

# REACTION VELOCITY IN IONIC SYSTEMS

## I. INTRODUCTION

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*Received December 31, 1931*

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It has been known for over forty years that measurements of the velocity of chemical reactions in solutions containing ions frequently yield results which are unexpected and inexplicable on the basis of the theory of Arrhenius and the classical laws of reaction velocity.

According to the theory of chemical reaction velocity as developed by van't Hoff, Wilhelmy, and Harcourt and Esson, each molecule entering into the kinetic scheme influences the velocity in proportion to its concentration. Accordingly Ostwald proposed that the catalytic inversion of cane sugar could be employed as a method for the determination of the hydrogen ion concentration furnished by different acids. The results agreed quite well with the concentrations of hydrogen ion as determined by other methods based upon the Arrhenius theory, except when salts were present. For example, the addition of 0.1 mole of

potassium chloride to a liter of solution containing cane sugar increased the velocity of inversion by about 40 per cent when dilute acetic acid was the catalyst, but only 4 per cent when dilute hydrochloric acid was used. On the other hand, the addition of sodium acetate to acetic acid produced a greatly decreased rate in reasonably good agreement with expectations based on the mass law, recognized as valid for weak electrolytes.

Later experiments demonstrated that the velocity of reactions between ions, such as the reduction of ferric ion by stannous ion, yielded reaction velocity "constants" which changed in a very pronounced manner when the initial concentrations were varied in an endeavor to discover the true order of the kinetic reaction.

In spite of extensive researches by many competent investigators, this problem of neutral salt or—better—electrolyte effect, remained an enigma until recently. It had to await the development of the modern theory of electrolytes to which it is closely related.

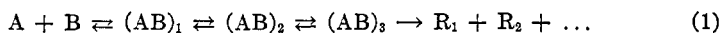
As the result of an extensive survey of the data on reaction velocity, Brönsted has formulated a theory which has at last brought order out of chaos. He divides the kinetic anomalies into three classes: (1) primary salt effect, which involves a purely kinetic effect confined to the reacting ions; (2) secondary salt effect, produced by a shift in the degree of dissociation of a weak electrolyte when one of its ions is involved in the kinetic process; (3) generalized acid-base catalysis. Since the latter has been the subject of a previous review in *This Journal* (1) and is discussed elsewhere in this symposium it will not be discussed further here. Instead the present review will be confined principally to a critical presentation of the primary salt effect and some recent experimental results bearing upon it (2).

## II. THE BRÖNSTED FORMULA

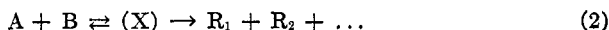
The fact that many chemical reactions follow an order different from that predicted from the stoichiometric equation for the process requires that the reaction molecules do not pass directly from the initial to the final state, but involve a series of more or less unstable intermediary complexes. The widespread ex-

istence of catalysis, the success of the Arrhenius equation, and the phenomena of induced reactions all bear evidence of the correctness of this point of view.

For a bimolecular reaction, Brönsted assumes that the reacting molecules A and B after colliding with each other pass through a series of such states as indicated by the scheme:



where  $(AB)_1$ ,  $(AB)_2$ ,  $(AB)_3$  represent the intermediate complexes. Their exact nature is not clearly understood, but the development of the quantum theory of band spectra furnishes ample evidence for the existence of a host of such states differing but slightly in energy content from one another. For our purposes it can be demonstrated that the tempo of the process will be determined by the rate of transformation of the most unstable complex, designated as the critical complex, (X). The kinetic process may be written more simply as:



Since the various complexes are in equilibrium with one another they may be eliminated successively in setting up the rate equation by introducing the equilibrium constants appropriate for each stage in the reaction; thus the final equation will involve only a concentration function of (A), (B), and (X) and the products of these equilibrium constants, all fused into one constant,  $k$ .

On the basis of this mechanism, Brönsted gives as his more general velocity formula:

$$v_1 = k_0 C_A C_B \frac{f_A f_B}{f_X} \quad (3)$$

Here,  $v$  equals  $-\frac{dC_A}{dt} = \frac{dC_B}{dt}$ ;  $k_0$  is independent of concentration,

so that the factor  $\frac{f_A f_B}{f_X} = F$ , representing the salt effect in terms of the ratio of the activity coefficients of A, B, and X, enters as the sole correction to the classical rate equation. Brönsted restricts equation 3 to dilute solutions since he makes no claim

that his theory will account for non-thermodynamic factors which may affect the velocity in concentrated solutions or on passing to a totally different solvent.

### III. INTERIONIC ATTRACTION THEORY OF ELECTROLYTES

To illustrate the usefulness of equation 3 for the interpretation of the neutral salt effect it becomes necessary to outline some of the salient features of the modern theory of electrolyte solutions. Reactions involving ions are best adapted for testing equation 3, owing to the simplicity with which the activity coefficient of an ion can be expressed as a function of the concentration in dilute solution. However, the theory is by no means restricted to this class of substances.<sup>1</sup>

The factor,  $F$ , vanishes whenever  $f_A f_B = f_X$ . This will be true for extreme dilution in any given reference solvent. How far this cancellation will persist upon passing to finite concentrations depends upon the extent to which each species obeys the laws of ideal solutes. It is well known that most non-electrolytes obey these laws reasonably well to about 0.1 molal. On the other hand, the hypothesis of the complete dissociation of strong electrolytes demands that the ions exhibit a uniform divergence from the simple gas laws solely by virtue of the interionic attraction arising from their net charges (5). In other words, the activity coefficient of an ion of a strong electrolyte is determined solely by its valence (charge) and the concentrations and valences of all the surrounding ions. This principle culminates, finally, in the limiting law of Debye and Hückel (6):—

$$-\log f_i = 0.50 Z_i^2 \sqrt{\mu} \quad (4)$$

valid for water ( $D = 78.8$ ) at 25°C. Here,  $\mu$  is the ionic strength equal to one-half the summation of the products of the concentrations of every ion in the solution, multiplied by the square of its respective electric charge,  $Z_i$ . That is,

$$\mu = \frac{1}{2} \sum C_i Z_i^2 \quad (5)$$

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<sup>1</sup> For a more complete presentation and the significance of the activity concept see reference 3. For a presentation of the theory of kinetic salt effect see reference 4.

Specific individual behavior due to such causes as the ionic diameters, changes in dielectric constant produced by the presence of the ions, enter only in terms of the concentration to a power greater than the one-half power. Specific individual deviations from equation 4 should vanish, therefore, for a region of sufficiently dilute solutions.

#### IV. EXPERIMENTAL VERIFICATIONS OF THE PRIMARY SALT EFFECT

Figure 1 represents the general dependence of the activity coefficient of a particular ion, as determined by solubility and

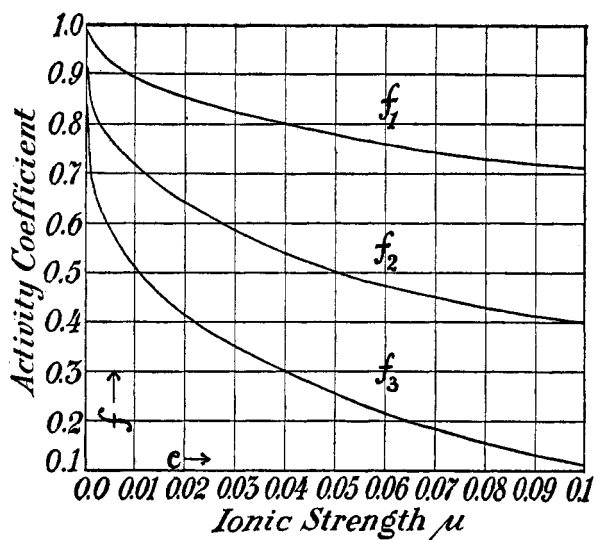


FIG. 1. THE DEPENDENCE OF THE ACTIVITY COEFFICIENT OF A UNIVALENT ( $f_1$ ), A BIVALENT ( $f_2$ ), AND A TRIVALENT ION ( $f_3$ ) AS A FUNCTION OF THE IONIC STRENGTH  $\mu$

related thermodynamic methods, as a function of its electric charge and as a function of the total concentration in terms of the ionic strength  $\mu$ . For  $\mu = 0.1$ , the activity coefficient for a neutral molecule ( $f_0$ ) is practically unity, i.e., 0.96 to 1.04 for most molecules, while the activity coefficients of ions assume values approximately equal to  $f_1 = 0.7$ ,  $f_2 = 0.4$ , and  $f_3 = 0.1$ . Since the fugitive nature of X precludes its isolation, and the

instability of A and B when in the presence of each other prevents a determination of  $f_A$  and  $f_B$  for the exact conditions under which the reaction proceeds, it is necessary to appeal to the principle of ionic types to test equation 3.

Table 1 classifies some reactions according to their electric types and presents numerical values for  $F$  for a total concentration of  $\mu = 0.10$ . In his first paper Brönsted compared the salt effects of a large number of ionic reactions with such predictions based on the solubility data then available. He showed that positive salt catalysis is always obtained for reactions between

TABLE 1  
*Salt effects as a function of the electric charge type*

TYPE	$F$	PREDICTED SALT EFFECT AT 0.1 $\mu$	CONCENTRATION DEPENDENCE
$A^+ + B^0 \rightleftharpoons X^+$ .....	$\frac{f_1 f_0}{f_1}$	0.96-1.04	Linear Positive or negative
$A^+ + B^+ \rightleftharpoons X^{++}$ .....	$\frac{f_1 f_1}{f_2}$	1.22	Exponential Positive
$A^+ + B^- \rightleftharpoons X^0$ .....	$\frac{f_1 f_1}{f_0}$	0.49	Exponential Negative
$A^{++} + B^- \rightleftharpoons X^+$ .....	$\frac{f_2 f_1}{f_1}$	0.40	Exponential Negative
$A^{++} + B^+ \rightleftharpoons X^{+++}$ .....	$\frac{f_2 f_1}{f_3}$	2.80	Exponential Positive

ions of the same sign, whereas negative salt catalysis always results when the reacting ions are of opposite sign. This prediction can be demonstrated more convincingly by using equation 4 to evaluate the factor  $F$  for high dilutions. If we integrate equation 3 under the assumption that the activity coefficients remain unchanged during the reaction<sup>2</sup> we obtain:

$$\log k = \log k_0 + \log \frac{f_A f_B}{f_X} \quad (6)$$

<sup>2</sup> G. Scatchard (J. Am. Chem. Soc. 52, 52 (1930)) by employing a simplified approximation to equation 4 has integrated equation 3, taking into account changes in the activity coefficients due to a change in the ionic strength with the progress of the reaction.

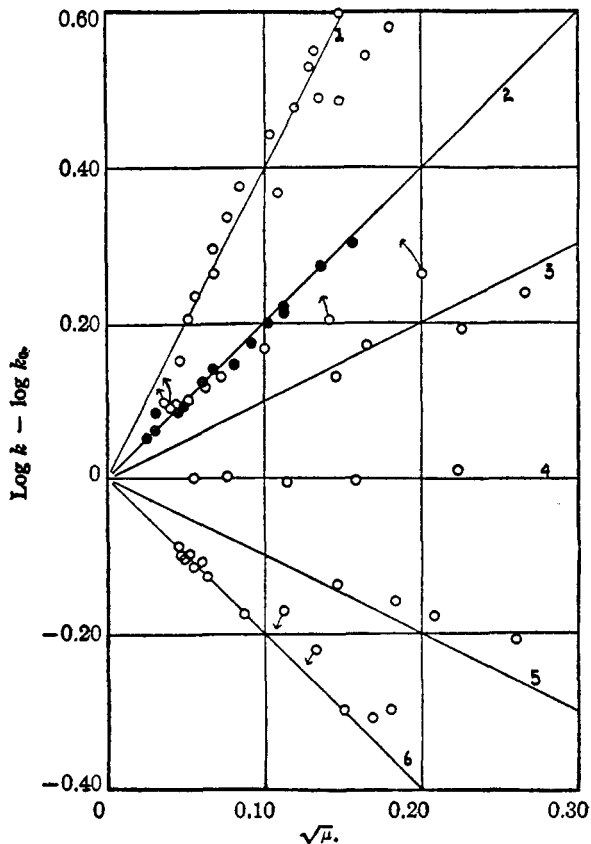


FIG. 2. THE INFLUENCE OF IONIC STRENGTH ON THE VELOCITY OF THE IONIC REACTIONS

1.  $2 [\text{Co}(\text{NH}_3)_5\text{Br}]^{++} + \text{Hg}^{++} + 2 \text{H}_2\text{O} \rightarrow 2 [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++} + \text{HgBr}_2$  (Bimolecular). No foreign salt added. Brönsted and Livingston: *J. Am. Chem. Soc.* **49**, 435 (1927).

2. Circles.  $\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{--} \rightarrow \text{CH}_2\text{S}_2\text{O}_3\text{COO}^- + \text{Br}^-$  as the sodium salt. No foreign salt added. La Mer: *J. Am. Chem. Soc.* **51**, 334 (1929).

Dots.  $\text{S}_2\text{O}_3^{--} + \text{I}^- \rightarrow \text{I}_2 + \text{SO}_4^{--}$  as  $\text{Na}_2\text{S}_2\text{O}_3$  and  $\text{KI}$ . King and Jacobs: *J. Am. Chem. Soc.* **53**, 1704 (1931).

3. Saponification of nitrourethane ion by hydroxyl ion.  $[\text{NO}_2 = \text{N} - \text{COOC}_2\text{H}_5]^- + \text{OH}^- \rightarrow \text{N}_2\text{O} + \text{CO}_3^{--} + \text{C}_2\text{H}_5\text{OH}$ . Brönsted and Delbanco: *Z. anorg. Chem.* **144**, 248 (1925).

4.  $\text{C}_{12}\text{H}_{22}\text{O}_{11}^0 + \text{OH}^- \rightarrow \text{Invert Sugar}$ . Arrhenius: *Z. physik. Chem.* **1**, 111 (1887).

5.  $\text{H}_2\text{O}_2 + \text{H}^+ + \text{Br}^- \rightarrow \text{H}_2\text{O} + \text{Br}_2$ . Livingston: *J. Am. Chem. Soc.* **48**, 53 (1926).

6.  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{++} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{++} + \text{Br}^-$ . Brönsted and Livingston: *J. Am. Chem. Soc.* **49**, 435 (1927).

A large number of reactions corresponding to the type  $\text{A}^+ + \text{B}^0 \rightleftharpoons [\text{X}]^+$  yielding a linear salt effect are to be found in the studies of Harned and Åkerlöf, and Brönsted and his collaborators. See *J. Am. Chem. Soc.* **50**, 358 (1928); **51**, 248 (1929); *Trans. Faraday Soc.* **25**, 59 (1929).

Introducing equation 4 for  $f_A$ ,  $f_B$  and  $f_X$ , and noting that  $Z_X = Z_A + Z_B$ , the result is

$$\log k = \log k_0 + Z_A Z_B \sqrt{\mu} \quad (7)$$

or

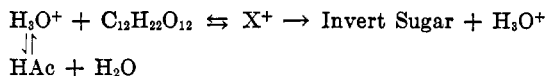
$$v = k_0 C_A \cdot C_B 10^{Z_A Z_B \sqrt{\mu}} \quad (8)$$

The velocity is consequently an exponential function of the square root of the ionic strength. When  $Z_A =$  zero, the factor  $Z_A Z_B$  vanishes. When A and B have the same sign,  $Z_A Z_B$  is positive; when A and B are opposite in sign,  $Z_A Z_B$  is negative.

Since the principle of ionic types assumes greater validity the more dilute the solution, the best test of the theory is obtained by plotting  $\log k$  against  $\sqrt{\mu}$ , and noting if the experimental curve *approaches* a slope equal to  $Z_A Z_B$ . Figure 2 shows that this requirement is met by six distinct types of reactions. In the case of reaction 1, studied by Brönsted and Livingston, it is difficult to say whether the deviations are due to experimental errors,<sup>3</sup> or to a failure of the formula for such high valence types at the concentrations studied (7). This point will be treated more critically in section IX.

#### V. SECONDARY SALT CATALYSIS

If one of the reacting ions is furnished by a weak electrolyte, as is the case when cane sugar is inverted by acetic acid (HAc), we have a situation represented by the scheme:



If now an inert foreign salt such as potassium chloride be added to this reacting mixture, we have in addition to the primary kinetic effect of about 4 per cent as found for hydrochloric acid,

<sup>3</sup> Most of the data for reaction 1 have not been plotted, as they deviate considerably within a given series. The circles refer to a series in which no foreign salt has been added. It is the most consistent of all.



an additional effect due to the displacement of the equilibrium between  $H^+$ ,  $Ac^-$  and undissociated  $HAc$ . Since at equilibrium we always have

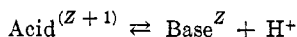
$$a_{H_3O^+} \cdot a_{Ac^-} = K'_a \cdot a_{HAc} \quad (9)$$

$$C_{H_3O^+} = K'_a \cdot \frac{C_{HAc}}{C_{Ac^-}} \cdot \frac{f_{HAc}}{f_{Ac^-} \cdot f_{H_3O^+}} \quad (10)$$

When the ionic strength increases from nearly zero to  $0.1 \mu$ ,  $f_{Ac^-}$  and  $f_{H_3O^+}$  change from about unity to about  $0.7$ ;  $f_{HAc}$  remains practically equal to unity. The decrease in  $f_{Ac^-}$  is balanced by the increase in  $C_{Ac^-}$  so that the only factor of importance is  $1/f_{H_3O^+} \cong 1/0.7 \cong 1.43$ . That is, a 43 per cent increase in inversion rate, as predicted for these limiting conditions, due simply to a 43 per cent increase in  $C_{H_3O^+}$  is in good agreement with the experiment. It should be pointed out that if the dissociation of the acetic acid has been repressed by an addition of a strong acid such as hydrochloric acid before adding the neutral salt, the secondary effect will disappear. On the other hand if sodium acetate is added, the effect of a neutral salt addition will be greater than in the absence of sodium acetate. When a common ion is present it is best to solve for the change in stoichiometric dissociation constant  $K_c$  by a formula like

$$K_c = K_a \cdot \frac{f_{HAc}}{f_{H_3O^+} \cdot f_{Ac^-}}$$

and then compute  $C_{H_3O^+}$  from  $K_c$  by successive approximations. For the case of a weak acid of the electric type  $(Z + 1)$



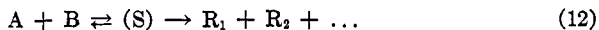
the Debye-Hückel limiting law gives

$$\log K_c = \log K_a - Z_B \sqrt{\mu} \quad (11)$$

Since the secondary salt effect is not a true kinetic effect we leave the matter with the remark that the dissociation of weak acids has been shown in several cases to approach the limiting behavior predicted by equation 11.

## VI. BJERRUM'S DERIVATION. THE CONCENTRATION HYPOTHESIS

Although we shall be obliged later to point out that this simple derivation of Brönsted's formula encounters grave objections, nevertheless it furnishes an excellent starting point for a discussion of the rôle played by activities and concentrations in the development of the theory of reaction velocity—the more so, since in most current derivations the matter is not clearly stated. Bjerrum (8) assumes that the purely physical collision complex (S), (Stosskomplex), determines the rate of the reaction through a spontaneous monomolecular decomposition induced by thermal agitation. Thus,



He assumes that the velocity is directly proportional to the concentration of collision complexes,  $C_S$ , at any moment, i.e.,

$$-\frac{dC_A}{dt} = k_S C_S \quad (13)$$

The generally valid mass law, in terms of activities, yields for the *collision equilibrium*

$$\frac{a_S}{a_A a_B} = K_a$$

or

$$C_S = K_a \cdot C_A C_B \cdot \frac{f_A f_B}{f_S} \quad (14)$$

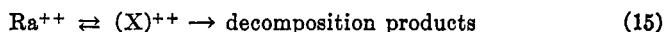
Substituting this value of  $C_S$  in equation 12, Brönsted's formula follows easily, provided we make no distinction between the critical complex, (X), and the collision complex, (S). From an experimental point of view, no distinction is possible, at the present time, since neither  $f_X$  nor  $f_S$  can be measured directly; we can only predict their ideal values from the total electric charge which is identical for X and for S.

At first sight, equation 13 appears entirely satisfactory; it is identical with the classical law and offers a ready explanation for

the observation that a radioactive ion decomposes as rapidly in a salt solution as in pure water. Accordingly, Bjerrum advanced the proposition that "the rapidity with which a spontaneously reacting molecule (or molecular complex) is transformed is independent of whether or not it exists in a place of high or of low chemical potential," to counteract what he believed to constitute an unwarranted and indiscriminate substitution of activities for concentrations, in rate equations.

Radioactive transformations are not cogent examples. Such transformations are due to the instability of the nucleus for which there is a finite probability of decomposition, quite independent of any external physical condition (9). This process is situated so deeply within the atom that it cannot be affected by changes in electric potential produced by the presence of an atmosphere of surrounding ions.

In terms of the theory of the intermediate critical complex we should have



$$v = kC_{\text{Ra}^{++}} \cdot \frac{f_{\text{Ra}^{++}}}{f_{\text{X}^{++}}} = k \cdot C_{\text{Ra}^{++}} \quad (16)$$

Since the radium ion and its reactive form, denoted by  $\text{X}^{++}$  have identical structures they will have identical activity coefficients. The example, although of interest, is incompetent to distinguish between the theory of collision complexes and the theory of unstable intermediate complexes.

The incorrectness of the concentration hypothesis may be demonstrated most convincingly by the following pure thermodynamic argument. Consider a reversible monomolecular reaction such as



assume the validity of the S formula and the concentration hypothesis (equation 13). Since the mass action law in terms of concentrations must now hold, the expression

$$\frac{C_{\text{A}}}{C_{\text{Y}}} = \text{constant} \quad (18)$$

is obligatory. Equation 18 permits of no displacement of the equilibrium on changing the properties of the medium. However, experience teaches otherwise. For example, in the case of the equilibrium between two modifications of "Zwitterions," a displacement occurs on the addition of salts, except in the trivial case where the two activity coefficients are affected equally.

#### VII. BRÖNSTED'S DERIVATION

This argument, due to Brönsted (10), led him to reject the concentration hypothesis in favor of the hypothesis that reaction velocity is determined by the *difference* in the potentials of the initial and critical states of the reacting system but is independent of the potential of the final state of the system. This is equivalent to saying that the rate of reaction depends upon the ratio of the activity coefficients of the substances in the initial and critical states.

He bases his argument upon the classical Guldberg and Waage kinetics for the dynamic equilibrium represented in the case of a bimolecular reaction by:



When the reaction is carried out in a medium of constant environment we may write the component velocity expressions as:

$$v_1 = k_1 C_A \cdot C_B = k_1 a_A a_B \quad (20)$$

$$v_2 = k_2 C_Y C_Z = k_2 a_Y a_Z \quad (21)$$

yielding for the equilibrium state where  $v_1 = v_2$

$$\frac{C_A C_B}{C_Y C_Z} = \frac{k_2}{k_1} = K_c \quad (22)$$

and

$$\frac{a_A a_B}{a_Y a_Z} = \frac{k_2}{k_1} = K_a \quad (23)$$

It is permissible to substitute the relative activities,  $a_A \dots a_Z$  as equivalent to the stoichiometric concentrations,  $C_A \dots C_Z$ , since under the stipulation of a constant medium, activity is always proportional to concentration. By the assumption of a suitable choice of standard state, the relative activities in equations 20 and 21 may be set equal to the concentrations without affecting the values\* of  $k_1$  and  $k_2$ .

If the medium in which the reaction proceeds is changed, equations 20 and 21 are no longer valid;  $a$  and  $c$  no longer exhibit linear proportionality. To account for changes in the medium, introduce coefficients  $\alpha$  and  $\beta$  as follows:

$$v_1 = k_1 \alpha_1 \cdot C_A C_B = k_1 \beta_1 a_A a_B \quad (24)$$

$$v_2 = k_2 \alpha_2 C_Y C_Z = k_2 \beta_2 a_Y a_Z \quad (25)$$

The coefficients  $\alpha$  and  $\beta$  vary independently of each other on changing the medium.  $k_1$  and  $k_2$  continue to be independent of concentration.

The unknown manner in which  $\alpha$  and  $\beta$  are affected by concentration, makes them appear at first sight to be of little value. For the equilibrium state, equation 23 must always be true regardless of concentration changes. By equating the right hand members of equations 24 and 25 we obtain

$$K_c = \frac{k_2}{k_1} \cdot \frac{\beta_2}{\beta_1} \quad (26)$$

Consequently,  $\beta_1$  always equals  $\beta_2$ , which proves that the generally valid velocity function for a bimolecular reaction has the form:

$$v = k \beta a_A a_B \quad (27)$$

Completely analogous expressions can be obtained of course in terms of the concentrations instead of the activities by equating the second members of equations 24 and 25. However the resulting quantity,  $K_c$ , is not, in general, independent of concentration on varying the medium. Therefore,  $\alpha_1$  and  $\alpha_2$  may vary independently of each other, a circumstance which makes them

worthless for further development. It emphasizes the usefulness of the activity concept.

Since the two reciprocal systems  $A + B$  and  $Y + Z$  involve substances of entirely different chemical character, they must be considered as behaving independently of each other with respect to variation in the medium. Consequently, the equality  $\beta_1 = \beta_2$  means that the reciprocal transformations must involve a common critical transition state, (X). Therefore, the two kinetic processes are to be formulated as



and



Nevertheless a change in the medium, in which the activities of the reacting molecules are held constant, may produce changes in the velocity of the two reactions without shifting the point of equilibrium. Accordingly, the common  $\beta$  coefficients are properties of the critical complex.

To determine the form<sup>4</sup> of  $\beta_1$  restrict equation 27 for simplicity to a monomolecular reaction, and write

$$v = k\beta C_A f_A \quad (30)$$

an expression which differs from Bjerrum's hypothesis (equation 13) by containing, in addition, the necessary factors  $\beta$  and  $f_A$ .

To elucidate the form of  $\beta$  consider the familiar diagram shown in figure 3, where the ordinates refer to the energy levels of A, X and Y which we may take as equivalent to the respective partial molal free energies,  $\overline{F}_A$ ,  $\overline{F}_X$ ,  $\overline{F}_Y$ . It has been a customary

<sup>4</sup> The presentation departs, at this point, from that given by Brönsted, who justifies the transformation of the classical laws simply on the following hypothesis:

(1) The probability of a molecule or a system of molecules passing from ordinary conditions into a state of great improbability varies proportionally to the ratio of activity coefficients in the ordinary and improbable state; or, identically,

(2) The probability for a molecule in a very improbable state to pass into ordinary conditions is independent of its activity coefficients in the two states.

assumption in chemical kinetics that reaction velocity is determined exponentially by the critical increment of energy necessary to raise the A molecules to the state X; i.e.,

$$\Delta F_{\text{critical}} = \bar{F}_X - \bar{F}_A$$

Introducing the universally valid expression

$$\bar{F}_i = RT \ln C_i + RT \ln f_i + \bar{F}_i^0$$

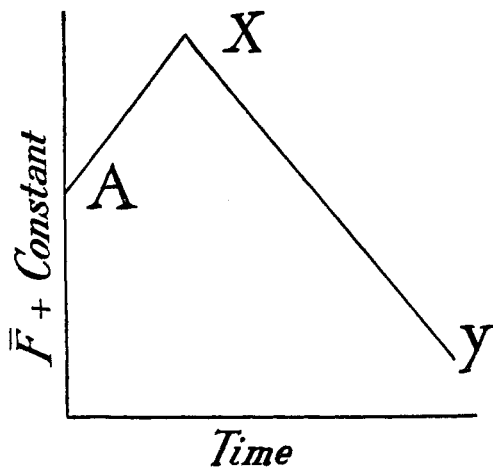


FIG. 3

we obtain

$$-\Delta F_{\text{critical}} = RT \ln \frac{C_A}{C_X} + RT \ln \frac{f_A}{f_X} \quad (31)$$

OR

$$\text{Exp} \left( -\frac{\Delta F_{\text{critical}}}{RT} \right) = \frac{C_A}{C_X} \cdot \frac{f_A}{f_X} \quad (32)$$

Of these two factors, the level of the potential of the A molecule in a given medium with respect to the standard medium is measured by the absolute activity coefficient  $f_A$ , and the reaction velocity will increase proportionally to the  $f_A$  coefficient if, on changing the medium, the  $\beta$  factor maintains a constant value.

But as stated above, certainly, the velocity does not depend upon the potential of the initial state, alone, but depends more upon the difference in level between the initial and critical states. If the medium is constant, the ratio  $\frac{f_A}{f_X}$  is unity and the reaction proceeds at a rate proportional to  $C_A$ , since  $\frac{1}{C_X}$ , being in equilibrium with A, can be absorbed in the velocity constant,  $k$ , by introducing an equilibrium constant. Ascribing the changes in velocity on changing medium to changes in the critical increment,  $\Delta F_{\text{critical}}$ , it is obvious that the velocity must be proportional to the ratio  $\frac{f_A}{f_X}$ . Consequently,  $\beta$  in equation 30 equals  $\frac{1}{f_X}$ . The argument can be extended to bimolecular or higher orders yielding equation 3. Brönsted's formula follows logically from principles which have been generally accepted by investigators in the field of gaseous kinetics.

#### VIII. ACTIVITIES VERSUS CONCENTRATIONS—THE EXPERIMENTS OF EYRING AND DANIELS

The question—"should activities or concentrations be employed in formulating rate equations"—was presented for discussion at this symposium as a result of the very interesting experiments of Eyring and Daniels on the monomolecular decomposition of nitrogen pentoxide in chemically inert solvents. These authors (11) have demonstrated—contrary to earlier less precise observations—that the specific velocity constant,  $k = -\frac{dc}{cdt}$  has different values in solutions than for the gaseous state. Furthermore,  $k$  increases perceptibly in the solvents nitromethane and carbon tetrachloride with increase in the initial concentration of  $N_2O_5$ , although the monomolecular character of the reaction is preserved. Table 2 gives a summary of the results for saturated solutions.

The authors state, "the experimental data in saturated solutions offer an unusually favorable means of distinguishing be-



tween the use of total concentrations and activities in reaction rate measurements. Neither is completely satisfactory. Crystalline nitrogen pentoxide, gaseous nitrogen pentoxide and saturated solutions in the various solvents, are all in equilibrium. The escaping tendency of simple  $N_2O_5$  molecules is the same in every case, but the total concentrations in moles per liter are widely different. . . . If the activity determines the reaction rate, the evolution of oxygen  $\left(-\frac{dc}{dt} = r\right)$  per liter should be the same in all cases because the escaping tendency is the same in all. . . . Such a result would be obtained if the solvated molecules did not decompose at all. If the total concentrations

TABLE 2

*Decomposition of nitrogen pentoxide in solutions saturated with crystalline nitrogen pentoxide at 15°C.*

Eyring and Daniels

SOLVENT	$C_{\text{sat.}}$ <i>moles per liter</i>	$-\frac{dc}{dt} \cdot 10^3$	$10^3 k = \frac{-dc}{cdt} \cdot 10^3$
Vacuum (gas phase).....	0.0102	0.0080	0.79
Nitromethane.....	4.38	5.92	1.35
Carbon tetrachloride.....	4.78	8.75	1.83
Liquid $N_2O_4$ .....	—	—	1.59

determine the decomposition rate, then the *specific* reaction rate,  $k$ , should be the same in all solvents. Such a result would be obtained if all the molecules, solvated and unsolvated, decomposed at the same rate. Obviously, both these views are incomplete.”

The development given in section VII suggests one reason why they are incomplete. The simple substitution of the activity of nitrogen pentoxide for the concentration of nitrogen pentoxide cannot suffice unless the activity coefficient of normal inactive nitrogen pentoxide,  $f_{N_2O_5}$  is identical with that of the activated form designated as  $f_{N_2O_5^*}$  in each of the solvents under discussion. Eyring and Daniels propose a different rate of decomposition for solvated as opposed to unsolvated molecules as an ex-

planation of their results. Without entering upon this question, it is important to point out that the tacit assumption of Eyring and Daniels that  $f_{N_2O_5}$  is identical with  $f_{N_2O_5^*}$  is tantamount to assumption that the solubility of the activated molecules relative to the normal molecules remains unchanged on passing from solvent to solvent. In other words, the solutions studied are presumed to be saturated to the same degree with respect to the activated forms.

The assumption that  $f_{Ra^{++}}$  is identical with  $f_{Ra^{++*}}$ , regardless of the solvent and offered as an explanation for the invariance of radioactive decompositions, was justified on the ground that any possible activation process in this case would be so deeply seated within the atom as to be completely shielded from all environmental influences. In the case of nitrogen pentoxide, the activation process is conceived as an increase in the (quantized) frequency of vibration of the atoms to the point of incipient dissociation. The molecular fields surrounding such an activated molecule can hardly be identical with those surrounding the inactive form. It seems logical to expect differences in the relative solubilities of the active and inactive nitrogen pentoxide molecules on changing the solvent.

The explanation offered demands a change in critical increment on changing the solvent; a variation of 500 calories is sufficient to account for all the data in table 2. Until a theory—comparable in its powers of prediction to the principle of electric charge types is developed for non-electrolytes—it does not seem likely that rate measurements on non-electrolytes will furnish a conclusive answer to the question raised at the beginning of this chapter, although the experimental results will unquestionably prove of great value in leading to a proper solution of the problem. Finally, it should be remarked that the assumption that the collision number is unaffected by change in solvent may not be strictly true.

#### IX. LIMITATIONS IN HIGH VALENCE TYPE MIXTURES

From their studies on the solubility of (3, -1) type salts, in the presence of salts of high valence types, La Mer and Mason

(12) found that the limiting law of Debye and Hückel was not obeyed when the cation of the saturating salt and the anion of the solvent salt were of high charge. Figure 4 is taken from their paper. In this example the cation of the saturating salt is trivalent. When the anion of the solvent salt is univalent, as is the case with potassium nitrate and barium chloride, there is excellent agreement with the Debye-Hückel limiting law. On the other hand, when the anion of the solvent salt is bivalent, as, for example, in the case of potassium sulfate or magnesium sulfate,

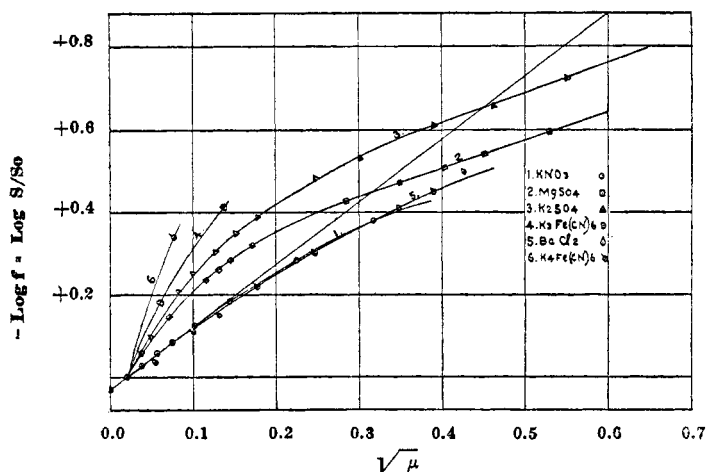
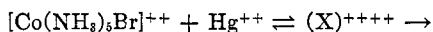


FIG. 4. EFFECTS OF VARIOUS SALTS UPON THE SOLUBILITY OF  
 $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{C}_2\text{O}_4]_3^-$

the *experimental limiting slope* in the region of concentration  $\mu = 0.001$  is two to three times that predicted by the Debye-Hückel theory. The figure shows that for such high valence type mixtures the specific characteristics of the activity coefficient do not become negligible for any region of dilution that can be investigated with the experimental methods now available. These results have been confirmed (13, 14) for other (3, -1) type cobalt amines and for lanthanum iodate. The anomaly may be considered as a general phenomenon whenever the product of the charges of the ions of opposite sign is equal to or

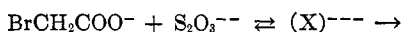
greater than four. It is not inconsistent with the fundamental postulates of the Debye-Hückel theory, provided a more complete solution of the equation of Poisson and Boltzmann is employed as has been demonstrated by La Mer, Gronwall and Greiff. Their analysis has demonstrated (15, 16) that the theoretical curve frequently passes through a point of inflection in its approach to the limiting law, the validity of which is restricted in such examples to extreme dilution.

If equation 3 is a correct expression for the velocity of an ionic reaction, this highly characteristic type of curve should be manifested for the salt effect in reaction velocity studies under similar conditions. A closer examination of the experimental data of Brönsted and Livingston for the reaction



labelled (1) in figure 2 where the critical complex is tetravalent and the ion of the medium (nitrate), is monovalent, strongly indicates that the *experimental limiting* slope is considerably greater than the theoretical value  $Z_A Z_B = 4$  which was accepted by the authors in their discussion. The discrepancies between equation 7 and their data may be due to a failure of the activity coefficients to obey the limiting law and not to experimental error.

To settle this point, La Mer and Fessenden (17) investigated the reaction



by introducing the reactants in the form of their calcium, barium and magnesium salts. Figure 5 gives the results of their kinetic experiments, which prove to be practically identical with the characteristic curves obtained for the solubilities of similar valence types shown in figure 4. In this reaction the product of the negative charge on the critical complex and that on the cations ( $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ) in the medium equals six. The results when small amounts of lanthanum chloride are added to very dilute solutions of the reactants in the form of their sodium salts are shown in figure 6. In this case the product of the charge on the critical complex and on the cation (lanthanum) being

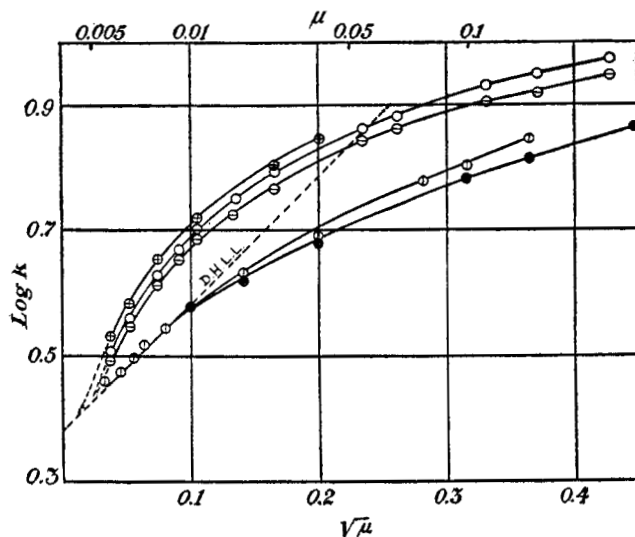


FIG. 5. THE VELOCITY OF THE BROMOACETATE-THIOSULFATE REACTION AS A FUNCTION OF CONCENTRATION, SHOWING THE SPECIFIC EFFECTS OF VARIOUS CATIONS

⊕ Barium; ○ Calcium; ⊖ Magnesium; ⊙ Potassium; ● Sodium salts

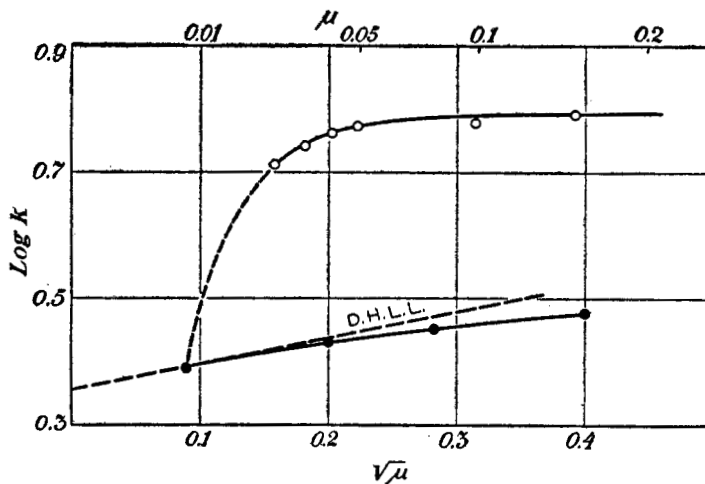


FIG. 6. THE VELOCITY OF THE BROMOACETATE-THIOSULFATE REACTION AS INFLUENCED BY SMALL ADDITIONS OF LANTHANUM CHLORIDE

● Sodium salts. ○ Lanthanum chloride added to lowest concentration of sodium salts of reactants.

nine, an even greater catalytic effect is produced. Although these results limit, seriously, the applicability of equation 7 based upon the Debye-Hückel limiting law for extrapolation to infinite dilution, nevertheless they are to be considered as furnishing one of the most decisive confirmations of Brönsted's velocity equation (6) yet obtained.

#### X. CHRISTIANSEN'S THEORY

Christiansen (18) develops the theory of bimolecular reactions in solution; this theory introduces several new and important factors in the mechanism of the salt effect. Only the salient features will be presented.

He points out that Bjerrum's use of a physical collision complex requires that  $C_s$  in equation 13 vary but little with the temperature, whereas in Brönsted's development the concentration of the critical complex would vary exponentially with the temperature. There is an important theoretical difference between the two viewpoints in spite of their formal similarity. Christiansen's treatment focuses attention upon the number of collisions between reacting molecules. He thus avoids the problem of the concentration of the collision complex, or of the critical complex.

Christiansen proposes that the expression

$$v = C_1 C_2 Z_{12} \sqrt{T} e^{-\frac{Q_{12}}{RT}} \Omega \frac{\rho}{\rho + \Sigma \eta c} \quad (33)$$

generally accepted for gaseous reactions between molecules 1 and 2 be employed as a more complete expression for solution reactions. Here the number of collisions per second per liter,  $S_{12}$ , equals  $C_1 C_2 Z_{12} \sqrt{T}$ , where  $Z_{12}$  is a characteristic quantity, depending upon the diameters of the molecules, but independent of the concentrations  $C_1$  and  $C_2$ . The term  $e^{-\frac{Q_{12}}{RT}}$  results from the assumption that two molecules react only when they strike each other with such velocities that the resulting kinetic energy exceeds the mean kinetic energy for the molecules by an amount  $Q_{12}$ . The factor  $\Omega$  is introduced to account for spatial orientation necessary for a fruitful collision.  $\rho$  represents the probability

per second of the spontaneous elementary reaction in the activated complex and  $c$  is the concentration of the various molecules present in the *immediate neighborhood* of the reacting molecules. This concentration can be different from the bulk concentration in the reacting mixture.

For gases, it has been emphasized repeatedly that collision with a third body is necessary to dissipate the energy liberated by the reaction. In solutions the solvent performs this function. The  $\eta$ 's are numerical coefficients of such size that the sum of their products with the respective local concentrations  $c$  expresses the probability per second of deactivation of the reacting molecules by surrounding solvent and solute molecules. The

factor  $\frac{\rho}{\rho + \sum \eta c}$  approaches unity for very small concentrations

while for large concentrations it approaches the value  $\frac{\rho}{\sum \eta c}$ . It cannot be evaluated, at present, but suggests that the simpler formulas (24, 25) may not always suffice.

To make equation 33 useful for ionic reactions, consider the influence of interionic attraction upon the number of impacts. According to the Boltzmann principle the average concentration of ion 2 at a distance  $r$  from ion 1 is given by

$$C = C_2 e^{\frac{-Z_2 e}{kT} \phi_1} \quad (34)$$

where  $C_2$  is the average concentration in the entire solution of ion 2,  $Z$  equals valence, and  $\phi_1$  equals average electrostatic potential at the distance  $r$  from ion 1. Christiansen points out that although this equation requires that ions of opposite sign congregate near one another as a result of electrostatic attraction, they do not collide with any greater average kinetic energy than they would in the absence of electrostatic attraction. This is an important principle<sup>5</sup> of statistical mechanics which has not been recognized by some more recent workers in this field (19).

<sup>5</sup> For a clear elementary proof see Herzfeld, *Kinetic Theory of Gases*; Müller-Pouillet, *Lehrbuch der Physik*, Volume III, page 137. (Braunschweig, 1925.)

The increased velocity which results when a foreign inert salt is added to a reaction between ions of the same sign is due simply to the increase in the number of collisions of the reacting ions resulting from the local increase in their concentration in the neighborhood of the inert ion of opposite sign. This is in harmony with the Debye-Hückel theory of electrolytes. By introducing Debye's value for the electric potential

$$\phi_1 = \frac{\epsilon Z_1}{Dr} e^{-\kappa r} \quad (35)$$

Christiansen obtains, finally, on setting  $\Omega$  and  $\frac{\rho}{\rho + \Sigma \eta c}$  equal to unity, an expression which we shall write as

$$\log k = \log k'_0 - \frac{Z_1 Z_2 \epsilon^2}{2.3 DkT} \frac{1}{r} + Z_1 Z_2 \sqrt{\mu} \quad (36)$$

Equation 36 differs from equation 7 only by the term in  $r$  representing the distance (in  $10^{-8}$  cm. units) of closest approach of the charges on the two ions at the moment of reaction. For a given value of  $r$  this term may be included in the constant  $\log k'_0$  since it is independent of concentration. Substituting numerical values for  $\epsilon$ ,  $D$ ,  $k$ ,  $T$ , valid for  $25^\circ\text{C}$ ., we can write

$$\log k_0 = \log k'_0 - \frac{Z_1 Z_2 3.06}{r} \quad (36a)$$

$k'_0$  represents the velocity constant for infinite dilution, freed from all effects due to the net electric charges but not to effects arising from electric moments.

From Christiansen's treatment we may conclude that the velocity of ionic reactions is influenced primarily by the distribution of the concentrations arising from interionic attraction. This means that the local concentration in the vicinity of the reacting ions is quite different from the experimentally determined concentration. On this basis, highly specific changes in reaction velocity are to be expected when highly charged ions of sign opposite to that of the critical complex constitute the environment. Such effects have been observed in the work of La Mer and Fessenden reported in the preceding section.



It is a source of regret that Ingold's important extension (20) of Bjerrum's fundamental contribution (21) that the Boltzmann distribution law can be successfully applied to the field of reaction velocity came to our attention too recently to be accorded the attention which it merits.

### XI. MOLECULAR STRUCTURE AND ORIENTED COLLISIONS

#### A. Effects of substitution

Table 3 gives a summary of the reaction velocity constants obtained for the replacement reaction, of type:  $X \cdot \text{CH}_2\text{COO}^- +$

TABLE 3  
*Influence of halogen substitution*

SUBSTITUENT IN THE ACETATE ION	REACTING ION		
	CNS <sup>-</sup>	SO <sub>3</sub> <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>-</sup>
Cl.....	0.00021	0.00461	0.00860
Br.....	0.023	0.454	0.888
I.....	0.0323	0.793	1.32

TABLE 4  
*Values of table 3 expressed as relative rates of reaction*

SUBSTITUENT	CNS <sup>-</sup>	SO <sub>3</sub> <sup>-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	REACTING ION	Cl	Br	I
Cl.....	1	22	41	CNS <sup>-</sup>	1	110	154
Br.....	1	19	39	SO <sub>3</sub> <sup>-</sup>	1	98	172
I.....	1	24.5	41	S <sub>2</sub> O <sub>3</sub> <sup>-</sup>	1	103	154

$\text{B}^{--} \rightarrow \text{B} \cdot \text{CH}_2\text{COO}^- + \text{X}^-$  to illustrate the effects of interchanging the halogen substituent  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ , in the acetate ion when it reacts with the ions  $\text{B}^{--}$  (CNS<sup>-</sup>, SO<sub>3</sub><sup>-</sup>, S<sub>2</sub>O<sub>3</sub><sup>-</sup>). By considering the rate constant with the CNS<sup>-</sup> ion as equal to unity, as shown in table 4, the ratios of the velocities for CNS<sup>-</sup>:SO<sub>3</sub><sup>-</sup>:S<sub>2</sub>O<sub>3</sub><sup>-</sup> are practically the same when reacting with the Cl, Br or I derivatives, namely, 1:23:41. In a similar way, by setting the rates of the chloro-substituted ion equal to unity (table 4) the ratio of the Cl:Br:I rates becomes about 1:105:155. These data are taken from several sources but principally from

the papers of Backer and Van Mels (22, 23, 24). They are not strictly comparable with one another since in some cases the reactants were present as the potassium salts and in other examples as their sodium salts at 0.1 molar concentration. In the case of the bromoacetate-thiosulfate reaction, the interchange of potassium for sodium as the chemically inert cation brings about a 12

TABLE 5

*Velocity constants for the reaction of sulfite ion ( $\text{SO}_3^{--}$ ) with halogenated fatty acid ions at 0.1 M and 25°C.*

HALOGENATED ION	Cl	Br	I	Cl:Br:I
Acetic.....	0.00461	0.454	0.793	1:98:172
$\alpha$ -Propionic.....	0.000160	0.0134	0.0252	1:84:157
$\beta$ -Propionic.....	0.000532	0.0205	0.0326	1:39:61

TABLE 6

*Velocity constants for ( $\text{SO}_3$ )<sup>-</sup> ion with halogenated fatty acid ions at 0.1 M and 25°C.*

	Cl	Br	I
Acetate $\text{C}_2$ .....	0.00461	0.454	0.793
$\alpha$ -Propionate $\text{C}_3$ .....	0.000160	0.0134	0.0252
Ratio $\text{C}_2:\text{C}_3$ .....	29	34	31

TABLE 7

*Influence of lengthening the carbon chain upon the velocity constants for ( $\text{SO}_3$ )<sup>-</sup> ion with  $\alpha$ -bromo-substituted acids*

NUMBER OF CARBON ATOMS	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$	$\text{C}_5$	$\text{C}_6$
$k$ .....	0.454	0.0134	0.0045	0.00234	0.0015
Ratio.....	1	0.0295	0.0099	0.0052	0.0033

per cent change in  $k$  at 0.2 molar concentration. This is of the same order as the discrepancies in the ratios. It is a fair presumption that measurements in more dilute solutions, where specific ion effects are negligible, would exhibit even greater regularity for the series of ratios in table 4.

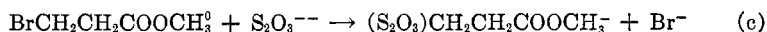
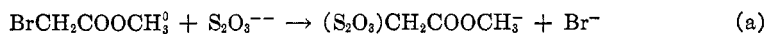
This simple regularity obtains only when the point of attack (X atom) in the molecule is kept at the same (alpha) position

relative to the charge on the carboxyl group, as is true in table 6, and in table 5 for the comparison between acetic and  $\alpha$ -propionic acid ions but not for the comparison with the beta derivative.

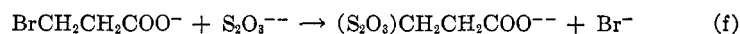
Table 7 shows the influence of lengthening of the carbon chain upon the velocity constant for the reaction between sulfite ion and  $\alpha$ -bromo-substituted fatty acids.

*B. Relative position of electric charge and point of attack in a reacting molecule*

La Mer and Kammer (25) have made an extensive experimental study to determine the cause of the change in reaction velocity which occurs when an attackable atom is moved from the alpha to the beta position in the ion of a fatty acid series. For this purpose, they measured, over a wide range of concentrations, the velocities of the reactions of the ester-thio type:



and the corresponding reactions of the ion-thio type:



The reactions involve, in each case, the replacement of a bromine atom by a thiosulfate ion. By comparing the results of the ester-thio types with those of the ester-ion types they ascertain the influence which the presence of an electric charge exerts on the reaction velocity as a function of its position relative to the bromine atom which is replaced by the thiosulfate ion.

The ester-thio reactions belong to Brönsted's zero type reactions so that the velocity should not change appreciably with change in total ionic concentration. This proves to be the case.

The ion-thio reactions belong to the type  $\text{A}^- + \text{B}^{--} \rightleftharpoons (\text{X})^{---}$

→R. Figure 7 illustrates that in the case of the  $\alpha$ -brominated ion the concentration dependence is in accord with the limiting requirements of equation 7 as has been proved many times for the

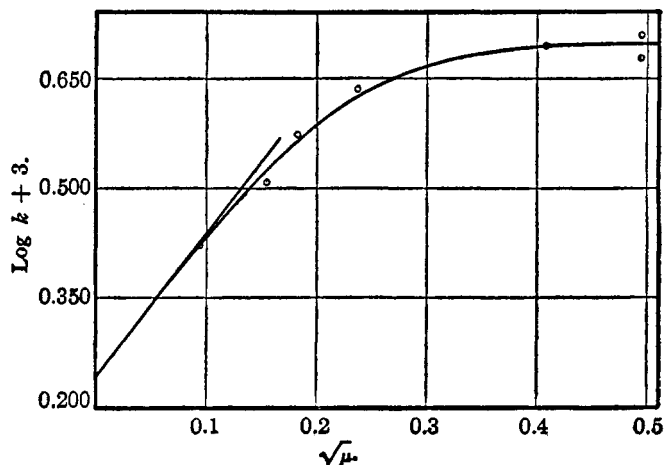


FIG. 7.  $\alpha$ -BROMOPROPIONATE ION AND THIOSULFATE ION

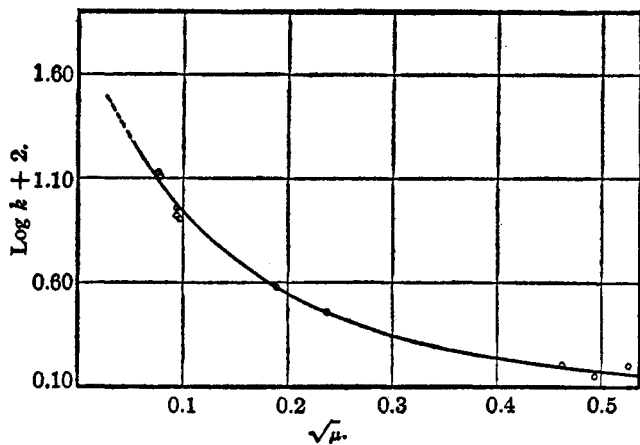


FIG. 8.  $\beta$ -BROMOPROPIONATE ION AND THIOSULFATE ION

bromoacetate-thiosulfate reaction (figures 2 and 5) when carried out in the presence of sodium and potassium ions (26, 27, 17).

The  $\beta$ -bromopropionate-thiosulfate reaction, (f), gives the sur-

prising result illustrated in figure 8; namely, that the *experimental limiting slope is of the opposite sign from that predicted for the electric charge type*. This interesting and important contradiction of Brönsted's theory will be interpreted in part C of this section.

Several significant conclusions can be drawn from the data of La Mer and Kamner given in table 8, valid for an ionic strength of  $\mu = 0.01$ . For the ester-thio type reaction, the rate decreases in the order bromoacetate,  $\alpha$ -bromopropionate, and  $\beta$ -bromopropionate, in accord with experience that the alpha position is more reactive than the beta position. This generalization is reversed when both reactants are charged; the  $\beta$ -bromopropionate ion reacts thirty times more rapidly with thiosulfate ion than does

TABLE 8

*Velocity constants for the reactions between the sodium salts of the brominated fatty acids (and methyl esters) and sodium thiosulfate at 25°C.  
for a concentration of  $\mu = 0.01$*

	ABSOLUTE VALUES OF $k$		RELATIVE VALUES OF $k$			
	Ester-thio type	Ion-thio type	Ester-thio type	Ion-thio type	Ester type	Ion type
Fatty acid:						
Bromoacetic.....	14.00	0.375	1	1	1	0.027
$\alpha$ -Bromopropionic.....	0.24	0.0027	0.017	0.0072	1	0.01
$\beta$ -Bromopropionic.....	0.03	0.080	0.002	0.21	1	2.7

the  $\alpha$ -bromopropionate ion. The reversal was predicted by the authors from electrostatic principles, since the number of collisions which the thiosulfate ion makes with the bromine atom is less in the alpha position than in the beta position as a result of the repelling action of the charge on the carboxyl group.

In considering the transition from the ester-thio to the ion-thio type reactions it should be noted that the rate *decreases* one hundred fold for the alpha derivative whereas it *increases* 2.7 fold for the beta derivative! An entirely analogous behavior was observed when the ion-thio reactions were carried out in media having pH values varying from 6.5 to 3. The dissociation constants of these fatty acids is of such an order that at pH = 3

they exist, for the most part, as neutral undissociated molecules so that the reaction is transformed to the zero type. The velocity constant of the alpha reaction is *increased sharply* upon passing to an acid solution while that of the beta reaction is *decreased*, but less markedly. The velocity curves for this change in pH have the general form of dissociation residue curves, as required by the explanation offered.

That the magnitude of the effect of transition from the ester-thio to the ion-thio reactions depends upon concentration is

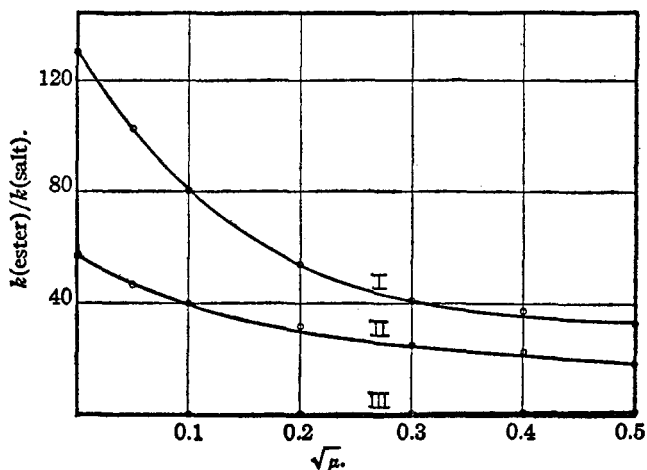


FIG. 9. I,  $\alpha$ -BROMOPROPIONIC ACID; II, BROMOACETIC ACID; III,  $\beta$ -BROMOPROPIONIC ACID

illustrated in figure 9, plotted from the data given in table 9. The increased reactivity of the beta ion as compared to that of the alpha ion was observed, but not interpreted, by Backer and Van Mels (22) for the reaction of sulfite ion with chloro-, bromo-, and iodo-propionates. Table 10 gives their results (in the presence of potassium ion), at 0.1 molar concentration ( $\sqrt{\mu} = 0.63$ ). Their alpha to beta ion reactivity ratio is smaller than that observed by La Mer and Kamner owing to the fact that the measurements of Backer and Van Mels were confined to the high concentration of  $\sqrt{\mu} = 0.63$ .

According to equation 36 the decrease in ion rates over ester rates should be accounted for by the term

$$-\frac{Z_1 Z_2 e^2}{2.3 DkT} \cdot \frac{1}{r} = -\frac{Z_1 Z_2 3.06}{r} \tag{37}$$

TABLE 9

The dependence of the ratios of the velocity constants of the thiosulfate reaction on concentration

	$\sqrt{\mu}$	0.00	0.05	0.10	0.20	0.30	0.40	0.50
$\frac{k_{ester}}{k_{salt}}$	Bromoacetate.....	(58)	46	40	32	26	23	20
	$\alpha$ -Bromopropionate.....	(131)	102	81	53	42	36	34
	$\beta$ -Bromopropionate.....	...	...	0.4	0.9	1.4	1.9	2.2
$\frac{k_{ester}}{k_{salt}}$ $\alpha$ -Bromopropionate	.....	...	...	218	58.5	28.9	19.7	15.7
$\frac{k_{ester}}{k_{salt}}$ $\beta$ -Bromopropionate	.....	...	...	32.2	9.1	4.8	3.5	3.0
$\frac{k_{salt}}{k_{salt}}$ $\beta$ -Bromopropionate	.....	...	...	0.25	0.08	0.04	0.03	0.02
$\frac{k_{salt}}{k_{salt}}$ $\alpha$ -Bromopropionate	.....	...	...	0.25	0.08	0.04	0.03	0.02
$\frac{k_{salt}}{k_{salt}}$ $\beta$ -Bromopropionate	.....	...	...	0.25	0.08	0.04	0.03	0.02
$\frac{k_{salt}}{k_{salt}}$ Bromoacetate	.....	...	...	0.25	0.08	0.04	0.03	0.02

TABLE 10

Reaction of sulfite ion with chloro-, bromo-, and iodo-propionates

	$k_\alpha$	$k_\beta$	RATIO $\alpha:\beta$
Chloropropionate.....	0.000160	0.000532	1:3.3
Bromopropionate.....	0.0134	0.0205	1:1.5
Iodopropionate.....	0.0252	0.0326	1:1.3

where  $r$  is the distance of closest approach of the charges at the moment of chemical reaction. It is only in the cases of the  $\alpha$ -bromopropionate and bromoacetate reactions that the velocity constant obeys the Debye-Hückel limiting formulas well enough to have confidence in the extrapolation to infinite

dilution using equation 7 to evaluate  $\log k_0$ , so that we may employ the equation

$$\log \left( \frac{k_{\text{ester}}}{k_{\text{ion}}} \right)_{\mu=0} = + Z_A Z_B \frac{3.06}{r} \quad (37)$$

The limiting values of this ratio are given in table 9 and figure 9; the value 131 for  $\alpha$ -bromopropionic acid corresponds to an  $r$  value of 2.88 Å, (using equation 37); the ratio for bromoacetate is 58 and gives an  $r$  of 3.47 Å. Both values of  $r$  are plausible.

### *C. Orientation in ionic reactions*

The introduction of the limiting forms of the Debye-Hückel theory employed in deriving equation 7 and Christiansen's equation (36) rests upon the validity of the simplifying assumption, necessary for mathematical development, that the charges on the ions may be considered as symmetrically distributed upon spheres of radius  $b$ . This assumption appears to be sufficiently valid to account for the bromoacetate and  $\alpha$ -bromopropionate data. It can hardly be considered a valid assumption for the collision between a thiosulfate ion and a  $\beta$ -bromopropionate ion if we are to accept the structural formulas of organic chemistry as representing even the approximate positions of the bromine atom and the charge on the carboxyl group. The models of organic chemistry require an orientation effect, superimposed upon the effects predicted for spherical ions.

La Mer and Kammer advance orientation as the explanation of the concentration dependence of the velocity of the  $\beta$ -bromopropionate-thiosulfate reaction shown in figure 8 and for the increased velocity which a charged beta ion exhibits over an uncharged beta molecule. Christiansen considered the possible influence of orientation, but expressed the opinion that in solutions it would probably prove to be of less importance than that of deactivating collisions.

That a molecular model consisting of a spherical and a non-spherical ion of like sign with the point of attack at a great distance from the electric charge on the non-spherical ion should



lead to a decreased velocity with increased ionic concentration may be demonstrated as follows:

Consider the extreme case of a volume of solution containing only one thiosulfate ion and one  $\beta$ -bromopropionate ion. Collisions will be very infrequent but, when they do occur, the probability that the bromine end will collide with the thiosulfate owing to the repulsive effect of the negative charges on the two ions is at a maximum. Practically every collision having a velocity sufficient to exceed the critical increment should, therefore, be fruitful. As we pass to slightly more concentrated solutions, the rapidly fluctuating fields produced by the thermal movement of the neighboring ions will disturb the ideal orientation of the collisions that prevails at extreme dilution. Many of the collisions predicted by the term  $C_A \cdot C_B$  in the rate equation (3)  $dx/dt = k \cdot C_A \cdot C_B$  will no longer occur with an orientation represented as lying within the critical solid angle necessary for chemical reaction. The result will be a decrease in the value of the velocity constant with increasing concentration which will be most pronounced in the highly dilute region. This effect for non-spherical ions is not adequately taken care of by the factor  $f_A f_B / f_X$ .

## XII. SUMMARY

1. A critical presentation of the derivations and theory underlying the primary kinetic salt effect is given.
2. The problem of substituting activities for concentrations in rate equations is discussed.
3. The customary limiting form of Brönsted's theory, based on the Debye-Hückel limiting law for activity coefficients, fails for high-valence type mixtures in highly dilute solutions. This failure, however, does not represent a contradiction of the theory of reaction velocity.
4. The influence of substitution and molecular architecture is discussed. Orientation is a factor that must be considered in the velocity of reactions involving long chain type molecules.

It is a pleasure to acknowledge the assistance which Miss Mildred Kammer has given in the preparation of this review.

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