

These experiments show that the separation of these two oxides is possible by means of selenium oxychloride and sulfuric acid.

Summary.

A new method has been described for the separation of molybdenum and tungsten, consisting in the extraction of molybdenum trioxide from a mixture of the ignited oxides by means of selenium oxychloride.

This work was performed by the writer while acting as research assistant to Professor Victor Lenher, whom the writer takes this occasion to thank for all his help and kindness.

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THE SPEED OF REACTION IN CONCENTRATED SOLUTIONS AND THE MECHANISM OF THE INVERSION OF SUCROSE.

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Introduction.

Although the speed of inversion of sucrose in acid solutions has been studied more than the kinetics of any other reaction,¹ there are two anomalies which were discovered by the earliest workers, but which have not yet received an adequate explanation. According to the accepted theories of chemical kinetics, the speed of reaction ought to be independent of the concentration of sucrose and proportional to the concentration of the hydrogen ion. Experimentally, the speed increases more rapidly than the concentration of the hydrogen ion when that of the sugar is kept constant; and when the concentration of acid is unchanged the speed increases rapidly with increasing sugar concentration.

There have been three types of explanation of these anomalies offered. The one most generally accepted at the present time explains only the abnormal increase with increased acid concentration or on the addition of a salt. This theory assumes that the non-ionized acid exerts a catalytic effect, which may be even greater than that of the hydrogen ion itself.² However, this theory alone is not sufficient as is shown by the facts that it will not explain the change in speed with changing sugar concentration, and that different values are calculated for the activity of the non-ionized

¹ A good bibliography up to 1906 is given by R. J. Caldwell, *Brit. Assoc. Rep.*, (York), 1906, pp. 267-92.

² The following references are typical of a voluminous literature in this field. H. C. S. Sneath, *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 211 (1913).

S. F. Acree, *Am. Chem. J.*, **49**, 345 (1913).

H. S. Taylor, *Medd. K. Vetenskapsakad. Nobelinst.*, **1913**; *Z. Elektrochem.*, **20**, 201 (1914).

acid from the effect of increasing acid concentration and from the effect of the addition of a salt with a common anion.³

A second method of explaining these anomalies is based on the assumption that the speed of reaction in solutions is not strictly proportional to the concentrations in moles per liter of the reactants. Wilhelmy,⁴ the pioneer in this field, empirically divided the weight of acid by that of water and found the resulting speed much more nearly constant. Spohr⁵ considered the effect due to the displacement of water by sugar, and he found that the speed of reaction was independent of the sugar concentration if the ratio of water to acid was kept constant. This method is equivalent to the use of the weight-normal concentrations of Morse,⁶ and it has been much used by Armstrong and his co-workers.⁷ Cohen⁸ accomplishes practically the same result by making a correction for the volume occupied by the sugar, similar to the "b" term in van der Waals' equation. All these methods neglect the fact that the water takes part in the reaction.

The third type of explanation is that of Arrhenius⁹ that the speed of reaction in solutions is proportional, not to the concentrations of the reactants, but to their osmotic pressures. The difficulty of this idea is the ambiguity of the osmotic pressure of a single component of a solution. At times the osmotic pressure seems to be identical with the activity as defined by G. N. Lewis,¹⁰ and for such cases the theory of Arrhenius is identical with that which will be presented in this paper.

A great step in advance was made when Jones and Lewis¹¹ measured the activity of the hydrogen ion by means of the hydrogen electrode. Assuming that the speed of reaction is proportional to this activity of the hydrogen ion rather than to its concentration, they find it also proportional to the concentration of water in moles per liter, and they draw the conclusion that the reaction proceeds by the combination of a molecule of sugar with a hydrogen ion, and that this complex ion reacts with one molecule of water to form glucose and fructose and to re-form the hydrogen ion. The present paper is an extension of the substitution of activity for

³ For example see H. S. Taylor and H. W. Close, *THIS JOURNAL*, **39**, 422 (1917).

⁴ L. Wilhelmy, *Pogg. Ann.*, **81**, 499 (1850).

⁵ J. Spohr, *J. prakt. Chem.*, [2] **33**, 265 (1886).

⁶ H. N. Morse, *Carnegie Inst. Pub.*, **198**, 97 (1914).

⁷ H. E. Armstrong and others, "Studies of the Processes Operative in Solutions," in the *Proc. Roy. Soc. (London)*, *J. Chem. Soc.* and *Chem. News*, **1906-13**.

Especially R. J. Caldwell, *Proc. Roy. Soc.*, **78A**, 272 (1906), and F. P. Worley, *J. Chem. Soc.*, **99**, 349 (1911).

⁸ E. Cohen, *Z. physik. Chem.*, **23**, 442 (1897).

⁹ S. Arrhenius, *Z. physik. Chem.*, **28**, 317-35 (1899).

S. Arrhenius and E. Andersson, *Medd. K. Vetenskapsakad. Nobelinst.*, **3**, No. 25 (1917).

¹⁰ G. N. Lewis, *Proc. Am. Acad.*, **37**, 49 (1901); *THIS JOURNAL*, **35**, 16 (1913).

¹¹ C. M. Jones and W. C. McC. Lewis, *J. Chem. Soc.*, **117**, 1120 (1920).

concentration to the other reactants as well as to the hydrogen ion. The conclusions as to the mechanism of the reaction are very different from those of Jones and Lewis.

The Formula for the Speed of Reaction in Solutions.

The formula for the speed of reaction in perfect gas systems is derived very simply from the kinetic theory: the speed is proportional to the concentration of each reacting species raised to the power which represents the number of molecules of that species which enter into the reaction according to the chemical equation. Given the reaction



the speed of reaction would be given by

$$s = dx/dt = K(C_1 - n_1'x)^{n_1} (C_2 - n_2'x)^{n_2} (C_3 - n_3'x)^{n_3} \quad (1)$$

where A_1 , etc., represent the chemical formulas of the substances; n_1 , etc., represent the number of molecules reacting; and n_1' , etc., represent the number of molecules which disappear when n molecules react. n_1' will be less than n_1 when the substance A_1 acts catalytically; it will be greater than n_1 if A_1 disappears in a subsequent reaction whose speed is greater than that of the reaction measured. C_1 , etc., represent the initial concentrations in moles per liter; s is the speed of reaction; K is a constant of proportionality; and x is a concentration term of such magnitude that $n_1'x$ is the number of molecules of A_1 that have disappeared from one liter in time t . When applied to the speeds of the opposing reactions of a reversible process, this formula gives the same result for the equilibrium constant as that derived by thermodynamics.

The speed of reaction in liquid systems, however, is treated only by analogy. From van't Hoff's classic exposition of the similarity of *dilute* solutions to perfect gases, Equation 1 has been extended to *all* solutions. Historically, this formula was arrived at empirically by Wilhelmy⁴ for this same reaction long before van't Hoff's theories, but the great success of these simple views is responsible for its retention long after it had been found not to fit the facts.

Thermodynamics requires that the general expression for the equilibrium constant be in terms of the activities as defined by Lewis.¹⁰ Since the ratio of the speeds of the opposing reactions of a reversible process must give the same equilibrium constant, it is a much more logical analogy to express the speed of a reaction (in a homogeneous system) in terms of activities. That is, the speed of any reaction in a homogeneous system is proportional to the activity of each reacting molecular species raised to the power which represents the number of molecules of that species which enter into the reaction according to the chemical equation. Lewis and Randall¹² have recently stated that this is a thermodynamic necessity for any reaction near equilibrium conditions.

¹² G. N. Lewis and M. Randall, *THIS JOURNAL*, **43**, 1150 (1921).

If we take the same chemical reaction as for Equation 1, the formula for the speed of reaction would be given by

$$s = K a_1^{n_1} a_2^{n_2} a_3^{n_3} \quad (2)$$

where a_1 , etc., represent the activities of the various reactants, and the other symbols have the same meaning as before. Since we already have an undetermined factor of proportionality we can use relative activities, assigning unit activity to any desired state. However, we encounter difficulty in interpreting the quantity s . It must be measured by the number of molecules which react in unit time, but in what units should it be expressed? The answer to this question will be made simpler by the introduction of a new term—"semi-ideal solution."

By semi-ideal solution will be meant one in which the polarity or thermodynamic environment is independent of the concentration; it differs from an ideal solution in that there may be chemical reactions between the components, although it includes ideal solutions as a special case. A semi-ideal solution might also be called physically ideal, since all the variations from ideality are due to chemical changes. The chief characteristic of a semi-ideal solution is that the activity of each component is proportional to the molar fraction of that component which actually exists in the solution. Neither the number of moles of any component nor the total number of moles can be determined from the quantities added to the solutions; but, in many cases, the actual calculation of these quantities is unnecessary. The assumption of semi-ideality is customarily made in treating chemical action in solution, be it dissociation, association or compound formation, when the solution is considered as too concentrated for the simple laws of dilute solutions. Dolezalek¹³ has gone so far as to claim that all solutions fulfil this condition. It is probable that most solutions are so nearly semi-ideal that the deviation from equality between activity and molar fraction is small.

For such solutions, as for ideal solutions, the quantity which is analogous to the volume of a perfect gas system is one mole of total substance, or the volume containing one mole. Replacing the total volume of a perfect gas system by the volume containing one mole of a semi-ideal liquid system is, at least approximately, the same as correcting the volume for the space occupied by all the molecules. If the polarity of the various kinds of molecules is the same, the forces of attraction and the distances between molecules will be independent of the nature of the molecules. Therefore the space between them will be approximately the same for any given number of molecules regardless of their size. But the space between the molecules is the free space, or the volume corrected for that part of it occupied by all the molecules, solvent as well as solutes. Then a dilute

¹³ F. Dolezalek, *Z. physik. Chem.*, **64**, 727 (1908); see, however, J. J. vanLaar, *ibid.*, **72**, 723 (1910), and J. H. Hildebrand, *THIS JOURNAL*, **38**, 1457 (1916).

solution would be one in which the free volume is proportional to the total volume. If we must give up our picture of rigid molecules, and consider them as fields of force without any definite boundary where they can be said to end, this is probably as definite an idea of free space in a liquid system as we can obtain.

Pursuing our analogy to a perfect gas, we will consider that the speed s is measured by the number of molecules transformed in unit time in a volume which contains one mole of total substance. If x is the number transformed in time t in one liter, then $s = \frac{1}{\Sigma C} \times \frac{dx}{dt}$, where ΣC is the total number of moles per liter. Let us consider the special simple case where x is measured for the substance A_3 , for which the solution is semi-ideal and for which n_3 is equal to unity. The activity of A_3 is $a_3 = (C_3 - x)/\Sigma C$, and Equation 2 becomes

$$s = \frac{1}{\Sigma C} \times \frac{dx}{dt} = K a_1^{m_1} a_2^{n_2} \left(\frac{C_3 - x}{\Sigma C} \right)$$

$$\text{or } dx/dt = K a_1^{m_1} a_2^{n_2} (C_3 - x). \quad (3)$$

It will be noted that a_1 and a_2 will in general be functions of the time or of x . For the third component we have reduced the formula to the same type as for perfect gases. If we can determine the functional relationship between a_1 , a_2 and x , we will not be restricted to solutions which are semi-ideal to more than one component. Obviously for dilute solutions, where the activity is proportional to the concentration, Equation 3 reduces to Equation 1.

We have now an expression for the speed of reaction in terms of thermodynamic quantities. It is not, of course, a thermodynamic theory of chemical kinetics, for the equation is derived only by a reasonable analogy.

The Inversion of Sucrose.

The inversion of sucrose as catalyzed by the hydrogen ion involves three reactants, sucrose, water and the hydrogen ion. If our formula is correct, its formulation when measured by the disappearance of sucrose is (from Equation 3),

$$dx/dt = K a_w^{n_w} a_h^{n_h} (C_s - x) \quad (4)$$

where the subscript (w) refers to water; the subscript (h) to the hydrogen ion and the subscript (s) to sucrose.

We can learn much about this reaction from the fact that, starting with any given concentration of sucrose and acid, the reaction gives a constant for a unimolecular reaction as measured by the disappearance of sucrose. Expressed mathematically,

$$\frac{dx}{dt} = k(C_s - x), \text{ or } k = \frac{1}{t} \ln \frac{C_s}{C_s - x}; \quad (5)$$

k is the K_{uni} of Jones and Lewis, and is constant only for a single con-

centration of sugar and acid. The fact that k so determined is a constant shows that n_s is equal to unity, and that, for the special case where each molecule of sucrose which disappears is replaced by one of glucose and one of fructose, we are justified in replacing the activity of sucrose by its concentration. This is a matter of some importance since we have no direct means of measuring the activity of the sucrose. It also shows that the activities of the water and of the hydrogen ion may be considered as remaining constant during the course of the reaction. For the present we will assume that we can employ the same measure of the speed of reaction when the original concentration of the sugar is varied, and we will leave the justification of that assumption until we discuss the mechanism of the reaction.

The results of Palmaer¹⁴ on solutions so dilute that the activity of the hydrogen ion is proportional to its concentration indicate that the speed of reaction is proportional to the first power of the hydrogen ion activity, or that n_h is also equal to unity. Unpublished work of Fales and Vosburgh and of Fales and Morrell, in which the activity of the hydrogen ion was measured directly, shows that this is also the case in the higher concentrations as studied by Jones and Lewis, and also shows that the hydrogen-ion activity does actually remain constant during the course of the reaction.

With these simplifications, Equation 4 becomes

$$dx/dt = Ka_w^n a_h^n (C_s - x) \quad (6)$$

where x and t are the only variables. Integrating, this becomes

$$K = \frac{1}{a_w^n a_h^n} \times \frac{1}{t} \ln \frac{C_s}{C_s - x} \quad (7)$$

Comparing Equations 5 and 7, we see that

$$K = k/a_w^n a_h^n \quad (8)$$

If we can measure k , a_w , and a_h , we can determine the value of n which gives a constant value of K , and so determine the number of molecules of water which enter into the reaction. Jones and Lewis¹¹ have measured k and a_h for solutions containing 10, 20, 30, 40, 50, 60 and 70 g. of sucrose per 100 cc. of solution and 0.1 N with respect to sulfuric acid at 20° and at 40°. They have expressed the activity in terms of moles of hydrogen ion per liter; but, in order not to change the magnitude of our constants more than necessary, we will adopt the convention that the activity of the hydrogen ion in 0.1 N solution of sulfuric acid in water alone is unity.

The activity of the water can be interpolated from the vapor-pressure measurements of Berkeley, Hartley and Burton.¹⁵ Water vapor at or

¹⁴ W. Palmaer, *Z. physik. Chem.*, **22**, 493 (1897).

¹⁵ Earl of Berkeley, E. G. J. Hartley and C. V. Burton, *Phil. Trans.*, **218A**, 295 (1919).

below room temperature behaves so nearly like a perfect gas that the vapor pressure of an aqueous solution may be taken as an exact measure of the activity of the water in that solution. These authors have measured very accurately the vapor pressures relative to that of pure water at the same temperature. If we adopt the convention that the activity of pure water is unity, these measurements give directly the relative activities required.

The Activity of the Water.—The method of determining the activity of the water is given in considerable detail since other workers might wish to use the same method.

The first step is to interpolate to the concentrations used by Jones and Lewis, but still at 0° and 30°, the temperatures of the vapor-pressure measurements. To do this the concentrations of Jones and Lewis are recalculated in terms of g. of sucrose per 100 g. of water by using the number of moles of water per liter given in their paper. The interpolation was then made graphically by two methods: in the first the activity was plotted against the concentration; in the second the ratio, $(1 - a_w)/\text{conc.}$, was plotted against the concentration. Each of these methods gave a graph of but slight curvature. Each curve was plotted twice on different scales, and the mean of the four determinations was taken as the best value. The greatest deviation of any individual value from this mean is 0.04% and the average deviation is less than 0.015%. The values of the activity used in plotting the curve are given in Table II (p. 2410) of the following article.

To determine the activities at 20° and at 40° from those at 0° and at 30°, the assumption is made that the relative activity is a linear function of the temperature. Since the maximum difference between 0° and 30° is 0.3%, this assumption cannot introduce an appreciable error. Table I gives the interpolated values at all four temperatures for solutions containing the same quantities of sugar as those used by Jones and Lewis but without sulfuric acid.

TABLE I.

INTERPOLATED ACTIVITIES OF WATER IN AQUEOUS SUGAR SOLUTIONS.

Concentration.		Activity (a).			
G. of sugar per 100 cc.	100 g. of water.	0°.	30°.	20°.	40°.
0	0.0	1.0000	1.0000	1.0000	1.0000
10	10.70	0.9940	0.9944	0.9943	0.9945
20	22.93	0.9868	0.9875	0.9873	0.9877
30	37.05	0.9782	0.9791	0.9788	0.9794
40	53.39	0.9676	0.9687	0.9683	0.9691
50	72.93	0.9539	0.9552	0.9548	0.9556
60	96.37	0.9360	0.9377	0.9371	0.9383
70	125.70	0.9119	0.9149	0.9139	0.9159

It is next necessary to correct the activity of the water for the sulfuric acid present. There are no data available for the temperatures in question, but the decrease in activity is so small that we are justified in assuming that it does not change with the temperature and in calculating it from the freezing-point depression. Noyes and Falk¹⁶ give the best value for the freezing-point depression of 0.05 *M* sulfuric acid as 0.2056°. Using the formula of Washburn¹⁷ quoted by these same authors, $1 - a_w = (p_o - p)/p_o = 0.00969 \Delta t (1 - 0.0043 \Delta t)$, we obtain $1 - a_w = 0.0021$. This holds for zero sugar concentration.

The next step is to calculate the decrease in solutions containing sucrose. The most obvious assumption is the ordinary one for dilute solutions, that the decrease due to the sulfuric acid is the same for all solutions. This assumption undoubtedly gives too small values for the decrease, but calculations are made on this basis and will be designated as results according to the first assumption.

A better value can be obtained by treating the sugar solutions as semi-ideal solutions in which the degree of the ionization of the sulfuric acid is independent of the sugar concentration, the degree of association of the water is constant, and there is no polymerization of any other substance. Our symbols will be the same as before with the addition that: C_w, a_w , etc., apply to solutions containing both sugar and acid; C'_w, a'_w , etc., to solutions of sugar without acid; C''_w, a''_w , etc., to solutions of acid without sugar; the subscript (_w) to monohydrol and the subscript (_p) to polymerized water; N_o is the molar fraction of monohydrol in pure water.

The sucrose in solution may be partially hydrated and partially not, but the total concentration of all its forms will be the amount of sucrose added per liter, C_s . The sulfuric acid will exist as $H_2SO_4, HSO_4^-, SO_4^{--}$ and H^+ , any one of which may be hydrated to various degrees. But the sum of the first three will always equal the quantity of sulfuric acid added, 0.05 moles per liter; the quantity of hydrogen ion per liter will be C_h . The activity of monohydrol in pure water is one, but its molar fraction is N_o . So in any solution the activity of monohydrol is equal to the molar fraction divided by N_o . The molar fraction of polymerized water in pure water is $1 - N_o$. Since the ratio of molar fractions of monohydrol and polymerized water is constant, the following holds true for all solutions.

$$\frac{C_p}{C_w} = \frac{N_p}{N_w} = \frac{1 - N_o}{N_o}, \quad C_p = \frac{C_w(1 - N_o)}{N_o} \quad \text{and} \quad C_p + C_w = C_w/N_o.$$

The total number of moles per liter will be,

$$C_w + C_p + C_h + C_s + 0.05 = C_w/N_o + C_h + C_s + 0.05.$$

From the hypothesis that the activity of each substance is equal to its molar fraction we have,

¹⁶ A. A. Noyes and K. G. Falk, *THIS JOURNAL*, **32**, 1013 (1910).

¹⁷ E. W. Washburn, *Technology Quart.*, **21**, 373 (1908).

$$\begin{aligned}
\frac{C_w/N_0 N}{C_w/N_0 + C_s} &= a'_w; \quad \frac{C''_w N_0}{C''_w/N_0 + C_h + 0.05} = a''_w; \quad \frac{C_h}{C''_w/N_0 + C_h + 0.05} = a''_h; \\
\frac{C_w/N_0}{C_w/N_0 + C_h + C_s + 0.05} &= a_w; \quad \frac{C_h}{C_w/N_0 + C_h + C_s + 0.05} = a_h \\
&\text{since } \frac{C'_s}{C''_w/N_0} = \frac{C_s}{C_w/N_0}, \text{ and } C''_h = C_h, \\
1 - a''_w &= 1 - \frac{C''_w/N_0}{C''_w/N_0 + C_h + 0.05} = \frac{C_h + 0.05}{C''_w/N_0 + C_h + 0.05} \\
a'_w - a_w &= \frac{C_w/N_0}{C_w/N_0 + C_s} - \frac{C_w/N_0}{C_w/N_0 + C_h + C_s + 0.05} \\
&= \frac{C_w/N_0 (C_h + 0.05)}{(C_w/N_0 + C_s)(C_w/N_0 + C_h + C_s + 0.05)} \\
&= \frac{C_w/N_0}{C_w/N_0 + C_s} \times \frac{C_h + 0.05}{C_w/N_0 + C_h + C_s + 0.05} \\
&= \frac{C_w/N_0}{C_w/N_0 + C_s} \times \frac{C_h + 0.05}{C''_w/N_0 + C_h + 0.05} \times \frac{C_h}{C_h} \\
&= a'_w \times (1 - a''_w) \left(\frac{a_h}{a''_h} \right) \tag{9}
\end{aligned}$$

or the decrease in the activity of the water in a sugar solution due to the sulfuric acid is equal to the decrease in the solution without sugar multiplied by the activity of the water in the sugar solution without acid and by the activity of the hydrogen ion in the final solution relative to that of an acid solution of the same concentration in the absence of sugar. Table II gives the activity of the hydrogen ion in the various solutions relative to that of 0.1 *N* sulfuric acid in pure water as unity, and the decrease in the activity of the water due to the sulfuric acid as calculated by Equation 9. Probably this decrease is a trifle too large. We will find later that the sugar solutions behave like semi-ideal solutions in which the degree of ionization of the sulfuric acid increases a little with increasing sugar concentration; and, assuming that whatever causes the apparent increased ionization would have the same effect on the activity of the water as though the increase were real, this would tend to give values for the decrease a little too large. Values calculated from these decreases are designated as results according to the second assumption.

The values of the activity of the water used in Tables III, etc., are rounded off to three places. The calculations are made on both assumptions since the true value probably lies between the two. The author believes that the final values of the activity as calculated by the second assumption are correct to one or two parts per thousand.

TABLE II.
DECREASE IN ACTIVITY OF WATER DUE TO SULFURIC ACID ACCORDING TO EQUATION 9.

Conc.	20°.		40°.	
	Activity of H ⁺ . $a_h/a^*h.$	Decrease. $a'_w - a_w.$	Activity of H ⁺ . $a_h/a^*h.$	Decrease. $a'_w - a_w.$
0	1.00	0.0021	1.00	0.0021
10	1.13	0.0024	1.12	0.0023
20	1.30	0.0027	1.24	0.0026
30	1.49	0.0031	1.56	0.0032
40	1.75	0.0036	1.82	0.0037
50	1.97	0.0039	2.18	0.0044
60	2.32	0.0046	2.60	0.0051
70	2.70	0.0052	3.04	0.0058

It is interesting to compare the calculated decrease in activity with the measurements of Rivett¹³ on the effects of various salts. Rivett measured the freezing points of 77 solutions of 14 salts in concentrations ranging from 0.1 *N* to *N* with respect to the salt and up to 40 g. of sugar per 100 g. of water. The different salts should not be expected to behave exactly like the sulfuric acid, but might be expected to have a somewhat similar behavior. The relative depression in the presence and in the absence of sugar is within the limits set by our two assumptions in all but 10 cases. Of these 5 are apparently errors in measurement or in tabulation, since they differ widely from the other results on the same salts. The other 5 are concentrated copper sulfate solutions, which appear to give regularly higher values than the sulfuric acid. The 67 values which fall within the limits are distributed nearly uniformly between the two.

The Order of the Reaction with Respect to the Water.—To determine the number of water molecules which enter into the reaction, we use Equation 8 and substitute various integral values for n_w to determine which will give constant values of K independent of the sugar concentration. Tables III A and IV A gives these values at 20° and 40° according to the first assumption. K_1 is the value of K when n_w equals 1; K_5 when n_w equals 5, etc. Tables III B and IV B give the corresponding results when a_w is calculated according to the second assumption. The values of k and a_h are, of course, the same for either assumption. In the B tables, C_w is the concentration of water divided by that in 0.1 *N* sulfuric acid without sugar—the relative concentration of the water—and K_c in the last column is $\frac{k}{a_h \times C_w}$. This is the value of K derived by Jones and Lewis multiplied by the number of moles per liter of water and of hydrogen ion in 0.1 *N* sulfuric acid without sugar; these values are included for comparison.

It is evident that when $n_w=1$, the values of K decrease rapidly with increasing sugar concentration. It is necessary to raise the activity of

¹³ A. C. D. Rivett, *Medd. K. Vetenskapsakad. Nobelinst.*, 2, No. 9 (1911).

the water to a much higher power. The results are tabulated for $n_w = 5, 6$ and 7 . The values of K_5 still decrease, those of K_7 increase, while those of K_6 remain sensibly constant.

The average values of the K 's are given, and the square root of the mean of the squares of the deviations of the individual values from the average value is given in the row designated R. M. S. D. (root mean square deviation). This is the best method of determining constancy. The values for zero concentration of sugar are given in parentheses, but they are not used in calculating the average values since the corresponding value of k is obtained by extrapolation.

TABLE III A.
VALUES OF K AT 20° BY FIRST ASSUMPTION.

Conc.	$k \times 10^6$.	a_h .	a_w .	$K_1 \times 10^6$.	$K_5 \times 10^6$.	$K_6 \times 10^6$.	$K_7 \times 10^6$.
0	(4.14)	1.00	0.998	(4.15)	(4.18)	(4.19)	(4.20)
10	4.43	1.13	0.992	3.94	4.07	4.10	4.13
20	4.79	1.30	0.985	3.74	3.97	4.03	4.10
30	5.21	1.49	0.977	3.57	3.92	4.02	4.11
40	5.54	1.75	0.966	3.28	3.76	3.90	4.03
50	5.95	1.97	0.953	3.17	3.85	4.04	4.24
60	6.22	2.32	0.935	2.87	3.76	4.02	4.30
70	6.29	2.70	0.912	2.55	3.69	4.05	4.44
			Average		3.86	4.02	4.19
			R.M.S.D.		0.127	0.057	0.131

TABLE III B.
VALUES OF K AT 20° BY SECOND ASSUMPTION.

Conc.	a_w .	$K_1 \times 10^6$.	$K_5 \times 10^6$.	$K_6 \times 10^6$.	$K_7 \times 10^6$.	C_w .	$K_c \times 10^6$.
0	0.998	(4.15)	(4.18)	(4.19)	(4.20)	1.000	(4.14)
10	0.992	3.94	4.07	4.10	4.13	0.935	4.18
20	0.985	3.74	3.97	4.03	4.10	0.872	4.22
30	0.976	3.58	3.94	4.04	4.14	0.810	4.31
40	0.965	3.28	3.78	3.92	4.06	0.749	4.23
50	0.951	3.18	3.89	4.09	4.30	0.686	4.41
60	0.933	2.88	3.80	4.07	4.36	0.623	4.31
70	0.909	2.56	3.75	4.13	4.54	0.557	4.18
		Average	3.89	4.05	4.23		4.26
		R.M.S.D.	0.108	0.063	0.161		0.078

TABLE IV A.
VALUES OF K AT 40° BY FIRST ASSUMPTION.

Conc.	$k \times 10^6$.	a_h .	a_w .	$K_1 \times 10^6$.	$K_5 \times 10^6$.	$K_6 \times 10^6$.	$K_7 \times 10^6$.
0	(5.98)	1.00	0.998	(5.99)	(6.04)	(6.05)	(6.06)
10	6.73	1.12	0.992	6.06	6.26	6.31	6.36
20	7.37	1.24	0.986	6.03	6.38	6.47	6.56
30	8.04	1.56	0.977	5.28	5.79	5.93	6.07
40	8.80	1.82	0.967	5.00	5.72	5.91	6.12
50	9.53	2.18	0.954	4.58	5.53	5.80	6.08
60	10.22	2.60	0.936	4.20	5.47	5.85	6.25
70	10.92	3.04	0.914	3.93	5.63	6.16	6.74
			Average		5.83	6.06	6.31
			R.M.S.D.		0.330	0.237	0.239

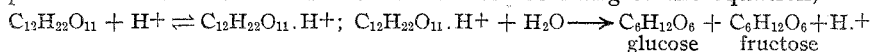
TABLE IV B.
 VALUES OF K AT 40° BY SECOND ASSUMPTION.

Conc.	a_w .	$K_1 \times 10^5$.	$K_5 \times 10^5$.	$K_6 \times 10^5$.	$K_7 \times 10^5$.	C_w .	$K_c \times 10^5$.
0	0.998	(5.98)	(6.04)	(6.05)	(6.06)	1.000	(5.98)
10	0.992	6.06	6.26	6.31	6.36	0.935	6.43
20	0.985	6.03	6.41	6.51	6.61	0.872	6.81
30	0.976	5.28	5.82	5.96	6.11	0.810	6.36
40	0.965	5.01	5.78	5.99	6.20	0.749	6.45
50	0.951	4.60	5.62	5.91	6.21	0.686	6.38
60	0.933	4.21	5.56	5.96	6.39	0.623	6.31
70	0.910	3.95	5.76	6.33	6.95	0.557	6.45
	Average		5.89	6.12	6.40		6.46
	R.M.S.D.		0.298	0.222	0.269		0.152

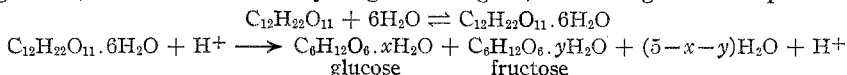
It is clear that the values of K_6 are much more nearly constant than those of K_5 or K_7 , and this conclusion is independent of the assumption as to the effect of the acid on the activity of the water, showing that a small error introduced by these assumptions will not affect the conclusions. The results at 40° are not so sharply conclusive as those at 20° . Apparently the experimental results are considerably less accurate due to the greatly increased speed of reaction, and the experimental errors introduce a variation of nearly the same magnitude as the differences between the results for K_5 , K_6 and K_7 . However, K_6 is still the best constant.

These results show conclusively that, if our conception of the speed of reaction is correct, a large number of molecules of water enter into the reaction. In order to establish that this number is 6 rather than 5 or 7 and that the number is independent of the sugar concentration, etc., a larger number of experiments with various acids at different concentrations will be necessary. Professor Fales has kindly consented to direct his work on sucrose inversion to a thorough test of the theory. To make the following discussion clearer we will assume that 6 molecules of water enter into the reaction, while we recognize that more complete results may change this number slightly. But such a change will not greatly change the nature of the discussion. If it be found that 7 molecules react rather than 6, the discussion will hold true if 7 be substituted for 6 wherever it occurs.

The Mechanism of the Reaction.—With 6 molecules of water taking part in the reaction, the number of possible ways of picturing the mechanism is very large. It seems probable, however, that the activity of the hydrogen ion in catalysis is the same as its activity measured by the hydrogen electrode. Then the 6 water molecules must react with the sugar or with a complex of sugar and the hydrogen ion. Jones and Lewis come to the conclusion that the sucrose and the hydrogen ion react to form a complex ion which then reacts with the water according to the equation,



If a large number of water molecules react instead of only one, this mechanism shows no reason why it should be 6 independent of the temperature and sugar concentration. The saccharated hydrogen ion also seems improbable, because, if it existed in the solution to any extent, it should reduce the activity of hydrogen ion in concentrated sugar solutions. It is much more probable that the water molecules react with the sugar first, and that this hydrate of sucrose then reacts with a hydrogen ion to give glucose, fructose and the hydrogen ion again, according to the equation:



These results cannot show whether the action of the hydrated sugar and the hydrogen ion is to form an intermediate complex ion or not.

The Activity of the Sugar.—If this picture of the mechanism of the reaction is correct, the reaction whose speed we are really discussing is the disappearance of the anhydrous (unhydrated) sugar. Also, if the measurements of the extent of hydration¹⁹ in the following paper are even approximately correct, we cannot assume that the sugar is almost all either hydrated or unhydrated; but both forms exist in our solutions to a considerable extent and their relative quantities vary widely with the concentration. It is necessary, then, to question critically our use of the disappearance of total sugar as a measure of the speed of reaction.

We will let the subscript (anh) apply to the anhydrous (unhydrated) sugar, and the subscript (hyd) apply to the hydrate. Then $C_s = C_{\text{anh}} + C_{\text{hyd}}$, and similarly for the other properties. The equations we used as a measure of the speed of reaction are

$$\frac{dx}{dt} = K a_w^n w_{ah} (C_s - x), \quad (6)$$

and

$$K = \frac{1}{a_w^n w_{ah}} \times \frac{1}{t} \ln \frac{C_s}{C_s - x}. \quad (7)$$

The corresponding equations for the disappearance of anhydrous sugar are

$$dy/dt = K a_w^n w_{ah} (C_{\text{anh}} - y), \quad (10)$$

and

$$K = \frac{1}{a_w^n w_{ah}} \times \frac{1}{t} \ln \frac{C_{\text{anh}}}{C_{\text{anh}} - y} \quad (11)$$

where y is the quantity of anhydrous sugar which disappears from one liter in time t .

$$\text{The } K\text{'s will be identical in case } \frac{C_s - x}{C_s} = \frac{C_{\text{anh}}}{C_{\text{anh}} - y}. \quad (12)$$

Let us consider the hydration of sucrose from the viewpoint of the law of mass action expressed in terms of activities, the holding of which is a thermodynamic necessity if the substances exist at all.

¹⁹ "Extent of hydration" is used to indicate the fraction of the sugar molecules hydrated; "degree of hydration," the number of molecules of water combined with one of sugar in the hydrate.

$$K_{\text{hyd}} = \frac{a_{\text{hyd}}}{a_{\text{anh}} \times a_w^6}, \text{ or } \frac{a_{\text{hyd}}}{a_{\text{anh}}} = K_{\text{hyd}} a_w^6 \quad (13)$$

$$\frac{a_{\text{hyd}} + a_{\text{anh}}}{a_{\text{anh}}} = \frac{a_s}{a_{\text{anh}}} = 1 + K_{\text{hyd}} a_w^6. \quad (14)$$

If, during the course of a single reaction, the activity of the water is constant, the right-hand side and therefore the left-hand side of Equation 14 will be constant. Now let us assume that the solutions are semi-ideal with respect to the hydrated and unhydrated sugar. Then for the activities we may substitute molar fractions, and we have,

$$\text{const.} = \frac{a_s}{a_{\text{anh}}} = \frac{N_s}{N_{\text{anh}}} = \frac{\frac{C_s}{\Sigma C}}{\frac{C_{\text{anh}}}{\Sigma C}} = \frac{C_s}{C_{\text{anh}}}. \quad (15)$$

If we substitute the values of C at time zero and time t , we have,

$$\frac{C_s}{C_{\text{anh}}} = \frac{C_s - x}{C_{\text{anh}} - y}, \text{ or } \frac{C_s}{C_s - x} = \frac{C_{\text{anh}}}{C_{\text{anh}} - y},$$

which is identical with Equation 12. We are therefore justified in taking the rate of disappearance of the total sucrose as a measure of the speed of disappearance of anhydrous sucrose when the activity of the water remains constant.

But the assumption of constant activity of the water is not in accord with experiment. Invert sugar depresses the activity of water very nearly twice as much as the sucrose from which it is derived, and this fact has been used to follow the course of the reaction by the change in boiling point²⁰ and in freezing point.²¹ For the most concentrated solutions the activity of the water would be reduced about 1/10 during the course of the reaction. This would mean that our integration of Equations 6 and 10 with the assumption of constant activity of the water is not exact. Equations 14 and 15 still hold, however, and combining them we have,

$$C_s/C_{\text{anh}} = 1 + K_{\text{hyd}} a_w^6 \quad (16)$$

Then, as the activity of the water decreases, the ratio of anhydrous to total sugar will increase. This will cause an acceleration of the reaction when measured in terms of the disappearance of total sugar (Equation 6) which will tend to compensate for the retardation due to the decreased activity of the water, and there will be a smaller error in assuming the activity of the water to be constant than if Equation 10 itself were used.

It does not seem worth while to follow the analysis of this factor more rigorously, since there are at least two other factors which tend to produce a variation in k as determined by the optical rotatory power. The first

²⁰ J. E. Trevor and F. C. Kortright, *Z. physik. Chem.*, **14**, 149 (1894).

²¹ L. Kahlenberg, D. J. Davis and R. E. Fowler, *THIS JOURNAL*, **21**, 1 (1899).

is the mutarotation of the products of inversion;²² the second, the reversion²³ or slow change in the final rotation which makes it difficult to determine the true end-point. This reversion is apparently due, in part at least, to a recombination of the glucose and fructose to disaccharides other than sucrose.

Worley made some very careful measurements and determined the change in k with time by using Equation 5 integrated between the limits t_1 and t_2 , which gives the formula,

$$k = \frac{1}{t_2 - t_1} \ln \frac{C_s - x_2}{C_s - x_1} \quad (17)$$

This formula has the single disadvantage that it multiplies the experimental error, since the time intervals must always be small. Worley found that for his experiments the total effect of the interfering factors was to give increasing values of k , while the decrease in the activity of the water would tend to give decreasing values.

Our problem is not to determine the exact kinetics of this reaction, actually of the eighth order and complicated by subsequent reactions, but simply to ascertain whether the value of k as calculated from the experimental results is really the k we have used in Equation 8. This will be true if the experimental k is the initial k —that at the beginning of the reaction—when the activity of the water has not appreciably changed and may be regarded as constant. A sufficient condition will be that k as determined by Equation 17 does not vary during the reaction.

Jones and Lewis give only one pair of results from which this condition may be tested, those for 70 g. of sucrose at 40°. These results are, however, the ones most likely to give a variation in k , since the activity of the water changes most for the concentrated solutions. Table V gives the constants for two duplicate experiments calculated by Equation 17 and by Equation 5. Those by Equation 17 are tabulated in the same row as t_2 , while t_1 is the next preceding time. It will be seen that the value of k from Formula 17 shows no systematic trend and that the average is practically the same as that calculated from Formula 5. Due to the magnification of the experimental errors with the shorter time intervals, the variation in the individual values is considerably greater for Formula 17. The results show that we are justified in using in Equation 8 the values of k as measured by Jones and Lewis.

²² J. Meyer, *Z. physik. Chem.*, **62**, 59 (1908); **72**, 117 (1910).

C. S. Hudson, *THIS JOURNAL*, **30**, 1160 (1908); **32**, 885 (1910).

²³ A. Wohl, *Ber.*, **23**, 2084 (1890). E. Fischer, *ibid.*, **23**, 3687 (1890).

F. P. Worley, *J. Chem. Soc.*, **99**, 349 (1911); *Proc. Roy. Soc. (London)*, **87A**, 555 (1912).

TABLE V.
RATE OF INVERSION OF SUCROSE.
70 g. per 100 cc. at 40°.

Time Sec.	Expt. 1.		Time. Sec.	Expt. 2.	
	$k \times 10^6$ Eq. 5.	Eq. 17.		$k \times 10^6$ Eq. 5.	Eq. 17.
780	10.82	1200	10.81
1500	11.03	11.25	1950	10.81	10.81
2100	10.98	10.87	2460	10.83	10.90
3060	11.00	11.04	3060	10.77	10.52
3900	11.03	11.13	3960	10.89	11.30
5160	11.07	11.20	4440	10.86	10.63
6420	11.11	11.28	6360	10.96	11.20
7500	10.98	10.20	6900	10.97	11.07
Av.	11.00	11.00	Av.	10.86	10.92

Reaction 55% complete. Reaction 53% complete.

The Activity of the Hydrogen Ion.—Jones and Lewis account for the increased activity of the hydrogen ion in the concentrated sugar solutions by a difference in the catalytic environments of sucrose and of water. Since the activity (as measured by the catalytic effect) does not change during the course of the reaction, the catalytic effect of the sucrose must be the same as that of the corresponding amount of invert sugar, and they therefore assume that it is zero, and that the whole change is due to the negative catalytic effect of the water. This they find expressible as an exponential function of the water concentration.

A very simple explanation is obtained from the view of semi-ideal solutions. If this view is correct, the activity of the hydrogen ion is proportional to its molar fraction, and the great change with changing sugar concentration is due to a change in the number of total moles per liter. By using the activity of the water and that of the hydrogen ion and applying the concept of a semi-ideal solution in which the degree of association of the water remains constant and no other substances are polymerized, it is possible to calculate the concentration of hydrogen ions in moles per liter. For the water we have,

$$\frac{C_w/N_0}{C_w/N_0 + C_h + C_s + 0.05} = a_w; C_w/N_0 = \frac{a_w}{1-a_w} (C_h + C_s + 0.05).$$

According to our convention, the activity of the hydrogen ion is not equal to its molar fraction, since we have assigned unit activity, not to a solution of unit molar fraction, but to a water solution of 0.1 *N* sulfuric acid. However, the activity will be proportional to the molar fraction, and we will let *K* be the proportionality constant.

$$\frac{C_h}{C_w/N_0 + C_h + C_s + 0.05} = Ka_h$$

Substituting the value of C_w/N_0 obtained above and solving for C_h , we have

$$C_h = \frac{Ka_h}{1-a_w - Ka_h} (C_s + 0.05). \quad (18)$$

The value of K may be obtained for each temperature by solving the equation for the solution without sugar where the hydrogen-ion concentration is known. At 20° , $C_h=0.06$, $a_h=1$, $a_w=0.998$, $C_s=0$; at 40° , $C_h=0.05$ and the others have the same values as at 20° . Table VI gives the values of the hydrogen-ion concentration calculated from Equation 18 at 20° and at 40° . In each case the values are calculated according to both assumptions as to the effect of the sulfuric acid on the activity of the water. The fact that the results are only a few per cent. different in the two cases shows that, even though the form of the mathematical equations is similar to those used in calculating the change in activity according to the second assumption, the results cannot depend upon that assumption.

TABLE VI.

CONCENTRATION OF HYDROGEN IONS IN AQUEOUS SUGAR-SULFURIC ACID SOLUTIONS.

Conc. of sugar.	Concentration of hydrogen ions.			
	20°		40°	
	1st assumpt.	2nd assumpt.	1st assumpt.	2nd assumpt.
0	0.060	0.060	0.050	0.050
10	0.062	0.062	0.056	0.056
20	0.066	0.066	0.062	0.057
30	0.070	0.067	0.067	0.064
40	0.072	0.070	0.071	0.067
50	0.072	0.069	0.075	0.070
60	0.073	0.071	0.076	0.073
70	0.072	0.070	0.077	0.073

Since the solutions are 0.1 N , multiplication of the hydrogen-ion concentration by 1000 will give the degree of ionization of the sulfuric acid in percentages. In each case the degree of ionization increases with increasing sugar concentration, but the increase is not very large, and for the more concentrated solutions it disappears within the rather large experimental error. This error is due to the fact that the hydrogen-ion concentration is calculated from small differences. A slight variation of the solutions from semi-ideality or a different assumption as to the degree of ionization without sugar would also change the table somewhat. If allowance were made for the smaller degree of association of the water in the solutions where its molar fraction is smaller, the concentration of hydrogen ion in the more concentrated solutions would be reduced. Certainly these results are too few for theorizing on the efficiency of water and of sugar solutions as ionizing media except to point out that they are not very different, and that we have eliminated the anomaly of an ionization greater than 100%.

Jones and Lewis reduced the negative catalytic effect of water on the inversion of sucrose as observed by Rosanoff and Potter²⁴ to a catalytic

²⁴ M. A. Rosanoff and H. M. Potter, *THIS JOURNAL*, 35, 248 (1913).

effect on the ionization of the acid. Our interpretation of the nature of sugar solutions reduces it to a difference in molar volume between sucrose and water. The fact that it may be expressed as an exponential function of the water concentration can give no new information on the nature of anticatalytic action.²⁵

The Relation to the Neutral Salt Effect.—If this theory as to the dependence of the speed of reaction on the activities of the reactants is correct, the effect of a neutral salt on the speed of reaction should be a complicated one. The addition of a neutral salt will affect the activity of each component. The activity of the water will be decreased as is shown by the decrease of vapor pressure or corresponding change in the other colligative properties. The activity of the hydrogen ion will be increased, as has been shown by the work of many observers.²⁶ Most of these observers interpret the effect as due to a decrease in the apparent volume of the solvent. In the terms of our theory this would mean an increase in the molar fraction of the hydrogen ion due to a decrease in the number of moles of water. Lack of knowledge of the degree of dissociation of the added salts prevents an analysis of this effect similar to that made on the sugar solutions to determine whether these solutions may also be interpreted as semi-ideal.

The effect of the salt on the activity of the sucrose has never been measured, but it would probably increase it. By decreasing the activity of the water it would decrease the extent of hydration of the sucrose. It is also a general characteristic of salts that they increase the activity of organic

²⁵ A paper by Garner and Masson (*Phil. Mag.*, **41**, 484-6 (1921)) on this subject has just come to the author's attention (September 29, 1921). They note that the ratio between the activity of hydrogen ions in a sugar solution and in pure water is approximately equal to the ratio between the osmotic pressure of the solution and that calculated by van't Hoff's Law and to the inverse ratio of the solubility of hydrogen in that solution and in pure water. They explain all three by the removal of water, probably to form a hydrate of sucrose. The assumptions upon which this is based for the solubility of gases are discussed in the following paper. For the osmotic pressure it must be assumed that the Morse formula gives an accurate expression for the osmotic pressure of an ideal solution; this is probably correct within the limits of their approximations. For the hydrogen ion activity one must assume that the activity of the hydrogen ion is inversely proportional to the quantity of water in which it is dissolved and independent of the other components of the solution. The present author can see no reason for assigning this unique position to water. It would certainly lead to astonishingly large results for the activity of hydrogen ion in nearly anhydrous alcohol or glycerine.

²⁶ G. Poma, *Z. physik. Chem.*, **88**, 671 (1914).

H. S. Harned, *This Journal*, **37**, 2460 (1915).

H. A. Fales and J. M. Nelson, *ibid.*, **37**, 2769 (1915).

A. W. Thomas and M. E. Baldwin, *ibid.*, **41**, 1981 (1919).

J. A. Wilson, *ibid.*, **42**, 715 (1920).

solutes, as shown by the decreased solubility and coefficient of partition with organic solvents.²⁷

It will be necessary to include all these effects in the consideration of neutral salt action. This becomes particularly important in the determination of the catalytic effect of the non-ionized acid. If this is to be calculated from the change in catalytic effect with changing acid concentration or on the addition of neutral salts, all the factors must be taken into consideration. It is not sufficient to follow the customary procedure of assuming the activity of the water and of the substrate to remain constant and to calculate the activity of the hydrogen ion from the law of mass action in terms of concentrations. The writer does not desire to question the existence of a catalytic effect of non-ionized acid, which, for certain reactions, seems to be firmly based on a variety of grounds, but he does wish to question the ordinary methods of calculating the relative catalytic effect of non-ionized acid and hydrogen ion.

Arrhenius and Andersson⁹ have studied the neutral salt effect on sucrose inversion from their viewpoint of osmotic pressures, and conclude that there is no evidence for a catalytic action of the un-ionized acid. Their osmotic pressure of the hydrogen ion is the same as its activity and is calculated with some extrapolation from the hydrogen-electrode measurements of Harned; the osmotic pressure of sugar they calculate from freezing-point measurements by a method which seems to me entirely unjustified; and they ignore the part of the water in the reaction. At present there are not enough data available for the analysis of this very important problem.

Summary.

1. A method has been outlined for calculating the activity of water in sugar solutions of any concentration at temperatures near room temperature. The method has also been extended to solutions containing a small amount of other solute (sulfuric acid).

2. A formula for the speed of reaction in solutions in terms of the activities of the reactants is developed and suggested as the most logical formula for solutions.

3. By the application of this formula to the inversion of sucrose it is shown that the available data indicate that the reaction is of the sixth order with respect to water.

4. The results are interpreted as indicating the existence of a hexahydrate of sucrose.

5. The effect of the addition of sugar in increasing the activity of the hydrogen ion is explained as being very largely due to an increase in the

²⁷ For ethyl acetate: H. Lunden, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 15 (1911); for benzoic and salicylic acids: B. de Szyszkowski, *ibid.*, **2**, No. 41 (1913).

molar fraction of hydrogen ions without any large change in the actual degree of ionization.

6. A warning is given concerning the customary method of calculating the catalytic effect of un-ionized acid.

In conclusion the author wishes to express his hearty thanks to Professor H. A. Fales and Mr. J. C. Morrell for their courtesy in giving him access to unpublished work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF AMHERST COLLEGE.]

THE HYDRATION OF SUCROSE IN WATER SOLUTION AS CALCULATED FROM VAPOR-PRESSURE MEASUREMENTS.

By GEORGE SCATCHARD.

Received, July 27, 1921.

Introduction.

The determination of the existence of hydrates of sucrose in its aqueous solutions and the calculation of the average degree of hydration of the sucrose have been made from various properties of these solutions. Jones and Getman,¹ Callendar,² Washburn³ and Bousefield⁴ calculated the degree of hydration from the freezing point; Bousefield, Frazer and Myrick⁵ and Porter⁶ used the osmotic pressure; and Philip,⁷ the solubility of hydrogen in sugar solutions. Einstein⁸ concluded from a kinetic treatment of viscosity that the sugar must be very heavily hydrated, but he did not determine the degree.

The calculation of hydration from the solubility of a gas depends on two assumptions: that the power to dissolve hydrogen of a given mass of water is independent of anything with which it may be mixed, and that the dissolving power of sucrose and of the hydrates of sucrose is zero. The principal justification for these assumptions is that, in the case of cane sugar and chloral hydrate, they give results in agreement with those from the colligative properties.

Washburn³ gives a very good review of hydration in solution, and notes that the colligative properties do not give mutually independent measures of the degree of hydration. The most rigorous treatment of either the

¹ H. C. Jones and F. H. Getman, *Am. Chem. J.*, **32**, 327 (1904).

² H. L. Callendar, *Proc. Roy. Soc. (London)*, **80A**, 466 (1900).

³ E. W. Washburn, *Technology Quart.*, **21**, 376 (1908).

⁴ W. R. Bousefield, *J. Chem. Soc.*, **105**, 600 (1914); *Trans. Faraday Soc.*, **13**, 141-55 (1917).

⁵ J. C. W. Frazer and R. T. Myrick, *THIS JOURNAL*, **38**, 1907 (1916).

⁶ A. W. Porter, *Trans. Faraday Soc.*, **13**, 123 (1917).

⁷ J. C. Philip, *J. Chem. Soc.*, **99**, 711 (1907); *Trans. Faraday Soc.*, **3**, 140-5 (1907).

⁸ A. Einstein, *Ann. Phys.*, [4] **19**, 301 (1906).