

ACID AND BASIC CATALYSIS

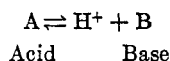
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Catalytic studies have played an important rôle in the development of the theories of solution and of acids and bases. It was not, however, until the publication of the paper by Brönsted (1) dealing with the effect of the concentration of electrolyte upon reaction rate that rapid progress began to be made in the field of acid and basic catalysis.

An acid was commonly regarded as a substance which gave hydrogen ions (H_3O^+) to aqueous solution, a base as a substance which gave hydroxyl ions. In 1923 there was put forward independently by Brönsted (2) and by Lowry (3) a new concept of acids and bases, according to which an acid is a substance which can split off a proton or unsolvated hydrogen ion, and a base a substance which can take up a proton to form an acid. Thus



REACTIONS EXHIBITING GENERAL ACID OR BASIC CATALYSIS

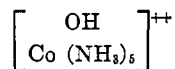
The new concept was soon verified experimentally. In studying the decomposition of nitramide in aqueous solution, a reaction extremely sensitive to hydroxyl ions, Brönsted and Pedersen (4) found that in a series of acetate-acetic acid buffer solutions the rate of reaction was proportional to the concentration of acetate ion and independent of the hydroxyl-ion concentration. Similarly the anions of other acids were shown to catalyze the decomposition, the catalytic effect of the anion decreasing with increase in the strength of the corresponding acid. The relationship

$$k_b K_A^{0.83} = 6.2 \times 10^{-5} \text{ or } k_b = 6.2 \times 10^{-5} K_B^{0.83}$$

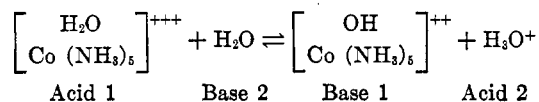
where k_b is the catalytic constant, K_A is the dissociation constant of the corresponding acid, and K_B is $1/K_A$, was found to hold exactly for the anions of monobasic carboxylic acids, and also for the anions of polybasic acids if a so-called statistical correction was made. The statistical correction will be discussed later. The catalytic effect of primary amines on the decomposition of nitramide was demonstrated by Brönsted and Duus (5). For these catalysts the relationship

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

was found valid. Brönsted and Volqvartz (6) studied the decomposition of nitramide catalyzed by hydroxo ion bases of the type of the ion



formed by action of the corresponding aquo ion with water



Their data conform to the equation

$$k_b = 0.083 K_B^{0.66}$$

or, when statistical corrections are made, to the equation

$$k_{b(\text{corr.})} = 0.0045 K_B^{0.84}$$

Dawson and his coworkers (7) have shown that the reaction between acetone and iodine in aqueous solution exhibits general acid and basic catalysis. If for all the acid catalysts studied one plots the logarithm of the catalytic constant¹ against the logarithm of the dissociation constant, one obtains the distribution of circles shown in figure 1. And if for all the basic catalysts one plots the logarithm of the catalytic constant against that of the dissociation constant of the corresponding or "conjugate" acid, one obtains the

¹ The value for the catalytic constant of the bisulfate ion is that calculated by Rice and Urey (*J. Am. Chem. Soc.* **52**, 95 (1930)).

distribution of squares shown in the figure. The slopes of the lines drawn are 0.36 and -0.58 , respectively. From the plot, which covers a range of 18 powers of 10 in the dissociation constant, it appears that a roughly linear relationship may be expected between the logarithms of catalytic and dissociation constants. For catalyzing acids of the monobasic carboxylic type an exact relationship between catalytic effect and acid strength can be formulated (8). In figure 2 the logarithm of the catalytic

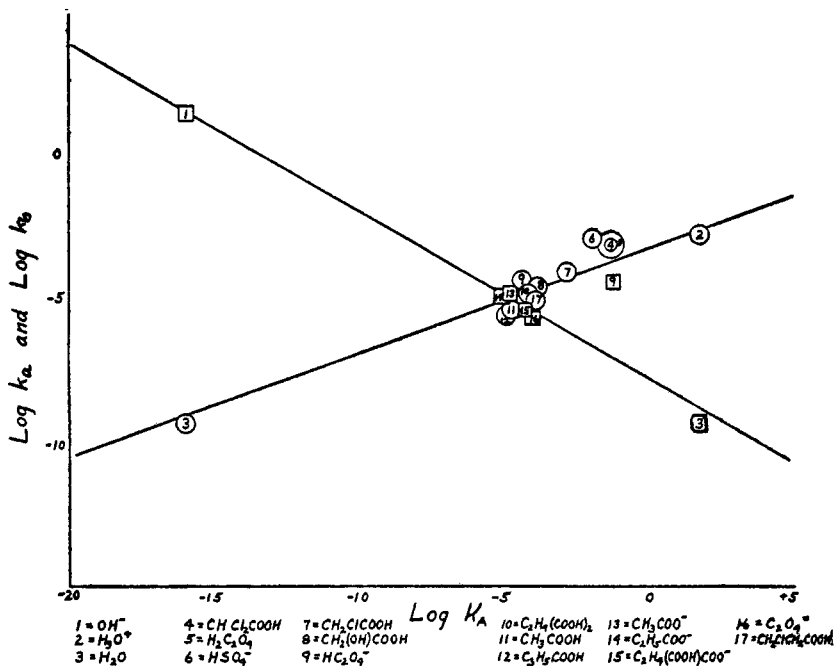


FIG. 1. THE ACETONE-IODINE REACTION

constant is plotted against the logarithm of the dissociation constant for the acids from propionic to dichloroacetic. The line in figure 2 corresponds to the equation

$$k_a = 0.0050K_A^{0.64}$$

The mutarotation of glucose furnishes another instance of general acid and basic catalysis. Brönsted and Guggenheim (9)

determined the catalytic effects of a considerable number of bases of diversified types, and the catalytic effects of several monobasic carboxylic acids. They plotted their values in the way in which those for the acetone-iodine reaction are plotted in figure 1, and concluded that one could predict the catalytic effect, correct to one power of 10, of any acid or basic molecule or ion from a knowledge of its acid or basic strength.

The existence of general acid catalysis in the hydrolysis of ethyl orthoacetate, ethyl orthopropionate and ethyl orthocarbonate was

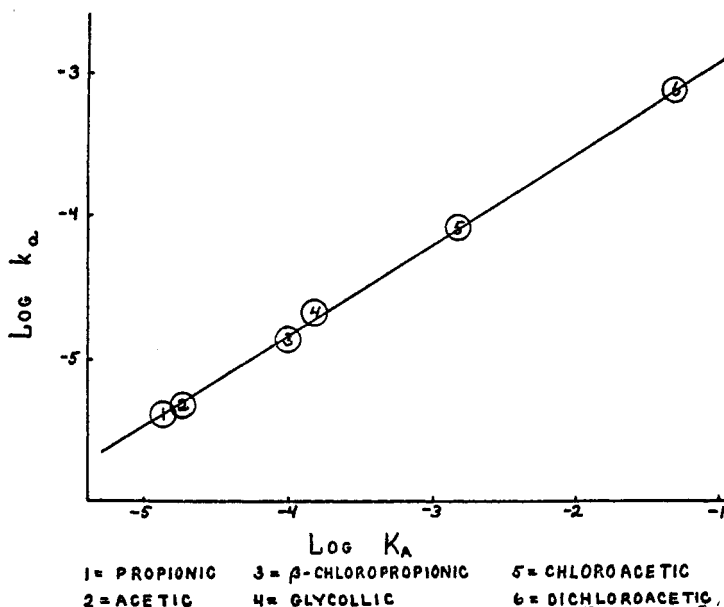


FIG. 2. THE ACETONE-IODINE REACTION

demonstrated by Brönsted and Wynne-Jones (10). For any one of the three reactions, the relationship between the logarithms of the catalytic and dissociation constants was found to be roughly linear, the exponent x in the equation.

$$k_a = G_1 K_A^x$$

being appreciably greater than that found in the case of the mutarotation of glucose. Brönsted and Wynne-Jones point out that as

x approaches unity it becomes increasingly difficult to detect the effect of acids other than the hydrogen ion, H_3O^+ . They also point out that if on the other hand x is zero, all catalytic constants become the same, which means that if the solvent is an acid its effect predominates over all other catalytic effects, since it is present in greatest amount. As a criterion for the detectability of general acid and basic catalysis they suggest the following: "If in a reaction catalyzed by hydrogen or hydroxyl ions there is a

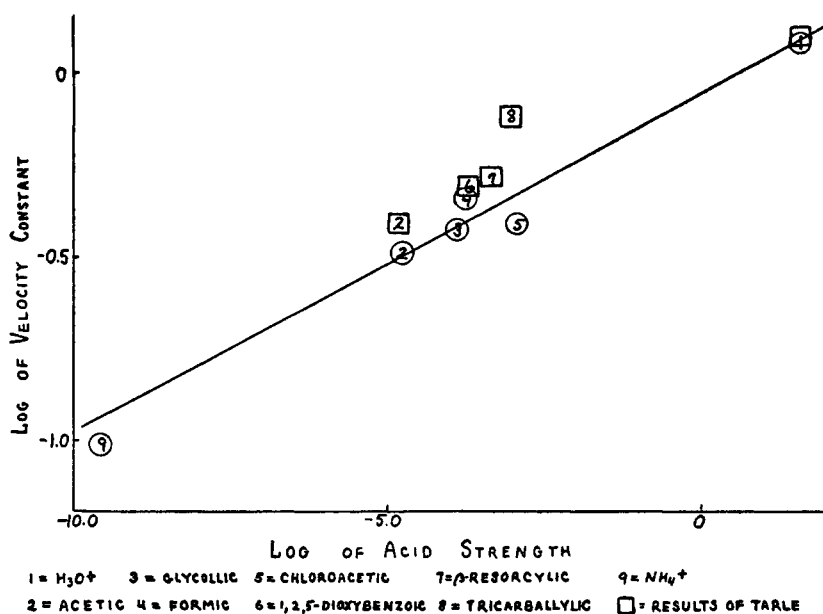


FIG. 3. THE DISSOLUTION OF MAGNESIUM IN ACIDS

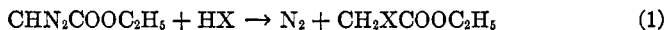
detectable but not too large 'spontaneous' reaction, then the conditions are favorable for the detection of effects by acids and bases in general."

The hydration of acetic anhydride is a reaction which is catalyzed by hydrogen and hydroxyl ions, and which proceeds at a measurable rate in water alone. Kilpatrick (11) found that the hydration was accelerated by basic anions, but that the order of acceleration was not that of basic strength.

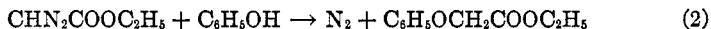
It was found by Miller and Kilpatrick (12) that the decomposition of diacetone alcohol, known to be catalyzed by the hydroxyl ion, is catalyzed by other bases also. Miller and Kilpatrick determined the catalytic constants of ammonia and three amines.

As Kilpatrick and Rushton (13) have shown, when magnesium dissolves in a solution of a weak acid the great part of the reaction is with the molecular acid rather than with the hydrogen ion. When the logarithms of the velocity constants are plotted against those of the dissociation constants of the reacting acids (figure 3) there appears the same approximately linear relationship which exists in the cases of acid and basic catalysis cited. The study has been extended to amalgams of the alkali metals; these also react with acids other than the hydrogen ion (14).

In solvents such as water and alcohol the catalytic effect of an acid is made up of the effect of the "hydrogen ion," formed by action of the acid with the solvent, and of the effect of the molecular acid. The former often obscures the latter. In inert media like benzene, where there is no action with the solvent, acid catalysis should be simpler. Brönsted and Bell (15) studied a number of reactions of diazoacetic ester in benzene solution. Acids react with the ester according to the equation



In the absence of acid there is no detectable reaction between diazoacetic ester and phenol; in the presence of acid, there occurs the reaction written above, and also



Having determined the velocity constant of reaction 1, Brönsted and Bell were able from the observed velocity constant of the complex reaction to evaluate that of reaction 2, which they found proportional to the concentration of acid. The catalytic constants for the substituted acetic acids which catalyze reaction 2 stand in the order of the dissociation constants of the acids in water; in fact they satisfy the equation

$$k_a = G_1 K_A^z$$

where α is one. Picric acid also catalyzes the reaction between diazoacetic ester and phenol in benzene solution; its catalytic constant, however, is much smaller than would be expected. The conclusion drawn by Brönsted and Bell is that in a solvent of low dielectric, where the structure of the acid molecule is of greater influence than in water, the equation relating catalytic and acid strength may hold for acids of the same chemical type only.

THE EQUATION RELATING CATALYTIC AND ACID OR BASIC STRENGTH

The equation relating catalytic and acid strength was proposed by Brönsted (16) on the basis of the following considerations. The dissociation process of an acid, in which a proton is given to a molecule of solvent, is similar to the catalytic process, in which a proton is given to a molecule of reactant. It is therefore to be expected that the catalytic constant k_a is more closely related to the velocity constant of dissociation k_{diss} , than it is to the equilibrium constant of the dissociation. According to the Arrhenius equation

$$k_{\text{diss}} = B e^{-E_{\text{diss}}/RT}$$

where E_{diss} is the energy of activation of the dissociation process, and

$$k_a = B e^{-E_a/RT}$$

where E_a is the energy of activation of the catalytic process. Hence

$$k_a/k_{\text{diss}} = e^{-(E_a - E_{\text{diss}})/RT}$$

If from the analogy between the two processes it may be inferred that the difference between the energies of activation is, for a given reaction in a given medium, independent of the catalyst, at any temperature k_a is proportional to k_{diss} .

The equilibrium constant of the dissociation process is equal to the ratio of the velocity constants of dissociation and association

$$K_A = k_{\text{diss}}/k_{\text{ass}} \quad (3)$$

If the assumption be made that for a series of analogous acids increase in K_A is brought about by a simultaneous increase in $k_{\text{diss.}}$ and decrease in $k_{\text{ass.}}$, it follows that from one acid to another K_A will change more rapidly than $k_{\text{diss.}}$ and $k_{\text{ass.}}$. This is expressed by the equation

$$k_{\text{diss.}} = GK_A^x \quad (4)$$

where G is a constant and x a proper fraction. Introducing the proportionality between k_a and $k_{\text{diss.}}$,

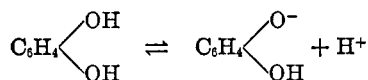
$$k_a = G_1K_A^x \quad (5)$$

For basic catalysis the relationship is derived in the same manner, on the assumption that the catalytic process is analogous to the association process. The resulting equation is

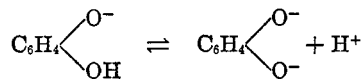
$$k_bK_A^{1-x} = G_2 \text{ or } k_b = G_2K_B^{1-x} \quad (6)$$

where $K_B = 1/K_A$.

The development thus far given applies to acids having one ionizable hydrogen atom and to bases having one point at which a proton can attach itself, i.e., acids of the type of phenol and bases of the type of the phenolate ion. For more complex types a statistical correction must be made (17). Let us compare the acids phenol and hydroquinone, and for the time being consider only the first dissociation of hydroquinone



For equal fixity of the ionizable hydrogen atoms in the two acid molecules, twice as many protons leave the hydroquinone molecule in unit time as leave the phenol molecule, whereas in each case the chance of union of a proton with the basic molecule is the same. That is to say, if we wish from the dissociation constants of the two acids to estimate the relative fixity with which the hydrogen atoms are held, we must compare the dissociation constant of hydroquinone with twice that of phenol. Considering now the second dissociation of hydroquinone



and the dissociation of phenol, for equal fixity of the ionizable hydrogen atoms the same number of protons leave each acid molecule in unit time, but there are twice as many chances of combination of a proton with the basic molecule in the case of hydroquinone, as there are in the case of phenol. Therefore we should compare the second dissociation constant of hydroquinone with one-half the dissociation constant of phenol, if we wish to estimate the relative fixity of the hydrogen atoms in the two acid molecules. Letting p represent the number of ionizable hydrogen atoms in the acid molecule, and q the number of points at which a proton may be attached in the molecule of the conjugate base,

$$K_A = p/q K_{A_0} \quad (7)$$

where K_{A_0} is the dissociation constant of a hypothetical acid in which the hydrogen atoms are held with the same firmness as in the acid under consideration, but for which $p = 1$ and $q = 1$. Therefore, as far as the influence of firmness of attachment of the hydrogen atoms is concerned, for the more complex types equations 5 and 6 become

$$k_a = G_1 (q/pK_A)^x \text{ and } k_b = G_2 (p/qK_B)^{1-x} \quad (8)$$

If in addition, however, the catalytic effect of an acid is proportional to the number of ionizable hydrogen atoms, and that of a base to the number of points at which a proton may be attached,

$$k_a = pk_{a_0} \text{ and } k_b = qk_{b_0} \quad (9)$$

where k_{a_0} and k_{b_0} are the catalytic constants of the acid A_0 and the base B_0 , respectively, having $q = p = 1$. The original equations, which for clearness might have been written

$$k_{a_0} = G_1 K_{A_0}^x$$

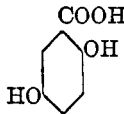
$$k_{b_0} = G_2 K_{B_0}^{1-x}$$

now become, by substitution from equations 7 and 9,

$$k_a = G_1 K_A^x q^x p^{1-x} \text{ and}$$

$$k_b = G_2 K_B^{1-x} q^x p^{1-x} \quad (10)$$

The selection of the values of p and q is somewhat arbitrary. For example, for the ion RCOO^- the assumption is made that q is two, i.e., that the two oxygen atoms are equally available to the proton; similarly for the PO_4^{--} ion it is assumed that q is four; for the HPO_4^{--} ion, that q is three. It is assumed that for the NH_4^+ ion p is four, i.e., that all four hydrogen atoms are equally ionizable; for the H_3O^+ ion, that p is three; presumably for an acid such as 2,5-dihydroxybenzoic acid



that p is three.²

If this derivation of the relationship between catalytic effect and acid or basic strength were complete, it would be expected that the exponent x or $1 - x$ would remain constant, for a given set of catalysts, from reaction to reaction. For the catalysis by the anions of monobasic carboxylic acids, Brönsted and Pedersen found the exponent to be 0.83 in the decomposition of nitramide, while Brönsted and Guggenheim found 0.34 in the mutarotation of glucose. Similarly Brönsted and Wynne-Jones found higher values of x for the acid catalysis of the hydrolysis of the

² Certain inconsistencies appear in the application of the statistical correction.

In making the statistical correction for the anions of monobasic carboxylic and of polybasic acids, Brönsted and Pedersen used formula 8 and employed p/q ratios which differ from those given in a later publication (16).

Brönsted and Duus made no statistical correction in their study of the decomposition of nitramide catalyzed by bases of the type of aniline.

In their study of the catalysis by the hydroxo ion bases, Brönsted and Volquartz made the statistical correction by plotting $\log K_A - \log p$ against $\log k_b$ in accordance with equation 10.

The equations given for the relationship between catalytic constant and basic strength in the decomposition of nitramide catalyzed by the three types of bases are, therefore, not strictly comparable.

ortho esters, than found by Brönsted and Guggenheim for the acid catalysis of the mutarotation of glucose. Other examples can be cited. It must be accepted that the exponent varies from reaction to reaction, and that accordingly there is an effect of the substrate for which the present theory does not account.

It is to be observed that in the decomposition of nitramide the hydroxo ion bases are far more powerful catalysts than are the amines or the anion bases of the same basic strength. If the analogy between the catalytic process and the association process of a base is justifiable, this condition is to be expected. The association involves a reaction between the base and a positively charged hydrogen ion; the catalytic process involves a reaction between the base and an uncharged molecule. If the catalytic effects of bases B and B^{++} are the same, their tendencies to take up a proton are the same, but owing to the repulsion between the positively charged base and the hydrogen ion the rate of association is less in the case of B^{++} than in the case of B . Conversely, for equal rates of association (equal basic strength), a greater catalytic effect is to be expected in the case of the positively charged base than in the case of the uncharged. The assumption is made that for bases of different type as well as for bases of the same type equal rates of association mean equal basic strength.

THE TEMPERATURE COEFFICIENT

Although considerable effort has been devoted to the detection and study of reactions showing general acid and basic catalysis, little is known of the change, with change in temperature, of the rates of the catalyzed reactions. In the case of a reaction catalyzed by acids HA_1, HA_2, \dots and by bases A_1, A_2, \dots it is unlikely that the energies of activation $E_{HA_1}, E_{HA_2}, \dots, E_{A_1}, E_{A_2}, \dots$ are all equal. It is, therefore, to be expected that the relationship between catalytic strength and relative acid or basic strength would change with change in temperature.

It is generally accepted that, in ester hydrolysis, the temperature coefficient of the hydroxyl-ion catalyzed reaction is lower than that of the hydrogen-ion catalyzed reaction. The same is probably true of the hydrolysis of the amides, in spite of the dis-

crepancies between the experimental results of different workers. In the case of the hydration of acetic anhydride Kilpatrick (11) estimated from the velocity constants of Szabó (18) at 18°C., and his own at 0°C., that for the reaction in water alone

$$k_0^{18}/k_0^0 = 3.6$$

and for the catalysis by the acetate ion

$$k_{Ac}^{18}/k_{Ac}^0 = 2.6$$

The heat of activation of the reaction between acetone and iodine, catalyzed by the hydrogen ion, is 20,540 cal. (19). From the experimental results of Rice and Lemkin (20), Rice and Urey (21) concluded that the heat of activation of the reaction between acetone and iodine, catalyzed by the bisulfate ion, is smaller by several thousand calories.

The authors (22) have recently made a study of the temperature coefficient of the mutarotation of glucose (*a*) in water alone, (*b*) catalyzed by pyridine, (*c*) catalyzed by the acetate ion, and (*d*) catalyzed by the hydrogen ion. In the list are three basic catalysts—water, the acetate ion, and pyridine—and two acid catalysts—water and the hydrogen ion. Experiments were carried out at 0°, 20° and 25°C. In figure 4 the logarithms of the catalytic constants are shown plotted against the reciprocal of the absolute temperature. Included on the plot are the results of Brönsted and Guggenheim at 18°C. The slopes of the lines in figure 4, multiplied by 4.574, give the values of the heat of activation listed in the following table.

<i>Heats of Activation</i>				
Catalyst.....	Hydrogen ion	Acetate ion	Pyridine	Water
Heat of activation.....	19,300	19,100	18,000	17,600

It has been pointed out that for reactions showing general acid or basic catalysis a linear relationship may be expected between the logarithm of the catalytic constant and the logarithm of the dissociation constant of the catalyzing acid or base. Since no reaction has been examined at several temperatures with sufficient thoroughness, it is not known whether the slope of the line ob-

tained by plotting the logarithm of the catalytic constant against that of the dissociation constant changes with temperature, or not. Assuming that the changes in the dissociation constants with temperature are small, one sees that if the heats of activation for the different catalysts are the same, the slope of the line remains constant, and that if the heats of activation change regularly with the acid or basic strength of the catalyst, the slope changes with temperature. If, in the mutarotation of glucose, pyridine, the

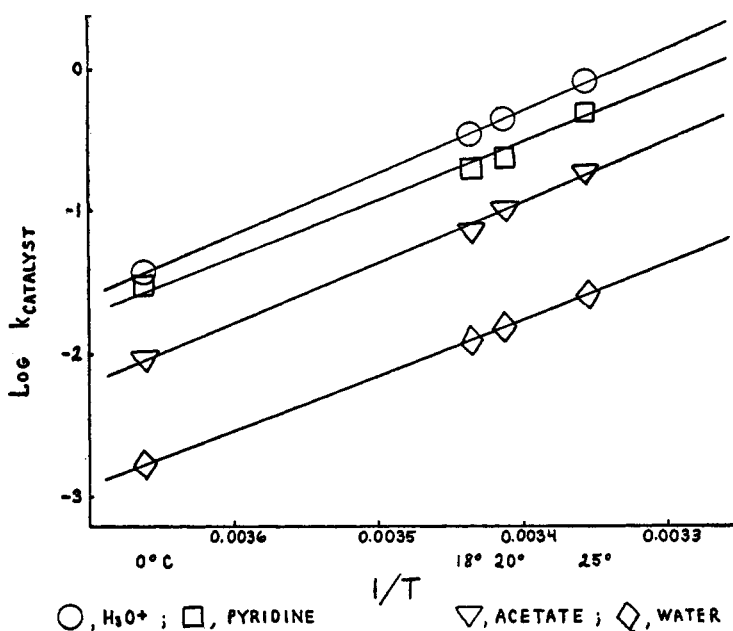


FIG. 4. THE MUTAROTATION OF GLUCOSE

acetate ion and water can be regarded as representative basic catalysts, and the hydrogen ion and water as representative acid catalysts, little change in the relationship between catalytic strength and relative acid or basic strength is to be expected with change in temperature.

SUMMARY

A number of reactions in solution are now known which exhibit general acid or basic catalysis, i.e., catalysis by acids other than

the hydrogen ion, or by bases other than the hydroxyl ion. In most cases the relationship between catalytic effect and strength of the acid catalysts is represented by the equation

$$k_a = G_1 K_A^x$$

and the relationship between catalytic effect and the strength of the basic catalysts by the equation

$$k_b = G_2 K_B^y$$

The equations hold roughly over a range of many powers of 10 in K_A in the mutarotation of glucose, the acid hydrolysis of the ortho esters, the acetone-iodine reaction, and the dissolution of magnesium in acids. For a series of catalysts of the same chemical type the equations have been found in a number of instances to hold exactly.

These equations were proposed by Brönsted on the assumption that the process of acid catalysis is analogous to the dissociation process of an acid, and that of basic catalysis to the association process of a base. Experiment shows that for a given series of catalysts the exponent varies from reaction to reaction, whereas according to the theoretical development constancy is to be expected. There is therefore an effect of the substrate for which the theory does not account.

Little is known of the temperature coefficients of the catalytic processes in reactions showing general acid or basic catalysis. An appreciable difference appears to exist between the heat of activation of the hydration of acetic anhydride in water alone, and the heat of activation of the hydration catalyzed by the acetate ion. Between the heats of activation of the acetone-iodine reaction catalyzed by the hydrogen and by the bisulfate ion there is a difference of about 15 per cent. A study of four catalytic processes in the mutarotation of glucose yielded values of the heats of activation ranging from 17,600 cal. for the water reaction to 19,300 cal. for the hydrogen-ion catalyzed reaction.

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