

In other words, the presence of a positive ion affects the whole structure of the chloride ion. It is obvious, then, that the total energy change cannot be found from the change in potential energy of the ions as a whole considered as rigid structures, but must take into account the changes of potential (and probable kinetic) energy of the electrons in each ion as well.

The approximate treatment of the electrons in a dynamic atom, as located in definite positions, may be justified on the ground that these positions represent time average or effective positions.<sup>14</sup> The greatest objection, however, to the treatment of Born and his associates is the assumption of a rigid structure and thus a complete neglect of changes in energy due to the distortion of the electronic arrangement. It would seem that further attempts in this direction are not likely to be profitable.

### Summary

A tabulation has been made of the heats of ionization in the gaseous state of the hydrogen and alkali chlorides, bromides and iodides.

The ionization constant of sodium chloride at its boiling point has been found to be  $4 \times 10^{-13}$ .

From a consideration of the fields of force about the ions and the molecular diameters it would seem that the heats of ionization cannot be calculated by any method which treats the ions as rigid structures of electrons about a positive center.

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## A THEORY OF CHEMICAL REACTIVITY

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The influence of temperature on the rate of chemical change is so marked that it is obviously a very important factor in any theory of chemical reactivity. Explanations for the high temperature coefficients of chemical reactions usually center round the empirical equation of Arrhenius<sup>1</sup> connecting velocity of reaction and temperature, which in the integrated form is  $2.3026 \log k_1/k_2 = \frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$ . Considering the hydrolysis of cane sugar by hydrochloric acid in aqueous solution, Arrhenius suggested that the cane sugar was present in two forms, active and inactive, in mass-action equi-

<sup>14</sup> Thus, the fundamental idea of G. N. Lewis' theory of valence, that in non-polar compounds a chemical bond consists of a pair of electrons, remains essentially the same whether we consider the electrons as actually located between the atoms or rotating in orbits with that position as their effective location.

<sup>1</sup> Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

librium, the equilibrium concentration of the active form being very small. In such a case as this it is evident that the concentration of the active form will vary rapidly with the temperature, for it will be proportional to the equilibrium constant of the reaction, active  $\rightarrow$  inactive molecules, and the quantity  $Q$  in the Arrhenius equation will be the heat of the reaction, active  $\rightarrow$  inactive molecules. The radiation theory offers a similar explanation, except that the two forms of the sugar molecules are not in mass-action equilibrium, the difference between the two forms being due to absorption by the sugar molecule of infra-red radiation, the molecule becoming active when its total energy exceeds a certain value.

It should be noted, however, that there is no *a priori* reason for supposing that the cane sugar exists in two forms; we might select any one of the three entities, cane sugar, water and hydrogen ion, taking part in the reaction, and by saying that it was present in two forms, we could deduce the Arrhenius equation. The justification for the particular selection would of course depend on the further development of the theory. The criticisms which were made during a recent discussion of the radiation theory,<sup>2</sup> and the inability of the theory to explain certain results recently obtained in this Laboratory<sup>3</sup> have led me to propose a modification of the Arrhenius theory in which the hydrogen ion is supposed to exist in two forms, active and inactive, in mass-action equilibrium. The active form is identified as the unhydrated hydrogen ion, the hydrated form and the undissociated acid having no catalytic activity; similar assumptions are made for hydroxyl-ion catalysis. Whereas on both the Arrhenius theory and the radiation theory every chemical reaction should have a unique temperature coefficient depending on the heat of activation of the substance undergoing change, it is evident that this new theory predicts that chemical reactions will fall into comparatively few classes, each having a characteristic temperature coefficient. That there is this tendency may be seen from the temperature coefficients obtained in the acid hydrolysis of substances containing the carbonyl group. A very great number of studies of this type of reaction have been made, and almost without exception the value of  $k_{35}/k_{25}$  lies between 2.2 and 2.5. The value of  $k_{35}/k_{25}$  for the acid hydrolysis of ethyl acetate,<sup>4</sup> formyl acetic acid<sup>5</sup> and ethyl cyano-acetate<sup>6</sup> are all 2.4, within experimental error; on the old theories we have to assume that these compounds all have the same heat of activation or critical increment.

Perhaps the most striking deduction which may be made from this new theory is that stoichiometrically neutral water may not be neutral cata-

<sup>2</sup> *Trans. Faraday Soc.*, 17, 546 (1922).

<sup>3</sup> Rice and Kilpatrick, *THIS JOURNAL*, 45, 1401 (1923). Rice and Lemkin, *ibid.*, 45, 1896 (1923).

<sup>4</sup> Taylor, *THIS JOURNAL*, 37, 551 (1915).

<sup>5</sup> Senter and Ward, *J. Chem. Soc.* 101, 2534 (1912).

<sup>6</sup> Dushrel, *Am. J. Sci.*, 33, 27 (1912).

lytically. We consider water to be neutral when the total hydrogen- and hydroxyl-ion concentrations are equal, and since the unhydrated ions are present in very minute concentrations we shall also have the concentrations of the hydrated ions equal at this point. The concentrations of the unhydrated ions will not be equal, however, and if, as I shall show later, the affinity of the hydrogen ion for water is greater than the affinity of the hydroxyl ion, a stoichiometrically neutral solution will be alkaline catalytically. It is only by making the solution acid stoichiometrically that the concentrations of the two unhydrated ions will become equal and the solution will have a minimum catalytic activity.

### Theoretical Outline

Since the views herein expressed are somewhat at variance with those currently accepted I will state briefly the assumptions made in the development of the theory. It is assumed that the law of mass action first enunciated by Guldberg and Waage is correct in its classical form, namely, that the concentration of a substance is a sufficiently exact and complete mode of representing its chemical reactivity. Such statements as "One and the same substance exhibits a different degree of reactivity according to the nature of its surroundings, that is, according to the nature of the medium in which it is dissolved," are explicitly denied. It is not the mass-action law but our system of stoichiometric equations that has broken down. For example, it will be shown that if we assume that only the unhydrated hydrogen ion is catalytically active we obtain a satisfactory explanation of experimental results, yet in our stoichiometric equations and in our methods of determining hydrogen-ion concentrations it is implicitly assumed that the total hydrogen ion is catalytically active. It is not surprising, therefore, that the mass-action law fails to hold.

That our stoichiometric equations do not truthfully represent what occurs may easily be seen by considering such reactions as that between the thiosulfate ion and iodine, or between silver nitrate and sodium chloride; even if the reacting species are present in concentrations as low as 0.00001 *N* the reaction proceeds practically instantaneously, and a great many other cases may be mentioned in which there is practically instantaneous reaction, although the concentrations of the reactants may be very low. It follows, therefore, that even at concentrations as low as 0.00001 *N* the number of molecular collisions is sufficient to permit a reaction to be practically instantaneous. If, however, we consider reactions which proceed with measurable velocity, the stoichiometric concentrations of the reactants may all be 0.1 *N* or even higher, yet it may take over an hour for  $\frac{1}{10}$  of the reactants to disappear. The theory explains this difficulty by postulating that in such cases the reactants are not those represented by the stoichiometric equations, but that due to combinations with the

solvent at least one of the reactants is present in very minute concentration with consequent reduction in the number of molecular collisions. On the other hand the radiation theory<sup>7</sup> explains the difficulty by assuming that only a small fraction of the collisions are effective. It may be pointed out here that the rule<sup>8</sup> that the temperature coefficient of a strongly catalyzed reaction should be less than that of a feebly catalyzed one depends upon the possibility of changing a large proportion of inactive to active molecules, in other words of bringing the concentration of the active molecules to ordinary stoichiometric concentrations. In this case the reaction should be practically instantaneous, so that we must conclude on the basis of both the Arrhenius theory and the radiation theory that the temperature coefficient is independent of the velocity of the reaction in those cases in which the velocity is measurable.

I will now consider a particular class of reactions, namely, the case where we have hydrogen-ion catalysis by a strong acid in which the solvent does not enter directly into the reaction. Assuming that the strong acid is practically entirely dissociated, the total hydrogen ion will be present as hydrated hydrogen ion and a minute quantity as unhydrated hydrogen ion; in this case the unhydrated hydrogen ion is supposed to be the only active molecule, so that all these reactions should have the same temperature coefficient. This would hold for any solution in which the hydrogen ion is combined only with water, for the variation with temperature of the concentration of the unhydrated ion depends on its heat of combination. Therefore the temperature coefficient should not be affected by the presence of non-electrolytes or neutral salts, since the affinity of hydrogen ion for water is so great<sup>9</sup> that it is unlikely that there will be any extensive combination between the hydrogen ion and these substances. For this conclusion regarding the temperature coefficient to be true, it is necessary to assume that the mass-action law holds and that viscosity effects are negligible. A study of the reaction between acetone and iodine showed that the value of  $k_{35}/k_{25}$  was  $3.0814 \pm 0.20\%$  whenever the catalyst was a strong acid, although in some cases neutral salts in concentrations from 1 to 4 *N*, and non-electrolytes in concentrations from 5 to 30% were present. This result is very striking because we were unable to alter the tem-

<sup>7</sup> W. C. M. Lewis [*Scientia*, **25**, 450 (1919)]. "The fact, that many reactions occur with a finite and measurable velocity, shows us that all the molecules are not in the same chemical state. If they were, the speed of the reaction would either be zero or infinite." Taylor [*J. Phys. Chem.*, **27**, 322 (1923)] has put forward a theory of negative catalysis based on these considerations. "The theory emphasizes anew the fact that the concentration of a substance is not the active mass of the substance, but a very much greater quantity."

<sup>8</sup> Lamble and Lewis, *J. Chem. Soc.*, (a) **105**, 2330 (1914); (b) **107**, 233 (1915).

<sup>9</sup> Born, *Ber. physik. Ges.*, **21**, 679 (1919). Fajans, *ibid.*, **21**, 649 (1919). A résumé of this work is given by Taylor, *Newer Aspects of Ionization Problems*, *Trans. Am. Electrochem. Soc.*, **43**, preprint (1923).

perature coefficient in the slightest degree when the catalyst was a strong acid. When, however, weaker acids were used as catalysts, that is, when the state of combination of the hydrogen ion was affected, the temperature coefficient fell. It will be shown in a later section that with weaker acids the concentration of the hydrated hydrogen ion diminishes with rise in temperature thus giving a lower temperature coefficient.

In reactions which are hydrolytic in character I assume that a compound is formed between the substance A undergoing hydrolysis and the water; that in general only a small fraction of the substance A is present as hydrate, and that the hydrolysis takes place by collision of the unhydrated hydrogen ion with the hydrate. It will be seen that the hydrate of the substance A now becomes an active molecule and the temperature coefficient of the reaction will depend on whether the heat of hydration of A is positive or negative. I have thus covered practically all cases of hydrogen-ion catalysis, and the treatment of hydroxyl-ion catalysis is exactly similar.

We can conclude, therefore, that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient. The temperature coefficient of a reaction is fixed by the number and nature of the active molecules, and all types of reaction which have the same active molecules will have exactly the same temperature coefficient. The variation with temperature of the concentration of the active molecule will depend on its heat of combination with the solvent or other constituents of the solution with which it combines. According as its heat of formation is positive or negative the concentration of the active molecule will decrease or increase with rise of temperature; an active molecule, therefore, on this theory has no particular virtue because of its internal energy content. If we measure the velocity of a reaction at two temperatures, and substitute the values in the Arrhenius formula we shall obtain directly the heat of combination of the active molecule if its formation is represented by an equation such as  $B + C \rightleftharpoons A$  where A is the active molecule. In other cases the calculated value of  $Q$  will usually be a simple multiple or sub-multiple of the heat of reaction, and in cases where there is more than one active molecule the value of  $Q$  will be the algebraic sum of these quantities. Since  $Q$  is a heat of reaction, it will vary slightly with the temperature, and this variation could be calculated if the specific heats of the reactants and resultants were known as functions of the temperature. In those reactions which have the same active molecules, the value of  $Q$  and its variation with the temperature will be the same.

In concluding this section I wish to refer briefly to unimolecular chemical changes. Perrin<sup>2</sup> in support of the radiation theory, has pointed out that in unimolecular chemical reactions the velocity is independent of the number of collisions per second and can, therefore, be due only to some out-

side agency, presumably radiation. This argument would be much more convincing if we had an example of a chemical reaction which proceeded with measurable speed and was really unimolecular; all the examples quoted<sup>10</sup> by Perrin are really pseudo-unimolecular, in which catalysts or traces of water vapor are required for the reaction to proceed. There does not appear to be a single case of a chemical reaction which proceeds with measurable speed and which we are reasonably certain is a true unimolecular reaction. It may be pointed out here that the decomposition of nitrogen pentoxide<sup>11</sup> which appeared to be a case of a unimolecular change has now been shown<sup>12</sup> to be at least bimolecular, small traces of the decomposition products being necessary to secure a constant specific rate of decomposition.

### Hydrogen-Ion Catalysis by Strong Acids

That there exists in aqueous solution more than one type of hydrogen ion has long been recognized. In a recent paper<sup>13</sup> Kendall states "the hypothesis of the catalytic activity of the undissociated molecule which purports to explain why the speed of reactions such as ester catalysis is not exactly proportional to hydrogen-ion concentration may be discarded in favor of a view which recognizes several types of hydrogen ion (*e. g.*,  $H^+$ ,  $[H(H_2O)]^+$ ,  $[H(R.COOR)]^+$ ) each possessing a different catalytic activity." The view which I have adopted in this paper is that only the free hydrogen ions are catalytically active, and that these correspond with the active molecules of Arrhenius. When the hydrogen ion is in combination, either as the undissociated molecule or as hydrated hydrogen ion, the resulting compound has no catalytic activity, or a relatively small catalytic activity; these compounds would correspond to the inactive molecules of Arrhenius.

Lapworth<sup>14</sup> and his co-workers first put forward the view that the unhydrated hydrogen ion was the catalytically active particle and that the hydrated hydrogen ion had little or no catalytic activity. They examined a number of widely different cases of hydrogen-ion catalysis in alcohol and showed that all occurred enormously faster in alcohol than in water, and further that the addition of minute quantities of water caused a marked retardation of the velocity. He states, "The proposition that free hydrogen ions are responsible for the catalytic activity of acids leads to the conclusion that they must be relatively few in number in aqueous solution. On the other hand the original conception of hydrogen ions was applied

<sup>10</sup> Lowry, *Trans. Faraday Soc.*, 17, 596 (1922).

<sup>11</sup> Daniels and Johnston, *THIS JOURNAL*, 43, 53 (1921).

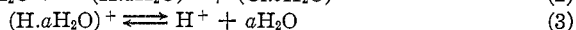
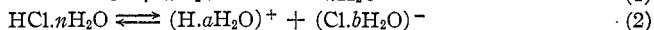
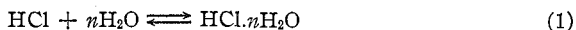
<sup>12</sup> Daniels, Wulf and Karrer, *ibid.*, 44, 2402 (1922).

<sup>13</sup> Kendall, *Proc. Nat. Acad. Sci.*, 7, 56 (1921).

<sup>14</sup> Fitzgerald and Lapworth, *J. Chem. Soc.*, 93, 2163 (1908). Lapworth, *ibid.*, 93, 2187 (1908).

to explain the conductivity of acids in aqueous solution, so that the terms are not synonymous. In the latter case, they must be complex ions, probably of the form  $(\text{H}_2\text{O}\cdot\text{H})^+$ ." Dawson,<sup>15</sup> from experiments on the reaction  $\text{CH}_3\text{COCH}_3 + \text{I}_2$  in water and water-alcohol mixtures, also supported this view. He showed that in alcohol solutions containing small quantities of water the reaction velocity was proportional to the concentration of the acetone, but was not proportional to the concentration of the acid catalyst. In such solutions the velocity increased much more rapidly than the concentration of acid catalyst. He concludes, "By comparison of the observations in aqueous with those in alcoholic solution we are led to the conclusion that the ionic component responsible for the catalytic effect is the free hydrogen ion, and that the effect of the hydrated ion is relatively unimportant. The concentration of the free hydrogen ions is very small in comparison with the total ion concentration, and in order to produce the observed effects it must be assumed that their specific catalytic activity is very great. Since the ratio of the free hydrogen ion to the total hydrogen ion concentration is so small the electrical conductivity of the solution is mainly determined by the complex ions, and the catalytically active ions are of little consequence in so far as the conductivity of the acid solution is concerned."

I will first apply this theory to the case of hydrochloric acid in aqueous solution, since the reasoning applies equally well to all strong acids. Writing the equilibria involved,<sup>16</sup> we have



where  $n = a + b$ . The problem is to find out how the unhydrated hydrogen ion in Equation 3 varies with the temperature, for this variation determines the temperature coefficient of the reaction. In the first place I will assume that at temperatures of  $0^\circ$  to  $35^\circ$  Reactions 1 and 2 go practically to completion, that is, that in aqueous 0.1 *N* solution hydrochloric acid is almost entirely dissociated. The concentration of the hydrated hydrogen ion will not vary, therefore, very much with the temperature, and for small temperature intervals we may write it as a constant without making much error. Considering Reaction 3 at  $25^\circ$  and  $35^\circ$  we have the ratio of the equilibrium constants  $K_{35}/K_{25} = \frac{(\text{H}^+)_{35} \times (\text{H}_2\text{O})_{25}^a}{(\text{H}^+)_{25} \times (\text{H}_2\text{O})_{35}^a}$  and since the heat of hydration<sup>17</sup> per g. of hydrogen ion is 262,000 cal., this ratio is of the order of 10.<sup>14</sup> Increase in temperature, therefore, strongly favors the formation of the unhydrated hydrogen ion, but unfortunately since we do not know

<sup>15</sup> Dawson, *J. Chem. Soc.*, 99, 1 (1911). Dawson and Powis, *ibid.*, 105, 1093 (1914).

<sup>16</sup> See Kendall and Gross, *THIS JOURNAL*, 43, 1416 (1921).

<sup>17</sup> Fajans, *Ber. phys. Ges.*, 21, 709 (1919).

the concentration of the simple water molecules present in the solution nor the number of water molecules in combination with the hydrated hydrogen ion we cannot calculate the change in concentration of the unhydrated hydrogen ion with temperature, which would give us the temperature coefficient of a reaction catalyzed by this acid. We can state, however, that a reaction will have the same temperature coefficient provided it is catalyzed by a strong acid, for the temperature coefficient is fixed by Reaction 3 and this is independent of the kind of acid used provided it is almost entirely ionized. A search of the literature showed that very few such measurements have been made, the great bulk of the studies having been made on reactions which are hydrolytic in character. Harned and Seltz<sup>18</sup> have measured the temperature coefficient of the change, acetyl-chloro-amino-benzene  $\rightarrow$  *p*-chloro-acetanilide, catalyzed by hydrochloric acid. Their results give the mean value of  $k_{35}/k_{25}$  as 3.14, which is in fairly good agreement with the theoretical value, 3.0814. Slator<sup>19</sup> has studied the temperature coefficients of the reactions between a great number of alkyl halides and sodium thiosulfate. The temperature coefficients in all cases had the value 3 within experimental error, which suggests that these reactions are really cases of hydrogen-ion catalysis. A more rigid test of the theory is at present being conducted in this Laboratory, by measuring the temperature coefficients of the reactions of iodine with various ketones and aldehydes. Mr. C. F. Fryling, using the improved technique<sup>3</sup> already described, has found that although the velocities vary widely, all of the temperature coefficients  $k_{35}/k_{25}$  have the value  $3.081 \pm 0.16\%$ , without a single exception. A description of this research will be communicated shortly. Work is also in progress to extend these measurements to other reactions.

### Hydrogen-Ion Catalysis by Moderately Strong and Weak Acids

If we write Equations 1 and 2 of the previous section as one equation and generalize by writing X for the acid radical we have:  $\text{HX} + n\text{H}_2\text{O} \rightleftharpoons (\text{H}.a\text{H}_2\text{O})^+ + (\text{X}.b\text{H}_2\text{O})^-$ . In general, this reaction will be exothermic, so that a rise in temperature will send the reaction towards the left. In the case of strong acids where the concentration of the undissociated acid (HX) is very small, an increase of temperature will not affect the concentration of the hydrogen ion  $(\text{H}.a\text{H}_2\text{O})^+$  appreciably, because only a slight movement of the equilibrium towards the left is necessary to alter markedly the value of the equilibrium constant. In the case of weaker acids where the undissociated molecule is present in appreciable amounts, increase in temperature should cause an appreciable diminution in the concentration of the hydrated hydrogen ion  $(\text{H}.a\text{H}_2\text{O})^+$ , and this diminution should be

<sup>18</sup> Harned and Seltz, *THIS JOURNAL*, **44**, 1475 (1922).

<sup>19</sup> Slator, *J. Chem. Soc.*, **85**, 1286 (1904).



greater the weaker the acid. The presence of neutral salts might be expected to increase this effect, since their effect is to make the acid appear weaker. It is evident, therefore, that in the case of weaker acids, since the concentration of the hydrated hydrogen ion diminishes with rise in temperature, the increase in concentration with temperature of the unhydrated hydrogen ion is partly neutralized; this means that weaker acids should have lower temperature coefficients than strong acids, a result which is in accord with experiment. The values of  $Q$  for the reaction between acetone and iodine when catalyzed by 0.1  $N$  hydrochloric acid and 0.1  $N$  sulfuric acid are 20,540 and 19,070, respectively, so that the ratio  $Q(\text{HCl})/Q(\text{H}_2\text{SO}_4) = 1.077$ ; this same ratio should be found for any other reaction whatsoever, provided that it is carried on in moderately dilute aqueous solution.

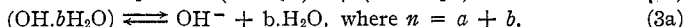
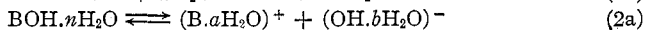
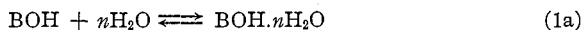
### Hydrogen-Ion Catalysis. Hydrolysis

Consider the hydrolysis of ethyl acetate by hydrochloric acid. Writing the equilibrium for ethyl acetate and water we have:  $\text{CH}_3\text{COOC}_2\text{H}_5 + n\text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 \cdot n\text{H}_2\text{O}$ . I will assume that only a small fraction of the ethyl acetate is present as hydrate and that the hydrolysis takes place by collision of the unhydrated hydrogen ion with the ethyl acetate hydrate. If the bulk of the ethyl acetate were present as hydrate or if the heat of hydration of the ethyl acetate were zero we should have a case similar to that treated in the section previous to the last, and the temperature coefficient,  $k_{35}/k_{25}$ , would be 3.08. Since, however, we have assumed that the ethyl acetate hydrate is present only in small concentration compared with the total ethyl acetate, the temperature coefficient will be lowered if the hydrate is formed with evolution of heat, and raised if the hydrate is formed with absorption of heat. The heat of dilution of aqueous methyl acetate is positive, which indicates that the hydrate is formed with evolution of heat and hence its concentration will diminish with rise in temperature. The heat of hydration of all esters containing the carbonyl group will probably have about the same value, so that in all cases of hydrolysis of such esters by strong acids the temperature coefficient should be about the same and be less than 3.08. Inspection of the literature shows that almost without exception the values of  $k_{35}/k_{25}$  for such reactions lie between 2.2 and 2.5. If instead of ethyl acetate in the above equation we substitute another substance capable of hydrolysis but having a negative heat of hydration, the concentration of the hydrate will increase with rise in temperature and the temperature coefficient,  $k_{35}/k_{25}$ , will be greater than 3.08. The value of  $k_{35}/k_{25}$  for the hydrolysis of cane sugar<sup>8b</sup> is slightly over 4, which indicates that the combination of the cane sugar with the water molecule *which takes part in the hydrolysis*, is an endothermic reaction. It does not seem possible, however, to test this experi-

mentally at present. The results given in the literature for the acid hydrolysis of amides are so contradictory that it is not possible to test the theory in this case either. From the results of Crocker<sup>20</sup> and of Kilpi,<sup>21</sup>  $k_{35}/k_{25} = 3.4$ . Peskoff and Meyer<sup>22</sup> studied the hydrolysis of six amides; the values of  $k_{35}/k_{25}$  which they obtained for the different amides were erratic and varied between 2.52 and 3.29.

### Hydroxyl-Ion Catalysis

If we write the equilibria involved when a base (B) is dissolved in water we have,



I assume here that only the free hydroxyl ion has any catalytic activity, and that when the hydroxyl ion is combined either with water or in the base, the resulting compound has no catalytic activity. The reasoning to be followed then becomes exactly the same as in hydrogen-ion catalysis; all reactions catalyzed by a strong base where the hydroxyl ion is the only active molecule, will have the same temperature coefficient, reactions catalyzed by weaker bases will have a lower temperature coefficient, and reactions involving the hydrolysis of compounds containing the carbonyl group will have a still lower temperature coefficient. As in the case of hydrogen-ion catalysis hardly any data are available for testing this except for the case of hydrolytic reactions. The value of  $k_{35}/k_{25}$  for the reaction between acetone and iodine has been measured in this Laboratory by Mr. M. Bergstein, and found to be 2.52 when the reaction was catalyzed by an alkaline buffer solution. Reicher<sup>23</sup> measured the rate of hydrolysis of ethyl acetate by sodium hydroxide at 24.22° and 35.14°; the value of  $Q$  calculated from these two results is 10,950, whence  $k_{35}/k_{25} = 1.82$ .

Wilsdon and Sidgwick,<sup>24</sup> and also Boeseken and Verkade<sup>25</sup> have studied the rate of hydration of acid anhydrides. These reactions are not catalyzed by hydrogen ions but are very strongly catalyzed by hydroxyl ions. It is suggested, therefore, that they are really cases of alkaline hydrolysis similar to the case of nitrocamphor investigated by Lowry,<sup>26</sup> the hydroxyl ion being derived from the glass or from organic alkaline impurities in the acetic anhydride. Wilsdon studied the rate of hydration of acetic, propionic and camphoric anhydrides at 18° and 25°. The average value of  $k_{25}/$

<sup>20</sup> Crocker, *J. Chem. Soc.*, **91**, 593 (1917).

<sup>21</sup> Kilpi, *Z. physik. Chem.*, **80**, 165 (1912).

<sup>22</sup> Peskoff and Meyer, *ibid.*, **82**, 129 (1913).

<sup>23</sup> Reicher, *Ann.*, **232**, 103 (1886).

<sup>24</sup> Wilsdon and Sidgwick, *J. Chem. Soc.*, **103**, 1959 (1913). Wilsdon, *ibid.*, **107**, 679 (1915).

<sup>25</sup> Boeseken and Verkade, *Verslag Akad. Wetenschappen Amsterdam*, **22**, 634 (1914).

<sup>26</sup> Lowry, *J. Chem. Soc.*, **93**, 107 (1908).

$k_{18}$  was 1.57, average deviation 3.6%, maximum deviation 5.7%. These deviations are probably within experimental error, yet the rate of hydration of acetic anhydride is almost ten times as great as that of camphoric anhydride. Using this average value,  $Q = 11,100$  and  $k_{35}/k_{25}$  (calculated) is equal to 1.84 as compared with 1.82 for the alkaline hydrolysis of ethyl acetate. Boeseken and Verkade studied the rate of hydration of propionic, butyric and *isobutyric* anhydrides at  $0^\circ$  and  $25^\circ$ , and obtained similar results.

The temperature coefficient for the hydrolysis of amides by alkalis should be somewhat greater than 2.52 which was obtained for the reaction between acetone and iodine when catalyzed by the hydroxyl ion. Peskoff and Meyer have obtained an average value for  $k_{35}/k_{25}$  equal to 2.65 for the alkaline hydrolysis of six amides.

### Point of Minimum Catalytic Activity

An aqueous solution is ordinarily considered neutral when the total hydrogen-ion concentration is equal to the total hydroxyl-ion concentration, in which case the hydrated forms of the two ions will be present in practically equal concentrations. It will be readily seen that in such a solution the concentrations of the unhydrated forms of the two ions may be very far from being equal, so that a stoichiometrically neutral solution may not be neutral catalytically. Indeed, from the work of Fajans and of Born<sup>9</sup> it is clear that the smaller the ion, the greater is its affinity for water; therefore, we should expect the hydrogen ion to have a much greater affinity for water than the hydroxyl ion, and consequently in a stoichiometrically neutral solution where the hydrated forms of the hydrogen ion and hydroxyl ion are present in equal concentrations, the unhydrated hydroxyl ion will be present in much greater concentration than the unhydrated hydrogen ion. By acidifying the solution we should reach a point where the concentrations of the two unhydrated ions are equal, and this would be the point of minimum catalytic activity, assuming that the catalytic activities of the two ions are about equal. The phenomenon was first noticed in this Laboratory in some preliminary work concerned with the measurement of reaction velocity. It was found that the saturated borax-boric acid buffer which was supposed to be neutral, catalyzed the reaction at about the same rate as 0.001 *N* hydrochloric acid. The acetone was finally converted into iodoform which indicated that the catalyst was hydroxyl ion. The matter was not investigated further at that time, the difficulty being overcome by rapid titration of the iodine. Since then the catalytic activity of buffer solutions on the reaction has been studied in this Laboratory by Mr. M. Bergstein, and the results will be communicated shortly. In all the cases investigated a point of minimum catalytic activity was found to lie about  $P_H$  5. This abnormal behavior

of aqueous solutions near the neutral point has been commented on in two papers. Karlsson<sup>27</sup> investigated the effect of hydrogen-ion concentration on the stability of methyl acetate and ethyl acetate. The experiments were made at 75° and 85° in presence of a buffer solution of known hydrogen-ion concentration and the esters showed greatest stability at Sørensen ( $P_H$ ) values between 4.7 and 5.1. Dawson and Powis<sup>28</sup> investigated the auto-catalytic reaction,  $\text{CH}_3\text{COCH}_3 + \text{I}_2 = \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$ . "If  $x$  represents the concentration of hydrogen iodide which has been set free after time  $t$  in an originally 'neutral' aqueous solution containing  $c$  molecules of acetone per liter and a relatively small quantity of iodine, then the velocity at this moment should be given by  $dx/dt = kcx$ , where  $k$  denotes the velocity in a solution containing one molecule of acetone per liter and one molecule of halogen acid per liter." The integrated form of the equation is  $\ln x = kct + \text{a constant}$ , and by extrapolation of the straight line obtained by plotting  $\ln x$  as a function of  $t$ , the initial speed of the reaction was found. This corresponded to a hydrogen-ion concentration of  $P_H$  4.7.

It would appear, therefore, that in order to attain a minimum rate of reaction in aqueous solution, or maximum stability of compounds which are decomposed catalytically, it is necessary to keep the stoichiometric hydrogen-ion concentration near  $10^{-5}$ . The hypothesis that the unhydrated hydrogen and hydroxyl ions are the catalytically active particles provides a satisfactory explanation of these abnormalities. Stoichiometrically neutral water is distinctly alkaline catalytically and it is only when the stoichiometric concentration of the hydrogen ion approaches  $P_H$  5 that the solution has minimum catalytic activity. The explanation of Karlsson that the hydrogen and hydroxyl ions do not have the same activity is probably only partly an explanation of the phenomenon, because on his explanation we have to assume that the hydroxyl ion is several hundred times as active catalytically as the hydrogen ion and that this same ratio holds for many different reactions.

### Summary

1. An explanation for the high temperature coefficient of chemical reactions is offered in which it is assumed that the mass-action law in its classical form is true, and that its apparent failure is due to using stoichiometric equations which do not represent even approximately the reactions taking place in the solution.

2. When the ordinary stoichiometric equations are replaced by equations representing more nearly what occurs, it has been shown that certain molecules are connected with an equilibrium constant in such a way that their concentrations vary rapidly with the temperature. These are re-

<sup>27</sup> Karlsson, *Z. anorg. Chem.*, 119, 69 (1921).

<sup>28</sup> Dawson and Powis, *J. Chem. Soc.*, 101, 1503 (1912).

ferred to as active molecules, and it is due to these that "slow" reactions have a high temperature coefficient.

3. The theory predicts that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient.

4. In this theory the assumption is made that the unhydrated hydrogen and hydroxyl ions are the catalytically active particles, and this leads to the conclusion that stoichiometrically neutral water is distinctly alkaline catalytically, and it is not until the hydrogen-ion concentration has a value about  $P_H$  5 that the concentrations of the unhydrated ions become equal, and the catalytic activity is at a minimum.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS, UNITED STATES DEPARTMENT OF COMMERCE]

## INVESTIGATIONS ON THE PLATINUM METALS. IV.<sup>1</sup> THE DETERMINATION OF IRIIDIUM IN PLATINUM ALLOYS BY THE METHOD OF FUSION WITH LEAD<sup>2</sup>

BY RALEIGH GILCHRIST<sup>3</sup>

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### Introduction

A critical study of the Deville and Stas<sup>4</sup> method for the determination of iridium in platinum alloys was undertaken at the Bureau of Standards as the first of a series of investigations into the analytical methods for the metals of the platinum group.

### The Deville and Stas Method

Deville<sup>5</sup> found that when platinum alloyed with iridium, rhodium, palladium, iron and copper is dissolved in lead at a high temperature, the lead forms alloys with all of the platinum, rhodium, palladium and copper, and with a very small proportion of the iron. The iridium, ruthenium and iron form a separate alloy containing no lead. Boiling dil. nitric acid removes the bulk of the lead together with the palladium and copper and

<sup>1</sup> (a) I. The Preparation of Pure Platinum, by Edward Wichers, *THIS JOURNAL*, **43**, 1268 (1921). (b) II. Investigations on Platinum Metals at the Bureau of Standards, by Edward Wichers and Louis Jordan, *Trans. Am. Electrochem. Soc.*, **43**, 385 (1923). (c) III. The Preparation of Platinum and of Platinum-Rhodium Alloy for Thermocouples, by R. P. Neville, *Trans. Am. Electrochem. Soc.*, **43**, 371 (1923).

<sup>2</sup> Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.

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<sup>4</sup> Deville and Stas, "Procès-verbaux, Comité International des Poids et Mesures," 1877, p. 185.

<sup>5</sup> Ref. 4, p. 162.