TABLE III

EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF 1-IODO-2-HYDROXYNAPHTHALENE

Salt	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$	Time, min.	0.1 N I_2, cc.	$k \times 10^{-2}$
...	15	12.7	4.51	15	12.7	4.51
KCl	15	11.3	5.29	15	11.2	5.35
NaCl	15	10.8	5.59	15	10.8	5.59
KBr	15	10.5	5.78	15	10.6	5.72
NaBr	15	10.1	6.04	15	10.2	5.98
LiCl	15	10.0	6.10	15	10.2	5.98
$SnCl_4$	15	10.4	5.84	15	10.2	5.98

Stannic chloride is not a neutral salt but it was added to the list because in the former method of preparing standard solutions of stannous chloride[3] there were always appreciable quantities of this salt present due to the oxidation of the stannous chloride during storage. We were not able to include sodium or potassium iodide in Table III, because they decomposed quite rapidly with the liberation of free iodine.

Summary

1. Water decreases the rate of hydrolysis of 1-iodo-2-hydroxynaphthalene in alcoholic and acetic acid solutions of hydrochloric acid.
2. Stannous chloride and iodine do not react appreciably in hydrochloric acid solutions of acetic acid containing little moisture.
3. Neutral salts increase the rate of hydrolysis of positive halogens.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND COLUMBIA UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF REACTIONS IN SOLUTION

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The generally accepted explanation for the temperature coefficient of reactions in general is essentially the Arrhenius hypothesis of activated molecules. This has been worked out rather completely for gaseous reactions on the assumption that there is a whole series of such active molecules in statistical equilibrium with the inactive molecules and that the active molecules differ from the inactive molecules only in their energy content; each of these active molecules has a finite probability of reacting which depends upon this energy content. On this hypothesis the energy of activation is the difference of the mean energy of the molecules which react and the mean energy of all the molecules.[1] It is generally supposed that the temperature coefficients of reactions occurring in solution has a similar explanation but so far there has been no theory generally

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[1] Tolman, THIS JOURNAL, **47**, 2652 (1925).

accepted which accounts for the experimental facts observed in the study of the temperature coefficient of reactions in solution.[2] It is the purpose of this paper to discuss an application of the temperature coefficient of gaseous reactions to reactions in solution.

Brönsted's Theory.—Brönsted[3] has obtained formulas accounting for many of the apparently anomalous facts in the field of reaction kinetics involving ions. It may be assumed that the first reaction between two molecules in a solution is to form a fugitive reactive complex which is in statistical equilibrium with the reacting molecules and it is this reactive complex which decomposes spontaneously and unimolecularly or reacts with another molecule in the system. The equations representing the change may be given as

$$\mathrm{A} + \mathrm{B} \leftrightarrows \mathrm{A{\cdot}B}$$
$$\mathrm{A{\cdot}B} = \mathrm{C} + \mathrm{D} + \ldots.$$

or

$$\mathrm{A{\cdot}B} + \mathrm{C} = \mathrm{D} + \mathrm{E} + \ldots.$$

The velocity of the reaction is assumed to be proportional to the *concentration* of the fugitive reactive complex A·B. The concentration of this complex is related to its activity by the equation

$$C_{\mathrm{A\cdot B}} = \frac{C_{\mathrm{A}}C_{\mathrm{B}}f_{\mathrm{A}}f_{\mathrm{B}}}{f_{\mathrm{A\cdot B}}}$$

where the f's are the activity coefficients.

The success of this theory lies in its ability to predict the changes in the velocity of such reactions due to the addition of electrolytes to the solution. These additions of salts will change the activity of the ions present in accordance with the principles first proposed by Lewis and by Brönsted.[4] The theory predicts the general nature of the change in velocity due to the addition of such salts; in some cases it gives correctly the sign and magnitude of the change, which is a remarkable contribution to our knowledge of these reactions when we consider the confusion in this field before the theory was developed.

An extension of the theory has been proposed to account for the phenomenon of acid and basic catalysis. It is only necessary to replace the fugitive complex between two reacting molecules by a fugitive complex between a molecule and the hydrogen ion or the molecule and a basic ion. The reaction rate is again assumed to be proportional to the *concentration* of the reactive complex and this concentration is again calcu-

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[2] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924), has developed a theory for the velocity of bimolecular reactions in solution.

[3] Brönsted, *ibid.*, **102**, 169 (1922); Bjerrum, *ibid.*, (a) **108**, 82 (1924); (b) **118**, 251 (1925); see also Brönsted, *ibid.*, **115**, 337 (1925).

[4] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**; Brönsted, This Journal, **42**, 761 (1920).

lated in the same way. Brönsted[5] was led to this concept of acid and basic catalysis from his previous proposal of a new definition of acids and bases according to which an acid is defined as a substance that can give up a proton to another molecule, while a base is one which can accept a proton from another molecule. Acid catalysis consists then in the addition of a hydrogen ion to a molecule with the subsequent reaction to give the final products and the final liberation of the proton, and basic catalysis in the addition of a basic ion to a molecule with the subsequent reaction and removal of a proton by the basic ion. Brönsted[6] has found some interesting empirical relationships between the acid and basic strength as determined from the ordinary dissociation constants of the acids and bases involved and the velocity of the reaction.

In all of this development, however, there has been a notable lack of any suggestions to account for the observed facts in connection with the temperature coefficients of these reactions. Moreover, in spite of the enormous amount of work done in support of Brönsted's theory, this work has mostly been done at only one temperature and in consequence there are comparatively few experimental data to test any theory.

Observed Temperature Coefficients.—A comprehensive review of the experimental facts has been given by Rice and his co-workers,[7] and in addition they have made the most accurate measurements of the rate of reaction between halogens and ketones in dilute aqueous solutions. They also studied the effect of adding various amounts of electrolytes and non-electrolytes. The essential observed facts are that the temperature coefficients of all these reactions are the same; when catalyzed by strong acids, the addition of salts of strong acids or non-electrolytes does not change the temperature coefficient even when present at high concentrations, though the absolute values of the reaction rate change considerably and follow the prediction of Brönsted's theory. These same reactions have a lower temperature coefficient when catalyzed by weak acids and the temperature coefficient is diminished still more by the addition of salts of these weak acids. The available data for sulfuric acid have been collected and are shown in Table I, from which it appears that there is first a rapid decrease in the energy of activation which finally approaches a constant value.

The small amount of experimental data available show that the change in temperature coefficient by changing the conditions in the solution is in general small, so that only high precision work is useful for any theory of the effect.

[5] Brönsted, *Chem. Reviews*, **5**, 231 (1928).

[6] Brönsted, *Trans. Faraday Soc.*, 630 (1928).

[7] Rice and Kilpatrick, THIS JOURNAL, **45**, 1401 (1923); Rice and Lemkin, *ibid.*, **45**, 1896 (1923).

TABLE I

DATA FOR SULFURIC ACID

Acid	Salt	Q
0.1 N HCl	None	20,540
.1 N H_2SO_4	None	19,070
.15 N H_2SO_4	0.05 M Na_2SO_4	18,700
.1 N H_2SO_4	.434 M Na_2SO_4	17,610
.1 N H_2SO_4	.87 M Na_2SO_4	17,010
.097 N H_2SO_4	1.69 M $(NH_4)_2SO_4$	17,150

Theoretical

The Debye–Hückel theory predicts that the activity coefficient of an ion of a strong electrolyte will approach in the limit for zero concentration[8]

$$-\ln f_i = Z_i^2 \frac{e^3}{4k} \sqrt{\frac{\pi}{k}} \frac{1}{(DT)^{3/2}} \sqrt{\sum_1^s n_i Z_i^2}$$

where Z_i is the valence of the ion, e the atomic charge, K the Boltzmann constant, D the dielectric constant and N_i the number of ions of the i^{th} kind per cc. The rate of change of the ln f_i with temperature is easily shown to be of the order of $2 \times 10^{-4} \sqrt{\mu}$, where μ is the ionic strength. This formula is only a limiting law and does not apply in the range of concentrations used in the experiments discussed in this paper, but it seems improbable that the change of the activities of strong electrolytes with temperature can account for more than a small part of the observed temperature coefficients of these reactions and some other hypothesis must be developed.

It has occurred to the authors that the following mechanism provides a means of accounting for the observed facts discussed in the previous section. The reactive complex postulated by Brönsted undoubtedly consists of a whole series of molecules which differ from each other only in energy content. It is only necessary to assume that the probability of a molecule (AH^+) reacting is a function of its energy content and that it increases with increasing energy content. This is the generally accepted hypothesis in gaseous reactions and leads to the conclusion that the energy of activation as determined from the measured temperature coefficient of the reaction is equal to the difference of the mean energy of the molecules that react and the mean energy of all the molecules. The reaction scheme which we propose is then

$$A + H^+ \rightleftharpoons AH^+$$
$$AH^+ \rightleftharpoons (AH^+)'$$
$$(AH^+)' + B = H^+ + C + D + \ldots.$$

where $(AH^+)'$ represents a whole series of high energy molecules of the variety (AH^+). This differs from the usual scheme used by Brönsted only in the introduction of an additional step. Its extension to other

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[8] La Mer, *Trans. Am. Electrochem. Soc.*, **51**, 530 (1927).

cases besides hydrogen-ion catalysis is obvious. It remains now to show that this scheme does agree with the experimental facts.

The addition of salts to such a reaction catalyzed by a strong acid changes the velocity of the reaction by changing the concentration of the reactive complex and this change in the concentration of the critical complex is characteristic of the charges of A, (AH^+) and $(AH^+)'$ to a first approximation and is not due to any other specific properties which they may have. It, therefore, affects the whole series of molecules of the (AH^+) type regardless of their energy contents. The energy distribution of these molecules will therefore not be disturbed. There is the possibility that the addition of the salt will change the probability of reaction of a given member of this series of $(AH^+)'$ molecules. However, if this were true, it would change the velocity of the reaction and it would not be possible, therefore, to predict the general nature of the primary salt effect. We conclude, therefore, that the distribution of molecules with different energy contents and their probabilities of reaction do not change with the addition of salt and, therefore, the temperature coefficient should be independent of the concentration of salts of strong acids, which is in agreement with experimental results. Rice and Lemkin[7] showed that the temperature coefficient is unchanged even when the reaction between acetone and iodine occurs in solutions of salt concentrations up to saturation, *i. e.*, at concentrations far beyond the range in which Brönsted's theory for the salt effect can be applied. The addition of non-electrolytes such as methyl acetate or acetic acid did not change the velocity of the reaction, while cane sugar increased the velocity of the reaction; in no case was the temperature coefficient changed, which on our theory means that the relative concentrations of high energy and low energy (AH^+) molecules were unchanged.

We will now consider catalysis by weak acids. We have now present two acids, one being the (H_3O^+) and the other the undissociated acid molecule; the reaction will be catalyzed by both these acids and it is possible that it may also be catalyzed by the basic anion of the weak acid. Each of these simultaneous reactions will have its own characteristic temperature coefficient and in addition there may be an effect upon the measured temperature coefficient due to side equilibria changing the relative amounts of these catalysts. Rice and Lemkin[7] investigated the catalysis of the acetone–iodine reaction by weak acids and found in all cases that the temperature coefficient was decreased. The temperature coefficient of this same reaction when catalyzed by sulfuric acid is less than when catalyzed by hydrochloric acid and the addition of sulfates lowers the temperature coefficient still further; the experimental facts have been summarized in Table I.

We shall try to give a general interpretation of this behavior by considering the catalysis by sulfuric acid in detail. In this case we must consider the two simultaneous reaction schemes

$$\begin{aligned}&A + H_3O \rightleftharpoons (A{\cdot}H_3O^+)\\&(A{\cdot}H_3O^+) \rightleftharpoons (A{\cdot}H_3O^+)'\\&(A{\cdot}H_3O^+)' \longrightarrow H_3O^+ + B + C + \ldots\end{aligned}$$

and

$$\begin{aligned}&A + HSO_4^- \rightleftharpoons (A{\cdot}HSO_4^-)\\&(A{\cdot}HSO_4^-) \rightleftharpoons (A{\cdot}HSO_4^-)'\\&(A{\cdot}HSO_4^-)' \longrightarrow HSO_4^- + B + C + \ldots\end{aligned}$$

We assume that these are the only catalysts present since basic catalysis by the SO_4^{--} ion is negligible. The observed velocity is due, therefore, to the joint catalytic effect of the (H_3O^+) and (HSO_4^-) and the observed temperature coefficient will depend upon the heats of activation of $(A{\cdot}H_3O^+)$ and $(A{\cdot}HSO_4^-)$ and their relative amounts.

The observed velocity constant of the reaction k will be

$$k = \frac{k_1c_1 + k_2c_2}{c_1 + c_2}$$

where c_1 and c_2 are the concentrations of H_3O^+ and HSO_4^-, respectively, and k_1 and k_2 are the velocity constants for the reaction catalyzed by these ions at unit concentration. Since $(c_1 + c_2)$ is the total acidity we can rewrite this in the form

$$k = k_1F + k_2(1 - F)$$

where F is the fraction of the total hydrogen present as (H_3O^+). Using the values for the concentration of hydrogen ion and hydrogen-sulfate ion secured by Sherrill and Noyes[9] and the measured values for the velocity constant of the reaction as catalyzed by strong acids which we assume gives k_1 together with the measured velocity constant catalyzed by 0.08060 N sulfuric acid, it is possible to calculate k_2. Interpolating Sherrill and Noyes' data for this concentration, we secure 0.0547 and 0.02525 for the normalities of H_3O^+ and HSO_4^-, respectively. Using these values and the observed values of k and k_1, namely, 15.55×10^{-4} and 17.1×10^{-4}, we secure 12.6×10^{-4} for the value of k_2. Further, by extrapolating Sherrill and Noyes' data to 0.15 N sulfuric acid, we find 0.0982 and 0.0520 for the normalities of H_3O^+ and HSO_4^-, respectively. Using these values, the observed value of k_1, and the value of k_2 calculated above, we find the value of k for this higher concentration to be 15.5×10^{-4}. This shows that the specific velocity constant should not change with a variation of the concentration of the sulfuric acid, in agreement with observation.

The observed temperature coefficient of the reaction is given by the equation

$$\frac{\mathrm{d}\ln k}{\mathrm{d}T} = \frac{1}{k}\frac{d}{\mathrm{d}T}\left[k_1F + k_2(1 - F)\right]$$

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[9] Sherrill and Noyes, THIS JOURNAL, **48**, 1870 (1926).

There are two limiting cases for this relationship. In the case of strong acids $F = 1$, $k = k_1$ and the heat of activation is that for the reaction scheme I; in the case of the reaction catalyzed by sulfuric acid in the presence of a high concentration of sulfate, there will be only a very low concentration of hydrogen ion, and thus $F = 0$ and $k = k_2$, so that the measured heat of activation is that of scheme II. These two heats of activation are 20,540 and 17,100 cal., respectively. Without knowing the way F changes with temperature, it is impossible to calculate the intermediate values, but we can expect that there will be a gradual transition in agreement with Table I.

Similar considerations will apply to basic catalysis and ionic reactions in general but we must emphasize the point that it does not seem possible to make any sweeping generalization as to the magnitude of the temperature coefficient, since each reaction is a special case.

Summary

1. Up to the present there has been no satisfactory explanation developed for the temperature coefficient of reactions in solution. The present paper proposes such an explanation based on Brönsted's theory and current theories for the temperature coefficient of reactions in the gaseous state.
2. It is suggested that there is a whole series of fugitive complexes of the type postulated by Brönsted which differ from each other only in energy content. The energy of activation is defined as the difference between the mean energy of the critical complexes which react and the mean energy of *all* the molecules.
3. When there is only a primary salt effect the temperature coefficient should be independent of the addition of salt.
4. In the case of catalysis by weak acids we may expect that there will be several simultaneous reactions, each with its own characteristic energy of activation. This has been discussed for the catalysis of the acetone–iodine reaction by sulfuric acid and the experimental results are shown to be in agreement with theory.

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