ACID AND BASIC CATALYSIS

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CONTENTS

PREFACE

The present review is a translation of a monograph: *"Om Syre- og Base-katalyse"* published by the University of Copenhagen September, 1926. The field is covered in the text up to March, 1926.

In order to bring the article up to date a short *Appendix* has been added in which the progress in 1926–1927 has been presented.

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INTRODUCTION

Acid and basic catalysis constitutes an important chapter in the history of physical chemistry. From studies in this field originated the chief contributions to our knowledge of homogeneous catalysis. In the formulation of the laws governing the velocity of chemical reactions in general, investigations of acid and basic catalysis have played a conspicuous part as appears from the classical investigations of Wilhelmy (180) on the inversion of cane sugar by acids and from the various catalytic studies by Ostwald (149) and Urech (176). Furthermore consideration of the phenomena of acid and basic catalysis has contributed to the understanding of the mechanism of chemical reactions in general and also has in many cases been useful in the verification of Arrhenius' theory of electrolytic dissociation (8).

The ideas of acid and basic catalysis, developed by Arrhenius (9, 10, 11, 12) on the basis of his dissociation theory, are still commonly recognized as principally correct. The chemist still considers the phenomena of acid and basic catalysis as due to the effect of hydrogen and hydroxyl ions respectively and makes use in numerous ways of such a dependence as a means of determining the concentration of these ions.

This simple conception of catalytic phenomena to which the investigations of Arrhenius have led, however, failed to prove entirely satisfactory. First, as is natural, certain factors used in the theory have on closer examination revealed incompleteness of definition. Secondly it must be admitted that the difficulties, encountered from the very beginning in the quantitative working out of the theory of electrolytic dissociation, have presented themselves with especial emphasis in the field of reaction velocity. Arrhenius (11) himself called attention to the difficulties caused by such anomalies in the consideration of catalytic phenomena from the point of view of electrolytic dissociation: thus for the interpretation of the effect of acids on the inversion of cane sugar he found it necessary to assume an increase in the "activity" of the sugar molecules on addition of the acid besides the ordinary catalytic effect of the hydrions. Later on as a result of similar difficulties he resorted to formulating the velocity law by means of osmotic pressure instead of concentration.

Other authors, engaged in the field of catalytic phenomena, have felt the same difficulties in different ways. In the course of time numerous attempts have been made to effect a closer approach to the experimental data by introducing suitable modifications in the original theory. While most of these attempts have failed in presenting decisive results, they have brought about a collection of data, which should be of value in future work. The influence on the catalytic velocity of reaction produced by addition of salts or more generally by a change in the concentration of electrolytes forms the chief basis for these modifying theories. It is primarily this conception called "Neutral salt effect" or more correctly "Salt effect," that has given rise to difficulties in the interpretation of the kinetic phenomena of reaction. In some respects these difficulties when closely studied are quite imaginary. In other respects, however, points of great kinetic significance are attached to the term "Salt effect," the understanding of which has been rendered possible only by means of the new theory of ionic solutions, which stands out as one of the chief advances in the recent development of modern chemistry.

In addition, views of interest for acid and basic catalysis have been developed in other directions. This applies to the ideas advanced on the state of the catalyst in solution and to the theory ascribing catalysis to the ionization of the substrate or to the formation of an intermediate product which reacts spontaneously.

One of the aims of this review is to give a critical exposition of the theories of acid and basic catalysis, without in any way laying claim to having attained a complete survey of this intricate subject. The intention is furthermore to give a brief outline of the modern views on catalytic salt effect. Finally there will be given certain ideas and considerations concerning the phenomena of acid and basic catalysis based upon views of the acid-basic function which have recently been advanced and for the development of which the catalytic decomposition of nitramide and certain analogous reactions like the mutarotation of glucose have furnished the experimental foundation.

The much disputed question as to a general definition of the concepts of catalysis and catalyst will not be treated in this paper, the laws governing the catalytic processes discussed here being considered as quite identical to those valid for other homogeneous reactions. Thus for example the catalytic decomposition of cane sugar by hydrions will be considered as a bimolecular reaction between the sugar molecule and the hydrion, for which the differential equation for bimolecular reactions is supposed to be applicable to the same extent as for non-catalytic reactions. The fact that one of the reacting molecules, viz. the catalyst, is to be found among the products of the reaction according to our view cannot possibly affect the laws governing the process.

I. THE INFLUENCE OF SOLVATION IN CATALYSIS BY HYDRIONS

Arrhenius' theory of acid catalysis as a catalysis caused by hydrions does not distinguish between the hydrion in the free and in the hydrated state. When we realize that the water-free and the hydrated hydrion in reality are two entirely different molecules, the question then arises as to their relative rôle in the hydrion catalysis. Resulting differences in the effects of the two ion species might perhaps offer a possibility of interpreting some of the anomalies, brought about by addition of salt or by some other change in the solvent.

Lapworth (66, 122) was the first to subject this question to a thorough treatment. According to his theory, which in many ways may seem plausible, the catalytic effect in acid catalysis is due solely to the non-hydrated or more generally to the non-solvated hydrion. The solvated hydrion is supposed to be inactive. Nowadays it is well known, that the free hydrion—an electron-free nucleus—is altogether different from any other chemical molecule, and it might therefore appear well founded to attribute special catalytic properties to the hydrion. On the other hand this would give the hydrion an unique position which is not supported by experimental evidence. The hydroxyl ion for instance, is equally as effective in catalytic processes as the hydrion.

The most important experimental foundation on which Lapworth's theory is developed comprises the results obtained by studying the effect of small quantities of water on saponification and other reactions catalyzed by hydrions, for example the hydrazobenzene-benzidene arrangement and the bromination of ketones in non-aqueous solutions. About 1895 H. Goldschmidt (72, 73) showed that hydrion catalysis in alcoholic solution is considerably depressed on addition of water. In subsequent papers he has studied the phenomenon thoroughly and developed a theory, which will be extensively dealt with below. Other authors have also (179, 105, 24, 175, 50) examined the influence exerted by water on various reactions catalyzed by hydrions in alcoholic and related solutions, and in this way have in the main confirmed the existence of the anti-catalytic effect of very small concentrations of water.

Lapworth explains the effect by the assumption that most of the hydrions in aqueous solution are hydrated having taken up a molecule of water to form the ion H_3O^+. In accordance with recent authors this ion will be termed here the oxonium ion, its great importance in the theory of acid and basic catalysis being further developed in chapters 6, 7 and 8. The free hydrion is, however, supposed to exist in the solution in small quantities, according to the following equilibrium:

$$H_3O^+ \rightleftarrows H_2O + H^+.$$

In an alcoholic solution for instance, an increase in the concentration of water will diminish the quantity of free hydrions, these being now transformed into oxonium ions. The depression of the catalytic action will, according to Lapworth, be naturally explained as due to a decrease in concentration of the effective catalyst.

The bromination of acetone may be taken as an example. The partial reaction which is measurable kinetically and which is strongly catalyzed by hydrions, consists most probably in the enolization (121) of the acetone, the depression caused by addition of water being about proportional to the quantity added. Only 2 per cent of water is necessary for reducing the velocity to 1/10 of the original value in a water free solvent.

Lapworth tries to support his views on the free hydrion by some other methods as well. For this purpose Hardman and Lapworth (92) have carried out a series of E.M.F. measurements in cells of the following type:

$$H \left| \underset{\text{Alcohol}}{HCl} \right| \underset{\text{Alcohol + Water}}{HCl} \left| H, \right.$$

in which the quantity of water is small as compared to the quantity of alcohol, but great as compared to that of hydrochloric acid. The E.M.F. of such a cell is given by the formula:

$$E = RT \ln \frac{P}{P_0}$$

where P is what the author calls the "availability of the acid," a term which evidently is identical with what we now would call the activity of the free hydrion. The measurements conform with the expression:

$$\frac{P}{P_0} = \frac{r}{r + w} \tag{1}$$

where *r* is a constant and *w* denotes the molarity of water in the alcoholic solution.

In reality a formula in agreement with (1) can easily be derived from the classical law of mass action. By using the following three equations

$$\frac{c_{H^+}\, c_{C_2H_5OH}}{c_{C_2H_5OH_2^+}} = K_1,$$

$$\frac{c_{H^+}\, c_{H_2O}}{c_{H_3O^+}} = K_2,$$

and

$$c_{C_2H_5OH_2^+} + c_{H_3O^+} = C_{H^+}$$

where C_{H^+} is the total concentration of acid, assuming complete dissociation we get:

$$\frac{c_{H^+\ (\text{alcohol} + \text{water})}}{c_{H^+\ (\text{alcohol})}} = \frac{\dfrac{c_{C_2H_5OH}}{K_1}}{\dfrac{c_{C_2H_5OH}}{K_1} + \dfrac{c_{H_2O}}{K_2}} = \frac{r}{r + c_{H_2O}}.$$

According to the terminology proposed in Chapter 7, *r* is the conventional dissociation constant in alcoholic solutions. The hypothesis of the existence of the free hydrion is consequently not in conflict with the results of the E.M.F. measurements. Lapworth considers this to be a support of the theory attaching importance especially to the fact (124) that the two catalytic constants k and k_0 for different catalytic reactions with and without addition of water respectively follow a formula analogous to (1):

$$\frac{k}{k_0} = \frac{r}{r + w} \tag{2}$$

r has here approximately the same value as given by the E.M.F. measurements.

Lapworth's theory has been given much credit and has been supported chiefly by English authors (42, 46). It will be shown, however, that there are decisive difficulties opposed to the theory.

In their first paper Fitzgerald and Lapworth call attention to the conflict between their views and those of Goldschmidt, without making any effort to test the relative soundness of the two theories. Goldschmidt, who as before mentioned, was the first to observe the anti-catalytic effect of water, explains the phenomenon by ascribing the catalytic effect to the hydrogen ion-alcoholate (83, 74, 80). The effect of the water depends consequently upon a partial decomposition of the alcoholate converting the hydrion into the oxonium ion according to the scheme:

$$C_2H_5OH_2^+ + H_2O \rightleftarrows C_2H_5OH + H_3O^+$$

In this system the alcohol serves as the solvent and hence may be considered to be present in constant concentration. The mass action law applied to this system yields:

$$\frac{c_{C_2H_5OH_2^+}c_{H_2O}}{c_{H_3O^+}} = r.$$

where *r* as previously mentioned corresponds to the dissociation constant of the oxonium ion in alcoholic solutions. If C_{H^+} means the total hydrion concentration regardless of solvation, the following equation is easily derived:

$$\frac{c_{C_2H_5OH_2^+}}{C_{H^+}} = \frac{r}{r + w}$$

If the hydrion alcoholate functions as the catalyst this equation may be transformed into the following:

$$\frac{k}{k_0} = \frac{r}{r + c_{H_2O}}$$

k and k_0 being the velocity constants in alcoholic solutions with and without water respectively. The assumption of the hydrion alcoholate as the active catalyst then leads to the same formula for the anti-catalytic effect as does the assumption of the catalytic activity of the free hydrion. This is also a simple consequence of the fact that the hydrion alcoholate and the free hydrion must be present in the alcoholic solution in a constant ratio with respect to their concentrations. The existing data cannot therefore be interpreted as verifying one of these theories at the expense of the other; they both explain equally well the experimental facts.

Furthermore it should be noted that the E.M.F. measurements mentioned above can not possibly prove anything as to the real existence of the free hydrion. The idea is frequently met that the validity of Nernst's formula (145) for the electromotive force, from which formula (1) is derived virtually presupposes a real concentration of the ion under consideration. However, a well defined chemical potential, for instance of a metal in a salt solution, may be obtained, even when no appreciable concentration of the metal ions exists in the solution. In the numerous instances in which Nernst's formula leads to absurd ion concentration—as for instance in the case of a copper electrode in a potassium cyanide solution—it is therefore unjustified to consider the reaction

$$\text{metal} \rightleftarrows \text{metal ion} + \ominus,$$

where $\ominus$ denotes the electron, as always determining kinetically the potential at the electrode. Under such circumstances and also in general the potential between electrode and electrolyte might be defined by means of more indirect reactions. For the copper-copper-cyanide system we might for instance have:

$$Cu + CN^- \rightleftarrows CuCN + \ominus$$

or

$$Cu + 2CN^- \rightleftarrows Cu(CN)_2^- + \ominus$$

As regards the hydrion potential in presence of water the indirect kinetic reaction:

$$H + H_2O \rightleftarrows H_3O^+ + \ominus$$

can just as well as the direct reaction:

$$H \rightleftarrows H^+ + \ominus$$

account for the existence of a well defined potential at the electrode.

The definition of the potential cannot therefore give any information as to the real existence of the water-free hydrion. Nor can the agreement between the electromotive force and the catalytic measurements from Lapworth's point of view be of decisive importance, as may also be seen from the thermodynamic scheme of equilibrium:

$$AH^+ \rightleftarrows A + H^+,$$

where A is the alcohol molecule, or more generally, the molecule of the solvent employed. According to this scheme the concentration of the hydrion alcoholate is proportional to the concentration calculated for the free hydrion. The relation between catalytic activity and electromotive force, which is derived if the free hydrion is supposed to be the active molecule in the catalysis as well as in the creation of the electromotive force, will consequently be maintained if the hydrion alcoholate be considered active in both respects.

It is thus impossible on this basis to choose between Lapworth's and Goldschmidt's theories, although other considerations might be taken into account to show the doubtful character of ascribing any kinetic significance to the free hydrogen nucleus. It is hard to believe that the hydrogen nucleus with one positive charge and without protecting electrons should be capable of existence amidst other molecules possessing electron systems acting as screens against the surroundings. This impossibility is according to

Fajans (62) manifested by the enormous heat effect of 232,000 cal. produced when the free hydrion unites with water. If this heat quantity is supposed to represent the affinity of the hydrion for water—as is approximately correct, the concentration of the free hydrion in an acid solution will be calculated equal to 10^{-150}. This calculation is based upon an application of the gas laws which naturally break down at these concentrations, but no doubt the order of magnitude of the figure demonstrates that the free hydrion cannot be present in aqueous solutions at kinetically significant concentration. The catalytic effect must consequently be assigned to the hydrion hydrate or the oxonium-ion, while in alcoholic solutions the hydrion alcoholate should be considered as the active catalyst in agreement with the view put forward by Goldschmidt.

Lapworth's theory on acid catalysis has recently been taken up by F. O. Rice (154) in his work on "chemical reactivity." Rice's views are based chiefly upon considerations regarding the temperature coefficient of catalytic reactions for which he takes advantage of Arrhenius' (11) well known theory of the dependence of the velocity of reaction upon the temperature, in which the equilibrium between the molecules of the substrate in normal and "active" state is supposed to be displaced in favor of the active molecules with increased temperature. This view is applied by Rice to the catalyst, whereby the shift of the equilibrium:

$$H^+ + \text{water} \rightleftarrows H^+-\text{hydrate}$$

is made to account for the dependence of the reaction upon variations in temperature. The solvent is not supposed to take part in the reaction and the whole catalytic effect is supposed to be exclusively due to the free hydrion.

The author presupposes (apparently as an obvious fact) that the temperature coefficient of all reactions belonging to this class must be the same provided the theory is true and he postulates, moreover, that the reactions catalyzed by hydrions and hydroxyl ions can be resolved into comparatively few classes. It is mentioned as a verification of the theory that the experimentally determined temperature coefficient $k_{35^\circ}/k_{25^\circ}$ in acid catalysis of esters is found to be between 2.2 and 2.5, while this identity can be explained from the old theories only by ascribing the same heat of activation to all the reacting molecular species. The temperature coefficient for the simple non-hydrolytic reactions catalyzed by hydrions is according to Rice:

$$\frac{k_{35^\circ}}{k_{25^\circ}} = 3.08.$$

This theory of the free hydrion as the only important factor in acid catalysis is extended further in deriving more general conclusions: The chemical reactions, pictured by the usual stoichiometric schemes, are as a rule far from giving the real mechanism. Products of dissociation and chemical compounds with the solvent, although present in exceedingly small concentrations, may be the true participants in the reaction. Such an assumption suffices for explaining apparent reaction anomalies, for the interpretation of which it will be unnecessary, therefore, to ascribe a kinetic effect to the surrounding medium.

In addition to what has been said before of the probable concentration of the free hydrion in water solution, there are further objections to which this "theory of reactivity" can be exposed. The contention that the theory of the free hydrion requires the same temperature coefficient for all simple reactions catalyzed by hydrions, can hardly be maintained because in that case the temperature coefficient for all bimolecular reactions involving the hydrion and generally also for all reactions with one common molecule ought to be the same. The identity of the temperature coefficients, experimentally found, cannot therefore be considered as evidence in favor of Lapworth's theory. Nor can the assumption that all reactions catalyzed by hydrions possess temperature coefficients belonging to comparatively few groups be taken as supporting the theory.

The hydrolytic decompositions catalyzed by hydrions may be considered as a separate group, different from the non-hydrolytic reactions mentioned above. In order to explain why the coefficient falls from 3.08 to 2.4 on proceeding to this type of reaction, Rice assumes the process to take place between the free hydrion and the hydrate of the substrate, at the same time pointing out that only a small quantity of the latter (dependent upon the temperature) is present in the hydrated state. This explanation will not fit, however, unless the decomposition of the hydrate varies in the same manner with the temperature for all hydrolytic decompositions, and this is again tantamount to the introduction of a constant heat of activation. While it is admitted that Rice, by making these assumptions, can arrive at the same temperature coefficients for all hydrolytic decompositions, the existence of the "comparatively" few groups of temperature coefficients has not by any means been proved in this way from theoretical views on acid catalysis.

The more general considerations made by Rice on the great difference between stoichiometric and kinetic conditions are no doubt quite sound. This question, which has been thoroughly treated by Kendall (109, 112, 110), has been generally recognized, although it might not always have been sufficiently respected. It ought to be emphasized, however, that the kinetic equations often are quite independent of whether the real equation or a thermodynamically equivalent equation is employed. (See section 3.) Be this as it may, it still remains unjustified to make the reactivity of the molecules independent of the medium in which the reaction proceeds.

Mention ought also to be made of the extension of the Lapworth-Rice theory of acid catalysis to account for the corresponding phenomena in basic catalysis. This extension made by Rice gives a comparison between the two kinds of catalysis. The hydroxyl ion is supposed to be almost completely hydrated, and the catalytic effect considered as due to the small amount of non-hydrated hydroxyl ions. Since the hydration tendency is much greater for the hydrion than for the hydroxyl ion the non-hydrated part will assume a higher value for the latter. The concentration of free hydrions in "neutral" solution will consequently be much lower than the concentration of the free hydroxyl ions although the hydrated ions are present in practically equal amounts.

There may be some reality in these qualitative considerations. Rice, however, makes the additional assumption that the real catalysts in acid and basic catalysis are of the same efficiency. If the real catalysts were the hydrated hydrions and hydroxyl ions, acid and basic catalysis ought then to be the same at the "neutral point." A solution, being "stoichiometrically neutral," would also be "catalytically neutral." The fact that the reaction minimum, or the stability maximum (Euler), for many reactions lies beyond the neutral point, for example, close to $p_H = 5$, is explained on the basis of the above assumption of the free ions being the active catalysts, whose concentrations at the neutral point are supposed to be quite different. The two water free catalysts are present in equal concentrations at the point of reaction minimum or at the "catalytic neutral point" as it is called by Rice; the location of this point on the acid side being due to the greater hydration of the hydrion as compared to that of the hydroxyl ion.

These considerations are, however, largely arbitrary. The assumption that acid and basic catalysts are equally effective is not well founded and may rather be considered as highly improbable. The interpretation given of the reaction minimum must therefore be rejected as being theoretically unsound. It is moreover well known that no fixed location can be attributed to this point, although it seems to lie about $p_H = 5$ in many cases. A great number of reactions are recorded where the effect of hydrions and hydroxyl ions is altogether different. Nitramide is completely unstable in alkaline solutions, while quite insensitive to acids. The salts of nitrosohydroxyl aminesulphonic acid are decomposed instantaneously in acid solutions while being reasonably stable to alkalis. Numerous examples of this kind exist, and are quite incompatible with an assumption of the same catalytic effect for the hydrion as for the hydroxyl ion, whether water-free or in the hydrated state.

An objection of more formal character may be added. As mentioned above, Rice formulates the concept of "catalytic neutrality" in relation to that of "stoichiometric neutrality." Stoichiometric neutrality is neutrality in the sense used by the chemist to denote the state in which the concentrations of hydrions and hydroxyl ions attain the same value. As pointed out elsewhere (30) it is intrinsically illegitimate, however, to make this conception of neutrality imply any sort of counterbalancing effects, such as in the case of electric neutrality. The reason is that ideas like acidity and basicity, strength of acid and strength of base do not have any common measure. Acidity can only be determined in relation to another acidity, basicity to another basicity. It is obvious that the acidity will decrease and the basicity increase, when sodium hydroxide is added to hydrochloric acid. It may be said that the acidity is diminished at the same rate as the basicity is increased, but the point where they become identical cannot be fixed, because this question has no logical sense.

There seems therefore no reason why the concept of stoichiometric neutrality should be generalized further into the field of kinetics. The common neutrality concept is based upon the idea of expressing equality of two effects of opposite kind, while the effects attaining the same value in the catalytic neutral point are entirely of the same kind. It is therefore advisable to omit the concept of catalytic neutrality.

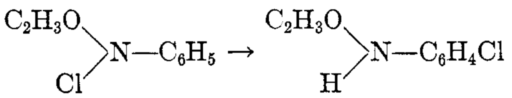
Although this is a purely formal question, it ought not to be dismissed as immaterial. The possibilities for development in a theoretical field are often dependent to a considerable extent upon suitable definitions and logical conceptions, whereas natural progress can be hampered or led astray if the definitions are lacking in clarity and cogency.

Nothing has been revealed in the theory of catalysis by adopting the theory of Lapworth, which can modify the result arrived at above as to the importance of solvation. Goldschmidt's views, in which the catalysis is ascribed to the hydrionhydrate in aqueous solutions, to the alcoholate in alcoholic solutions, to the anilinium ion (81) in aniline solutions etc. must still be considered to offer the best foundation for a theory of catalysis. This theory, so to speak, is imposed upon us by its own force, when we realize that the free hydrion is incapable of existence in any solvent and consequently either has to remain in the original acid molecule or to combine with the molecules of the solvent.

This mode of thinking leads to the assumption of different "hydrions" in different solvents, so that hydrion catalysis in different systems is really produced by different catalysts. This result is, however, as shown in Chapter 8, only the first step in the establishment of a more general theory of acid and basic catalysis.

II. THE DUAL THEORY OF CATALYSIS

The observations made by Blanksma (20) and later by Acree and Johnson (5), studying the transformation of acetyl chloroamino benzene into p-chloracetanilide:



$$\begin{matrix} C_2H_3O \\ Cl \end{matrix}\!\!>N{-}C_6H_5 \rightarrow \begin{matrix} C_2H_3O \\ H \end{matrix}\!\!>N{-}C_6H_4Cl$$

are among the first experimental data to have contributed to the formulation of the theory of catalysis later called the dual theory. This reaction is catalyzed by hydrochloric acid, but the velocity of reaction is proportional to the square of the acid concentration and not to the first power as in simple hydrion catalysis. If the phenomenon be interpreted as an effect due to the HCl molecule, a second power law will be obtained, provided that no other substances add to the catalytic effect. The more general conclusion has been drawn that the hydrion is not the only catalyst in acid catalysis, a greater or smaller effect being ascribed also to the undissociated acid molecules.

By studying the reaction mentioned above, many investigators (6, 148, 156, 96) have been able to show that the mechanism of the total reaction is more complicated and that the partial reaction determining the velocity is catalyzed by hydrions as well as by chloride-ions, which kinetically amounts to an HCl-catalysis. This reaction is not suitable, therefore, as a type of the ordinary hydrion catalysis, being more related to such reactions as the decomposition of diazo acetic ester by HCl (25, 67) and the addition of HCl by quinone (50). These processes will not proceed unless chloride ions as well as hydrions are present.

Investigations on catalytic salt effect in alcoholic as well as in aqueous solutions have given the dual theory a more solid foundation. On the whole, the development in theories on acid and basic catalysis might to a great extent be considered as a reflection of the interpretations given in the course of time for the influence of salt upon the velocity of reaction. The dual theory, as formulated by Senter (163) and Lapworth (124), has gained support from many sides, in fact it is represented in several text books (128, 181) as an unquestionable reality. It must be realized, however, that the results of the theory are due to wrong interpretations of experimental data.

Since the conditions in aqueous and alcoholic solutions are in a quantitative sense very different, it appears natural to deal first with the simpler aqueous solutions. The dual theory has been brought forth chiefly by H. S. Taylor (168, 169, 170, 171) and Dawson (44, 45) and his coworkers. Taylor worked especially on the hydrolysis of esters, catalyzed by strong or moderately strong acids with and without addition of neutral salts. By using hydrochloric acid as a catalyst and potassium chloride as neutral salt he thus found for five different esters the ratio between the catalytic constants in 0.1N HCl + 1.0N KCl and in 0.1N HCl without any KCl to be 1.24, the deviations from this value amounting only to a few per cent. 1N KCl consequently causes the velocity to rise 24 per cent. The ratio between the catalytic constant of the HCl-molecule and the hydrion can be calculated if the increase in undissociated HCl, brought about by addition of KCl and determined by conductivity measurements, is made to account for the effect observed. The experiments gave an average value 2.9 for this ratio. Other concentrations of the acid gave somewhat lower values, yielding the final average of 2.77, whereby the catalytic effect of the HCl-molecule would be about three times that of the hydrion.

It will be seen that this explanation necessitates the assumption that the salt effect would be zero if no increase in the concentration of the undissociated HCl had taken place on addition of KCl. This assumption, however, is absolutely without foundation. Changing the solution from 0 to 1N KCl means a very serious alteration of the medium kinetically. For instance Geffcken's (71) solubility measurements show that the activity coefficient of a non-electrolyte like oxygen, is subject to a change of about 38 per cent on addition of NaCl up to 1N concentration. It seems plausible, therefore, to interpret the catalytic effect mentioned above as a pure kinetic effect, independent of the formation of new molecules. This explanation conforms much better to the modern view on electrolytes, in which the hydrochloric acid under these conditions is supposed to be completely dissociated.

A more direct corroboration of this explanation may moreover be found in another experimental series by Taylor. An almost constant ratio, varying from 1.24 to 1.20, will be found if the effect of 1N KCl on the catalysis by hydrochloric acid in concentrations varying from 0.01N to 0.5N is calculated on the assumption of constant hydrion concentrations. These values of the ratio will amount to 1.42 and 1.55 respectively, i.e., much more diverging figures if the hydrion concentration is supposed to be reduced by addition of KCl according to the classical method of calculation.

This is only a single example of the simplification brought about in the field of kinetics by employing the stoichiometric concentration of strong electrolytes instead of introducing conductivity corrections or activities. This last point will be thoroughly treated in Chapter 6.

The calculations by Snethlage (165) on Palmaer's (150) inversion experiments are subject to similar objections as were brought against those by Taylor. The inversion velocity caused by 0.1N KCl is about 6 per cent higher than what is calculated from the velocity at concentrations lower than 0.01N. The catalytic effect may now be calculated if this 6 per cent increase is supposed to be due to the increase in undissociated HCl. The salt effect may, however, just as well be interpreted kinetically. The latter view seems to be supported by the minor variations in the inversion constant at concentrations lying between 0.01N and 0.001N HCl, because the formation of catalytically active HCl within this concentration range would give a considerably higher variation than what is observed.

Taylor's calculations lead also in the case of tri- and dichloroacetic acid to a catalytic effect of the undissociated molecules, although much less than for HCl. The experimental error is much greater for these weak electrolytes, however, while at the same time the application of the conductivity method and the fact that the primary and secondary salt effect are not taken into account make the results very problematic.

Results of somewhat greater significance for the dual theory have been obtained by H. M. Dawson (43, 44, 45) and his co-workers from investigations on enolization of acetone catalyzed by acids. The catalytic effect of certain organic acids was studied at various concentrations of acid, with and without addition of the corresponding salt. The results with monochloroacetic acid are of special interest. The ratio between the catalytic effect and the hydrion-concentration undergoes a considerable increase, when the concentration of the system with respect to either acid or salt is increased, this effect being much greater here than in the case of ester hydrolysis. The effect might be ascribed to the undissociated molecules, as assumed by Dawson. In order to enable any definite conclusions it is however absolutely necessary to take account also of the salt effect mentioned before, as well as of the influence of the monochloroacetic acid in changing the medium.

The catalytic values for stronger acids like trichloroacetic, trichlorbutyric and naphthalene sulphuric acids etc. are so uncertain that no importance can be attached to them, the reasons being the same as in the case of hydrochloric acid.

Dawson and Reimann (45) point out that their results do not agree with the investigations by Arrhenius (12) on the inversion of cane sugar with and without addition of the corresponding neutral salt. This is true also when the calculations are carried out according to more recent views. It seems as if the effect, for instance, of acetic acid on the inversion velocity is determined only by the hydrion concentration, if the various salt effects are taken into account. It must be considered, however, that acetic acid is much weaker than monochloroacetic acid, investigated by Dawson and Reimann, while also the nature of the catalyzed reactions certainly influences the law governing the process of catalysis. The importance of the latter point will be taken up in one of the following chapters.

The catalytic effect of an acid from the viewpoint of the dual theory may be expressed by the equation:

$$h = k_{H^+}c_{H^+} + k_Mc_M,$$

where *h* is the catalytic velocity, k_{H^+}, k_M, c_{H^+} and c_M being the catalytic constants and concentrations of the hydrion and the undissociated acid respectively. Taylor (171) and Snethlage (164) have discussed the importance of the dissociation constant *K* of the acid, and the former has given the following generalization:

$$\frac{k_M}{k_{H^+}} = \sqrt{K}.$$

According to this equation k_M must be greater than k_{H^+} for strong acids. In certain cases the effect of the hydrion ought to equal that of the undissociated acid, and the catalysis would consequently be independent of the degree of dissociation (78). The evidence given in support of this equation is, however, very scant.

Numerous investigations on the dual theory (1) have been carried out in alcoholic solutions, especially by Goldschmidt (75, 82, 76, 77), Bredig (23), Snethlage (164, 165) and Acree (3). Many of the results obtained give apparently good reasons for the maintenance of the dual theory. The calculations are, however, based upon the classical mass action law, and they generally assume the complete absence of kinetic salt effects. In both of these respects the alcoholic solutions deviate more from ideality than do water solutions, and therefore the results obtained on this basis must be considered very critically.

In the development of his theory on strong electrolytes Bjerrum (17) has pointed out that the catalytic velocity using strong acids is generally proportional to the total concentration of the acid, and he finds this to be an important evidence in favor of complete dissociation of strong electrolytes. In applying these points of view to Goldschmidt and Thuesen's (82) investigation on esterification of weak acids by using methyl alcohol as a solvent and picric and hydrochloric acids as catalysts he finds reasonable values for the ion activity in alcoholic solutions by assuming the hydrion to be the true catalyst. Goldschmidt himself later on (80) expressed doubt as to the applicability of the dual theory in the catalysis by strong acids in alcohol.

Similar results will be obtained by going through the work of Snethlage, which has often been considered as being of particular importance for the dual theory for alcoholic solutions. Mention will be made here of his application of Bredig's diazo acetic ester catalysis in absolute alcohol at constant concentrations of picric acid on addition of varying quantities of p-toluenepicrate and related organic picrates. The velocity of reaction proved to decrease with increasing concentration of picrate as the incomplete dissociation of picric acid in alcohol was further depressed. The decrease in velocity was comparatively slight, however, and could not be made to approach zero asymptotically even at high concentrations of picric acid as ought to have been the case if the classical laws were valid and the hydrion alone catalyzed the reaction. On the contrary by plotting the velocity against the reciprocal value of the picrate concentration as abscissa, Snethlage could extrapolate a value of the velocity equal to 0.013 at zero abscissa, while the acid without any picrate gave 0.058. The velocity could consequently not be reduced below 22 per cent of the initial value. The limiting value found in this way was attributed to the undissociated picric acid.

It will be shown later, however, that the dissociation of a weak acid is the more dependent upon the total salt concentration of the solution, the lower the dielectric constant of the solvent. In aqueous solution a weak acid at 0.1N salt concentration will possess a degree of dissociation twice as high as would have been the case if no salt effect had been present. The effect will be much greater when ethyl alcohol is employed as a solvent, the dielectric constant being only about one third of that for water. In this case the dissociation will be about ten times as great as calculated from the classical law of mass action. The catalytic effect at high concentrations of picrate need not therefore be due to the undissociated acid but might as well be interpreted as a hydrion effect. The extrapolation to an infinitely large salt concentration is under these circumstances misleading and fails to give any information whatsoever as to the effect of the undissociated acid.

A new calculation of the experiments of Snethlage is therefore needed. Our knowledge of the dependence of the dissociation upon salt concentration in ethyl alcohol is not sufficient for such a calculation, except in extremely dilute solution, and we can therefore only indicate that these experiments are not in conflict with the assumption that the diazo ethyl acetate reaction in alcohol solutions is catalyzed only by hydrions.

The principles for calculating the shift in equilibrium, which have been of kinetic influence in Snethlage's experiments, will be given in the chapter on the secondary kinetic salt effect. It will suffice to refer to the general existence of this effect without going into further details, since such a secondary salt effect has been present in all catalytic experiments on incompletely dissociated acids in alcoholic solution, also in the exact and exhaustive material produced by Goldschmidt and his co-workers.

The ideas characteristic of the dual theory for acid catalysis have been transferred to basic catalysis by S. F. Acree (4). He concludes from previous measurements in aqueous solutions and from his own measurements in alcoholic solutions that the catalytic effect is not only due to the hydroxyl ion or to the $C_2H_5O^-$—ion but also to the "undissociated bases" like NaOH and $NaOC_2H_5$ just as in the reaction between ethyl iodide and potassium ethylate both the latter as well as the ethylate ion are supposed to take part in the reaction (63). These views have brought forth extensive and important experimental material by Acree and his co-workers, but what has been said before of the experimental data on acid catalysis as a support of the dual theory applies equally well to Acree's measurements on basic catalysis. These experiments can only be made to fit the dual theory by neglecting the secondary and primary salt effects, known to exist.

Finally the views recently given by Hantzsch (90, 91) on the nature of acid and basic catalysis should be mentioned briefly. Hantzsch criticizes severely the importance usually attached to the dissociation as a measure of the strength of the acids, although he is not really opposed to the electrolytic dissociation theory. The dissociation, which a strong acid undergoes on solution in water involves, according to his view, both a depression of the acid properties and a levelling down of the great differences, displayed by the acids when in pure state. Hence the pure undissociated acids ought to possess a stronger catalytic effect than the dissociated aqueous solutions. This view is thus related to the dual theory of catalysis, although it was developed on a different basis.

However, while the dual theory has been restricted to the comparative study of catalysis in a definite solvent, and consequently has been able to work with the usual unprecise definition of acid and base strength, the Hantzsch theory is designed to apply to all solvents. It is quite crucial to this theory, therefore, that Hantzsch employs a completely undefined conception of acid strength. H. v. Halban (88, 89) has subjected this theory to a thorough criticism, to which here only reference can be made.

III. THE IONIZATION THEORY OF CATALYSIS

It is in many respects a reasonable idea to try to correlate the catalytic effect and the tendency of the catalyzed molecules to form more or less definite compounds with the catalyst. Such conceptions have appeared repeatedly in the development of reaction kinetics. Kastle (108) thus explains the catalytic effect of the hydrion by assuming the formation of an intermediate product between hydrion and catalyzed molecule and the subsequent spontaneous decomposition of the product formed. This view has been taken up by many authors, especially by Euler and Stieglitz, who have shown how to bring the theory into agreement with the experimental data.

In most of the reactions catalyzed by acids and bases, the substrate is electrically neutral and will therefore acquire an electric charge on addition of or reaction with hydrogen or hydroxyl ions. Since the assumption of such ion formation as a preliminary of the reaction itself is characteristic of the theory dealt with in this chapter this can appropriately be termed the ionization theory of catalysis. It seems practical to maintain this term also for the case of the substrate itself being already electrically charged.

As early as 1899 Euler (51, 54) launched the view that catalytic effect is always due to an increase in the concentration of reacting ions on addition of catalyst, basing this idea upon the fact that ionic reactions as distinguished from reactions between neutral molecules proceed instantaneously or in an immeasureably short time. Related theories have also been supported by other authors (131, 117, 120). The salt effect is explained by Euler (51) as an increased ionization of the reacting substances due to a collateral increase in the dielectric constant of the system. The ideas brought forth by these authors have been important for the development of the ionization hypothesis—as demonstrated through subsequent papers by Euler and his co-workers—although a general validity cannot be given to the old conception of ionic reactivity as quoted above.

As an example of the application of the ionization hypothesis, the mutarotation of glucose may be taken, a reaction which has been subjected to a thorough analysis from different angles by numerous investigators. This reaction is catalyzed by hydrions as well as by hydroxyl ions.

The velocity at 25°C according to Hudson (99) is given by the equation:

$$k = 0.0096 + 0.258\ c_{H^+} + 9750\ c_{OH^-}$$

where k is the monomolecular reaction constant, the time being expressed in minutes, and c_{H^+} and c_{OH^-} denote the concentration of hydrions and hydroxyl ions in the glucose solution. This equation shows that the process is composed of three partial reactions, independent of each other, viz. a spontaneous reaction independent of the acidity of the solution and two reactions catalyzed by hydrions and hydroxyl ions respectively. Riiber (155) has shown that the glucose transformation is a balanced reaction giving about 36.1 per cent α glucose and 63.9 per cent β glucose at equilibrium. In the preceding equation k is consequently equal to the sum of the two constants k_α and k_β corresponding to the two transformations $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ for which reason k must be independent of whether the reaction is started with the α or with the β form, as also shown by Riiber.

Euler (55, 56, 60) explains the partial reactions sensitive to hydrions and hydroxyl ions on the basis of the ionization theory. Since glucose is able to act both as an acid and as a base, it will be ionized amphoterically to glucose cations and glucose anions on addition of acid and base respectively, and these ions will in turn spontaneously break down. Other reactions catalyzed by acids or bases such as the decomposition of aceto acetic ester are interpreted by Euler (59) in the same manner.

The acid constant of glucose is approximately known, various authors (139, 116) having found values ranging between 10^{-12} and 10^{-13}. The addition of base will bring about an ionization of the glucose molecule according to the scheme:

$$C_6H_{12}O_6 + OH^- \rightleftarrows C_6H_{11}O_6^- + H_2O.$$

Application of the mass action law yields:

$$\frac{c_{C_6H_{12}O_6}\, c_{OH^-}}{c_{C_6H_{11}O_6^-}} = K,$$

showing that the spontaneous decomposition of the glucose anion obeys the same laws as a bimolecular reaction between glucose molecules and hydroxyl ions.

Basic properties may be attributed to the glucose molecule by assuming the existence of the following equilibrium:

$$C_6H_{12}O_6 + H^+ \rightleftarrows C_6H_{13}O_6^+,$$

showing in the same way that a spontaneous decomposition of the positive glucose ion yields the same course of reaction as would have been given by the bimolecular reaction between glucose and hydrions. Kinetic measurements cannot therefore furnish any evidence as to the validity of the ionization theory.

On the other hand it is not possible merely on the basis of the reaction type to refute the theory. Several facts seem to indicate that in some cases acid and basic catalysis are best interpreted from the hypothesis of ionization. It will in other cases, however, prove simpler to avoid such an explanation of the catalysis. To accept the theory as a *general* interpretation cannot be justified, the reasons being given in a subsequent chapter dealing with a general theory of acid and basic catalysis. An essential feature in Euler's view of catalysis is his idea of ascribing approximately the same velocity of decomposition to the two ions—the glucose anion and glucose cation—reacting in acid and basic solution respectively. From that point of view the difference in the behavior of the hydrion and hydroxyl ion as catalysts should be due entirely to differences in the magnitude of the acidic and basic constant of glucose.

Such an identity of the two velocities of decomposition seems *a priori* highly improbable. An experimental decision of this question is possible from the point of view of the ionization theory, provided the acid constant and basic constant of glucose are known. It would then be possible to calculate the quantities of glucose cation and glucose anion present under different conditions and then to make sure whether the ratio between these two velocities equals the velocity ratio. The basic constant, however, has not as yet been accessible to direct experimental measurement. Euler, therefore, simply assuming the correctness of this identity, calculates the ratio between the glucose anions and cations in basic and acid solutions of glucose, without of course getting any verification of his assumption by this procedure. The calculations are as follows:

The law of mass action gives for the two equilibria:

$$\frac{c_{Gl^-}\,c_{H^+}}{c_{Gl}} = K_A, \quad \frac{c_{Gl^+}\,c_{OH^-}}{c_{Gl}} = K_B$$

If the two solutions have the same c_{Gl}:

$$\frac{K_A}{K_B} = \frac{c_{Gl^-}\,c_{H^+}}{c_{Gl^+}\,c_{OH^-}}$$

The basic constant of dissociation K_B can consequently be evaluated when K_A, c_{H^+} and c_{OH^-} are known and the ratio $\frac{c_{Gl^-}}{c_{Gl^+}}$ is put equal to the ratio between the velocities of the two catalyzed reactions.

On the basis of the theory of the velocity minimum the calculations are as follows. If the ionization theory is valid we may write:

$$h = k_0 c_{Gl} + k_1 c_{Gl^-} + k_2 c_{Gl^+}.$$

The velocity minimum is determined by the equation:

$$k_1 c_{Gl^-} = k_2 c_{Gl^+},$$

since the product $k_1\, c_{Gl^-} \cdot k_2 \cdot c_{Gl^+}$ is constant. By introducing K_A and K_B:

$$k_1 \frac{K_A}{c_{H^+}} = k_2 \frac{K_B}{c_{OH^-}}$$

The hydrion concentration at the minimum of velocity is consequently given by:

$$c^2_{H^+} = \frac{k_1 K_A}{k_2 K_B} \cdot K_{H_2O}.$$

The square of the hydrion concentration at the iso-electric point is:

$$c^2_{H^+} = \frac{K_A}{K_B} \cdot K_{H_2O}.$$

The catalytic minimum and the iso-electric point will consequently coincide, when $k_1 = k_2$, i.e. when the anion and the cation of the glucose are decomposed at the same velocity, as assumed by Euler.

The basic constant K_B is thus given by the equation:

$$K_B = \frac{K_A \cdot K_{H_2O}}{c^2_{H^+ \text{(minimum)}}} \tag{1}$$

The point of minimum velocity, or the stability maximum, as it also has been expressed, plays an important rôle in the investigations on the glucose transformation and other reactions carried out by Euler and his co-workers. It has to be remembered, however, that the minimum is far from being sharp, the equation of Hudson corresponding to a very flat curve; secondary factors like salt effect, etc. are therefore likely to cause great displacements, while at the same time the calculations shown above are subject to the twofold uncertainty of the ionization theory itself and of the assumption of the same transformation velocity for cation and anion. It is therefore very doubtful whether any real significance can be attached to the calculated K_B values, and equation (1) must for the same reasons be considered as exceedingly hypothetical.

Kuhn and Jacob (116) have subscribed to Euler's opinion in as far as they assume the amphoteric character of glucose and a spontaneous decomposition of the glucose ions formed upon action with the acid and with the base. But contrary to Euler, they do not assume the same reaction constant for the glucose anion as for the glucose cation, ascribing to the former about double the reaction velocity of the latter. Much stress is laid by the authors on this result which in a subsequent article (115) is made the basis of further theoretical considerations. It is therefore necessary to examine this point more closely in order to show the decisive misconception involved in the development of their results.

Both Euler, and Kuhn and Jacob present the dependence of the velocity upon the hydrion and the hydroxyl ion concentration by means of a $k - p_{H^+}$-diagram, i.e., they have employed Sörensen hydrion scale as abscissa and the velocity constant as ordinate. If the catalytic effects of the hydrion and the hydroxyl ion are proportional to their concentrations—and only in this case can the ionization theory be maintained—the classical theory of dissociation will demand complete symmetry of the velocity curve in the diagram mentioned. Kuhn and Jacob now allege from their measurements that the basic branch of the curve has double the slope of that of the acid part and conclude from this that the ratio between the velocities is also 2 to 1. This conclusion, however, depends upon a mathematical mistake. If Kuhn and Jacob were right in their picture of the slopes, the correct inference would be that the velocity for the basic catalysis is proportional to the square of the hydroxyl ion concentration when a first power law is followed for the acid catalysis. The curve does not say anything, however, of the relative velocities of the two catalytic reactions. The conclusions drawn by Kuhn and Jacob are therefore not only unjustified but they are also in obvious conflict with their own equation for the catalytic process wherein proportionality with respect to both hydrion and hydroxyl ion concentration is expressed.

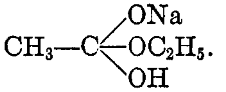
It is therefore not an exaggeration when Euler, Ölander and Rudberg in their studies on mutarotation (60) characterize the method of Kuhn and Jacob's calculation as "theoretisch nicht einwandsfrei." The mathematical and graphical procedure employed by these authors (60), however, does not seem very convenient either. They use a method of plotting p_{H^+} against log k, in which k is the constant directly observed comprising all the three partial reactions and they seem to interpret this curve as if the two branches represented the two partial catalytic reactions. However, a simple kinetic law cannot be obtained by introducing the logarithm of a velocity constant, representing the sum of two partial constants. Such a law can be derived only by introducing the logarithm of the partial constant, i.e. by using the term log $(k - k_0)$. On plotting this term against p_{H^+} the graph will consist of two straight lines of unit slope, showing the velocities to be proportional to the concentration of the catalysts. The curvature, displayed by the curves of Euler, Ölander and Rudberg at low concentrations of hydrions and hydroxyl ions will then of course disappear.

The results recorded so far are all based upon the application of the classical laws for dissociation and equilibrium, in which the gas laws are assumed to be valid for dissolved ions, thus justifying the expression of the mass action law in terms of concentrations. The data, produced hitherto on the kinetics of the glucose transformation are not sufficiently accurate for the purpose of applying the modern concepts to this reaction. An accurate experimental investigation of the reaction must, however, necessarily be accompanied by a corresponding theoretical treatment, based upon modern kinetic theories.

In this connection attention should be drawn to the fact that the great advantages of the p_{H^+} -scale in electrometric measurements, in which activity and not concentration values of the hydrogen ion are furnished are generally not present to the same extent in the field of kinetics. The tendency shown in many recent papers on kinetic questions to use the activity scale instead of the hydrion concentration scale has only hampered the interpretation of these phenomena. The question of activity versus concentration will however be taken up in detail in a subsequent chapter, in which the point just mentioned will be further elucidated.

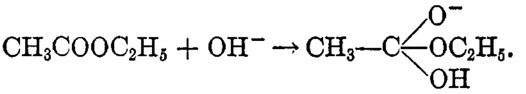
The same views brought forth in the interpretation of the glucose transformation have been applied by Euler and his co-workers (57, 58, 107) to other catalytic reactions especially the classical ester catalysis and the inversion of cane sugar (56). The investigation of the first reaction, which is catalyzed by hydrions as well as by hydroxyl ions, is chiefly directed towards the determination of the properties at the stability maximum.

The hydrolysis of ethyl acetate in aqueous solution in presence of a base is, according to Euler's theory of ionization, dependent upon the ionization of the ethyl acetate molecule. Euler and Laurin (57) assume sodium hydroxide to react with ethyl acetate forming



$$CH_3{-}C\begin{cases}ONa\\ OC_2H_5\\ OH\end{cases}.$$

This compound is presumably taken to be dissociated, so that the process really means an addition of hydroxyl ions according to the scheme:

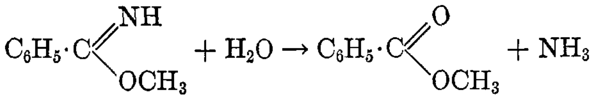


$$CH_3COOC_2H_5 + OH^- \rightarrow CH_3{-}C\begin{cases}O^-\\ OC_2H_5\\ OH\end{cases}.$$

The nature of the positive ethyl acetate ion is not mentioned but can most simply be considered as a direct addition product as follows:

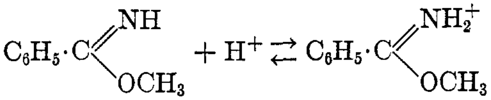
$$CH_3COOC_2H_5 + H^+ \rightarrow (CH_3COOC_2H_5, H)^+$$

By using the mass action law it becomes evident, however, that a bimolecular reaction between the catalyst and the ester molecule and a spontaneous reaction of the positive or negative ester ion lead up to results which are kinetically identical. As in the cases previously considered an agreement between the theory and the observed course of reaction cannot be taken as a support of the ionization theory. It has been mentioned already that Stieglitz has been one of the foremost advocates of what we have called the ionization theory. He has worked chiefly on imido esters and related compounds (166). The decomposition of methylimido benzoate by water according to the scheme:



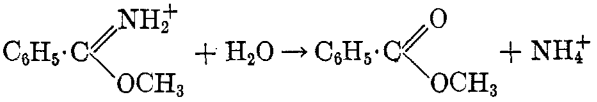
$$C_6H_5\cdot C\Big\langle{}^{NH}_{OCH_3} + H_2O \rightarrow C_6H_5\cdot C\Big\langle{}^{O}_{OCH_3} + NH_3$$

proceeds very slowly without catalysts, but is greatly accelerated in presence of acid. Stieglitz assumes the catalytic effect to be due to the formation of a positive ion:



$$C_6H_5\cdot C\Big\langle{}^{NH}_{OCH_3} + H^+ \rightleftarrows C_6H_5\cdot C\Big\langle{}^{NH_2^+}_{OCH_3} \qquad (2)$$

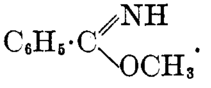
which then reacts spontaneously with the solvent:



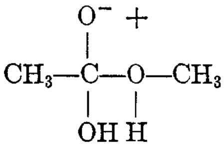
$$C_6H_5\cdot C\Big\langle{}^{NH_2^+}_{OCH_3} + H_2O \rightarrow C_6H_5\cdot C\Big\langle{}^{O}_{OCH_3} + NH_4^+ \qquad (3)$$

The catalytic effect of the hydrion is consequently interpreted in accordance with the ionization theory, and a closely related explanation has also been applied by Stieglitz to the ordinary ester hydrolysis.

Although the kinetic basis of these views is subject to the same objections as brought out previously, Stieglitz contends that these studies constitute a crucial proof of the validity of the theory and other authors particularly Acree (2, 5, 7) have in effect supported this view. Stieglitz admits in a later paper (167), however, that the form of the reaction curve fails to give any information concerning the real mechanism of the reaction, and now resorts to other propositions for confirming his theory.

Particularly he bases his ideas upon the rule that the catalytic effect of the hydrion is closely connected with the conversion of the cation of the weaker base into the cation of the stronger base to give the highest possible diminution in free energy: Reaction (3) ought to proceed easily since NH_3 is a stronger base than  $C_6H_5\cdot C\begin{smallmatrix}\diagup\!\!\!\diagup NH \\ \diagdown OCH_3\end{smallmatrix}$. It is easy to see, however, that Stieglitz's application of the principle of change in free energy is not correct and that his rule cannot be of general validity.

Similar considerations on the hydrolysis of esters have been brought forward by Lowry (134) who particularly endeavors to elucidate the chemical structure of the intermediate products formed by the reacting molecules. Since these intermediate compounds are supposed to react spontaneously, Lowry's views as to the mechanism of catalysis are practically congruent to those of the ionization theory. The following formula is ascribed to the active complex in the hydrolysis of ethyl acetate:



$$\begin{array}{ccccc} & & O^- & + & \\ & & | & & \\ CH_3 & — & C & —O— & CH_3 \\ & & | & | & \\ & & OH & H & \end{array}$$

which is an ampho-ion formed simply by addition of water to the ester molecule. Lowry's concept thus seems unable to convey any immediate understanding of the catalytic phenomenon.

It has now been shown for a number of reactions that a study of the kinetic course of reaction cannot provide any support in favor of the ionization theory. This has been pointed out on the basis of the classical expressions for the velocity of reaction and the mass action law, and the result is not therefore a priori applicable to such reactions, for which the classical formulas break down. It can be shown, however, that the new and more exact theories on velocity and equilibrium in dilute solutions lead to the same result.

Consider the following chemical state of equilibrium:

$$A_1 + A_2 \rightleftarrows B_1 + B_2.$$

The thermodynamic mass action law yields for the process:

$$\frac{a_{B_1} a_{B_2}}{a_{A_1} a_{A_2}} = K, \tag{4}$$

where *a* denotes the activity and K is the thermodynamic mass action constant, independent of the concentration. In the case of the A-system undergoing a change into a new system C, the velocity according to the new velocity theory is given by the formula:

$$h_A = k_A a_{A_1} a_{A_2} \cdot \frac{1}{f_X}$$

as will be explained in chapter 4.

If not A but the B system reacts, the analogous expression is:

$$h_B = k_B a_{B_1} a_{B_2} \cdot \frac{1}{f_Y}$$

where k_A and k_B are constants for dilute solutions and for the same solvent, while X and Y are the critical complexes, formed from the molecules of the A-system and the B-system, respectively. Combination of the two equations yields:

$$\frac{h_A}{h_B} = \frac{k_A}{k_B} \cdot \frac{1}{K} \cdot \frac{f_Y}{f_X}$$

The electrical charge on the critical complexes X and Y must be equal to the total charge of the A and B systems respectively, since these complexes are formed by collision within the A- and B-systems. The total charge however, is the same, in both systems, and X and Y must consequently also carry the same charge. This means that the corresponding activity coefficients f_X and f_Y vary with the concentration in the same way as long as the solution is moderately dilute. h_A in the above equation is consequently proportional to h_B, i.e. it is not possible from the kinetic course of reaction to distinguish between the decomposition of the A- and B-systems even by using the exact equations. At higher concentrations (change in medium, addition of salt etc.) the variations in f_X and f_Y will probably no longer be proportional, but this uncertainty as to the ratio between the two activity coefficients cannot of course offer any means for conclusions on the mechanism of reaction.

The above results are conclusive only if the changes A→C and B→C do not cause any disturbance in the equilibria, since equation 4 is valid only for the state of equilibrium. In other words the speed of these changes ought to be low as compared to that of the maintenance of the equilibrium $A \rightleftarrows B$. It is of course always possible to decide whether the A- or B-system reacts, if only the reaction proceeds sufficiently slowly.

These considerations can be formulated into a general rule since they are quite independent of the particular form of the equilibrium: In any reacting system in which an equilibrium $A \rightleftarrows B$ is instantaneously established it is impossible to decide from the course of the reaction whether the system A or the reciprocal system B reacts.

The two possibilities:

$$\begin{tikzcd} A \arrow[r, "\text{slow}"] \arrow[d, shift left] & C \\ B \arrow[u, shift left, "\text{Instantaneous}"] & \end{tikzcd}$$

and

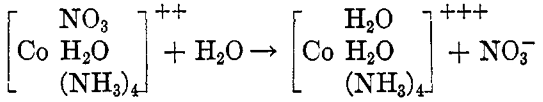
$$\begin{tikzcd} A \arrow[d, shift left] & \\ B \arrow[u, shift left, "\text{Instantaneous}"] \arrow[r, "\text{slow}"] & C \end{tikzcd}$$

are equivalent in this respect. This proves that one must relinquish as a general proposition the idea that a verification of the ionization theory can be obtained from the kinetics of the reaction.

On the other hand it is a question of considerable theoretical interest to decide whether this equivalence between the two schemes of reaction really means that f_X and f_Y are quite identical when the equilibrium is established instantaneously but this question is certainly not easy to answer.

It might be possible to distinguish between the two reciprocal systems, however, when other considerations besides the purely kinetic picture so far considered are taken into account. It has been mentioned above that Stieglitz found corroboration for the ionization theory in a principle involving the connection between the strength of the base and the velocity. No general validity could be assigned to this principle, but it might nevertheless be possible in certain cases to obtain some clues from similar considerations.

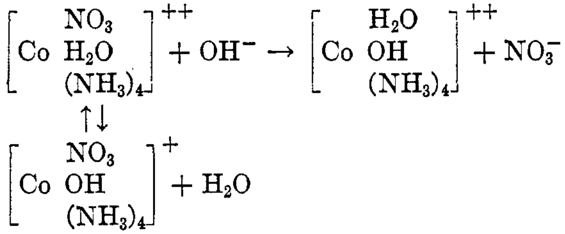
The following example from the field of the group of metal amines may be illustrative in this respect. The nitrato aquo tetramine ion is decomposed by water, splitting off the nitrato group and taking up a water molecule as follows:



$$\left[\begin{matrix} & NO_3 \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{++} + H_2O \rightarrow \left[\begin{matrix} & H_2O \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{+++} + NO_3^-$$

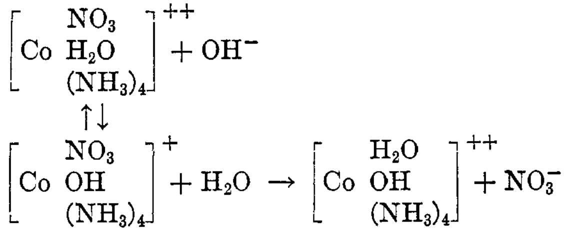
This "aquation" process is very sensitive to hydrions, the velocity in dilute acid being about inversely proportional to c_{H^+}. It might therefore seem possible to regard the reaction as an hydroxyl ion catalysis. On the other hand the nitrato ion is of slightly acid character, the hydrogen atoms of the constitutional water groups being ionizable, so the effect of diminished hydrion concentration may be to increase the acid dissociation forming the nitrato hydroxo ion which in its turn reacts spontaneously with the solvent. These possibilities may be written as follows:

(a)



$$\begin{array}{ll} \left[\begin{matrix} & NO_3 \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{++} + OH^- \rightarrow & \left[\begin{matrix} & H_2O \\ Co & OH \\ & (NH_3)_4 \end{matrix}\right]^{++} + NO_3^- \\ \quad\uparrow\downarrow & \\ \left[\begin{matrix} & NO_3 \\ Co & OH \\ & (NH_3)_4 \end{matrix}\right]^{+} + H_2O & \end{array}$$

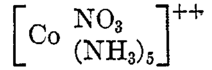
or (b)



$$\begin{array}{ll} \left[\begin{matrix} & NO_3 \\ Co & H_2O \\ & (NH_3)_4 \end{matrix}\right]^{++} + OH^- & \\ \quad\uparrow\downarrow & \\ \left[\begin{matrix} & NO_3 \\ Co & OH \\ & (NH_3)_4 \end{matrix}\right]^{+} + H_2O \rightarrow & \left[\begin{matrix} & H_2O \\ Co & OH \\ & (NH_3)_4 \end{matrix}\right]^{++} + NO_3^- \end{array}$$

where the process taken vertically represents the acid-base equilibrium which is instantaneously established. According to what was pointed out before it is impossible to decide from the kinetic course of reaction whether reaction (a) or (b) controls the catalysis.

The fact, however, that the nitrato pentammincobalt ion:



$$\left[\mathrm{Co}\,\begin{matrix}\mathrm{NO_3}\\(\mathrm{NH_3})_5\end{matrix}\right]^{++}$$

which is quite analogous to the nitrato aquo tetramine ion—but without acid character—shows no sensitiveness of this kind to hydrions, may be taken as strong indication that the acidity is the determining factor and, therefore the kinetic scheme is given by (b) and not by (a).

Similar deductions will surely give valuable information in many other cases as well.

More decisive criteria for the elucidation of these questions may be obtained however on the basis of new conceptions of acid and basic catalysis to be developed in the last chapter.

IV. PRIMARY SALT EFFECT. ACTIVITY AND CONCENTRATION

The fact that the addition of neutral salt with or without an ion in common with the catalyzing acid often causes considerable variations in the reaction constant, was one of the earliest objections against Arrhenius' hydrion theory of acid catalysis. The deviations from proportionality to the concentration of a strong catalyzing acid as exhibited for instance in the inversion of cane sugar have also been considered of the same nature as the salt effect. These points have been dealt with to a certain extent in the chapter on the dual theory. In the present chapter we will discuss the salt effects more generally from the standpoint of the modern theories of electrolyte activity and of velocity of ionic reactions. It may at once be stated that the influence of salt upon the reaction velocity is far from being a kinetic abnormality even in solutions of low concentration. It is entirely reasonable to expect a kinetic effect since as already mentioned the addition of salt changes considerably the properties of water as a solvent, the activity coefficient of dissolved non-electrolytes being increased 30 to 40 per cent (157) in some cases by simply adding NaCl up to 1N. There is no reason to consider this salt effect as an enigmatic phenomenon in conflict with the general kinetic views as seems to be the idea in Nernst's treatment (146) of this subject.

Nevertheless it is a question of great interest how this salt effect is to be properly interpreted. In this respect it is very conspicuous that the kinetic salt effects in dilute solution fall into two sharply distinguishable groups. For some reactions the effect upon the velocity constant is proportional to the concentration of the salt, in which case the effect is said to be *linear*. In other cases the effect is relatively greater the more dilute the salt solution: the variation in velocity seems rather to be proportional to the square root or to the cube root of the salt concentration, and the effect is then appropriately termed exponential in contradistinction to the linear effect (33).

A closer examination reveals that the exponential salt effect is always involved in reactions between two charged molecules, while the linear salt effect is peculiar to reactions between neutral molecules or between a neutral molecule and an ion. This observation has played an important part in the development of the general kinetic theory, in which not only the concentrations of the reacting substances but also their activity coefficients are supposed to govern the course of reaction.

It will be desirable to give a brief exposition of the general velocity theory for bimolecular reactions, since—as mentioned in the introduction—catalytic reactions can always be considered as bimolecular reactions between the molecules of the catalyst and the substrate. The velocity of a bimolecular process:

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

proceeding in dilute solution in an unchanging medium according to the classical theory is determined by the expression:

$$h = k \cdot c_A . c_B,$$

the concentration of the reciprocal system thus having no effect upon the velocity with which A and B react. From the standpoint of velocity being related to free energy this lack of dependence upon the chemical potential of the reciprocal system may appear striking. Realizing, however, that the reaction, stoichiometrically represented by: $A + B \rightarrow C + D$ is by no means expressed kinetically by this scheme, but actually consists in the formation of a "critical" collision complex (A, B) from collisions between A and B and a subsequent instantaneous decomposition of this complex to yield $C + D$, it appears quite natural that the chemical potential of the final system is without influence on the course of the reaction.

It is therefore essential to focus one's attention upon the process: $A + B \rightarrow (X)$, i.e. the process leading to the formation of the critical complex X. For this reaction it seems reasonable to attach great significance to the chemical potentials of all molecules taking part in the process. The chemical potential is intimately related to the activity coefficient, and the factor by which the concentration product in the classical velocity equation must be multiplied in order to take into account the influence of the activity coefficients upon the velocity, can be expressed as follows:

$$F = \frac{f_A f_B}{f_X}$$

which ratio has been called the *kinetic activity factor*.

A detailed treatment of this formula may be found in the original papers referred to previously (28, 31). It will suffice to mention here that the following hypothesis gives the foundation of the theory: "The probability of a molecular system passing from its normal state, into a state characterized by great improbability, is proportional to the ratio between the activity coefficients in the normal and the improbable state." From this rule the above kinetic activity factor is easily calculated, since the velocity of the process $A + B \rightarrow (X)$ is proportional to the probability of A and B getting into the critical state (X). This process being measurably slow the critical state must be characterized by a high degree of improbability.

The complete expression for the velocity of the bimolecular reaction according to this theory is consequently:

$$h = k\, c_A\, c_B \frac{f_A f_B}{f_X} \tag{2}$$

For other methods leading to related expressions see Bjerrum (18) and Christiansen (39).

Expression (2) has been verified most conspicuously in ionic reactions. From what is known of the effect of ionic charge upon the activity coefficient it may be concluded that a positive salt effect, i.e., a rise in the velocity on addition of salts, is to be expected from equation (2) if the ionic reactants carry charges of the same sign, while a negative salt effect or decrease in velocity is predicted in the case of ions of opposite sign. This is exactly what is borne out by experience. The magnitude of the concentration effect in dilute solutions may be calculated from the expression of Debye-Hückel for the dependence of the activity coefficient upon the concentration (47). This theory yields the formula (36):

$$\log_{10} f = -0.5\, z^2 \sqrt{\mu} \tag{3}$$

where z is the valence of the ion and μ is the ionic strength, defined for a simple salt solution by:

$$\mu = c \cdot \frac{z_1 + z_2}{2}$$

c denotes the equivalent concentration and z_1 and z_2 are the valences of the two ions of the salt. By substituting these expressions in (2) we get:

$$h = k\, c_A\, c_B\, 10^{z_A z_B \sqrt{\mu}} \tag{4}$$

The initial slope of the velocity-concentration curve is consequently infinite. If the equivalent salt concentration is changed from zero to 0.1 the change in velocity for two univalent ions will be about 100 per cent, and for two trivalent ions about 10^4 times the original value. These effects show what extraordinary significance must be assigned to the kinetic activity factor and demonstrates clearly the failure of the classical expressions—where the factor F is omitted—to give an even approximately correct formula for the velocity of ionic reactions. From equation (4) it can be seen that the above mentioned law relating the type of the reaction and the sign of the salt effect must be valid, and that the *numerical* value of the salt effect is independent of the sign of the ionic charges. The formula fails, however, to give exact quantitative results except for extremely dilute solutions.

In ordinary catalysis, however, the linear salt effect is of greater importance than the exponential. Before taking up the application of the formula in the linear salt effect, the relation between the new theory and the thermodynamic mass action law as well as the part played by the activity concept in this theory should be briefly considered. First of all the formula given above fulfills the obligation of yielding the thermodynamic mass action law when applied to a chemical equilibrium, e.g.

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

For the velocity from left to right we have the expression

$$h_1 = k_1 c_A c_B \frac{f_A f_B}{f_X}$$

and for the reverse process:

$$h_2 = k_2 c_C c_D \frac{f_C f_D}{f_Y}.$$

At equilibrium where the velocities must be equal, we get:

$$\frac{a_C a_D}{a_A a_B} = \frac{c_C c_D f_C f_D}{c_A c_B f_A f_B} = \frac{k_1}{k_2} \cdot \frac{f_Y}{f_X}.$$

According to the theory the critical complexes X and Y are, however identical; the right hand side of the equation is therefore a constant and the equation conforms with the thermodynamic law of mass action.

Another theory—the so-called activity rate theory—which also obeys this obligatory condition has been developed by H. Harned (93, 95, 96), W. C. McC. Lewis (103, 143) and other authors (158, 64). Here the velocity is assumed proportional to the activity of the reactants, and hence for the bimolecular process $A + B \rightarrow C + D$ we get:

$$h = k\, a_A\, a_B = k\, c_A\, c_B\, f_A\, f_B, \tag{5}$$

an expression which differs from (4) through the absence of the factor $\frac{1}{f_X}$.

The two theories lead to practically identical formulas, in the particular case of the critical complex being uncharged, i.e., if the two reacting ions carry charges of the same magnitude but of opposite sign. Such reactions can therefore naturally be mistaken as supporting the activity rate theory. In the case of the rearrangement of acetyl chloro amino benzene into p-chloro acetanilide, investigated by Harned and Seltz (96), the reaction may be considered to take place between the organic molecule, the H^+ ion, and the Cl^- ion. As shown by Bray and Livingston (22, 129) the same applies to the catalytic decomposition of hydrogen peroxide in an acid bromine-bromide solution, this reaction proceeding between the H_2O_2 molecule and the two ions Br^- and H^+. Both reactions follow equation (5) closely, since in these cases f_X is equal to unity.

For all other types of reactions the formulas of the two theories are quite different. The strong positive salt effect, displayed by reactions between ions of the same sign in dilute solutions, cannot be explained by the activity rate theory—nor can the linear effect in hydrion catalysis as will be shown later. In obvious conflict with facts, a negative salt effect is according to this theory, the only possible form of salt effect in dilute solutions. The reason why the activity rate theory nevertheless has found some supporting evidence is—aside from those cases where $f_X = 1$—that the data refer to solutions of such high concentrations as to obscure to a large extent the pure activity effects. The application of this theory to ordinary acid and basic catalysis will be dealt with below.

It is of essential importance for the salt effect in normal hydrion and hydroxyl ion catalysis—as exemplified by the inversion of cane sugar and ester hydrolysis—that the molecules of the substrate are electrically neutral. If this be the case the bimolecular reaction between the catalyst and the substrate is given by the scheme:

$$A + H^+ \rightarrow \text{Product of reaction.}$$

Application of formula (2) will yield for the catalytic velocity:

$$h = k\, c_A\, c_{H^+} \frac{f_A\, f_{H^+}}{f_X},$$

f_A, the activity coefficient of a neutral molecule, being at moderately high dilutions equal to unity, while at the same time f_{H^+} and f_X approach the same ideal value. The salt effect is consequently negligible at low concentrations, retaining for the classical expression:

$$h = k\, c_A\, c_{H^+}$$

its full validity. The value of the salt effect at somewhat higher concentrations can be determined by using the expressions for the dependence of the activity coefficient upon the salt concentration. The activitity coefficient of a neutral molecule seems—as far as our available data go—to be given by the equation:

$$-\ln f_0 = \beta_0\, c,$$

while univalent ions at moderately low salt concentrations obey the following formula (29, 36)

$$-\ln f_1 = \alpha \sqrt{c} + \beta_1\, c,$$

where α is a universal constant.

By substituting these expressions we get:

$$-\ln \frac{f_A\, f_{H^+}}{f_X} = (\beta_A + \beta_{H^+} - \beta_X)\, c,$$

and

$$h = k\, c_A\, c_{H^+}\, e^{(\beta_X - \beta_A - \beta_{H^+})\, c} \qquad (6)$$

or if the solutions are so dilute with respect to salt that the kinetic activity factor does not deviate too much from unity:

$$h = k\, c_A\, c_{H^+} [1 - (\beta_A + \beta_{H^+} - \beta_X)\, c]. \tag{7}$$

This equation states that the salt effect for the type of catalytic reactions under consideration varies linearly with the salt concentration, i.e., the total electrolyte concentration inclusive of the concentration of the catalyzing strong acid.

The coefficients β_A and β_{H^+}, and probably β_X as well, are of the same order of magnitude, so that the three species of molecules, involved in the reaction, can be expected to contribute equally to the salt effect. As to the absolute magnitude of β_A the evidence available from salting-out experiments has shown that the nature of both the A-molecule and the salt are of influence, so that neither the magnitude nor even the sign of the coefficient is certain. The same applies probably to β_{H^+} and β_X as well. An examination of the data available on the β-coefficient seems, however, to indicate that the following expression

$$1 > \beta_A + \beta_{H^+} - \beta_X > -1$$

is valid for most reactions, so that the maximum positive or negative salt effect would not exceed 10 per cent in a 0.1 N salt solution, while ordinarily it is considerably less. The data on kinetic salt effect confirm this supposition quite well. The fact that salt addition generally accelerates hydrion catalysis may also be explained from this formula, since β_{H^+} has a lower value than the corresponding coefficient for most other ions and since β_A, the coefficient for a non-electrolyte, is often negative.

The laws for hydroxyl ion catalysis are quite similar to those given above for acid catalysis; but the sign of the salt effect seems frequently to be negative in basic catalysis, e.g., in ester hydrolysis (9) and in the decomposition of triacetonamine (68, 69, 35). For the individual salt effects the ionic charge is important, the catalytic effect being independent of the positive ion, if the catalyst itself is positively charged while dependent upon the negative, and vice versa (33, 40).

This theory of the primary linear salt effect may be regarded as accounting for most of the phenomena described in this chapter, without implying, however, that all other effects are of no influence. It ought especially to be emphasized that the change in medium, brought about by addition of even moderately small quantities of salt, can affect the rate of chemical reaction noticeably. The effects of changes in the medium are probably proportional to the salt concentration, and they cannot therefore be distinguished from the effects determined by formula (7).

A linear salt effect has been found in many reactions, e.g., in the inversion of cane sugar (150), ester hydrolysis (53, 151, 169), lactone formation (97, 98) etc., many of these results having been taken as supporting the dual theory as mentioned in chapter 2. More recently, the diazo acetic ester catalysis (34) and the decomposition of triacetonamine (35) have been investigated, showing the existence of a linear salt effect—positive in the first case and negative in the latter.

The primary salt effect in the ordinary processes catalyzed by hydrions and hydroxyl ions is thus shown to be linear—i.e., proportional to the concentration—both from theoretical considerations and from experimental evidence. The conditions will of course be altered, when the substrate is no longer a neutral molecule. The effect is then determined by formula (2) as an exponential salt effect to account for the response of the ionic activity coefficients to changes in concentration. Such reactions are of great interest, but experimental data are not yet available for proving that this kind of catalysis actually exists.

The activity rate theory described previously has been based to some extent upon catalytic investigations. As the chief result in this field it has been pointed out that the activity of the catalyst and not its concentration is the essential factor in the catalysis.

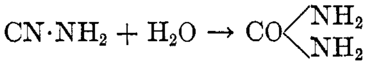
This view may possibly be traced back to Lapworth (122, 102) who attaches great catalytic significance to changes in the thermodynamic potential of the hydrion, caused for example by addition of water to an alcoholic solution. In his investigation on the catalytic decomposition of hydrogen-peroxide in presence of iodide ions Harned (93) claims proportionality between the rate of reaction and the chloride ion activity in solutions of sodium chloride and potassium chloride, a linear salt effect having been previously found for this reaction through work by Bredig and Walton (26). The activity of the catalyst has been introduced more directly in investigations by Jones and Lewis (103) on the inversion of cane sugar, by Harned and Seltz (96) on the transformation of acetyl chloro amino benzene into p-chloro acetanilide and by Harned and Pfanstiel (95) on the hydrolysis of ethyl acetate, these authors having emphasized the importance of the activity of the catalyst by more or less convincing arguments.

A thorough examination by Åkerlöf (1) of the acid catalysis of ethyl acetate in the presence of various salts at high concentrations has led to the following formula for the salt effect at constant hydrion concentration:

$$h = C\sqrt[3]{a_{H^+}}.$$

where C is a constant. Contrary to the activity rate theory the velocity is here supposed to be proportional to the cube root of the activity and Åkerlöf's equation, applied to dilute salt solutions, cannot therefore give the catalytic activity rate theory any support.

Grube and Schmid (87) have recently subjected the neutral salt effect in the acid hydrolysis of cyanamide according to the scheme:



$$CN{\cdot}NH_2 + H_2O \rightarrow CO\begin{cases}NH_2\\NH_2\end{cases}$$

to a close study with a special view to strongly concentrated salt solutions. They find the simple connection:

$$h = h_0e^{kc}, \tag{8}$$

where h and h_0 are the velocities with and without salt addition respectively, c is the salt concentration and k a constant dependent upon the nature of the salt. This equation, which shows that the same change in salt concentration produces the same percentage change in h analogous to the equation for salting out of a non-electrolyte (157), could also be made to fit other reactions, e.g. some of the systems examined by Harned and Åkerlöf quoted previously.

It is not unlikely that an equation like (8) might have approximate validity up to quite high concentrations, in which respect the concentration scale in which c is expressed is not without consequence. It is to be noted especially that equation (8), for sufficiently small values of c, can be written in the following manner:

$$h = h_0(1 + kc),$$

i.e., exactly analogous to the equation for the linear salt effect. The considerations, upon which the linear expression is based, lead in reality to formula (8), but the differences between the two equations can be neglected in dilute solutions. On the other hand the relation assumed by Grube and Schmid to exist between concentration and hydrion activity, and from which they conclude the importance of the latter in catalysis, is open to criticism. This relation is expressed as follows:

$$a = a_0 e^{k'c} \tag{9}$$

where a and a_0 are the hydrion activities with and without any salt addition respectively, c is the salt concentration and k′ a constant dependent upon the nature of the salt. Combination of (8) and (9) yields:

$$\left(\frac{h}{h_0}\right)^{k'} = \left(\frac{a}{a_0}\right)^{k}$$

or

$$h = Q \cdot a^{\frac{k}{k'}}. \tag{10}$$

This formula agrees with that of Åkerlöf, if k′/k be equal to 3, which, however, according to Grube and Schmid is not the case.

Expression (9) gives at low salt concentrations:

$$a = a_0(1 + k'c)$$

or if the concentration of acid is sufficiently low:

$$a_H = c_H (1 + k'c)$$

The hydrion activity ought therefore to vary linearly with the salt concentration—in obvious conflict with the well known connection between concentration and activity coefficient in dilute solutions. Equations (9) and (10) cannot therefore be of general validity.

Most of the experiments that have been done to construct an experimental basis for the activity rate theory of catalysis have, in order to get marked and conspicuous effects, been done at high salt concentrations. This procedure does not serve the purpose for several reasons: Firstly because the pure catalytic effect in these solutions is influenced and obscured by numerous factors, veiling the effect that is being sought. Secondly one is prevented from taking advantage of the pronounced and uniform variations with concentration shown by the activity coefficient in dilute solutions. The information obtained from a study of dilute solutions indicates beyond doubt that the important factor is the concentration of the catalyst and not its activity. The results arrived at in concentrated solutions cannot therefore be used for building up a general theory in conflict with the experimental foundation itself, but they might be combined to form empirical laws of more or less extended applicability, the experimental data being still far too scant for a satisfactory interpretation of such empirical rules.

Still one step further has been taken in support of the activity rate theory by assuming that the absolute activity of the hydrion is the governing factor in acid catalysis also when shifting from one solvent to another. This assumption in some way harmonizes with the general velocity theory developed by Dimroth (48). The fact that hydrochloric acid catalyzes lactone formation much more strongly in moist ether than in aqueous solutions of the same concentration, is explained by Taylor (172) as due to differences in the activity of HCl in the two solvents. On this point it will be sufficient to refer the reader to previous considerations (31) regarding the effect of a change in the medium.

In a conscious opposition to the concentration theory Kuhn and Jacob (116) have made the assumption that hydrion catalysis, particularly for the mutarotation of glucose, but also in general, is not proportional to the hydrion concentration but to the activity of the reacting molecules. Since their results are only of moderate accuracy and their paper does not contain any discussion at all of the mass of data contradictory to their assumption we need only quite briefly consider their statements.

Their own measurements can indeed, although with some difficulty, be interpreted in favor of the concentration theory. The difficulties lie in the authors' failure to state the acid concentration, giving only the p_{H^+} values electrometrically measured. For the most suitable experiments, viz., the measurements at $p_{H^+} = 2.09$ and 1.05 the ratio between the catalytic velocity (the total velocity minus the spontaneous) and the hydrion activity at the two concentrations is found to be 3.5 and 3.0 respectively. If the concentration is substituted for activity, the corresponding values will be 3.9 and 4.0 showing a much better agreement. The data of Kuhn and Jacob correspond, therefore, better to the concentration theory than to the activity theory.

The authors did not carry out this calculation. Their arguments for assuming proportionality with the activity are based upon their salt effect experiments. 1.0 N lithium chloride accelerates the reaction about 30 per cent in 0.1 N HCl, while the same concentration of LiCl is of no effect in 0.001N acid. This difference in the effects at different HCl concentrations is explained by the authors on the basis of changes in f_{H^+} caused by the salts. How this assumption can be made to account for the activity proportionality is not obvious.

The salt effect experiments are explained most simply by assuming the spontaneous reaction to be retarded about 10 per cent and the catalytic reaction to be accelerated about 40 per cent by 1 N LiCl. This is by no means unreasonable, since corresponding salt effects are known from analogous reactions. Both these effects are expected to be linear.

Although based upon an unsound theoretical foundation which weakens from the outset the whole conduct of their work the paper of Kuhn and Jacob contains in some respects an interesting experimental contribution to the study of the glucose transformation as will be described further in the last chapter.

V. SECONDARY SALT EFFECT

While the primary salt effect as pointed out in the previous chapter is a direct kinetic consequence of changes in the activity coefficient of the molecules involved, the effect called the secondary salt effect (27, 38, 37, 35) is of an indirect nature, caused by a displacement in the equilibrium on addition of salt, this displacement either increasing or decreasing the concentrations of ions, participating in the reaction.

In a well known investigation on inversion velocity, Arrhenius (13) showed in 1899 that the catalytic inversion of cane sugar is much more sensitive to addition of neutral salts like KCl when the catalyst is a weak acid than when it is a strong acid. He interpreted this phenomenon as the effect of an increase in the dissociation of the weak acid and consequently also in the number of catalyzing hydrions, connecting this change in dissociation with the general deviations from the ideal osmotic laws already at that time known to exist in the case of strong electrolytes. This explanation given by Arrhenius must be considered as being correct also from the standpoint of more modern ideas. In order to get a thorough understanding of the phenomena involved, i.e., to get a quantitative theory for the secondary salt effect, it is necessary, however, to consider the case in the full light of the modern electrolytic theory.

Numerous investigators during the last decades have developed a new concept of what has been called the anomalies of strong electrolytes. Van Laar (118, 119) seems to have been the first to advance the view that salts like potassium chloride and sodium chloride are ionized in aqueous solution, to a much higher extent than concluded from conductivity data. On this basis the electrolytic conductivity cannot be taken as a measure of the degree of dissociation—as was done by Arrhenius—but the variation in the molar conductivity with concentration has to be ascribed to the electric forces acting between the ions. The same idea has been developed independently of van Laar by Bjerrum (17), Milner (140) and Ghosh (84, 85, 86). While Milner and Ghosh have aimed at a theoretical evaluation of the effects caused by the electrostatic forces between the ions the credit for having been the first to realize the great chemical importance inherent in the theory of the complete dissociation of strong electrolytes rests with Bjerrum. He has also shown that the chemical phenomena in salt solutions are easily amenable to a simple treatment from the new viewpoints by applying the convenient concept activity—originally introduced by G. N. Lewis (126)—and the corresponding activity coefficient.

The following formula has been given by Bjerrum for the activity coefficient of an ion:

$$-\ln f = a\sqrt[3]{c} \tag{1}$$

where *c* is the salt concentration and *a* a constant dependent upon the ion charge and the type of salt. This expression, representing the logarithm of the activity coefficient as proportional to the cube root of the concentration, seems to hold quite well for concentrations from 0.01N to 0.1N, while a corresponding square root formula appears to be more exact at lower concentrations. As mentioned before the following formula (29, 36), is applicable also at somewhat higher concentrations:

$$-\ln f = \alpha\sqrt{c} + \beta c \tag{2}$$

It is beyond the scope of the present treatise to go into the details of this theory, and reference will therefore only be made to some reviews (14, 49, 100, 147) containing the chief characteristics of the theory. Concepts like "activity" and "activity coefficient" are supposed to be familiar to the reader.

An important contribution to the quantitative understanding of the conditions in solutions of strong electrolytes has been given recently by Debye and Hückel (47), who have developed theoretically an expression for the activity coefficient in dilute solutions, given in simplified form by the following formula:

$$-\log_{10} f = \frac{1.81}{(DT)^{3/2}} \cdot 10^6 z^2 \sqrt{\mu} \tag{3}$$

where μ denotes the ionic strength (see chapter 4), z the valence of the ion, D the dielectric constant of the medium and T the temperature, while at higher concentrations an additional term has to be included containing the first power of the concentration. This formula agrees well with (2), developed chiefly on an empirical basis.

The great value of these investigations in the interpretation of kinetic phenomena is due to the fact that both the kinetic activity factor and the shift of equilibrium which determines the secondary salt effect, depend upon the activity coefficients of the ions. This shifting of the equilibrium can be calculated in the following way:

If the catalyst be for example, acetic acid, dissociating according to the scheme:

$$\mathrm{EH} \rightarrow \mathrm{E}^- + \mathrm{H}^+,$$

the thermodynamic mass action law yields:

$$\frac{a_{\mathrm{E}^-}\, a_{\mathrm{H}^+}}{a_{\mathrm{EH}}} = \mathrm{K},$$

where a is the activity. Substituting $a = cf$:

$$\frac{c_{\mathrm{E}^-}\, c_{\mathrm{H}^+}}{c_{\mathrm{EH}}} \cdot \frac{f_{\mathrm{E}^-}\, f_{\mathrm{H}^+}}{f_{\mathrm{EH}}} = \mathrm{K},$$

A change in the degree of dissociation must consequently follow when the factor $\frac{f_{\mathrm{E}^-}\, f_{\mathrm{H}^+}}{f_{\mathrm{EH}}}$ is changed in the presence of electrolytes. For acetic acid in 0.01N solution f_{E^-} and f_{H^+} are reduced from about 0.98 to 0.7–0.75 by addition of salt up to 0.1N, while f_{EH} may be considered as approximately unchanged and equal to unity. The dissociation of the acetic acid has consequently to increase about 40 per cent, and a similar increase has to be expected in the catalytic effect, since the hydrion concentration is the deciding factor in the catalysis.

Schreiner (161) has worked out the dissociation of acetic acid from this point of view, finding agreement with the theory, and similar verifications have been obtained in numerous other measurements (27, 28, 38).

The secondary effect exerted by salts upon catalysis by weak acids depends according to this example upon changes in the activity factor, these changes being chiefly a function of the valence type of the weak electrolyte. The influence of salt in lowering the activity coefficient is greater the higher the charge of the ion—as shown by numerous experimental data (36), and as follows from the Debye-Hückel theory. For aqueous solutions at 20°C. the Debye-Hückel formula can be written:

$$-\log_{10} f = 0.5\, z^2 \sqrt{\mu} \tag{4}$$

where z is the valence of the ion. If this formula be used for calculating the activity factor in the dissociation equilibrium:

$$A \rightleftarrows B + H^+,$$

we get

$$-\log \frac{f_B\, f_{H^+}}{f_A} = (z_B^2 - z_A^2 + 1)\, 0.5 \sqrt{\mu}$$

or

$$\log \frac{f_B\, f_{H^+}}{f_A} = z_B \sqrt{\mu}$$

and the corresponding mass action expression becomes:

$$\frac{c_B\, c_{H^+}}{c_A} = K \cdot 10^{-z_B \sqrt{\mu}} \tag{5}$$

The dissociation constant is consequently independent of the salt concentration when z = 0, i.e., when the B-molecule is uncharged. Hence the equilibrium

$$NH_4^+ = NH_3 + H^+,$$

where $B = NH_3$, will not be shifted by addition of salt at moderately low concentrations. The acidity created by the above dissociation scheme or by a dissociation of the same electrical type will therefore be governed by particularly simple laws.

If z_B is negative, salt addition will evidently increase the dissociation of the acid as shown previously in the case of acetic acid. This effect will be designated a positive salt effect. It will be still more pronounced, if the charge of the acid itself is negative, as for example for the acid oxalate and tartrate ions.

If z_B is positive, the dissociation of the acid will decrease on addition of salt, the salt effect being in this case negative; as an example one may take the "hydrolytic" decomposition of the chromic ion (38), which can be considered most simply as a dissociation according to the scheme:

$$\left[\mathrm{Cr}\ (\mathrm{H_2O})_6\right]^{+++} \rightleftarrows \left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\ (\mathrm{H_2O})_5\end{matrix}\right]^{++} + \mathrm{H}^+$$

The secondary salt effect in hydroxyl ion catalysis can be calculated in a similar way by considering the equilibrium:

$$\mathrm{B} \rightleftarrows \mathrm{A} + \mathrm{OH}^-$$

The corresponding equations will be:

$$\frac{c_A\, c_{OH^-}}{c_B} \cdot \frac{f_A\, f_{OH^-}}{f_B} = K,$$

$$\log \frac{f_A\, f_{OH^-}}{f_B} = -\, z_A \sqrt{\mu},$$

and

$$\frac{c_A\, c_{OH^-}}{c_B} = K \cdot 10^{z_A \sqrt{\mu}}, \tag{6}$$

A positive salt effect ought consequently to be obtained, when z_A is positive, for example when the base is uncharged like NH_3 or when it carries positive charges. The salt effect is zero when $z_A = 0$, for example in the equilibrium:

$$\mathrm{E}^- + \mathrm{H_2O} \rightleftarrows \mathrm{EH} + \mathrm{OH}^-,$$

and finally negative salt effect has to be expected, when z_A is negative, e.g.:

$$\mathrm{PO_4^{---}} + \mathrm{H_2O} \rightleftarrows \mathrm{HPO_4^{--}} + \mathrm{OH}^-,$$

when $z_A = -2$.

As long as the solutions are sufficiently dilute with respect to salt, for example not exceeding 0.01N, the formulas (5) and (6) will permit of a fairly exact quantitative calculation of the salt effect. The deviations appearing at higher concentrations are probably as a first approximation best given as varying linearly with the salt concentration, the proportionality factors involved being of the same order of magnitude as the salting-out coefficient for non-electrolytes and the coefficient β in formula (2).

It should be noted that the magnitude of the effect here discussed is largely a function of the ratio in which the molecules are present in the equilibria considered. Three separate cases might here be distinguished. Consider the equilibrium:

$$A \rightleftharpoons B + H^+$$

and suppose the catalysis to be due to the hydrions. If $c_B = c_{H^+}$ (I), that is the solution can be made up from the weak electrolyte A and the solvent alone the salt effect will fall upon B and H^+ to the same extent. If $c_B >> c_{H^+}$ (II), i.e., in the case of a buffer solution, the whole change in concentration will be restricted to the hydrion, and the catalytic effect will be double that in case (I); and finally if $c_{H^+} >> c_B$ (III), the solution is regulated with respect to B-molecules and the secondary salt effect equal to zero.

It is evident from what has been stated that the secondary salt effect is dependent upon a number of factors and so may prove of a rather complicated nature. It is important therefore that the theory has been amply verified. The law of secondary salt effect is obeyed not only when a salt like KCl is added to acetic acid in the inversion of cane sugar or for the hydrolysis of esters [Arrhenius (13, 27)] but also in cases where salts with a common ion are added to weak acids or bases. The older data show on closer examination that considerable deviations from the simple classical laws exist. For instance when sodium acetate is added to acetic acid or when ammonium chloride (10, 35) is added to ammonia results are obtained which conform to the requirements of the secondary salt effect.

Furthermore the influence of differences in the type of dissociation has been verified by recent investigations. A strong negative salt effect has been found for the basic catalysis of nitroso triacetonamine (35), when the reaction proceeds in a mixture of secondary and tertiary phosphates. A negative effect has also been found for the diazo acetic ester catalysis in solutions of chromic salts (38). These phenomena are all in agreement with the theory of the secondary salt effect.

The considerations made in this and the preceding chapter in connection with the development of the theory of primary and secondary salt effects clearly show the inadequacy of attempting to relate the salt effects simply to the p_{H^+} values of the solutions. These values are only of indirect interest in the question of the rate of reaction—as pointed out before, while at the same time they fail to take into account the general change in medium brought about by shifting the equilibria in the solution. It has been overlooked in the numerous attempts of this kind not only that the p_{H^+}-function (or potential in general) is but indirectly of significance in the question of reaction rate, but also, that the effect of added salts is, as shown, very pronouncedly dependent upon the general nature of the system under investigation.

VI. THE ACID-BASIC FUNCTION

For a complete understanding of the phenomena in acid and basic catalysis, an analysis of the very concept of acids and bases is necessary. The historical development of this concept, as outlined for example in S. M. Jörgensen's (104) and Ramberg's (152) expositions of the subject, gives an impression of very fluctuating views in the course of time. Here we are not going to deal with the historical evolution but try to present the ideas to which recent studies of the nature of acids and bases have led.

The definition of an acid deduced from Arrhenius' dissociation theory may be considered as the one generally accepted nowadays. According to this any substance splitting off hydrions on solution in water is an acid. The definition in this form is hardly consistent since certain properties are attributed to the substance under circumstances different from those under which the observations are made. A substance ought to be pronounced an acid under certain conditions only if hydrions are released from it under the same conditions. Pure acids like acetic acid and nitric acid will perhaps not be considered as acids by this definition, if hydrions are undetectable when the substances are in a pure state, i.e., in the absence of solvent.

It is quite possible, however, that a substance which does not give off hydrions under certain conditions can nevertheless, possess properties which justify the application of the term acid. This is easily understood when realizing that the reaction indicating the acidity of the acid:

$$A \rightleftarrows B + H^+ \tag{1}$$

is not identical with the reaction governing the dissociation in a solvent, since it is not the free but only the solvated hydrions which attain perceptible concentrations in solution. The real dissociation always proceeds in cooperation with the solvent, and the degree of dissociation is dependent upon the readiness with which this cooperation is afforded. In defining an acid, however, it is preferable, to disregard this influence of the solvent and instead of the true process of dissociation to use scheme (1) as our definition of the acid A, expressing merely the splitting off of a hydrion, without saying anything concerning its subsequent fate.

Now considering the definition of a base it is well known that, since the formulation of the dissociation theory this has been closely associated with the hydroxyl ion. A substance, according to this view, is considered a base when it splits off hydroxyl ions in aqueous solutions. This definition, however, is much too narrow, even after being modified to include the solvent effect as in the definition of an acid given above. Those substances, designated as bases, are, quite generally and independently of the solvent, characterized by their *ability to take up hydrions.* Scheme (1) will consequently express both the acid character of the molecule A and the basic character of the molecule B and can therefore be used as the schematic definition for both; namely,

$$\left.\begin{array}{l} \mathrm{A} \rightleftarrows \mathrm{B} + \mathrm{H}^+ \\ \mathrm{Acid} \rightleftarrows \mathrm{Base} + \mathrm{H}^+ \end{array}\right\}. \qquad (2)$$

A base is necessarily formed whenever a substance functions as an acid giving off hydrions, and conversely an acid has always to appear when a base takes up a hydrion. Acids and bases related to each other by such a scheme are designated as conjugate acids and bases.

The advantages of this definition are developed elsewhere (30) and will not be treated in detail here. It suffices to mention that the scheme gives in all cases a logical and adequate expression of the properties which are generally recognized as being characteristic of acids and bases. The close relation between these two groups of substances is explained by their fundamental relation to the hydrion, while their unique position as compared with all other chemical substances is due to the uniqueness of the hydrion, consisting solely of an atomic nucleus. The only possible parallel to this class of substances is the oxidation-reduction system, in which the electron plays the same rôle as does the hydrogen nucleus or proton in the acid-base-system.

Furthermore the thermodynamic significance of the scheme (2) ought to be emphasized. Even if the two opposed reactions in the equilibrium given by (2) fail in giving the correct kinetic picture of the process, the thermodynamic mass action law may nevertheless be applied to the equilibrium, irrespective of whether or not actual existence is assigned to the hydrion. This point will be taken up in the next chapter in the problem of obtaining a suitable standard for the concepts of acidity and basicity as well as of acid and basic strength.

There can be inferred from scheme (2) as a result of particular importance that conjugate acids and bases cannot carry the same electric charge. If the acid is electrically neutral, the base must be negatively charged, e.g., in the acetic acid-acetate ion system.

$$\mathrm{EH} \rightarrow \mathrm{E}^- + \mathrm{H}^+,$$

while a neutral base requires a positively charged acid, e.g.

$$NH_4^+ \rightleftarrows NH_3 + H^+.$$

In this respect the new definition shows a distinctive departure from the old theory in which the electric neutrality of the acid and basic molecules was considered an essential feature (137). According to the new concept molecules exert their acid or basic functions independently of their electric charges, the acid and basic properties being ascribable in the same way to ions and uncharged molecules.

The recognition of this point of view implies an unusual extension of the acid-base concept, but at the same time creates a simplification and conformity in the treatment of the phenomena involved both in aqueous and non-aqueous solutions. Reference is made to earlier papers on this subject (30, 32).

The fact that a molecule may exhibit acidity or basicity independent of its charge does not mean, of course, that the charge is without influence upon the strength of the acid and the base. Nor does the omission of the solvent in scheme (2) imply that the solvent is immaterial for the manifestation of the acid and basic properties. On the contrary, as shown in chapter 7, the influence of the solvent is of the greatest importance. First of all the dissociation of an acid, as mentioned, takes place only under the influence of the solvent. For acetic acid in water the dissociation equilibrium will be given by the scheme:

$$EH + H_2O \rightleftarrows E^- + H_3O^+$$

in which EH and H_3O^+ according to (2) act as acids and H_2O and E^- as bases. It is reasonable to assume that the hydrion unites with one molecule of water, just as it takes up one molecule of ammonia. This is in agreement with the results obtained by numerous authors (83, 62, 90, 63, 160, 134, 32). The normal, hydrated hydrion, or the oxonium ion, may therefore be considered as an acid, possessing special significance not in any essential respect but only because of the practical consideration that its conjugate base is the most common solvent, water.

Addition of the base, ammonia, to the solvent water will in the same manner give rise to the equilibrium:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-,$$

where NH_3 and OH^- function as bases and H_2O and NH_4^+ as acids. The different rôle played by the water in these two examples makes clear its amphoteric character and may serve as an example in considering the *double acid-base equilibrium*, which will be established in a system comprising two pairs of conjugate acids and bases:

$$\text{Acid}_1 + \text{Base}_2 \rightleftarrows \text{Acid}_2 + \text{Base}_1, \tag{3}$$

In conformity with this scheme, the reaction taking place on mixing an acid and a base consists in the formation of a new acid and a new base. This result is in marked opposition to the usual ideas according to which the resulting reaction is a "neutralization."

$$\text{Acid} + \text{base} \rightleftarrows \text{salt} + \text{water} \tag{4}$$

Since, however, the concepts of "neutralization" and "neutrality," as has been shown before (30), are illogical and misleading, it seems desirable to subject scheme (4) which is fundamental to these concepts to a closer examination especially as to its relation to (3). One would expect that such an analysis would lead to a more satisfactory understanding of the "salt" concept and its relation to that of acids and bases than has hitherto been obtained.

The extent, to which acids and bases react upon mixing, is as is well known entirely dependent upon their strength. For "strong" acids and bases in aqueous solution the reaction is practically complete; for acetic acid and ammonia it is appreciably incomplete; for acetic acid and aniline only 50 per cent complete; while finally phenol and aniline scarcely react at all. Theoretically the reactions can be considered as incomplete in all cases, and the nature of the acid and basic properties is consequently analyzed most generally by taking acids and bases which do not exhibit extreme effects.

For that purpose consider the reaction between acetic acid and aniline

$$CH_3COOH + C_6H_5NH_2 \rightleftarrows CH_3COO^- + C_6H_5NH_3^+ \qquad (5)$$

and the reaction between acetic acid and the propionate ion:

$$CH_3COOH + C_2H_5COO^- \rightleftarrows CH_3COO^- + C_2H_5COOH \qquad (6)$$

The extent of reaction in both these cases is about 50%, so so that the concentrations of the two reciprocal systems are about the same at equilibrium. Scheme (5) taken from left to right denotes the reaction between a neutral acid and a neutral base and in the opposite direction a reaction between an ion base and an ion acid, while scheme (6) gives in either direction the reaction between an ion base and a neutral acid. Both reactions conform completely to scheme (3).

It is immediately apparent by comparison with scheme (4) that the water molecule is absent in (5) and (6). This might perhaps be considered as immaterial, since in aqueous solution it is always possible to introduce a water molecule in the equation by assuming hydration to take place. The effect of such a water molecule could not be distinguished, however, from the ordinary solvation effect, pertaining to all reactions proceeding in a solvent, and therefore cannot furnish a distinguishing characteristic in acid and basic reactions.

Furthermore it is seen in the case of reaction (4) that acetate ion + anilinium ion, i.e., acid and base with opposite charges, serve as a substitute for the "salt" in scheme (4). The definition of a salt given by (4) corresponds consequently in this respect to the ordinary concept of salts as substances being ionized into two or more oppositely charged ions. The product of reaction in (6), however, cannot possibly be covered by the salt concept, nor does the product in scheme (5), taken from right to left, viz. acetic acid + aniline, justify the application of this term.

Hence "salt formation" in reactions between acids and bases becomes restricted to cases, in which the acid-base system reacting is uncharged. If it be recognized, therefore, that the electric charge does not affect the characteristic properties of acids and bases, the conclusion seems inevitable that also "salt formation" is deprived of the rôle hitherto assigned to it in acid-basic reactions thus leaving the relation between salts, acids and bases involved in scheme (4) without general significance.

The usual scheme (4), comprising the old views on acid and basic reactions, is therefore certainly not adequate according to the new concepts. It ought to be stated, however, that this scheme has originated from considerations on "strong" acids and bases in aqueous solution. Since the base in this case is the hydroxyl ion, the "process of neutralization" will certainly be accompanied by the formation of water. This is naturally not in conflict with our point of view, according to which H_2O might take part in the reaction just as well as any other base and acid. If both the acid and the base are strong, the whole reaction will correspond to a water formation, thus:

$$H_3O^+ + OH^- \rightleftarrows 2H_2O, \tag{7}$$

and if the acid is weak and the base strong:

$$CH_3COOH + OH^- \rightleftarrows CH_3COO^- + H_2O \tag{8}$$

or the acid strong and the base weak:

$$H_3O^+ + NH_3 \rightleftarrows NH_4^+ + H_2O, \tag{9}$$

water and no salt will be formed. Previously it has been customary to consider $Na^+ + OH^-$ and not OH^- alone as the base; in the same way the term acid has been applied to $H_3O^+ + Cl^-$ and not to H_3O^+ alone. The products in the above equations would then be:

$$2H_2O + Na^+ + Cl^- \qquad (7)$$
$$H_2O + Na^+ + CH_3COO^- \qquad (8)$$
$$H_2O + NH_4^+ + Cl^- \qquad (9)$$

in agreement with the old idea of a salt formation. It seems self-evident, however, that an admixture of ions—already present in the original solutions—can hardly be characteristic of a chemical process, and also that the systems $H_3O^+ + Cl^-$ and $Na^+ + OH^-$ deserve the designation of salts just as much as do $Na^+ + Cl^-$, $Na^+ + CH_3\ COO^-$ or $NH_4^+ + Cl^-$. The acid-base reaction would then according to the old point of view hardly represent a salt formation, but rather a salt transformation.

Accordingly, since we are justified in concluding that the usual scheme:

$$\text{acid} + \text{base} \rightleftarrows \text{salt} + \text{water}$$

does not express the essential and characteristic features in the reaction between acids and bases, it becomes evident that the conception of a salt—if at all accessible for a proper delimitation—has to be established by definitions which have no relation to the conception of acids and bases.

E. Franklin (70) has pointed out that the common scheme (4) for acid, base and salt can be replaced in many reactions by other schemes in which the part played by H_2O is taken by other substances such as HF, H_2S, H_3N, etc., thus making a distinction between the "water system," the "hydrogen fluoride system" etc. for acid, bases and salts. These considerations being primarily systematic in character, do not add anything new concerning the characteristic functions of acids and bases. The objections brought against the ordinary ideas on the "water system," may be transferred unchanged in principle to Franklin's systems.

VII. ON THE STRENGTH OF ACIDS AND BASES

To the considerations on the acid-basic function given in the preceding chapter it is necessary to attach a definition of acid and basic strength as well as of the concepts of acidity and basicity. These terms have been confined primarily to aqueous solutions or, in any case, to solutions of constant environment, without much consideration as to how the concepts can be extended to include variations in solvent. Since in aqueous solutions acidity is most conveniently defined as the hydrion activity or the hydrion potential, it would appear reasonable to define the acidity of any homogeneous system as the hydrion potential in that system. Such a definition would be similar to the one suggested by Lapworth (123), whose views on this point, however, are far from being clear. Basicity is then the reciprocal value of the activity or the negative value of the hydrion potential.

Measurements of acidity and basicity, defined in this manner, could then, in principle, be carried out by determining the potential difference between two reversible hydrogen electrodes, one dipping into a standard solution of unit hydrion activity and the other into the solution in question, both solutions being brought to the same electrical potential. The activity concept to be used here is the same as the one originally proposed by G. N. Lewis, identity of activity of a substance in two solvents indicating that also its chemical potential is the same in these solvents. This activity may be called the absolute activity in order to avoid ambiguity. The activity of an acid is of course an entirely different concept from that of acidity since the former depends not only upon the H^+ ion but also upon the corresponding anion.

While fixing the conception of acidity and basicity by a theoretical definition is thus of no difficulty the problem of obtaining a general measure of *acid and basic strength* may appear a little more complicated. In conformity with the dissociation theory, it has become customary to determine the strength of an acid by its dissociation constant in dilute aqueous solution. This method is excellent also for non-aqueous solutions, as long as the problem is only to compare the strength of various acids in the same medium. Constancy of the medium obviously requires that the concentration of the acids under investigation should be very low, since a solution of finite concentration really is a medium different from the pure solvent.

The "dissociation constant" is however no longer a simple measure of acid and basic strength, when the medium is changed. It would therefore hardly be rational to use this constant for comparing acid strengths in different media. In searching for a more general measure of the strength, it would seem expedient to relate the question of strength to the general concept of acidity and basicity. Keeping in mind our scheme of definition:

$$A \rightleftarrows B + H^+$$

we will decide to measure the strength of acids and bases by the acidity and basicity, respectively, exhibited in the solutions under comparable conditions, i.e., when the ratio between the concentrations of acid and base is a constant. If unity is chosen for this constant ratio, we get the expression:

$$\frac{c_B}{c_A} \cdot a_{H^+} = K_{Acid} \tag{1}$$

as a measure of the acid strength for variations of both the acid and the medium, and similarly for the basic strength

$$\frac{c_A}{c_B} \cdot \frac{1}{a_{H^+}} = K_{Bas.} \tag{2}$$

The constants thus defined, for which the term *acidity constant* and *basicity constant* should be used, are—as a closer study shows—well adapted as measures of acid and basic strength.

In the above equations c refers to the stoichiometric concentrations of the acid and base involved, irrespective of their solvation in the solution. It is therefore very probable that what are called c_A and c_B for the same acid-base system in different solvents actually correspond to entirely different A- and B- molecules. It might perhaps have been preferable in the definition of $K_{Acid.}$ and $K_{Bas.}$ to let c_A and c_B denote the concentrations of the real, free A- and B-molecules, if it were not for our limited knowledge of the state of solvation, which does not suffice for calculating the concentration on this basis.

The above constants differ from the usual constants of dissociation by containing a_{H^+}—the absolute activity of the hydrion—instead of the hydrion concentration. One might wonder whether the substitution for c_A and c_B of the corresponding absolute activities would carry the problem still a step further. The strength constant defined in this way:

$$\frac{a_B}{a_A} a_{H^+} = K_{Act.}$$

is a real thermodynamic constant, the activity constant, quite independent of the medium, and this K might therefore seem suitable as an absolute definition of the acid strength.

A closer study, however, will easily reveal the failure of this method. The quantities involved in $K_{\text{Acid.}}$ viz. the absolute activity of the hydrion and the stoichiometric concentrations of A and B, are comparable for variations both of the acid and of the solvent, whereas the activities a_A and a_B entering in the definition of $K_{\text{Act.}}$ can quite well be compared for the same acid in different media, but by no means for different acids in the same medium. It is for instance impossible to measure the activity of hydrochloric acid in relation to the activity of acetic acid, before both of these values have been fixed by an arbitrary convention. Then, however, the strength constant $K_{\text{Act.}}$ will become a function of this convention and consequently will not afford the absolute measure sought for. For instance, this standardization might be brought about by assuming activity and stoichiometric concentration to attain the same value in ideally dilute aqueous solutions, as is usually done in the thermodynamic treatment of electrolytes dissolved in water. $K_{\overline{\text{Act.}}}$ would then be identical with $K_{\text{Acid.}}$ in the special case where water is the medium. A more general measure of acid and basic strength would be possible only if a particular state were found, which could represent a sort of general and ideal reference state. The attenuated vapor is actually such an ideal state, and from a theoretical point of view the best solution of the problem would be to refer the acid and basic strength to the vapor state. The activities of A and B would then be equal to the concentrations in the vapor system, and the acid strength would be the acidity in an attenuated vapor phase at equal concentrations of A and B. A practical application of this principle is precluded, however, since at least two different species of electrically charged molecules are involved in the acid-basic equilibrium.

Maintaining therefore the measures of acid and basic strength given above, viz:

$$\frac{c_B}{c_A} \cdot a_{H^+} = K_{\text{Acid.}}, \quad \frac{c_A}{c_B} \cdot \frac{1}{a_{H^+}} = K_{\text{Bas.}}$$

the next step will be to investigate more closely the influence of medium and ionic charge type upon these constants.

By introducing the relation between the absolute activity a, the absolute activity coefficient f and the concentration:

$$a = cf,$$

the expression for the acidity constant may be transcribed as follows:

$$K_{\text{Acid.}} = \frac{c_B}{c_A} \cdot a_{H^+} = \frac{a_B}{a_A} \cdot a_{H^+} \cdot \frac{f_A}{f_B},$$

in which $\frac{a_B}{a_A} \cdot a_{H^+} = K_{\text{Act.}}$ is a thermodynamic constant for each particular acid. Variations in the acidity constant by changing from one medium to another are consequently determined only by the ratio between the absolute, stoichiometric activity coefficients f_A and f_B and are notably not—as shown later to be the case for the dissociation constant—dependent upon the acid or basic character of the medium. The stoichiometric coefficients f_A and f_B include all the effects—especially also the solvation effect—produced by a change in medium, for which reason the variations in f_A and f_B with the medium are undoubtedly of an individual character. Nevertheless it can be stated as a general rule governing the dependence of this change upon the ionic charge, that the higher the charge on the ion the greater will be the increase in its activity coefficient on changing from a medium of high dielectric constant to one of lower dielectric constant. If a series of acids of different electric charges: A^-, A^0, A^+, A^{++} etc. be considered, the changes in f for these acids and the corresponding bases, when the medium is changed for example from water of high dielectric constant to alcohol of lower dielectric constant, will come out according to the following scheme:

Acid	Base	f_A	f_B	$\frac{f_A}{f_B}$	$K_{\text{Acid.}}$
A^-	B^{--}	+	++	−	−
A°	B^-	0	+	−	−
A^+	B°	+	0	+	+
A^{++}	B^+	++	+	+	+

where an increase is denoted by + and a decrease by −. This scheme represents clearly the effect that the medium exerts upon the acidity constant by virtue of its dielectric constant, since the ratio $\frac{f_A}{f_B}$, as shown previously, determines the change in $K_{\text{Acid.}}$ Thus on proceeding from water as a solvent to alcohol, the constant for acetic acid of type A° will decrease, while it will increase for the ammonium ion, which is of type A^+. The change will of course be opposite for the basicity constant, which is the reciprocal of the acidity constant of the conjugate acid.

The above rule that a decrease in the dielectric constant produces a higher increase in the activity of the ion, the higher the numerical value of the electric charge, follows simply from the electrostatic formula for the potential of a spherical particle in a medium of dielectric constant D:

$$\psi = \frac{\epsilon z}{Dr}$$

where ϵ is the unit charge of electricity, z the number of these charges on the particle and r the radius.

The electrical energy of the particle is then:

$$E = \frac{\epsilon^2 z^2}{2\ Dr}$$

and the work which can be gained by transference from medium 1 to medium 2:

$$A = \frac{z^2\epsilon^2}{2r}\left(\frac{1}{D_1} - \frac{1}{D_2}\right). \tag{3}$$

This work may also be written:

$$A = k\ T \ln \frac{f_1}{f_2} \tag{4}$$

where f_1 and f_2 are the absolute activity coefficients in medium 1 and 2, respectively. Hence:

$$\ln \frac{f_1}{f_2} = \frac{z^2\epsilon^2}{2\ rk\ T}\left(\frac{1}{D_1} - \frac{1}{D_2}\right) \tag{5}$$

By introducing:

$$K_{Acid.} = K_{Act.} \frac{f_A}{f_B} \qquad (6)$$

and

$$z_A = z_B + 1$$

we get:

$$\ln \frac{K_{Acid.\,(1)}}{K_{Acid.\,(2)}} = \frac{\epsilon^2}{2\ k\ Tr} \left(\frac{1}{D_1} - \frac{1}{D_2}\right) (2\ z_B + 1), \qquad (7)$$

where $r_A = r_B = r$.

Max Born (21) has made use of equation (3) for calculating ion sizes by assuming the work performed in the transference from vacuum to water to be equal to the heat of hydration. For calculation of the change in the acidity from water to methyl alcohol numerical values are now introduced:

$\epsilon = 4.77 . 10^{-10}$
$k = 1.37 . 10^{-16}$
$D_1 = 81$
$D_2 = 31$
$T = 290$
$r = 2 . 10^{-8}$

the latter value having of course only an approximate and uncertain character. By substitution:

$$\log \frac{f_1}{f_2} = 62.2 \left(\frac{1}{D_1} - \frac{1}{D_2}\right) z^2$$

$$\log \frac{f_1}{f_2} = 1.24\ z^2$$

and

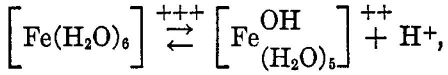
$$\log \frac{K_{Acid.\,(Methyl\,alc.)}}{K_{Acid.\,(Water)}} = 1.24\ (2\ z_B + 1).$$

The acidity constant for acetic acid, where $z_B = -1$ and for the ammonium ion where $z_B = 0$ ought accordingly to decrease and increase, respectively, by 1.24 logarithmic units on passing from water to methyl alcohol, i.e. the acid should become 17 times weaker or stronger by this change in solvent. The observed change agrees always in sign with the calculation, but the numerical value found by experiment is much higher than the calculated in spite of the fact that the value used for r is probably too small. There is nothing surprising in this disagreement, because the simplified picture of a molecule used in these calculations is certainly very far from representing its actual structure.

It has been pointed out previously (32) that the effect of the medium upon the dissociation constant may be estimated by considering the influence of a change in the dielectric constant upon the forces between the dissociation products of the acid, i.e. between the base and the hydrion. This effect depends upon the type of dissociation. On proceeding from a medium of a higher to a medium of a lower dielectric constant the forces between the charged particles will increase and the dissociation consequently decreases if the base is negatively charged and increases if the base is positively charged. The diminution in the dissociation of acetic acid:

$$\mathrm{EH} \rightleftarrows \mathrm{E}^- + \mathrm{H}^+,$$

brought about by changing the medium from water to aqueous alcohol, is therefore to be attributed largely to a corresponding rise in the electric attraction between the ions of the acid; conversely the increase in the dissociation of ferric ion:



$$\left[\mathrm{Fe(H_2O)_6}\right]^{+++} \rightleftarrows \left[\mathrm{Fe}^{\mathrm{OH}}_{(\mathrm{H_2O})_5}\right]^{++} + \mathrm{H}^+,$$

caused by addition of alcohol, is explained on the basis of an increase in the repulsive forces between the positive hydroxo-ion and the hydrion. It can be shown that this mode of attacking the problem gives the same quantitative results as the previous method.

As long as only the electric effect is taken into account the dissociation constant on changing from one medium to another may be considered as inversely proportional to the number of collisions per second between the basic molecule and the hydrion. Using the method given by J. A. Christiansen (39) the influence of the electric forces upon the number of impacts will be determined by Boltzmann's factor:

$$e^{-\frac{\epsilon}{kT}\psi_B}$$

where ψ_B, the potential at a distance r from the center of the B sphere, is given by the equation:

$$\psi_B = \frac{z_B\,\epsilon}{Dr},$$

r being the sum of the radii of the B-molecule and the hydrion. The influence of the electric forces upon the number of collisions is thus governed by the factor:

$$e^{-\frac{z_B\,\epsilon^2}{k\,T\,Dr}}$$

and consequently:

$$\ln \frac{K_{Dis.\,(1)}}{K_{Dis.\,(2)}} = \frac{\epsilon^2}{kTr}\left(\frac{1}{D_1} - \frac{1}{D_2}\right)z_B \tag{8}$$

This formula differs from (7) by containing the factor $2z_B$ instead of $(2z_B + 1)$. The reason for this difference is that (7) contains the acidity constant, whereas K in (8) stands for the following constant:

$$\frac{c_B}{c_A}\,c_{H^+}$$

the ratio between this constant and the acidity constant being $\frac{1}{f_{H^+}}$. By introducing (5):

$$\ln \frac{f_{H^+\,(1)}}{f_{H^+\,(2)}} = \frac{\epsilon^2}{2\,rk\,T}\left(\frac{1}{D_1} - \frac{1}{D_2}\right)$$

(7) and (8) are seen to be identical.

These formulas for the ratio between the absolute activity coefficients in two solvents usually yield as already mentioned values which are too low. These deviations are due first of all to the unjustified extension to real ions of the electrostatic laws for spherical particles but account ought also to be taken of both the "physical" and "chemical" solvates existing in solution in many cases.

Numerous authors have been concerned with the question of the dependence of dissociation and chemical potential upon the properties of the solvent. It is well known that Walden (177) has given the following empirical relation:

$$\frac{c_1}{c_2} = \left(\frac{D_1}{D_2}\right)^3$$

between the dielectric constants and the concentrations, for which a salt shows the same dissociation in two solvents. A corresponding equation has also been developed on theoretical grounds (16, 114). This formula gives qualitatively the same dependence of the ion potentials upon the medium as do the above equations, although the lack of concordance is otherwise obvious. Numerous experiments on solubility and E.M.F. (101, 144, 125, 94, 160) give further qualitative confirmation of these results.

Experimental data, on the influence of the medium upon what we have called the acidity and basicity constants are only meagre. The investigations have generally been concerned with the ordinary dissociation constant as for instance in recent papers by Schreiner (162) on strong acids in water, methyl and ethyl alcohol and by Bjerrum, Unmach and Zechmeister (19) on electrolytes in methyl alcohol.

A verification of the views developed here for the influence of the medium upon the acidity constant can be found, however, in a series of investigations by Michaelis and Mizutani (138, 141, 142). They determine electrometrically the hydrion potential in buffer mixtures in water and in water-alcohol solutions and compute from these measurements an expression identical with the acidity constant. A rise in the alcohol percentage from 0 to about 90 causes regularly a *decrease* in the acidity constant (2–3 logarithmic units) for neutral acids (acetic acid, benzoic acid etc.) and a corresponding, although numerically somewhat smaller, *increase* in the constant for positive ions (ammonium ion, anilinium ion etc.)—which is in good agreement with the views developed above. The changes in the dissociation of the negative acids and the amphoteric character of the amino benzoic acids are likewise in accordance with the theory. In the case of glycine the first dissociation step (the dissociation of the positively charged glycinium ion) shows a decrease in acidity on addition of alcohol, whereas the second step is not materially affected by the addition, this behavior being explained when the ampho-ion form of the glycine and ordinary singly-charged ions are supposed to possess a similar sensitivity to alcohol. In agreement with this view glycine which is highly soluble in water is mentioned as insoluble in absolute alcohol.

Whether the assumption made by Michaelis and Mizutani that the acid character of the carboxyl group is more sensitive to alcohol than is the basic character of the amino group is a question which cannot yet be definitely decided.

The acidity and basicity constants are, as mentioned before, subject to more individual effects in addition to those arising from variations in the dielectric constant and the electric charge of the acid and the base. The chemical potential of a particle in a solution depends upon the surroundings through influences other than those of the electric net charge. For some non-electrolytes the potential is for example higher in water than in benzene, while the opposite may be true in other cases. Such effects must of course be operating quite generally, an increase in the absolute activity coefficient of the acid causing the acidity constant to increase, whereas the constant will be influenced in the opposite manner by a corresponding rise in the activity coefficient of the base. For non-electrolytes the individual effects are easily accessible to observation. In the case of ions electromotive force measurements—as in the papers quoted above—may be applicable but high and difficultly accessible boundary potentials will most likely obscure the results. Comparing a series of salts with a common ion, e.g. in respect to their solubilities, it is possible to obtain data for the activity ratio of the non-common ions in the two solvents. The ratio for a single ion is however not accessible by this method.

The fact that the anilinium ion and particularly the dimethylanilinium ion shows greater increase in the acidity constant from water to alcohol than does the electrically analogous ammonium ion—as found by Michaelis and Mizutani—represents an individual activity effect which becomes intelligible in view of the considerable increase in the solubility ratio amine/ammonia brought about by changing the solvent from water to alcohol.

This survey will probably suffice for illustrating the convenience of the acidity and basicity constants as a measure of acid and basic strength. The change of the constants for the same acid and base passing from one medium to another is consistent with the terminology adopted, since an acid is said to possess the greatest strength in the medium, in which under equal conditions, i.e., at constant $\frac{c_A}{c_B}$, the highest acidity is produced. The definition gives to no less degree a rational comparison between the strengths of acids and bases in unchanged medium, since the strength in this case may also be measured by the acidity or basicity in the solution under equal conditions.

Before the investigation is extended to comprise the actual dissociation phenomena of dissolved acids and bases, the important question of the acidity and the basicity of the medium itself has to be studied. A certain acidity and basicity will exist in most solvents without any addition of acid or base, and this property of the pure solvent is highly important in acid-base equilibria. If, for example, the acidity of water is defined similarly to the acidity of an acid dissolved in water, we shall have:

$$K_{\text{Acid. }(H_2O)} = \frac{c_{OH^-}}{c_{H_2O}} \cdot a_{H^+},$$

and this quantity might well be termed the *rational acidity constant* of water. It is seen, however, that the same exact meaning cannot be assigned to this constant, since c_{H_2O} does not possess an explicit value as does the concentration of a dissolved substance. By analogy with the recognized custom of omitting the concentration of the molecules in the dissociation constant of a pure liquid, a new constant may be formulated as follows:

$$K_{\text{Acid. }(H_2O)} = c_{OH^-}\, a_{H^+}$$

which has a definite value and which therefore in contradistinction to the preceding constant may be called the *conventional acidity constant* of water.

The same complication appears also in the definition of the acidity constant for the H_3O^+-ion, since the corresponding base in this case is the pure solvent, the conditions being analogous also in the definition of the basicity constants. No difficulties are encountered, however, in the formulation of the corresponding formulas when the distinction between rational and conventional constants is maintained throughout the treatment.

The scheme, expressing the acid or basic function, together with the formulas for the two kinds of constants is given below. (Rational; conventional; acidity; and basicity are abbreviated to rat.; conv.; acid.; bas. respectively.)

The acid function for H_2O: $H_2O \rightarrow OH^- + H^+$

$$K_{\text{rat. Acid. }(H_2O)} = \frac{c_{OH^-}}{c_{H_2O}} \cdot a_{H^+}. \qquad K_{\text{conv. Acid. }(H_2O)} = c_{OH^-} \cdot a_{H^+}.$$

The base function for H_2O: $H_2O + H^+ \rightarrow H_3O^+$

$$K_{\text{rat. Bas. }(H_2O)} = \frac{c_{H_3O^+}}{c_{H_2O}} \cdot \frac{1}{a_{H^+}}. \qquad K_{\text{conv. Bas. }(H_2O)} = c_{H_3O^+} \cdot \frac{1}{a_{H^+}}.$$

The acid function for H_3O^+: $H_3O^+ \rightarrow H_2O + H^+$

$$K_{\text{rat. Acid. }(H_3O^+)} = \frac{c_{H_2O}}{c_{H_3O^+}} \cdot a_{H^+}. \qquad K_{\text{conv. Acid. }(H_3O^+)} = \frac{a_{H^+}}{c_{H_3O^+}}.$$

The base function for OH^-: $OH^- + H^+ \rightarrow H_2O$

$$K_{\text{rat. Bas. }(OH^-)} = \frac{c_{H_2O}}{c_{OH^-}} \cdot \frac{1}{a_{H^+}}. \qquad K_{\text{conv. Bas. }(OH^-)} = \frac{1}{c_{OH^-} \cdot a_{H^+}}.$$

It follows from the definitions of the constants for conjugate acids and bases, that $K_{\text{Acid }(H_2O)} \cdot K_{\text{Bas.}(OH^-)} = K_{\text{Bas.}(H_2O)} \cdot K_{\text{Acid}(H_3O^+)} = 1$, as may be seen from the above table both for the rational and conventional constants.

The corresponding expressions for other solvents may easily be formulated. The conventional basicity constant in methyl alcohol is thus:

$$K_{\text{conv. Bas. }(CH_3OH)} = \frac{c_{CH_3OH_2^+}}{a_{H^+}}$$

In order to give these constants numerical significance a general standardization of the hydrion activity a_{H^+} has to be made. This might be achieved by assuming the absolute stoichiometric activity coefficient of the hydrion equal to unity in an infinitely dilute aqueous solution, which means that $c_{H_3O^+} = a_{H^+}$ in this solution. The conventional acidity constant of water is then identical with the "dissociation constant" in the classical sense, whereas the corresponding basicity constant for water is equal to unity.

About the constants, derived from this standardization for other solvents only little is known. The hydrion potential in ethyl alcohol is, according to the E.M.F. measurements of Larsson 0.149 volts higher than the potential in water of the same hydrion concentrations($c_{H_3O^+} = c_{C_2H_5OH_2^+}$), i.e.:

$$K_{\text{conv. (Bas. }H_2O)} = 330\ K_{\text{conv. Bas. }(C_2H_5OH)}$$

Water is consequently from the conventional constants 330 times as strong a base as is ethyl alcohol, whereas the difference between the rational constants is somewhat less. Due to the existence of disturbing junction potentials, the figures thus obtained are of a considerable uncertainty.

It is of great importance to have these constants determined for different solvents. The general method for this purpose is to determine the hydrion activity in the two solvents after addition of known quantities of acid or base, sufficiently strong for producing in the solution the same concentration of the acid or base corresponding to the molecules of the medium. It might also be done by determining both the acidity or basicity constants and the dissociation constants of the acid and the base in the two solvents to be compared, as further explained below.

So far no attention has been paid to the actual "dissociation" of the acid and base, which is of such outstanding importance in the classical theory. Proceeding now to an analysis of this process of dissociation it will be well to bear in mind that the free hydrion, as shown before, hardly has any chance of existing in the solution. The "dissociation" of an acid, when introduced in a pure solvent, is therefore dependent upon the basic character of the solvent, since the "dissociation" really means nothing else but transference of the hydrion from the acid to the solvent. The reaction may be written for the acid A and water as solvent as follows:

$$A + H_2O \rightarrow B + H_3O^+ \tag{9}$$

If the solvent completely lacks the character of a base, no "dissociation" will take place and the acid will dissolve unchanged in the medium.

A reaction of the base similar to the above one (9) for the acid will take place only, when the solvent is able to yield the hydrion, necessary for the base if its basicity is to be manifested through a chemical reaction. In the case of water as a solvent the process is:

$$B + H_2O \rightarrow A + OH^- \tag{10}$$

The schemes (9) and (10) give the characteristic acid and base equilibria, independent of the charges on A and B. In spite of the reactions for acetic acid and the ammonium ion in water being quite analogous:

$$EH + H_2O \rightarrow E^- + H_3O^+ \tag{11}$$
$$NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+ \tag{12}$$

the first is normally called a dissociation and the second an hydrolysis. Similarly of the two reactions:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{13}$$
$$E^- + H_2O \rightarrow EH + OH^- \tag{14}$$

it is usual to call (13) a dissociation and (14) a hydrolytic reaction. One and the same terminology ought, however, to be used for reactions like (11) and (12) which conform to scheme (9)—and again for (13) and (14) conforming to (10). It does not follow directly from this view, however, that schemes (9) and (10) ought to be included in the same category, as has been the usual practice for acids and bases of the same charge.

A consideration of reaction (9) and analogous processes with the solvent shows that they do not represent a dissociation in the same sense of the word as applied to gaseous systems, but are in reality double decompositions, i.e., hydrolytic or solvolytic reactions. Nevertheless it seems adequate in the terminology of these reactions to disregard the solvent, the effect of which is the same in all cases, and call the process a dissociation in accord with the language historically recognized for neutral acids, the more so as the reaction in dilute solution is governed by laws conforming to the laws of a true dissociation. Once decided upon, this terminology has, however, to be carried through consistently in all cases, irrespective of the charge type. The formation of the H_3O^+-ion should always be described as a dissociation even when the dissociating acid is for example the ammonium ion or another molecule carrying an electric charge.

The application of the term dissociation to reaction (10) may be considered still more illogical, since the B-constituent does not decompose but on the contrary takes up a hydrion. Nevertheless the similarity of the two schemes (9) and (10) both representing an acid-base equilibrium makes it desirable to retain the term "dissociation" also for the case of a base dissolved in an acid solvent.

We find it convenient therefore not only to keep the term dissociation for the reactions characteristic of acids and bases in appropriate solvents but also to generalize the application to comprise all such reactions, regardless of whether the acid or base is charged or electrically neutral. The term hydrolysis, which has hitherto been applied to some of these acid-basic reactions, is in this way eliminated, and the ambiguity of having two expressions for the same phenomenon cleared away. On the other hand it would perhaps be preferable, to characterize the dissociation as being hydrolytic, alcoholytic, aminolytic etc. according to the solvent involved in the process.

For characterizing various dissociation equilibria the usual dissociation constant employed for neutral acids and bases is well suited. This constant will be denoted by K_A and K_B, for the acid and basic dissociations respectively. Here also, as for the acidity and basicity constant, the distinction between rational and conventional constants proves relevant, since the solvent participates in the process of dissociation.

If the acid and base dissociation be given by:

$$A + H_2O \rightleftarrows B + H_3O^+$$

and

$$B + H_2O \rightleftarrows A + OH^-,$$

respectively, the mass action law yields on including the solvent:

$$\frac{c_B \cdot c_{H_3O^+}}{c_A \cdot c_{H_2O}} = K_{\text{rat. A}} \tag{15}$$

and:

$$\frac{c_A \cdot c_{OH^-}}{c_B \cdot c_{H_2O}} = K_{\text{rat. B}} \tag{16}$$

and by leaving out the solvent:

$$\frac{c_B \cdot c_{H_3O^+}}{c_A} = K_{\text{conv. A}} \tag{17}$$

and

$$\frac{c_A \cdot c_{OH^-}}{c_B} = K_{\text{conv. B}}. \tag{18}$$

Without further specification K_A and K_B will be considered as denoting the conventional constants.

It follows from these considerations that an acid-base dissociation of the pure solvent can take place only if its character is amphoteric, i.e. if it possesses both acid and basic properties. The molecules of the solvent are then able both to give off and take up hydrions. For water the electrolytic dissociation is determined by the process:

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-,$$

one water molecule functioning as an acid forming OH^- and the other as a base forming H_3O^+. The analogous process in methyl alcohol will be:

$$CH_3OH + CH_3OH \rightleftarrows CH_3OH_2^+ + CH_3O^-.$$

A low electrolytic dissociation for a pure solvent is hence due to the weak development of either its acid or its basic character. The great influence which the dielectric constant is known to exert upon the dissociation is included in its effect upon the acidity and basicity constants.

Contrary to the acidity and basicity constants for which no common measure exists the acid and basic dissociation constants will be equal for the pure solvent. The previous distinction between rational and conventional constants must also be maintained here so we can write:

$$\frac{c_{H_3O^+} \cdot c_{OH^-}}{c^2_{H_2O}} = K_{rat.\,A\,(H_2O)} = K_{rat.\,B\,(H_2O)}$$

$$c_{H_3O^+} \cdot c_{OH^-} = K_{conv.\,A\,(H_2O)} = K_{conv.\,B\,(H_2O)}$$

and analogously for methyl alcohol and other media of amphoteric character.

The question now arises, what is the significance of the dissociation constants as measures of strength in relation to the acidity and basicity constants which we have introduced above as a general measure in this respect.

If the equations for the acidity and basicity constants of the solvent are combined with the expressions for the dissolved acids and bases (1)–(2) and (15)–(18), we get:

$$K_A = K_{Acid.}\, K_{Bas.\,(H_2O)} \qquad (19)$$

$$K_B = K_{Bas.}\, K_{Acid.\,(H_2O)} \qquad (20)$$

The dissociation constant of an acid is therefore the product of the acidity constant of the acid and the basicity constant of the medium, and the dissociation constant of a base is the product of the basicity constant of the base and the acidity constant of the medium. Both K_A and $K_{Acid.}$ as well as K_B and $K_{Bas.}$ are equally well suited as measures of strength so long as the medium is kept constant. We note that K_A and $K_{Acid.}$ are altered to the same extent by the change from one definite medium to another, since the ratio $K_A/K_{Acid.}$ is according to (19) independent of the nature of the acid. The bases of course follow the same rule.

For the medium itself we may write:

$$c_{H_3O^+}\, c_{OH^-} = K_{A\,(H_2O)} = K_{B\,(H_2O)} = K_{Acid.\,(H_2O)} \cdot K_{Bas.\,(H_2O)}. \tag{21}$$

The acid and basic dissociation constants of the amphoteric solvent are consequently identical and equal to the product of its acidity constants as in the case of (19) and (20) for dissolved acids and bases. This equation is valid for the rational as well as for the conventional constant.

Most quantitative measurements of acid and basic strength have had as their aim the determination of K_A and K_B. In order to estimate the change in these constants from one solvent to another, the formulas (19) and (20) have to be consulted. In addition to the effect of the medium upon the acidity and basicity constants which has already been discussed, these equations show that the dissociation is determined by the acid and basic nature of the solvent. The changes exhibited by the acidity and basicity constants on alteration of the medium as compared with the corresponding changes in the dissociation constants are thus able to give information concerning the acid and basic character of the medium. Exact investigations for the purpose of determining the acid and basic nature of pure solvents are however not available, and due to this lack of experimental data the interpretation of the dissociation phenomena as regards their dependence upon the medium is rendered feasible only to a very limited extent.

Bjerrum, Unmach and Zechmeister (19) have carried out exact measurements on the dissociation of acetic acid and ammonia in methyl alcohol as well as on the dissociation constant of pure methyl alcohol. The acid dissociation constants, calculated from the constants given by Bjerrum, viz.: $K_{EH} = 10^{-9.65}$,

$K_{NH_3} = 10^{-5.92}$ and $K_{CH_3OH} = 10^{-17.01}$, are tabulated below together with the corresponding acid constants in water:

ACID	K_A IN METHYL ALCOHOL	K_A IN WATER	LOGARITHMIC CHANGE
Acetic acid	$10^{-9.65}$	$10^{-4.76}$	4.89
Ammonium ion	$10^{-11.09}$	$10^{-9.39}$	1.70

We see from these figures that the change from water to methyl alcohol causes the constants of both acids to decrease but much more for acetic acid than for the ammonium ion. According to the previous considerations a decrease in $K_{Acid.}$ for acetic acid and an increase for the ammonium ion have to be expected. The diminution in both constants is then explained on the basis of equation (19) by the smallness of the basicity constant of methyl alcohol in comparison with that of water. The great decrease in the dissociation constant observed in the case of acetic acid is explained by the effects of the change of medium upon K_{Acid} and $K_{Bas.\ (Medium)}$ operating in the same direction, whereas the far smaller decrease in the case of the ammonium ion is due to the two effects counteracting each other.

The change in acidity constant from water to 95 per cent methyl alcohol has been determined by Mizutani (142) for a series of acids, his values being easily extrapolated to 100 per cent methyl alcohol. Acetic acid shows a decrease of 2.3 and ammonium ion an increase of 0.8 logarithmic units. From this change combined with the above change in the dissociation constants the following values are calculated by equation (19):

Change in constants from water to methyl alcohol

	$\Delta \log K_A$	$\Delta \log K_{Acid.}$	$\Delta \log K_{Bas.\ (Medium)}$
Acetic acid	−4.9	−2.3	−2.6
Ammonium ion	−1.7	+0.8	−2.5
Average			−2.55

The values obtained from the two independent computations are thus in good agreement, indicating that pure methyl alcohol is about 350 times as weak a base as is pure water.

An analogous calculation, although with greater uncertainty, can be carried out for ethyl alcohol. The basicity constant relative to that of water is found by comparison of the dissociation constants and acidity constants of acids in water and alcohol as exhibited in the following table. Δ is the increase from water to alcohol. The figures of the first column are taken from a survey by Larsson (125) and those in the second column from Michaelis and Mizutani (138).

Change in constants from water to ethyl alcohol

	$\Delta \log K_A$	$\Delta \log K_{\text{Acid.}}$	$\Delta \log K_{\text{Bas.}}$ (Medium)
Acetic acid	−5.5	−2.7	−2.8
Benzoic acid	−5.9	−3.2	−2.7
Salicylic acid	−5.7	−2.8	−2.9
Average			−2.8

According to these figures ethyl alcohol is about 600 times as weak a base as water. The value 330 found previously from Larsson's measurements are in moderate agreement with this result. If Larsson's figures are right methyl and ethyl alcohol should have practically the same basic strength.

It is now possible to calculate the acidity constants of the alcoholic media by means of formula (21). Thus for methyl alcohol:

$$\frac{K_{A(H_2O)}}{K_{A(CH_3OH)}} = \frac{K_{B(H_2O)}}{K_{B(CH_3OH)}} = \frac{K_{\text{Acid.}\,(H_2O)} \cdot K_{\text{Bas.}\,(H_2O)}}{K_{\text{Acid.}\,(CH_3OH)} \cdot K_{\text{Bas.}\,(CH_3OH)}}$$

or by introducing numerical values:

$$\frac{K_{\text{Acid.}\,(H_2O)}}{K_{\text{Acid.}\,(CH_3OH)}} = \frac{10^{-14.1}}{10^{-17.0}} \cdot 10^{-2.5} = 10^{0.4} = 2.5$$

By using Danner's (41) value for the dissociation constant of ethyl alcohol at 18°C.:

$$K_{A(C_2H_5OH)} = 10^{-19.1}$$

we get:

$$\frac{K_{\text{Acid.}\,(H_2O)}}{K_{\text{Acid.}\,(C_2H_5OH)}} = \frac{10^{-14.1}}{10^{-19.1}} \cdot 10^{-2.8} = 10^{2.2} = 160.$$

If the data—used for these calculations—be trustworthy, the acidity would change only slightly from water to methyl alcohol, but considerably from methyl alcohol to ethyl alcohol. This result seems somewhat improbable. The experimental results are, therefore, at least to some extent not satisfactory.

Further applications of the ideas developed in this chapter can be made on the basis of the important and extensive material produced by H. Goldschmidt and his pupils. The detailed treatment, necessary for investigating these results, are somewhat beyond the scope of this treatise, however, and cannot therefore be undertaken here.

VIII. AN EXTENDED THEORY OF ACID AND BASIC CATALYSIS

The change in the conception of acids and bases as developed in the two preceding chapters is likely to imply also a change in our views of the kinetic phenomena exhibited by this group of substances. In fact the subjection of the general thermodynamic properties of acids and bases to such an elaborate treatment was made partly because the kinetic significance of these general properties was to be expected. It might even be said that it is just in the field of catalysis that the effect of the reformulation of the acid-basic function manifests itself in a particularly definite and obvious manner.

That the hydrion in solution exists only in the solvated state is a fact of paramount importance in elucidation of the intrinsic nature of acid catalysis. It follows therefrom that hydrion catalysis in aqueous solution cannot be due to the free hydrion but has rather to be ascribed to the H_3O^+ or oxonium ion. However, this ion being an acid, which according to our previous statements cannot claim a unique position within the group of acids, there seems to be no a priori reason to try to reserve for it a unique position as an acid catalyst. On the contrary it would be logical to attribute the property of acid catalysis to all acid molecules, i.e. to all molecules capable of giving off a hydrogen nucleus. The effect of the various acids should then depend upon the readiness with which the nucleus is split off, this property being in its turn dependent upon the strength of the acid.

This mode of reasoning is valid, if the catalyzed reaction is not subject to a specific effect. However, the possibility of a reaction being catalyzed by the acid XH and not by YH must not be overlooked. The transformation of acetochloroamino-benzene into p-chloroacetanilide is thus catalyzed by hydrochloric acid, but not by nitric acid. Such specific phenomena are certainly of considerable interest but since we are going to develop the general theory of acid-basic catalysis, it will not be necessary to deal with them here.

The conclusions for basic catalysis will be quite analogous. Since the hydroxyl ion does not, in principle, assume any unique position among the bases, basic catalysis cannot be attributed solely to this particular ion. In general basic catalysis must be looked upon as the effect of the various bases involved and is therefore to be correlated with the ease with which a hydrogen nucleus is taken up, i.e. to the strength of the base.

The extended theory here outlined thus removes the hydrion and hydroxyl ion from the unique position held by them in the classical theory of dissociation and catalysis. It ascribes quite generally acid and basic catalysis directly to molecules of acid and basic character. On the basis of these ideas a number of questions of importance in catalysis arise, some of which will be discussed in the present chapter. First we shall have to consider however the new theory in its relation to the dual theory (Chap. 2), with which it might seem to have some points in common through the importance attached to the "undissociated acids" by both theories.

There is no doubt as to the similarities between the contents of the two theories, since the dual theory as well as the extended catalytic theory supposes the "undissociated acids" to exert catalytic effect. The former, however, considers the "hydrion" and the undissociated acid molecule as quite different species, thus setting up consciously a distinction between acid catalysis and hydrion catalysis. The present theory avoids such a dualism, looking upon hydrion catalysis simply as a particular instance of general acid catalysis. This consistency in the way of regarding catalytic phenomena is the theoretical strength of the extended theory of catalysis. The dual theory on the other hand does not rest upon theoretical considerations and is—as pointed out in Chapter 2—based more than anything else upon misinterpretation of the experimental facts. The catalytic effect used as evidence for the dual theory is in most of the cases caused by phenomena which are foreign to the views inherent in the dual theory. The foundation of the two theories are therefore entirely different, even if their contents exhibit a certain similarity.

Except for those presented in the dual theory no views have been advanced previous to the present theory of catalysis, which might render possible a similar explanation of catalytic phenomena. Still mention must be made, of an investigation by Fajans, (61) suggested to him by Bredig, in which the decomposition of camphor and bromocamphor-carbonic acid in presence of nicotine, quinine, quinidine, etc. is interpreted as a certain kind of basic catalysis. The reaction was however, explained, as being a decomposition of the "salt" formed with the base, i.e., more or less in conformity with the ionization theory of catalysis. The author mentions that a deeper insight into the reaction might be obtained when the investigation is extended to comprise a greater number of bases and consideration of their strength. An extension of our general ideas in catalysis is however not afforded by this work, its aim being rather to examine the stereochemical characteristics of the catalyst.

In some relation to this work Ljunggren (130) investigated the catalytic decomposition of acetoacetic acid in presence of several organic bases. His results are of considerable interest, but no new points of view for their interpretation appear to have been obtained.

Investigations of this nature may, however, prove of great value for the development of the present theory of catalysis. For example, this is the case in the mutarotation reaction of nitrocamphor in various solvents, as studied by Lowry (135), in which substances like piperidine, aniline, sodium ethylate, water, etc. showed great catalytic effect. It is probable that catalysis by basic molecules takes place, but the experimental data do not suffice for stating exactly the character of the reaction.

In later investigations on mutarotation by Lowry and his coworkers (65, 132, 134, 136), attention has especially been called to the acid or basic character of the solvent. Evidence of much greater consequence for the extended theory of catalysis has been furnished, however, by certain reactions in aqueous solutions especially by the catalytic decomposition of nitramide and the mutarotation of glucose. Before proceeding to present the experimental verifications of the theory obtained by means of these reactions we shall try to analyze the mechanism of catalysis in order to obtain some idea of the important question of the significance of the acid and basic strength of the catalyst.

The primary condition for catalysis is the possibility of the molecules of the catalyst and the substrate forming new molecular complexes on colliding. These complexes may in conformity with previous proposals be called critical complexes. If the catalyst be an acid it seems natural to picture the reaction in the first step as a transference of the hydrogen nucleus of the catalyst into the substrate molecule. The binding of the hydrogen nucleus occurring in molecules of high energy content, might then cause a disruption of the structure of the substrate molecule resulting in the formation of a stable product as the next step. The catalytic mechanism of the reaction A→B might then be presented as follows:

$$\mathrm{A} + \mathrm{KH} \rightarrow (\mathrm{A}, \mathrm{KH}) \rightarrow (\mathrm{AH}, \mathrm{K}) \rightarrow (\mathrm{BH}, \mathrm{K}) \rightarrow (\mathrm{B}, \mathrm{KH}) \rightarrow \mathrm{B} + \mathrm{KH},$$

where KH is the acid catalyst and the parentheses signify the molecular complexes reacting.

Similarly in basic catalysis the shock, initiating the reaction, is supposed to be caused by the transference of a hydrogen nucleus from the substrate to the catalyst within the complex. As an illustration of the mechanism of the process AH→BH we thus can write:

$$\mathrm{AH} + \mathrm{K} \rightarrow (\mathrm{AH}, \mathrm{K}) \rightarrow (\mathrm{A}, \mathrm{KH}) \rightarrow (\mathrm{B}, \mathrm{KH}) \rightarrow (\mathrm{BH}, \mathrm{K}) \rightarrow \mathrm{BH} + \mathrm{K},$$

where K is the catalyst base.

This picture can, of course, only give a rough sketch of what happens in the process, since the symbols in these schemes are rather undefined in their character. For example, nothing is said as to whether the passage of the hydrogen nucleus proceeds continuously or whether, as may be expected, it occurs as a quantum jump. Also the effect of the solvent molecules in acting as receivers and transmitters of energy has been left out of the considerations. Nevertheless the above schemes, however incomplete in presenting an exact picture of catalysis, seem to be serviceable as a basis for further conclusions in particular as regards the influence of the acid and basic strength.

The mechanism suggested contains an important consequence with respect to the nature of the substrate. It is obvious that acid and basic catalysis require a substrate of basic and acidic nature, respectively. These properties need not be developed, however, to such an extent as to permit of detection by general methods for measuring acidity and basicity. Only in the case of substrates and solvents containing no hydrogen can the absence of acid character and therefore of basic catalysis with certainty be predicted.

From the above one might perhaps feel inclined to believe that after all the distinction between the ionization theory and the present theory of acid and basic catalysis is comparatively slight. For instance the kinetic reaction determining the velocity in the acid catalytic transformation $A \rightarrow B$, according to the extended theory is:

$$(AH, K) \rightarrow (BH, K)$$

and according to the ionization theory:

$$AH \rightarrow BH$$

In the latter theory, however, AH is a normal molecule whose conversion into BH is no more intelligible than the original reaction $A \rightarrow B$ for which it was expected to furnish an explanation, whereas (AH, K) is a critical complex capable of instantaneous reaction. Furthermore, as pointed out in Chapter 3 the empirical consequences of the two points of view may differ fundamentally, which makes it possible to take a more definite standpoint towards the main idea of the ionization theory.

For this purpose consider the following process catalyzed by bases:

$$\mathrm{XH} \rightarrow \mathrm{YH}$$

As mentioned in Chapter 3, it is impossible from the shape of the reaction curve to make any distinction between a hydroxyl ion catalysis and a spontaneous reaction of the X^--ion. This is due to the proportionality between the concentration of the X^--ion and the product of the XH and OH^--concentrations in the equilibrium:

$$\mathrm{XH} + \mathrm{OH}^- \rightleftarrows \mathrm{X}^- + \mathrm{H_2O}$$

This proportionality in turn is conditioned by the fact that the fourth molecule in the equilibrium, the acid conjugate to the catalyzing base, is present, as the solvent, i.e. in unvariable concentration.

If the hydroxyl ion is present in non-aqueous solution, or if the basic catalysis in water is due to some catalyst other than the hydroxyl ion this difficulty obviously disappears. If the acetate ion, for example, be the catalyst the corresponding equilibrium:

$$\mathrm{XH} + \mathrm{E}^- \rightleftarrows \mathrm{X}^- + \mathrm{EH}$$

evidently permits of a change in the product of the XH and E^- concentrations without requiring a simultaneous change in the concentration of the X^- -ion. It should be possible from that kind of experiments to decide, which of the two theories is correct. For instance in acetate—acetic acid buffers of constant ratio between the buffer constituents but of variable total concentration, the ionization theory in the absence of salt effects demands constant rate of reaction whereas the extended theory of catalysis would require variations if a detectable catalytic effect can be ascribed to the acetate ion.

It should be noted, however, that even if the experimental test comes out in favor of the extended theory the possibility of a collateral spontaneous decomposition of the X^--ion in the course of the OH^--catalysis is not excluded. In order to study this possibility a closer investigation of the general laws governing acid and basic catalysis particularly as regards the effect of the strength of the catalyst is required.

The dependence of the catalytic effect upon the strength of the catalyzing acids and bases is actually a question of paramount importance in the present theory. The readiness with which a hydrogen nucleus is given off by an acid and taken up by a base may be assumed to be greater the greater the strength of the acid and the base, and hence the catalytic effect would be expected to increase with increasing strength of the acid and the base. The simplest scheme would be to assume direct proportionality between the catalytic constant and the strength constant of the acid or basic catalyst, in which case:

$$k_a = GK_A,$$

where k_a and K_A denote the catalytic and dissociation constant of the acid catalyst respectively and G is a constant dependent only upon temperature, pressure, medium and substrate. Obedience to such a simple relation, however, cannot be expected for the following reasons:

The probability of the hydrogen nucleus leaving the acid molecule and forming the reacting complex with the substrate can hardly be directly related to the strength of the acid but rather to the *rate* at which the acid dissociates, i.e. reacts with the solvent to form hydrion solvate and the conjugate base. The "dissociation" equilibrium in an acid solution is, like any other equilibrium, supposed to be kinetic in nature; so that the equilibrium for, say, acetic acid in water:

$$EH + H_2O \rightleftarrows E^- + H_3O^+$$

is the state in which the two opposing reactions proceed with the same velocity. If the reaction from left to right be (arbitrarily) called a dissociation, from right to left an association, and the corresponding velocity constants $k_{diss.}$ and $k_{ass.}$ the dissociation constant is given by:

$$K_A = \frac{k_{diss.}}{k_{ass.}} \tag{1}$$

It is obvious, then, that the same strength may correspond for different acids to quite different values of $k_{diss.}$ and $k_{ass.}$

We must expect that the catalytic constant k_a is more closely related to $k_{diss.}$ than to K_A because the processes of catalysis and of dissociation are of analogous character. In the former reaction the hydrion is given off to a complex, which undergoes a further decomposition, whereas in the latter the hydrion is given off to one of the solvent molecules, with which it might stay united for a certain length of time before being lost again. However, what happens after addition of the hydrion cannot be essential for the probability of the addition process and it is therefore most likely that the velocity of the two processes follows the same law.

This conclusion may be further defined by introducing the critical energy of reaction. The difference between the critical energies $E_{diss.}$ and E_a corresponding to the "dissociation" and the catalysis, is independent of the catalyst for a given reaction in the same solvent. If the velocity constant for the acid dissociation be $k_{diss.}$ and for the catalysis k_a we get:

$$k_a = k\, e^{-\frac{E_a}{RT}}$$

and

$$k_{diss.} = k\, e^{-\frac{E_{diss.}}{RT}}$$

whence the ratio between the two velocity constants is found equal to:

$$\frac{k_a}{k_{diss.}} = e^{-\frac{E_a - E_{diss.}}{RT}}.$$

This equation shows that for different catalysts in the same reaction and medium the velocity constants of the acid catalysis and the acid dissociation are proportional.

Experiments for determining the velocity of dissociation have shown it to be of a high order of magnitude without having succeeded in determining absolute values. As to the relative dissociation velocities we may, however, make certain conjectures.

According to the kinetic conception of the dissociation constant as expressed by formula (1), this constant can only vary simultaneously with $k_{diss.}$ and $k_{ass.}$ The simplest assumption is that —in any case for acids of the same type—an increase in the rate of dissociation from one acid to another is accompanied by a decrease in the rate of association and vice versa, so that in other words the change in strength, observed for a series of analogous acids, is caused by concerted changes in $k_{diss.}$ and $k_{ass.}$

This means that passing on from one acid to another K_A will have to change more markedly than do $k_{diss.}$ and $k_{ass.}$ This result may be expressed by the following equation:

$$k_{diss.} = G\,K_A^x \tag{2}$$

in which G is a constant and x a proper fraction. The numerical value of the latter cannot be estimated a priori, nor is it permissible to assign in advance any constant value to it, independent of the acid strength. It is however reasonable to assume x to be a continuous function of K for acids of the same type.

If the proportionality between the velocities of dissociation and of catalysis is introduced into equation (2) we get:

$$k_a = G_1\,K_A^x \tag{3}$$

as the relation which may be anticipated to exist between the catalytic constant and the dissociation constant of an acid.

Analogous considerations can be applied to basic catalysis. We assume proportionality between the catalytic constant and the velocity constant of association and further that the ratio between these constants does not change with the nature of the base. Furthermore from formula (1) and (2) is deduced:

$$k_{ass.} = G\,K_A^{x-1}$$

where K_A is the dissociation constant of the corresponding acid. If we now introduce the base constant from the relation:

$$K_A\,K_B = \text{dissociation constant of medium}$$

we get:

$$k_{ass.} = G'\,K_B^{1-x} \tag{4}$$

and consequently:

$$k_b = G_2 K_B^{1-x}. \qquad (5)$$

It follows from these equations first, that the value of x is independent of the nature of the substrate. Secondly the equations give information concerning the relation between the catalysis of conjugate acids and bases. It follows from the derivation that x has the same value in the two equations for conjugate acids and bases:

$$k_a = G_1 K_A^x, \quad k_b = G_2 K_B^{1-x}.$$

If x—as a proper fraction—varies from 0 to 1 the sensitivity of the acid catalysis to changes in K_A will rise gradually from 0 to 1, while at the same time the sensitivity of the basic catalysis will fall gradually from 1 to 0. A sensitivity equal to zero means that the catalytic constant does not change with the strength of the catalyst, whereas a sensitivity equal to unity means that the variation is directly proportional to it. These two cases are of course limiting cases, the sensitivity normally deviating from these minimum and maximum values. However, it appears from the formula, that if the acid catalysis displays great sensitivity to changes in the strength constant, the basic catalysis will display low sensibility and vice versa.

It is obvious that the views advanced here lead to a theory of acid and basic catalysis, which in its principle rests on a broader foundation than previous theories. It must be admitted, however, that the premises which lie at the root of the theory, although plausible, are not absolutely cogent in their nature, and it might therefore prove necessary on closer examination to modify these assumptions in different directions. Experimental test is of course the most direct way of attaining a measure of the value of the theory.

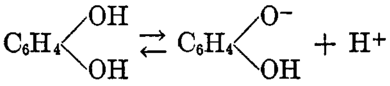
In the experimental investigation of the present theory of catalysis we have, however, to consider some particular circumstances of significance in correlating the efficacy of catalysts of different type with the corresponding strength constants. The catalytic as well as the acid and basic properties are generally not determined solely by the firmness with which the hydrion is attached to the acid molecule, but also depend upon the number of ionizable hydrogen nuclei possessed by the acid molecule and upon the number of points in the base molecule to which the hydrion can attach itself.

If the acid molecule contains only one acid hydrogen atom and the corresponding base only one point of attack, we have the statistically simplest acid-base system, represented for instance by the phenol-phenolate system:

$$C_6H_5OH \rightleftarrows C_6H_5O^- + H^+$$

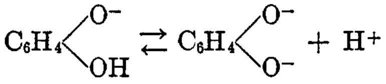
The number of acid hydrogen atoms in the acid molecule being denoted by p and the number of points of attack in the base molecule by q, we have for this simple case: $p = q = 1$.

In the first dissociation step for hydroquinone:



$$C_6H_4{<}\begin{matrix}OH\\OH\end{matrix} \rightleftarrows C_6H_4{<}\begin{matrix}O^-\\OH\end{matrix} + H^+$$

we have two ionizable hydrogen atoms in the acid and one point of attack in the base. Hence $p = 2$ and $q = 1$ in this case, whereas for the second dissociation step:



$$C_6H_4{<}\begin{matrix}O^-\\OH\end{matrix} \rightleftarrows C_6H_4{<}\begin{matrix}O^-\\O^-\end{matrix} + H^+$$

$p = 1$ and $q = 2$, etc.

For the purpose of studying the influence of these statistical conditions upon acid and basic strength we must attribute to all ionizable hydrions the same fixity in the molecule. Of course we must also assume the statistical conditions to be completely obeyed according to the above simple picture. It is then clear that in the above examples hydroquinone, in the first step of dissociation will be twice, and in the second step half as strong an acid as phenol, and that, in general, the dissociation constant of an acid will be given by:

$$K_A = \frac{p}{q} K_{A_0} \tag{6}$$

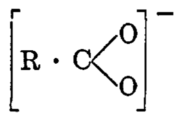
where K_{A_0} signifies the dissociation constant in the statistically simple acid-base system of the same hydrogen fixity. The ratio p/q will be called the statistical acid strength factor. For the conjugate base the relation:

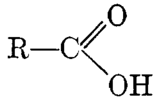
$$K_B = \frac{q}{p} K_{B_0} \tag{7}$$

analogous to (6) is easily seen to hold, the ratio q/p being termed the statistical basic strength factor. The following table gives the statistical factors for a series of acid-base systems as computed from the formulas (6) and (7). The systems are arranged in the order of decreasing values of p/q.

ACID	BASE	p	q	p/q
$Cr(H_2O)_6^{+++}$	$Cr(H_2O)_5OH^{++}$	12	1	12
NH_4^+	NH_3	4	1	4
$C_6H_5NH_3^+$	$C_6H_5NH_2$	3	1	3
OH_3^+	H_2O	3	1	3
$Co(NH_3)_5H_2O^{+++}$	$Co(NH_3)_5OH^{++}$	2	1	2
$Cr(NH_3)_2(H_2O)_2(OH)_2^+$	$Cr(NH_3)_2(H_2O)(OH)_3$	4	3	4/3
H_3PO_4	$H_2PO_4^-$	3	2	3/2
$C_2O_4H_2$	$C_2O_4H^-$	2	2	1
$C_6H_5NH^+$	C_5H_5N	1	1	1
$C_6H_5N(CH_3)_2H^+$	$C_6H_5N(CH_3)_2$	1	1	1
$H_2PO_4^-$	HPO_4^{--}	2	3	2/3
CH_3COOH	CH_3COO^-	1	2	1/2
$C_2O_4H^-$	$C_2O_4^{--}$	1	4	1/4
HPO_4^{--}	PO_4^{---}	1	4	1/4

It should not be overlooked, however, that these values are not entirely free of assumptions. For example, it has been assumed that the carboxyl group after the ionization of its hydrogen atom has two points of attack; in other words the two oxygen atoms of the ion:



are equally available for the hydrion. This implies that the negative charge is not specifically attached to the oxygen atom in the hydroxyl group and that the formula  $R-C\overset{O}{\underset{OH}{<}}$ is justified only as a description of the undissociated acid. Looking upon this condition from the standpoint of structural chemistry such cases may however be of special interest since the conclusions regarding statistical factors drawn from catalytic experiments might in many cases throw some light on difficultly accessible questions of structural chemistry.

For acid and basic catalysis the significance of the statistical strength factors is seen in the following manner. The previous deduction of the relation between the catalytic and strength constants:

$$k_a = G_1 K_A^x, \quad k_b = G_2 K_B^{1-x}$$

pre-supposes the simple statistical condition $p = q = 1$. These expressions ought now to be written:

$$k_{a_0} = G_1 K_{A_0}^x, \quad k_{b_0} = G_2 K_{B_0}^{1-x} \qquad (8), (9)$$

in order to distinguish between the simple and the more complicated cases. These expressions are also valid for the more complicated cases as far as the influence of firmness of attachment of the hydrion upon the catalysis is concerned. However, an additional factor enters, namely that the catalytic effect of an acid may be proportional to the number of acid hydrions and the effect of a base proportional to the points exposed to attack from the hydrion. Therefore:

$$k_a = p k_{a_0}, \quad k_b = q k_{b_0}$$

Introducing these equations together with (6) and (7) into (8) and (9) the following expressions for the acid catalysis are obtained:

$$k_a = p G_1 K_{A_0}^x = p G_1 \left(\frac{q}{p} K_A\right)^x$$

or

$$k_a = G_1 K_A^x q^x p^{1-x} \qquad (10)$$

and for the basic catalysis:

$$k_b = qG_2K_{b_0}^{1-x} = qG_2\left(\frac{p}{q}K_B\right)^{1-x}$$

or

$$k_b = G_2K_B^{1-x}q^x p^{1-x} \tag{11}$$

These equations require, just as in (6) and (7) a complete conformity to the statistical requirements.

As the chief result of these considerations we may state that the presence of complicated statistical conditions in the acid-base system will affect the catalytic activity of the acid and the base in proportion to the change in the factor:

$$q^x p^{1-x}$$

this effect according to formula (10) and (11) being the same in acid and basic catalysis. If it were permissible to consider x as independent of the nature of the reaction it would follow from the results of the nitramide catalysis that x is considerably smaller than $1-x$ and that the factor p therefore is of higher influence than is q. In this case the catalysis by bases would depend upon their strength constants to a greater extent than would catalysis by acids.

In the special case of hydrion catalysis in aqueous solutions p equals 3, since H_3O^+ acts as a catalyst, whereas p, for example, for acetic acid and related organic acids is equal to unity. This circumstance of course to some extent displaces the catalytic conditions in favor of the hydrion more or less obscuring the catalytic effect of the weak acid.

Investigations on the catalytic decomposition of nitramide have furnished the most important experimental evidence of the present theory of acid and basic catalysis. This substance discovered by Thiele and Lachmann (174) corresponds to the formula $H_2N_2O_2$ without showing the chemical properties expected of the amide of nitric acid. As already found by the discoverers, the substance is decomposed practically instantaneously in basic solutions according to the scheme:

$$H_2N_2O_2 \rightarrow N_2O + H_2O$$

A closer investigation (37, 34) of this reaction in aqueous solutions has shown that within certain limits of basicity the process is composed of two partial reactions; a spontaneous one, proceeding independently of the acidity of the solution, and a catalytic one. *All bases seem to act as catalysts,* the term base being used in conformity with the definition in Chapter 6. If the solution be sufficiently acid, the base effect is depressed, and the spontaneous reaction is the only factor of importance. This reaction is strictly monomolecular and has a half-period of 13.7 hours at 15°.

In an 0.01 equimolar acetate buffer solution (0.01 m. acetate + 0.01 m. acetic acid) the rate of decomposition is about 15 times as great as the velocity of the spontaneous reaction. This effect as may easily be shown by varying the ratio acetate/acetic acid, is proportional to the concentration of the acetate ion and should therefore be considered as an acetate ion catalysis. The anions of other organic acids such as propionic acid, benzoic acid, formic acid, salicylic acid, etc. have a similar effect. The same behavior is furthermore shown by anions of polybasic acids and by amines like aniline, toluidine, chloroaniline, etc. Since changes in hydrion concentration at constant concentration of anions or of amines do not affect the catalysis, the reaction conforms actually to the requirements of the extended theory of basic catalysis.

The determination of the constants in the catalytic decomposition of nitramide when brought into relation with the corresponding strength constants yields the following expression:

$$k_b = 6.2 \cdot 10^{-5} K_B^{0.83},$$

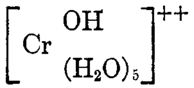
which is valid for basic anions of a series of organic acids, whereas the expression:

$$k_b = 1.7 \cdot 10^{-4} K_B^{0.75}$$

holds for cyclic amines.

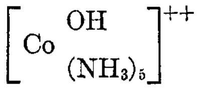
These equations conform to formula (5), deduced from theoretical considerations, the exponent $1 - x$ being a proper fraction while the above theoretical reasoning was unable to yield any information as to the variation of the exponent with the strength of the base, the measurements give the interesting result that $1 - x$ is constant within every group of bases, despite the considerable changes (from 2.10^{-6} to 10^{-2} for the anions and from $0.7.10^{-5}$ to 2.10^{-3} for the amines) in the dissociation constants.

While the effect of the cyclic amines and the anions of the weak acids are but slightly different other basic catalysts exhibit a much higher catalytic activity. The polyvalent basic cations, as for example:



$$\left[\mathrm{Cr}\begin{matrix}\mathrm{OH}\\ (\mathrm{H_2O})_5\end{matrix}\right]^{++}$$

and



$$\left[\mathrm{Co}\begin{matrix}\mathrm{OH}\\ (\mathrm{NH_3})_5\end{matrix}\right]^{++}$$

possess extraordinary catalytic effects easily noticeable even in strongly acid solution. The difference in the catalytic efficiency of different catalytic groups is not surprising, but on the contrary must be expected from a consideration of the catalytic mechanism. Since the association is a reaction between the base molecule and a positively charged hydrion, whereas the catalytic reaction takes place between the base molecule and a neutral nitramide molecule, parallelism between k_b and K_b is only to be expected as long as the catalyst is of unchanged charge type. If we consider the association and catalytic processes for two bases of different charge: B and B^{++}:

$$B + H_3O^+ \rightarrow (B,H_3O)^+, \tag{12}$$

$$B^{++} + H_3O^+ \rightarrow (B,H_3O)^{+++} \tag{13}$$

and

$$B + H_2N_2O_2 \rightarrow (B,H_2N_2O_2), \tag{14}$$

$$B^{++} + H_2N_2O_2 \rightarrow (B,H_2N_2O_2)^{++}, \tag{15}$$

and assume the velocity to be the same for (14) and (15), i.e. B and B^{++} having the same catalytic influence, reaction (12) must necessarily proceed faster than (13) owing to the marked repulsive forces affecting the latter reaction. In the case of the same catalytic effect B is consequently a stronger base than B^{++}, i.e. at the same rate of association—and this in turn, according to our theory, means the same basic strength—the catalytic effect is highest for the ion carrying the highest positive charge. This explains the high catalytic power of the bivalent hydroxo ions, but a similar effect called for by the theory when comparing bases having one negative and zero charge respectively does not seem to be present.

The problems of great physico-chemical interest further attached to the nitramide catalysis have been treated in the papers quoted above and need not be taken up here. The factors there discussed should, however, be taken into consideration in a general quantitative examination of the theory.

Another reaction probably of no less significance for importance in the theory of acid and basic catalysis is the mutarotation of glucose. Euler has found that certain ions have an anomalous effect upon the mutarotation of glucose, and Kuhn and Jacob have subjected this anomaly to a closer study in their paper previously mentioned. The phenomenon observed is the acceleration of the glucose transformation by certain ions like acetate, phosphate and citrate ions. The latter authors interpret the phenomenon as being an effect of these ions upon the activity of the reactants, this interpretation being obviously related to the view of the general significance of activity in catalytic reactions which has already been criticized in chapter 4. This explanation of the specific effect of the ions however offers no clue to the understanding of the phenomenon.

It is natural, however, to apply to this "anomaly" the same ideas which have proved so fruitful in the case of the nitramide catalysis. The reaction is a transformation of alpha-glucose into beta-glucose leading to an equilibrium between the two modifications (155). Hydrions and hydroxyl ions as well as acetate, phosphate and citrate ions act as catalysts. Furthermore the reaction is partly a "spontaneous" one; i.e. within a certain range of acidity the velocity is practically constant in absence of other catalysts.

All of these phenomena are undoubtedly to be interpreted on the basis of the extended theory of acid and basic catalysis.

Examination of this hypothesis by means of the data of Kuhn and Jacob is made difficult by the fact that these authors have conducted their experiments from the standpoint of the "activity theory" without, however, carrying through the work consistently on this basis. It is possible, however, by introducing concentration instead of activity throughout to obtain some idea of the magnitude of the catalytic effect.

The following equation for the spontaneous reaction by hydrions and hydroxyl ions according to Kuhn and Jacob is valid at 25°C.:

$$10^4\,k = 104 + 3300\,c_{H^+} + 9.3 \cdot 10^7\,c_{OH^-}$$

This equation does not differ much from the formula given by Hudson mentioned previously. In the experiments with acetate, phosphate, etc. that part of the reaction, not due to the presence of these anions, can be eliminated by this equation, c_{H^+} and c_{OH^-} being approximately known, and in this way the effect of the anions can be calculated approximately. This calculation shows primarily that the effect is nearly proportional to the concentration of the anion in agreement with the theory. Moreover the catalytic effect is found to increase with the basic strength of the anion as in the case of the nitramide catalysis; but scarcity of data does not permit a determination of the quantitative relation between catalytic constant and basic strength.

However, in a study of mutarotation at present in progress in this laboratory, we have been able to establish definitely the presence of such catalysis and to determine it quantitatively for a series of bases of varying type. Similarly—and in this respect the results extend further than those for nitramide—we have obtained an analogous effect for acids in agreement with the views given here. Experiments on mutarotation have therefore already contributed importantly to the establishment of the extended theory. When we consider that these new phenomena have been observed in the study of a reaction which for a generation has been the subject of extensive experimental research, we may well believe that a systematic study in the field of acid and basic catalysis will afford corresponding results in illustration of the ideas developed in these chapters.

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APPENDIX (1926-1927)

TO CHAPTER III

During the last two years Euler and Ölander (10, 11, 12, 13) have continued their catalytic studies from the standpoint of the ionization theory of catalysis. The opinion that the theory is supported by the catalytic phenomena observed in mutarotation seems also to be maintained in these recent papers, but a theoretical proof is still lacking. In order to explain the phenomena in the catalysis of mutarotation by acid and basic molecules other than hydrogen and hydroxyl ions Ölander (21), however, seems prepared to admit that a compound formed by the substrate and the catalysts in question (e.g., an acetate ion or a pyridine molecule) may well be taken as the reactive molecule characteristic of the theory. He is obviously unaware of the fact that when abandoning the idea of simple substrate ions as the reactive molecules in catalysis and permitting any complex, formed by the substrate and a catalyst, to perform the functions which have hitherto been attached to the substrate ions he actually gives up the fundamental principles of the Euler theory and in substance subscribes to the extended theory advocated in the present review.

A. Skrabal (22) has subjected the theory of Euler to an elaborate criticism in an article in which he also gives a review of his own work on hydrolytic reactions from the standpoint of structural chemistry. Strangely enough he seems to believe in the possibility of distinguishing between the two different mechanisms of catalysis by extending experiments to such concentrations of the catalyzing hydrogen and hydroxyl ions that a considerable part of the substrate is transformed into an ion. It is not clear, however, how this conclusion has been arrived at. If it were true, the quite recent paper by Euler and Ölander (13) dealing with the hydrolysis of acetamide by strong acids would have brought good evidence in favor of the ionization theory, as actually believed by these authors. However, it should be emphasized once more that the above disproof of the possibility of discriminating between the two pictures is general and conclusive, so it cannot be avoided by any special construction as to the nature and extent of the reaction considered.

TO CHAPTER IV

The question of primary kinetic salt effect has been dealt with by F. G. Soper (23), who derived a velocity expression for ionic reactions similar to Expression (4, IV). His formula deviates from (4), however, in that the exponent is two-thirds of the exponent in this equation. This divergence is due to a confusion of total and differential free energy (3, 5, 15). Furthermore it appears from another article by the same author (24) that the thermodynamic ideas underlying the derivation of the proposed formula are absolutely unsound, particularly as regards the free energy of the solvent and the part played by it in the charging processes of the Debye-Hückel theory.

Attempts to sustain different forms of the activity rate theory for the case of concentrated salt solutions have been published recently by Åkerlöf (1) and by Soper and Pryde (25). While Åkerlöf from measurements of the rate of decomposition of diacetone alcohol in alkaline solution concludes that the velocity is proportional to the activity of the hydroxyl and the alkali metal ion, Soper and Pryde, studying the rearrangement of chloroacetanilide catalyzed by hydrochloric acid—that is by H^+ and Cl^-—find the speed proportional to the activity of *all* three molecules reacting. From the standpoint of the general activity rate theory the two papers are incompatible. The last mentioned authors in arguing against Equation (2, IV) as applicable to their reaction in concentration up to 1.5 N HCl give no consideration to the fact that this equation is derived only for the domain of much more dilute salt solutions.

L. E. Bowe (4) has studied cane sugar inversion and ester hydrolysis by hydrochloric acid in the presence of concentrated alkali halides and has also determined electrometrically the hydrogen ion activity (called by him the apparent H^+) in the same solution. While for the cane sugar inversion a certain parallelism between speed and hydrogen ion activity was demonstrated, the ester hydrolysis was found to be much less affected by addition of the neutral salt. As was to be expected no general kinetic conclusion could, therefore, be arrived at on the basis of these experiments. Theoretically the work is characterized by the serious mistake of confusing activity and osmotic pressure and by making use of the concept of solution pressure, which, except for solutions following the gas laws, has no definite significance. In this respect he seems to be a follower of W. Bancroft (2) who evidently has not yet familiarized himself with the modern conceptions in the field of solutions.

TO CHAPTER V

M. Kilpatrick (18) has studied catalysis in buffer solutions and shown the presence of a secondary kinetic salt effect. Otherwise the importance of the theory of primary and secondary salt effect does not appear to be recognized as yet, even in very recent work on catalysis. Thus Dawson and Carter (8) still believe in the possibility of calculating hydrogen ion concentrations by the classical mass action expression and the simple Nernst formula in salt solutions the concentration of which varies from 0 to 1 normal. It will appear from the above theory of salt effect that the error involved in this way of calculation may easily amount to 100 per cent or more. Lowry and Smith (20) in their paper on mutarotation of glucose attribute high importance to Dawson's work on account of its "repudiation" of the theory of secondary salt effect as first demonstrated in Arrhenius' experiments quoted above. They fail to realise, however, that the effect of sodium chloride in accelerating the inversion of cane sugar by a weak acid is entirely different in nature from the accelerating effect of sodium acetate in the mutarotation of glucose. In the interpretation of catalytic phenomena in salt solutions there is no escape from the obligatory condition of considering three entirely different effects: *1*, primary salt effect, *2*, secondary salt effect, *3*, direct catalytic effect of the ions in conformity with the extended theory of acid and basic catalysis presented in chapter VIII of the present review. Owing to the magnitude of the last mentioned influence in the acetone-iodine reaction the conclusions of Dawson and Carter for this reaction are qualitatively correct in spite of their neglecting the effects mentioned under *1* and *2*. On the other hand in the investigation by Dawson and Lowson (9) on ester hydrolysis the same omission becomes fatal.

TO CHAPTER VI

The general question of the definition of an acid has been dealt with by A. F. Germann (14) and A. Hantzsch (17). The ideas of the first of these authors, although of a subversive tendency, are extremely vague and more likely to confuse than to clarify the conception. Hantzsch describes an acid as a compound of hydrogen with a negative group. Beside the uncertainty implied by using the undefined idea of a "negative" group the description of Hantzsch is not actually a definition, but rather an attempt to point out which characteristics are required to make a substance an acid. The inadequacy of the acid "dissociation" as a general measure of acidity is obviously what makes Hantzsch fall back on a more or less obsolete standpoint, as expressed by his considering "salt formation" as a property of fundamental significance for the concept of acidity. This idea disagrees entirely with our point of view. However, the inadequacy of measuring acidity in different solvents by means of dissociation has also been emphasized above, and we may find after all—in spite of much divergency—that the ideas of Hantzsch are, in many ways, not incompatible with those of the present review.

Conant and Hall (7, 16) have made an interesting investigation on acidity and basicity in acetic acid as a solvent and have shown how the possibility of titrating an acid or a base depends upon the acid and basic properties of the solvent.

TO CHAPTER VIII

The investigation on mutarotation referred to above has now been published (6). The results obtained are in full conformity with the extended theory of catalysis showing a marked catalytic effect of a number of acid and basic molecules. In a logarithmic plot of catalytic constant against strength constant for all the different electric types of catalysts including the solvent the results come out as a straight line with a slope of 0.4 and about 0.2 for bases and acids respectively. This relationship seems approximately fulfilled throughout a range of acid and basic strength of about 10^{18}, and it is possible therefore within this range to predict approximately the catalytic efficiency of any base or acid in the mutarotation merely from its strength.

Lowry and Smith (20) have studied the glucose reaction from a similar point of view and have obtained values for acetic acid, acetate and ammonium ion which agree well with our results. The value for the catalytic constant of the hydrochloric acid molecule cannot be accepted, however, because the authors have based their calculations upon the classical view of dissociation of strong electrolytes. Some aspects developed by Lowry (19) in a subsequent paper on the mechanism of catalysis are much in accord with the extended theory of catalysis presented above.

The paper by Dawson and Carter (8) on the acetone-iodine reaction mentioned above, is a continuation of previous work on the basis of the dual theory by Dawson and his coworkers. The new work, however, contains much more conclusive evidence in favor of the extended theory of catalysis although, as mentioned, the omission of salt effect from their considerations makes quantitative calculation difficult.

It should be mentioned finally that experiments now in progress in this Laboratory have brought further support to the ideas of the extended theory of acid and basic catalysis.

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