

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE]

## THE SPEED OF REACTION IN CONCENTRATED SOLUTION AND THE MECHANISM OF THE INVERSION OF SUCROSE. II

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The theory that the speed of reaction is proportional to the activities of the reactants rather than to their concentrations has apparently won general acceptance. Harned and Seltz<sup>1</sup> give a summary of much of the important work which supports this theory. Later work and some omitted by them will be referred to in what follows. Brönsted<sup>2</sup> has modified the theory by the addition of another factor which will be considered later.

There are two factors that have but little effect on most reactions, but which become enormously important in the inversion of sucrose. The first is the definition of reaction speed, and the second, the influence of viscosity on reaction speed. Since my interpretation of both differs from that of Moran and Lewis,<sup>3</sup> and since no progress can be made toward determining the mechanism of the inversion process until they are settled, it is important to review the evidence, both experimental and theoretical, on these questions.

### The Definition of Reaction Speed

In the concentration form of the equation for reaction speed it is obvious that the speed,  $s$ , must equal  $-dC_1/dt$ , or the quantity transformed per liter in unit time. This definition of  $s$  has been carried over to the equation in terms of activities, apparently without question of its validity. In a previous paper<sup>4</sup> I defined  $s$  as equal to  $-dN_1/dt$ , or the quantity per mole of all substances or per unit of free volume, and I gave reasons for considering this to be the best analogy to the volume of a perfect gas. The following is a more complete and detailed treatment of the same subject which includes a justification of the activity theory of reaction speed.

Activity is a thermodynamic function, while the speed of reaction can be expressed only in terms of the kinetic theory. To correlate the two it is necessary to interpret activity in terms of the kinetic theory, although such an interpretation obviously cannot replace the thermodynamic definition. For simplicity of treatment we will limit ourselves for the present to the case where only 1 molecule of each kind reacts, and to ideal solutions.

<sup>1</sup> Harned and Seltz, *THIS JOURNAL*, **44**, 1475 (1922).

<sup>2</sup> Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

<sup>3</sup> Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922).

<sup>4</sup> Scatchard, *THIS JOURNAL*, **43**, 2387 (1921).

Every method of measuring activity, except by the speed of reaction, depends upon the number of molecules passing through or reacting at a surface, which may be the surface of contact of the solution with a gas, with another liquid, with the solid form of the solute, or with an electrode. Since the activity is independent of the extent of this surface, it must be proportional to the number of molecules which collide with a unit surface. To account for different degrees of attraction of different surfaces, this may be expressed as the number which would collide with a unit standard surface multiplied by a coefficient for the particular surface. Also, the activity must be proportional to the fraction of colliding molecules that pass through or react at the surface, either of which we will call the fraction of reactive molecules. This may be summarized in mathematical form: activity = proportionality constant  $\times$  number of collisions against unit standard surface  $\times$  specific surface coefficient  $\times$  fraction of reactive molecules.

In an ideal solution the fraction of the molecules that are reactive is independent of the composition, and the activity of each component is proportional to its mole fraction. So the number of collisions of each component is proportional to its mole fraction, and not in general to its concentration.

In collisions between 2 molecules, let us picture the molecules of the first type as colliding with those of the second. Then the number of collisions will be proportional to the mole fraction of the molecules of the first type. For a single molecule of the second type the factor of proportionality will be its surface expressed in equivalents of a unit standard surface, which will certainly depend upon the size and nature of its surface, and perhaps also on its motion through the solution. In an ideal solution, however, this factor will be independent of the composition. The total number of collisions in a liter will be proportional to the concentration of the molecules of the second type, the number per mole of each component to its mole fraction. In either case the number of collisions will be proportional to the mole fraction of the molecules of the first type.

$$\text{Collisions per mole} = K \times N_1 \times N_2 \quad (1a)$$

$$\text{Collisions per liter} = K \times N_1 \times C_2 = K \times \Sigma C \times N_1 \times N_2 = K/\Sigma C \times C_1 \times C_2 \quad (1b)$$

The kinetic theory assumes that the speed of a bimolecular reaction is proportional to the number of collisions between reactive molecules of each sort. In an ideal solution, where the fraction of the molecules which are reactive is constant, the speed is proportional to the number of collisions between all the molecules. Using the two values of speed defined above, and recalling that in an ideal solution activity is proportional to mole fraction

$$-dN_1/dt = K' \times N_1 \times N_2 = K'' \times a_1 \times a_2 \quad (2a)$$

$$-dC_1/dt = K' \times \Sigma C \times N_1 \times N_2 = K'/\Sigma C \times C_1 \times C_2 = K'' \times \Sigma C \times a_1 \times a_2 \quad (2b)$$

The general equations are obvious. If  $m$  represents the number of molecules of each kind which react, they are

$$-dN_1/dt = K'' \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n} \quad (3a)$$

$$-dC_1/dt = K'' \times \Sigma C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n} \quad (3b)$$

This derivation holds only for ideal solutions, but it does show that, if its logic is correct, the term  $s$  for ideal solutions when the equation is written in terms of activities is the quantity transformed in unit time per single mole of all components.

For the purpose of integration, the activities which change during the course of the action must be expressed in the same units as the differential. For an apparently unimolecular reaction<sup>5</sup> the  $\Sigma C$ 's cancel in the second form, and the value of  $K$  is the same whether the speed is expressed in terms of mole fractions or of concentrations. In general  $K_C = K_N(\Sigma C)^{1-n}$  where  $n$  is the apparent order of the reaction. A dilute solution, as ordinarily considered, is one in which  $\Sigma C$  is constant and independent of the composition. For such a solution  $K_C$  is proportional to  $K_N$  for a reaction of any order.

To extend this treatment to semi-ideal solutions, in which all the deviation from ideality is due to chemical action, it is necessary and sufficient to express the mole fraction of each reactant as it exists in solution and not as moles added.

The extension to solutions in general must be made by analogy, but it is rendered more probable by the fact that most solutions do not deviate much from semi-ideality. At present we cannot apply the theory of the speed of reaction unless the activity of each reactant whose concentration changes during the course of the reaction is proportional to its mole fraction; so the extension need not be too general. We know that in a reversible reaction near equilibrium the speed of each of the two opposing reactions must be proportional to the activities of the reactants, regardless of the nature of the environment. From the above argument it is evident that the reaction speed is proportional to the activities of the reactants in any reaction in ideal or semi-ideal solutions. The only generalization which will include both these special cases is that the speed of all reactions is proportional to the activities of the reactants: that Equations 3a and 3b hold for all reactions. This is further justified by the conclusion that the activity contains factors for both the proportion of reactive molecules and the frequency of collision.

This interpretation of activity offers an explanation of the conclusions of Brönsted<sup>2</sup> concerning the salt effect on the speed of reactions, particularly between ions. Brönsted considers that every reaction takes place by the formation of an intermediate complex of extreme instability, whose activ-

<sup>5</sup> The order of a reaction is the number of molecules that react according to the equation; the apparent order is the number of those whose activity changes.

ity corresponds to its electrical charge which must equal the algebraic sum of the charges of the reactants. The speed of reaction is proportional to the activities of the reactants and inversely proportional to the activity coefficient ( $a/C$ ) of this critical complex.

The formation of a complex which reacts immediately is synonymous with reaction on collision. The salt effect on reaction speed might be due to a change in the proportion of reactive molecules or to a change in the collision frequency. The effect on the activity coefficient might be due to either of these same causes. The fact that these effects depend only on the ionic type indicates that it is the latter which is changed, for the fraction of the ions which are already active must vary greatly for ions of the same valence type. Both salt effects are probably due to a change in the medium which alters the effect of the electrical charges upon each other, the nature of which is such that, when the frequency of collisions between oppositely charged ions is increased, that between similarly charged ions is decreased, and *vice versa*. Since the effect on the speed of reaction is due to the same cause as that on the activity, it should be inversely proportional to the activity coefficient of the complex formed during collision. This factor represents a true catalytic action in the salt effect, distinct from and superposed on the change in activities of the reactants.

Brönsted's conclusions are based on results with solutions 0.1 *N* or more dilute, which may be considered as dilute solutions by the definition given above; in such solutions the activity coefficients are approximately equal for ions of the same valence type. To apply this theory to concentrated solutions, the activity coefficient of the complex should be defined as the activity divided by the mole fraction:  $f_C = a_C/N_C$ . Moreover, in concentrated solutions the activity coefficient is not the same for all ions of the same valence type. Since the activity coefficient of an extremely unstable substance can never be measured directly, this introduces a new source of uncertainty into the study of concentrated solutions. In ideal or semi-ideal solutions  $f_C$  is a constant. The general equations become

$$-dN_1/dt = K''/f_C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n} \quad (4a)$$

$$-dC_1/dt = K''/f_C \times \Sigma C \times a_1^{m_1} \times a_2^{m_2} \times \dots \times a_n^{m_n} \quad (4b)$$

### Viscosity and Speed of Reaction

Those who have assumed that the viscosity of a medium affects the reaction speed have generally assumed also that the speed of any reaction is inversely proportional to the viscosity, which seems to imply that the viscosity is a symptom of an inertia in the medium which affects anything happening in it. Others<sup>6,7</sup> have maintained that the effect of viscosity is at most very much smaller than that calculated by this assumption.

<sup>6</sup> Arrhenius, *Z. physik. Chem.*, **28**, 317 (1899).

<sup>7</sup> von Halban, *ibid.*, **67**, 129 (1909).

Moran and Lewis<sup>3</sup> consider that the frequency of collision is a function of the viscosity, and that it is only through influencing this frequency that the viscosity affects the reaction speed. Then the viscosity should have no effect on a unimolecular reaction. In the case of the reaction of sucrose with hydrogen ion, the heavier sucrose molecule moves so much more slowly that it may be considered as motionless, and the effect of viscosity on the reaction speed is proportional to its effect on the mobility of hydrogen ion as measured by conductivity: it is approximately inversely proportional to the square root of the viscosity.

I believe that the speed of reaction is independent of the viscosity. My conception of the influence of viscosity is essentially that of Arrhenius,<sup>6</sup> which deserves restatement and emphasis and requires some minor modifications. Since the influence of a substance on the viscosity of a medium depends largely upon the size of its molecule, we will simplify the discussion by neglecting other factors and defining size as effect on viscosity.

Conductivity is not proportional to fluidity (the reciprocal of viscosity) but to some fractional exponent of it. The usual explanation of this smaller exponent is that the ions are too small to obey Stokes's law and that, when the individual molecules are considered, a solution is heterogeneous. The fluidity measures the mobility of all the molecules, large and small, while the conductivity measures the mobility of the smaller ions past the larger molecules. The effect of the larger molecules on the average mobility, when they themselves take part in the motion, is greater than their blocking effect upon smaller molecules or ions.<sup>8,9,3</sup>

To extend this reasoning to the speed of reaction we must consider that both fluidity and conductivity depend upon the ordered motion of migration. Both are measured by the linear velocity over distances very large compared to the free path of the molecules. The speed of reaction, on the other hand, depends upon the frequency of collision and, therefore, upon the chaotic motion of thermal agitation. Although the free path in liquids is extremely small, an ion, when the direction of its motion is changed by collision, has exactly the same probability of colliding with a reactive molecule as though it had continued its motion in the original direction.

According to the theory of the equipartition of energy and the kinetic molecular concept of temperature, the speed of thermal motion is a function only of the temperature, and is independent of the viscosity or any other property of the medium. In fact, the kinetic explanation of viscosity considers that viscous resistance is exerted by means of the change of energy of ordered linear motion to that of chaotic thermal

<sup>8</sup> Green, *J. Chem. Soc.*, 93, 2049 (1908).

<sup>9</sup> MacInnes, *THIS JOURNAL*, 43, 1217 (1921).

agitation. Since the frequency of collision and the speed of reaction depend only on this latter type of motion they cannot be influenced by viscosity.

The experimental study of the effect of viscosity on reaction speed is inconclusive because of the failure to eliminate other factors. The viscosity of a medium cannot be changed without changing the medium, which may also change the activity coefficient of any reactant or the specific catalytic effect of the medium. The effect on activity coefficients may be determined by measuring the activities, and that on the catalytic effect only by measuring the speed of several reactions in the same media. The fact that viscosity and speed of reaction change together cannot show how the two are related, or even that they are related.

Very dilute solutions of agar-agar or of gelatin have very great viscosities, while the effect of these solutes on other properties is small. It has been found that the speed of hydrolysis of methyl acetate by hydrochloric acid in such solutions, even when set to a jelly, is almost as great as in water.<sup>10,11</sup> The small change can probably be accounted for by a change in the activity of the hydrogen ion. This eliminates the possibility of a general inertia due to viscosity. It cannot decide between the two other theories, for the conductivity and diffusion are also nearly the same in these jellies as in water.

Arrhenius<sup>6</sup> believed that the fact that non-electrolytes have a very small effect on the speed of sucrose inversion compared to their effect on viscosity<sup>12</sup> proves that the reaction speed is very nearly independent of viscosity. But there may be a compensating increase in the activity of one of the reactants; witness the effect of sucrose itself on the hydrogen-ion activity.

The same objection applies to the measurements of reaction speed in water-alcohol mixtures.<sup>13</sup> There must be a great change in the activity coefficients of most substances as the solvent changes, for the solubilities change greatly. The activity coefficients of ions apparently change also. The measurements of Pearce and Hart,<sup>14</sup> calculated for 0.1 mole in a liter of solvent, show that the mean activity of lithium and chloride ions is 5 times as great in methyl alcohol, and 8 times in ethyl alcohol, as in water; but no activities have been measured in connection with the speed of reaction measurements. Moreover, although the viscosities of mixtures of water-alcohol pass through a maximum, the speed of re-

<sup>10</sup> Reformatsky, *Z. physik. Chem.*, **7**, 34 (1891).

<sup>11</sup> Callow, *Trans. Faraday Soc.*, **11**, 55 (1915).

<sup>12</sup> Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

<sup>13</sup> This objection applies also, as regards the activity of the acid, to the work of W. H. Garrett and W. C. M. Lewis [THIS JOURNAL, **45**, 1091 (1923)] on the formation of valerolactone in solutions containing sucrose.

<sup>14</sup> Pearce and Hart, THIS JOURNAL, **44**, 2411 (1922).

action sometimes increases, sometimes decreases, and sometimes passes through a minimum, which does not, however, correspond to the viscosity maximum.<sup>15</sup>

Particularly interesting are the results of Kistiakowsky on the reaction of formic acid with ethyl alcohol and that of ethyl formate with water. When the reactions are catalyzed with hydrochloric acid the speeds of both decrease slowly as water is displaced by alcohol to a minimum at about 60% alcohol, and then increase rapidly. Without a catalyst both decrease much more rapidly and continuously to 90% alcohol. The difference in the reactions with and without catalyst is very possibly a measure of the hydrogen-ion activity.

The only measurements in which all the activities have been measured are those of Buchböck<sup>16</sup> on the hydrolysis of carbonyl sulfide in aqueous solutions of various salts and acids, published soon after the first suggestion of the activity theory, under the name of solubility theory, by Van't Hoff.<sup>17</sup> Probably the speed of this reaction should not be affected by the viscosity according to any kinetic theory of viscosity, since the reaction is unimolecular or with the solvent which is in large excess. The constants quoted do show that, corrected or not by multiplying by any power of the viscosity, the concentration theory, the simple activity theory, and the unmodified theory of Brönsted all fail to give constants. The modified theory of Brönsted explains the results if the speed is independent of the viscosity and the activity coefficient of the critical complex increases linearly with some function such as the "ionic strength" of Lewis and Randall.<sup>18</sup> The concentrations of the ions may be estimated roughly from the molality of the solution necessary to give the same freezing-point depression as does *N* hydrochloric acid.

### The Inversion of Sucrose

Most of the assumptions necessary to the application of this theory to the inversion of sucrose were discussed in my previous paper,<sup>4</sup> but some require reconsideration in the light of new work. The numbers following the subtitles refer to the pages of the previous paper.

**Activity of Sucrose** (2391-2, 2399-402).—There seems no reason to change the conclusions that the reaction is unimolecular with respect to

<sup>15</sup> Walker and Kay, *J. Chem. Soc.*, **71**, 489 (1897). Kistiakowsky, *Z. physik. Chem.* **27**, 250 (1898). Caldwell, *Proc. Roy. Soc.*, **78A**, 272 (1906). Acree, *Am. Chem. J.*, **41**, 457 (1909). Reid, *ibid.*, **41**, 483 (1909). Schilow and Pudovkin, *Z. Elektrochem.*, **16**, 125 (1910). Burrows and Fawsitt, *J. Chem. Soc.*, **105**, 609 (1914). Burrows, *ibid.*, **105**, 1260 (1914).

<sup>16</sup> G. Buchböck, *Z. physik. Chem.*, **34**, 229 (1900).

<sup>17</sup> Van't Hoff, "Lectures on Theoretical and Physical Chemistry," Eng. ed., **1898**, Part I, pp. 217 ff.

<sup>18</sup> Lewis and Randall, *THIS JOURNAL*, **43**, 1112 (1921).

sucrose, and that the activity of sucrose is proportional to its mole fraction.<sup>19</sup>

**Constancy of  $k$**  (2391-2, 2399-402).—Fales and Morrell<sup>20</sup> claim that  $k$ , the constant for a unimolecular reaction, is not always constant during the course of a single reaction. Unfortunately, their experiments were not carried out in duplicate, and it is difficult to determine what part of their variation should be attributed to a real lack of constancy and what part to experimental error. The more complete details in Morrell's dissertation indicate two types of variation from constancy.

The first is abnormally high values of  $k$  for the first 1 or 2 minutes. This is noticeable only in the 0.1  $N$  or more concentrated solutions, for in the more dilute solutions the total change in so short a time is negligible. The abnormality is irregular and bears no apparent relation to the acid or sugar concentration. Two probable causes are: (1) an error in the measurement of time, which is unavoidable when the time interval is not great compared to the time of delivery of the pipets; and (2) an increase in temperature for the first few minutes due to the heats of dilution. Fales and Morrell have discarded these abnormally high values in calculating their average constants. They probably do not indicate a real abnormally high initial speed.

The second is a gradual increase of the reaction speed, which appears only in the solutions more concentrated in hydrochloric acid than 0.3  $N$ . Their solutions of 0.3  $N$  acid have about the same hydrogen-ion activity as the upper limit in the solutions studied by Lewis.<sup>21,3</sup> We are, therefore, justified in assuming that such an increase does not exist in these solutions. Moreover, such a gradual variation would appear in their method.<sup>22</sup>

**Activity of Water** (2392-6).—The activity of the water cannot be determined directly, since it changes materially during the course of inversion. It is determined from the activity in solutions without acid, and corrected for the effect of the acid by two assumptions which seem to give the minimum and maximum probable values. For 0.1  $N$  sulfuric acid the greatest correction is 0.6% and the greatest difference between the two assumptions is 0.4%; for 0.1  $N$  hydrochloric acid the corresponding values

<sup>19</sup> In their statement that this question involves a difficulty to which attention had not hitherto been drawn, Moran and Lewis<sup>3</sup> apparently overlook the discussion in my previous paper referred to above.

<sup>20</sup> Fales and Morrell, *THIS JOURNAL*, **44**, 2071 (1922). Morrell, *Dissertation*, Columbia University, 1921.

<sup>21</sup> Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920).

<sup>22</sup> The agreement between the results of Moran and Lewis and of Fales and Morrell noted by Lewis, Merriman and Moran [*THIS JOURNAL*, **45**, 711 (1923)] does not depend on the form of constant used by the authors, but arises through agreement of the two observations in both  $k$  and  $a_{H^+}$ .



are twice as great. The two assumptions lead to practically the same conclusions as to the number of water molecules taking part in the reaction.

**Activity of Hydrogen Ion (2392).**—It was previously assumed that the hydrogen electrode with saturated potassium chloride bridge gave an accurate measure of the hydrogen-ion activity. The discussion in another paper<sup>23</sup> indicates that this cannot be true with varying acid concentration, but that it is probably true with varying sucrose concentration. However, this must be recognized as an assumption with some theoretical justification. Without it, the measurements of sucrose inversion are worthless as a test of theories of the mechanism of reaction.

Fales and Morrell<sup>20</sup> claim that the reaction speed is not exactly proportional to the hydrogen-ion activity with varying acid concentration. Their results can be explained by the error in the determination of the hydrogen-ion activity and by the theory of Brönsted.

**Activity Coefficient of Critical Complex.**—If Equations 4a and 4b are correct, the activity coefficient of the critical complex must be taken into account, but it cannot be measured directly and cannot be assumed to be equal to that of the hydrogen ion. It was shown<sup>23</sup> to be probable that the two most important reasons for the change in activity coefficients are the change in the fraction of unhydrated ions and the effect of electrical charges on one another. In the case of a critical complex the first is already taken into account in the activities of the reactants. With varying sucrose concentration the total ionic concentration is probably unchanged, so we will assume that the activity coefficient of the critical complex is constant. This assumption has about the same degree of substantiation as the one that the saturated potassium chloride bridge gives constant liquid-junction potentials with these solutions.

For varying acid concentration the best we can do is to assume that the activity coefficient of the critical complex is the same as that of the potassium and chloride ions, which appear not to be greatly affected by varying water activity but to depend on the changing concentration of ionic charges. Frankly discarding the experimental determinations of hydrogen-ion activity, and taking the activities of hydrogen ion and of chloride ion in the dilute sucrose solutions as the same as in water solutions of the same molality, we find for the results of Fales and Morrell constants within the variation of their two series from each other, except for the 0.001 *N* solutions, where the concentration of acid may well be reduced by some side reaction.<sup>24</sup> It is not worth while publishing the details with so many approximate assumptions involved.

<sup>23</sup> Scatchard, *THIS JOURNAL*, **45**, 1716 (1923).

<sup>24</sup> A similar treatment of the results of Harned and Pfanstiel [*THIS JOURNAL*, **44**, 2193 (1922)] on ester hydrolysis gives less constant values than those quoted and explained in their article. This may be due to the uncertainty about the activity of the ester and about the number of water molecules which enter into the reaction.

**Equation for Sucrose Inversion.**—It is convenient to collect here the definitions of the various symbols.

$N$  = mole fraction;  $C$  = concentration in moles per liter;  $\Sigma C$  = total moles of all components per liter;  $a$  = activity, on a scale such that it is unity for pure water or for solutions without sucrose;  $f = a/N$ ;  $\eta$  = viscosity;  $x = 0.52$  at  $20^\circ$  and  $25^\circ$ ,  $0.55$  at  $35^\circ$  and  $40^\circ$ ;  $n$  = an integer (trial values = 5, 6, 7); subscript  $w$  applies to water,  $H$  to hydrogen ion,  $s$  to sucrose, and  $c$  to the critical complex;  $k = 1/C_s \cdot dC_s/dt = k_{obs.}$  of Moran and Lewis.

Since the reaction is unimolecular with respect to sucrose and hydrogen ion and the activity of the sucrose is the only one that changes enough to need consideration, Equation 4b becomes;

$$-dC_s/dt = K''/f_c \times \Sigma C \times a_s \times a_H \times a_w^n = K''/f_c \times \Sigma C \times 1/\Sigma C \times f_s \times C_s \times a_H \times a_w^n$$

$$K'' = f_c/(f_s \times a_H \times a_w^n) \cdot 1/C_s \cdot dC_s/dt = f_c/(f_s \times a_H \times a_w^n) \cdot k \quad (5)$$

We have assumed that  $f_c$  and  $f_s$  are constant; by Brönsted's theory we might make the less sweeping assumption that their ratio is constant. By the simple activity theory  $f_c$  should be replaced by 1. In any case the ratio may be incorporated in the constant, and we reach a result identical with that of the previous paper.

$$K_s = \frac{k}{a_H \times a_w^n} \quad (6)$$

**Other Constants.**—Lewis and his co-workers have proposed two constants for this action, which we will designate by the initials of the authors.

$$K_{J+L} = \frac{k}{a_H \times C_w} \quad (7) \qquad K_{M+L} = \frac{k \times (C_w - 4C_s) \times a_w^2 \times \eta^x}{a_H} \quad (8)$$

$K_{J+L}$  differs from  $K_s$  only in the replacement of the activity of water by its concentration. It depends upon all the assumptions mentioned above except those concerning the activity of water. It must be rejected, however, unless the activity theory is correct for some substances but not for others.

$K_{M+L}$  differs in the definition of reaction speed and in assuming that the speed is inversely proportional to  $\eta^x$ . For these solutions  $(C_w - 4C_s)$  is approximately equal to  $a_w^{10}$ , and  $\eta^x$  to  $a_w^{-18}$ , when all are expressed on such a scale that they are unity for pure water. Then the insertion of these terms makes a difference corresponding to + 10 and - 18, respectively, molecules of water reacting with each molecule of sucrose. Obviously, no conclusions can be drawn regarding the mechanism of the reaction until both of these two factors are settled.  $K_{M+L}$  depends upon all the other assumptions that does  $K_s$ .

**Experimental Results.**—The work of Moran and Lewis with hydrochloric acid as catalyst offers another check of the theory. In calculating the activity of water its activity in 0.1  $N$  hydrochloric acid is taken as 0.9965 (determined from freezing-point measurements).  $K_{J+L}$  is 55.55 times as great as the value given in the formula. The values of  $K_{M+L}$ ,

are taken directly from the paper of Moran and Lewis and also differ from the value given by the formula by a constant factor, different for each temperature. These differences arise from different units for activities and concentrations, but they can make no difference for a comparison of relative values.

TABLE I  
SPEED CONSTANTS BY VARIOUS FORMULAS

Conc. sugar	$K \times 10^6$	$a_H$	—First assumption—			—Second assumption—			$K_{J+L} \times 10^6$	$K_{M+L} \times 10^6$		
			$a_W$	$K_S \times 10^6$ $n = 5$	$K_S \times 10^6$ $n = 6$	$K_S \times 10^6$ $n = 7$	$a_W$	$K_S \times 10^6$ $n = 5$			$K_S \times 10^6$ $n = 6$	$K_S \times 10^6$ $n = 7$
At 25°												
0.0	(1.21)	1.00	0.997	(1.23)	(1.23)	(1.24)	0.997	(1.23)	(1.23)	(1.24)	(1.21)	(1.31)
10.0	1.36	1.20	.991	1.19	1.20	1.21	.990	1.19	1.20	1.22	1.21	1.28
20.0	1.52	1.44	.984	1.14	1.16	1.18	.982	1.16	1.18	1.20	1.21	1.25
30.0	1.68	1.74	.976	1.09	1.12	1.14	.973	1.11	1.14	1.17	1.19	1.24
40.0	1.83	2.09	.965	1.05	1.08	1.12	.961	1.07	1.11	1.16	1.17	1.24
50.0	1.99	2.50	.952	1.02	1.07	1.12	.947	1.05	1.10	1.17	1.16	1.24
60.0	2.15	3.00	.934	1.01	1.08	1.16	.928	1.04	1.12	1.21	1.15	1.27
70.0	2.30	3.60	.911	1.02	1.12	1.23	.903	1.06	1.18	1.30	1.15	1.28
Av.				1.07	1.12	1.17		1.10	1.15	1.20	1.18	1.26
At 35°												
0.0	(5.00)	1.00	0.997	(5.08)	(5.09)	(5.11)	0.997	(5.08)	(5.09)	(5.11)	(5.00)	(12.5)
10.0	5.65	1.19	.991	4.97	5.01	5.06	.990	4.99	5.04	5.09	5.08	12.4
20.0	6.33	1.42	.984	4.83	4.91	4.99	.983	4.86	4.94	5.03	5.11	12.3
30.0	7.00	1.71	.976	4.62	4.74	4.85	.973	4.69	4.82	4.96	5.05	12.2
40.0	7.66	2.05	.965	4.47	4.63	4.80	.962	4.54	4.71	4.90	4.99	12.2
50.0	8.33	2.45	.952	4.33	4.55	4.78	.947	4.45	4.69	4.96	4.94	12.1
60.0	9.07	2.95	.935	4.30	4.60	4.92	.928	4.47	4.81	5.19	4.94	12.5
70.0	9.66	3.53	.912	4.34	4.76	5.21	.904	4.53	5.01	5.55	4.91	12.3
Av.				4.55	4.74	4.94		4.65	4.86	5.10	5.00	12.3

TABLE II  
ROOT-MEAN-SQUARE DEVIATIONS DIVIDED BY AVERAGE

Formula	$n$	H <sub>2</sub> SO <sub>4</sub> 20°	H <sub>2</sub> SO <sub>4</sub> 40°	HCl 25°	HCl 35°	Av.
$K_S$ First assumption...	5	0.033	0.057	0.060	0.054	0.051
	6	.014	.039	.040	.033	.031
	7	.031	.038	.034	.029	.033
$K_S$ Second assumption.	5	.028	.051	.048	.041	.042
	6	.016	.036	.032	.027	.028
	7	.038	.042	.037	.040	.039
$K_{J+L}$ .....		.018	.024	.021	.014	.019
$K_{M+L}$ .....			.031	.036	.014	.023

The values of the constants are given in Table I. Table II contains the relative root-mean-square deviations of the experimental values from their averages for both 0.1 N sulfuric and hydrochloric acids, and the last column gives the average of the 4 series. These values are equal, within 1%, to the relative probable error of a single determination, and offer the simplest means of comparing the constancy of the constants.

Examining first the application of my formula to the inversion catalyzed

by hydrochloric acid, it is evident that the constancy is not so good as with sulfuric acid and that all the results show a minimum for medium concentrations. Remembering that the second assumption for determining  $a_w$  is more probable than the first, we see that these results confirm those with sulfuric acid in indicating that  $n$  is 6, although the possibility that it is 7 is not eliminated.

To compare the three formulas we will take  $K_S$  for the second assumption with  $n$  equal to 6. Of the three formulas,  $K_{J+L}$  fits the experimental data best, in spite of the fact that  $K_S$  contains an arbitrary integer and  $K_{M+L}$  an arbitrary non-integral constant, both chosen to give the best agreement with experimental data. The difference between the latter two is small and may be accounted for by the greater flexibility of the arbitrary constant in  $K_{M+L}$ . It is doubtful if any of the variations exceed the sum of the experimental errors. The experimental results certainly cannot serve as a criterion to choose between the several formulas; this choice must be based on the accuracy and reasonableness of their assumptions. Only after the formula is established can the experiments determine the number of water molecules which react with one molecule of sucrose.

**The Hydration of Sucrose.**—Moran and Lewis find confirmation of their formula from their conclusion that osmotic-pressure measurements prove that sucrose exists in water solution entirely as a tetrahydrate. I have already discussed the accuracy of the various methods of determining the extent of hydration, the fact that all methods point to decreasing hydrate formation with increasing concentration, and that the most accurate results (from vapor pressures) are best accounted for by the formation of a hexahydrate in accordance with the law of mass action.<sup>25</sup>

**The Critical Increment.**—Moran and Lewis claim further confirmation of their theory from the fact that it gives probable values of the critical increment, that is values which agree with Lewis's radiation theory. The critical increment is a function of the fraction of reactive molecules. The activity must be a function of the same quantity, whether the nature of that function is correctly derived above or not. It follows that the critical increment cannot be derived from the reaction speed in terms of activities, but must be in terms of concentrations or mole fractions. Since the volume changes very little with the temperature, the difference between these last two is negligible. A detailed discussion of this complicated question is out of place here, but the critical increment, calculated from concentrations or mole fractions, is practically the same for the two theories of the reaction mechanism.

### Summary

1. A kinetic interpretation of activity is given which justifies the expression of reaction speed in terms of activities and which demands that the

<sup>25</sup> Scatchard, *THIS JOURNAL*, 43, 2406 (1921).

speed so expressed be defined as moles transformed in 1 mole of all components.

2. This interpretation offers a possible explanation of the salt effect on reaction speed. The expression of Brönsted must be modified for concentrated solutions.

3. An analysis of experimental work shows that it is of little value for determining the relation of reaction speed to viscosity. The kinetic theory, however, demands that reaction speed be independent of viscosity.

4. These conclusions lead to the formula for the inversion of sucrose previously presented when the concentration of electrolyte is unchanged.

5. The experimental measurements cannot serve as a criterion for choice between the various theories of the mechanism of the reaction, for the difference in agreement between the formulas is too small.

6. Any interpretation of the experiments depends upon the assumption that the liquid-junction potential with saturated potassium chloride is independent of the sucrose concentration.

7. Interpreted by the formula previously presented, the speed of inversion catalyzed by hydrochloric acid adds confirmation that 6 molecules of water react with each molecule of sucrose. The agreement is not quite so good as with sulfuric acid.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## THE SEPARATION OF ISOTOPES. APPLICATION OF SYSTEMATIC FRACTIONATION TO MERCURY IN A HIGH-SPEED EVAPORATION-DIFFUSION APPARATUS

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### Introduction

**Important Factors for Rapid Operation of Diffusion Methods.**—In the separation of isotopes, the small separating power of the diffusion methods (including evaporation) must be compensated by very rapid operation, if large separations are to be obtained in a reasonable time. The apparatus described below was designed to accomplish this object for mercury. In the course of the work, systematic fractionation as applied to diffusion methods has been rather thoroughly studied.

The most important factors for maximum speed of separation fall into two classes: those of operating speed and those of operating efficiency.<sup>2</sup>

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<sup>2</sup> By the efficiency of any given operation is meant the ratio of *actual* separation to the separation obtained under *ideal* conditions. The separation obtainable under ideal conditions by a process either of evaporation or of molecular diffusion, is given by Equations 7, 16 and 19 of a previous paper [(a) Mulliken, *THIS JOURNAL*, **44**, 1034 (1922)].