CXXVI.—*Studies in Catalysis. Part XIV. The Mechanism of the Inversion of Sucrose.*

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IN connexion with the investigations carried out in this laboratory on the chemical reactivity of molecular and ionic species from the point of view of the radiation hypothesis, it was found necessary, in one section of the work, to make a series of determinations of velocity-constants in the case of a few familiar reactions, such as the inversion of sucrose, with the object of studying more particularly the influence of change of environment on the rate of the reaction. The principle of mass action, in its usual formulation, affords no information of an a priori kind regarding the effect of environment. It is hoped that the radiation hypothesis may be of assistance in this connexion (compare Lewis, *Scientia*, 1919, 25). As a preliminary, it is necessary to possess as clear a view as possible of the actual material mechanism of the selected reaction in order to be able to proceed with some degree of confidence to the further problems involved in alterations of material and temperature environment. The inversion of sucrose is a reaction particularly suitable for the purpose in view in so far as precision of measurement is concerned. Further, this reaction has been frequently investigated, but, in spite of this, the inversion process

obviously requires further investigation, more particularly as regards the way in which the hydrogen ion enters into the process.

The present research was undertaken primarily for this purpose. As will be seen, the experimental measurements consist on the one hand of determinations of reaction velocities, and on the other of determinations of the average (geometric mean) activities of the hydrogen ions, obtained by the electrometric method. In agreement with the conclusion already reached by Harned (*J. Amer. Chem. Soc.*, 1918, **40**, 1461) in connexion with other reactions catalysed by ions, it has been found that the activity of the hydrogen ion, as defined by G. N. Lewis, is the determining factor for the rate of the reaction. This conclusion is of great importance, as it not only includes to a certain extent the phenomenon known as the solvent displacement effect, but also, as pointed out by Harned, appears to exclude the necessity of ascribing any catalytic influence to the undissociated molecule of the acid. In order to obtain data which could be employed for various kinds of calculation, care has been taken to determine the amounts of all constituents, water included, in known volumes of the various solutions.

As will be shown later, the most probable material mechanism of the inversion reaction is that expressed by $\text{RH}^+ + \text{H}_2\text{O} \rightarrow \text{dextrose} + \text{lævulose}$. That is, the reaction is a true bimolecular one, between a molecule of water and a complex ion, formed by the addition of hydrogen ion to the sucrose molecule.

EXPERIMENTAL.

Reaction Velocity Measurements.

The rate of inversion of sucrose was carried out in the ordinary manner with the usual precautions at 20°, 30°, 40°, and 50° in the presence of *N*/10-sulphuric acid, the initial concentration of sucrose being varied over a wide range, namely, from 10 to 70 per cent., in order to bring into prominence any effect produced by the displacement of the solvent, water, the volume of the various solutions being maintained constant. All determinations were carried out in duplicate, and satisfactory unimolecular velocity-constants were obtained throughout the entire range examined. To save space, the mean values only of the observed velocity-constants, referred to the base *e* and in seconds⁻¹, as well as the initial concentrations of sucrose and water, are given in the following table.

TABLE I.

Catalyst : 0.1*N*-H₂SO₄.

Grams of sucrose in 100 c.c. of solution.	Gram- molecules of water (<i>M</i> =18) per litre.	Unimolecular velocity-constant.			
		× 10 ⁶ at 20°.	× 10 ⁵ at 30°.	× 10 ⁵ at 40°.	× 10 ⁴ at 50°.
10	51.95	4.43	1.83	6.73	2.29
20	48.45	4.79	1.97	7.37	2.55
30	44.99	5.21	2.12	8.04	2.81
40	41.62	5.54	2.29	8.80	3.08
50	38.09	5.95	2.45	9.53	—
60	34.59	6.22	2.58	10.22	—
70	30.94	6.29	2.66	10.92	3.94

It will be observed that in all cases displacement of the water by the sucrose causes a definite increase in the velocity-constant, a further illustration of the anti-catalytic effect of water already observed in other reactions, for example, hydrolysis of esters. If the reaction is a true bimolecular one, it is necessary to divide the velocity-constants by the corresponding concentration of water in order to obtain comparable quantities in so far as this stoicheiometric correction is concerned. Whether the observed velocity-constants require to be thus divided or not, it is possible to obtain values for the critical increment, E , by means of the equation $d \log k / dT = E / RT^2$, from the velocity-constants at different temperatures. It was thus found that with an increasing initial concentration of sucrose, the value of E rises steadily over all three ranges of temperature investigated, namely, 20° to 30°, 30° to 40°, and 40° to 50°. That is, the critical increment (or the temperature-coefficient) apparently rises, whilst the velocity-constant itself also increases. As this is in direct contradiction to the conclusion already drawn, namely, that the greater the critical increment the smaller, *ceteris paribus*, the velocity-constant, it was concluded that the catalytic conditions were not comparable at any pair of temperatures, as the content of sucrose was varied. The behaviour, in fact, could be accounted for on the assumptions that (*a*) the catalytic influence of the acid at any given temperature increases with increasing concentration of sucrose, and (*b*) that this increase in catalytic activity is greater the higher the temperature. This conclusion did not appear to be a very probable one on the basis of the degree of electrolytic dissociation of the acid, for in the case of sulphuric acid the catalytic effect ascribed to the undissociated molecule is approximately the same as that of the hydrogen ion, and in general the ratio of the catalytic effect ascribed to the molecule to that of the ion decreases as the temperature increases. Owing to the large viscosity effects produced by a variation in the

concentration of sucrose, electrical conductivity measurements could not give direct information, even assuming that the original equation of Arrhenius was valid, an assumption which has recently been called in question. On this account, it was decided to determine the activity or thermodynamic concentration of the hydrogen ions (strictly speaking, the geometric mean of the activity of hydron and HSO_4') by means of electromotive-force measurements.

Activity of Hydrogen Ion in Aqueous Solutions of Sucrose.

The cell employed was of the following type:

The use of a saturated solution of potassium chloride as a middle liquid, to eliminate contact potential differences, has been frequently recommended (compare Fales and Vosburgh, *J. Amer. Chem. Soc.*, 1918, **40**, 1291). The absolute value of the normal calomel electrode was taken to be +0.56 volt at 18°. Using T. W. Richards' value for the temperature-coefficient of this electrode, namely, 0.0006 volt per degree, the potential difference of the calomel electrode at 20° was taken to be 0.5612 volt, at 40° 0.5732 volt. The value of π_{H} , the potential of the hydrogen electrode in the sulphuric acid-sucrose solutions, was obtained by means of the following equations:

$$\pi_{\text{H}} = 0.277 + 0.058 \log_{10} \text{H}^+ \text{ at } 20^\circ$$

and

$$\pi_{\text{H}} = 0.296 + 0.062 \log_{10} \text{H}^+ \text{ at } 40^\circ,$$

where the electrolytic potential of hydrogen has been assumed to vary directly as the absolute temperature. The absolute value may not be correct on this basis, but as the quantity involved is a constant at any given temperature, the relative values of π_{H} at two different temperatures are comparable.

Table II contains the *E.M.F.* data obtained at 20°, the last column giving the average activity of the hydrogen ion expressed in gram-molecules per litre. Table III contains similar data for 40°. In all cases, dissolved oxygen was removed from the sucrose solutions to prevent any change in the sucrose in contact with the platinised platinum electrode.

TABLE II.

Temperature, 20°. 0.1N-H₂SO₄.

Grams of sucrose in 100 c.c. of solution.	Gram-molecules of sucrose per litre.	Gram-molecules of water ($M = 18$) per litre.	<i>E.M.F.</i> of cell observed, in volts.	P.d. of hydrogen electrode, π_H .	Activity of hydrogen ion in gram-molecules per litre.
0	0	55.55	0.3555	0.2057	0.060
10	0.292	51.95	0.3520	0.2092	0.068
20	0.585	48.45	0.3485	0.2127	0.078
30	0.877	44.99	0.3450	0.2170	0.0895
40	1.169	41.62	0.3410	0.2202	0.105
50	1.460	38.09	0.3380	0.2282	0.118
60	1.755	34.59	0.3345	0.2267	0.139
70	2.047	30.94	0.3313	0.2299	0.162

TABLE III.

Temperature, 40°. 0.1N-H₂SO₄.

Grams of sucrose in 100 c.c. of solution.	<i>E.M.F.</i> of cell, in volts.	P.d. of hydrogen electrode.	Activity of H ⁺ in gram-molecules per litre.
0	0.3580	0.2152	0.050
10	0.3545	0.2187	0.056
20	0.3522	0.2210	0.062
30	0.3460	0.2272	0.078
40	—	—	0.091*
50	0.3370	0.2362	0.109
60	—	—	0.130*
70	0.3280	0.2452	0.152

(Values marked with an asterisk are interpolated from the curve.)

It will be observed that the activity of the hydrogen ion is less at 40° than it is at 20°. This would be expected for the *concentration* of the ion, since the dissociation of the acid is accompanied by an evolution of heat.

The first conclusion to be drawn from the above data is that the activity of the hydrogen ion increases appreciably at both temperatures with an increase in the concentration of the sucrose, and further, as shown later in the figure, the rate of increase in activity is greater at 40° than it is at 20°. The bearing of these results on the velocity-constants will be considered in the next section.

The second conclusion is that the activity of an ion is related to its concentration in a very secondary manner. This has already been shown to be the case by several American investigators. The effect is well marked in the present instance. Thus, when the sucrose content is 70 per cent., the thermodynamic concentration of the hydrogen ion is 0.162 at 20° and 0.152 at 40°, although the

maximum actual concentration of hydrogen ion cannot exceed 0.10.

The third conclusion is that the displacement of the solvent by a non-electrolyte, sucrose, produces effects entirely analogous to those produced by addition of neutral salts, the addition of the sucrose, and consequent elimination of water, causing an increase in the activity of hydrogen ion from two- to three-fold. It is proposed to investigate this aspect of the displacement effect (compare Griffith and Lewis, T., 1916, **109**, 67) in further researches in this laboratory. The activity of ions in presence of a non-electrolyte appears to have been investigated in a single instance only, namely, by Harned (*J. Amer. Chem. Soc.*, 1915, **37**, 2467), who determined the activity of the hydrogen ion from hydrochloric acid, in the presence of mannitol, without observing, however, any marked effect over the concentration range employed.

THE PROBABLE MECHANISM OF THE INVERSION PROCESS.

It was found that the directly observed velocity-constants (table I) at 20°, when divided by the concentration of the water and also by the corresponding activity of the hydrogen ion, gave a quantity which was a constant within the limit of the experimental error. Similarly, the data at 40° gave a constant independent of the sucrose or water content, the numerical value being, of course, greater than that at 20°. These constants represent bimolecular velocity-constants reduced to unit activity of hydrogen ions. The values are given in tables IV and V.

TABLE IV.

Temperature, 20°. 0.1N-H₂SO₄.

Grams of sucrose in 100 c.c. of solution.	Gram- molecules of water (<i>M</i> =18) per litre.	Unimolecular velocity- constant observed. × 10 ⁶ .	Unimolecular velocity- constant divided by water concentration. × 10 ⁸ .	Unimolecular velocity- constant × 10 ⁶ divided by water and also by activity of H ⁺ ions.
0	55.55	4.14*	7.46*	1.24
10	51.95	4.43	8.53	1.25
20	48.45	4.79	9.88	1.27
30	44.99	5.21	11.58	1.29
40	41.62	5.54	13.31	1.27
50	38.09	5.95	15.61	1.32
60	34.59	6.22	17.97	1.29
70	30.94	6.29	20.33	1.25

Mean = 1.27×10^{-6} .

(Values marked with an asterisk are obtained by extrapolation.)

TABLE V.
Temperature, 40°. 0.1N-H₂SO₄.

Grams of sucrose in 100 c.c. of solution.	Gram- molecules of water per litre.	Unimolecular velocity- constant observed. × 10 ⁵ .	Unimolecular velocity- constant divided by water concentration. × 10 ⁶ .	Unimolecular velocity- constant divided by water and also by H' activity. × 10 ⁵ .
0	55.55	5.98*	1.08*	2.16
10	51.95	6.73	1.30	2.31
20	48.45	7.37	1.52	2.46?
30	44.99	8.04	1.79	2.30
40	41.62	8.80	2.11	2.31
50	38.09	9.53	2.50	2.30
60	34.59	10.22	2.96	2.27
70	30.94	10.92	3.53	2.33

Mean = 2.305×10^{-5} .

(Values marked with an asterisk are obtained by extrapolation.)

The two mean values, 1.27×10^{-6} at 20° and 2.305×10^{-5} at 40°, represent the true bimolecular velocity-constant, k_{bi} , of the reaction, where k_{bi} is defined by

$$k_{bi} = k_{uni} / [\text{H}_2\text{O}] [\text{H}'],$$

where k_{uni} is the observed unimolecular velocity-constant, $[\text{H}_2\text{O}]$ the concentration of the water ($M=18$), and $[\text{H}']$ is the activity of the hydrogen ion. The values of k_{bi} as thus defined are independent of the concentration of sucrose or water, and also of the activity of the acid catalyst. The values of k_{bi} depend only on the temperature.

Since the change in the observed velocity-constant with the composition of the solution is entirely accounted for, after the introduction of the necessary stoichiometric correction for water, by the activity of the hydrogen ion, it follows that the undissociated molecule of the acid possesses no catalytic effect in this case. This conclusion has already been drawn by Harned (*loc. cit.*) in other cases in the presence of neutral salts. It is hoped that further investigation with other acids will settle the question as to whether this conclusion is a general one for aqueous solutions. In the case of gaseous systems, catalysis by means of acid is scarcely known. De Hemptinne (*Zeitsch. physikal. Chem.*, 1892, **13**, 561) states that a positive catalytic effect is produced by hydrogen chloride gas in the hydrolysis of gaseous esters. In these circumstances, and probably therefore in non-ionising solvents, the undissociated molecule of the acid is the catalysing individual.

The fact that constant values for k_{bi} , as defined above, are

obtained at a given temperature, removes the difficulty already mentioned in connexion with the apparent variation of the critical increment with composition of the system. When the catalytic conditions are really made the same at two different temperatures, a single value for E , the critical increment per gram-molecule of sucrose inverted, is obtained, this value being independent of the concentration of sucrose or water in the system. The value of E calculated from k_{bi} at 20° and 40° is 26,390 calories. The accuracy of this value depends on the relative accuracy with which the activities of the hydrogen ions at 20° and 40° have been determined. This numerical value represents the sum of the critical increments of the reactants, which will be shown later to be the complex ion (sucrose H^*) and water.

The constancy of k_{bi} may be employed as a criterion in attempting to determine the mechanism of the inversion process by means of stoichiometric equations, for these equations must be such as to lead finally to an expression of the form

$$k_{bi} = k_{uni} / [H_2O] [H^*].$$

Apart from this consideration, many alternative modes of expressing the inversion process suggest themselves. We shall consider five of the most probable of these, and show that only one of them is in agreement with the criterion. The latitude of choice arises from the doubt as to whether (a) the hydrogen ion which reacts is hydrated or not, (b) whether the sucrose which reacts is hydrated or not. The problem of hydration is one of the least satisfactory aspects of the theory of solutions, the evidence in most cases being conflicting.

Possibility 1.—Assume that practically all the sucrose is hydrated and that the same is true for the hydrogen ions, but that it is the non-hydrated sucrose which reacts with a hydrated hydrogen ion (H_2O, H^*). Applying the law of mass action to the hydration of the sucrose, $R + H_2O = (R, H_2O)$, we have $K = [R, H_2O] / [R] [H_2O]$, where K is the equilibrium constant of hydration and R stands for non-hydrated sucrose. The inversion process assumed to be correct is $R + (H_2O, H^*) \rightarrow$ dextrose + levulose. Hence, rate of inversion = $k_{bi} [R] [H_2O, H^*]$. But rate of inversion = k_{uni} observed $[(R, H_2O)]$, since practically all the sucrose has been assumed to be hydrated. Hence,

$$k_{bi} = k_{uni} [(R, H_2O)] / [R] [H_2O, H^*] = k_{uni} \cdot K \cdot [H_2O] / [H_2O, H^*].$$

This mechanism requires, therefore, that the product of the observed velocity-constant by the water concentration divided by the activity of the hydrogen ions should be a constant independent of the initial concentration of sucrose. This differs from the true

criterion, and, in fact, the right-hand side of the equation is not a constant. Hence, possibility 1 is incorrect.

Possibility 2.—Assume that practically all the sucrose is hydrated, but that the hydrogen ion is practically all unhydrated, and that the inversion process is $(R, H_2O) + H^+ \rightarrow$ dextrose + laevulose. This leads finally to the conclusion that

$$k_{bi} = k_{uni} / [H^+].$$

The right-hand side of this expression is not constant. Hence, possibility 2 is incorrect.

Possibility 3.—Assume that practically all the sucrose is hydrated and that the hydrogen ion is also practically all hydrated, but that it is the non-hydrated hydrogen ion which reacts with hydrated sucrose, as in possibility 2. We have now to allow for K_i , the equilibrium constant of hydration of the ions,

$$K_i = [H_2O, H^+] / [H^+][H_2O].$$

This assumption leads finally to $k_{bi} = k_{uni} \cdot [H_2O] \cdot K_i / [H_2O, H^+]$, which is indistinguishable from possibility 1, and is therefore incorrect.

Possibility 4.—Assume that the sucrose and the hydrogen ions are practically all hydrated, and that it is the hydrated form of each which reacts according to the equation

Then, $k_{bi} = k_{uni} / [H_2O, H^+]$, which, being equivalent to possibility 2, is incorrect.

Possibility 5.—Assume that the sucrose as well as the hydrogen ions is practically all non-hydrated, and that the first stage is addition to form a complex ion, thus: $R + H^+ = RH^+$, which is followed by the true inversion reaction,

We then have, rate of inversion $= k_{uni} [R]$, also, rate of inversion $= k_{bi} \cdot [RH^+][H_2O]$, whence $k_{bi} = k_{uni} [R] / [RH^+][H_2O]$. Now, K_c , the equilibrium constant of the complex-ion formation, is given by $K_c = [RH^+] / [R][H^+]$, whence $k_{bi} = k_{uni} / K_c \cdot [H_2O][H^+]$. This is in agreement with the criterion, the right-hand side being a constant, since it only differs from the criterion in containing the constant, K_c . It may be shown, further, that if the above mechanism is assumed, with the modification that the sucrose is nearly all hydrated, an expression is obtained which is not in agreement with the experimental result. Also, if possibility 5 is employed, with the modification that the ions are practically all hydrated, an equally incorrect expression is obtained. Finally, if possibility 5 is employed, with the modification that both sucrose and the ions are practically all hydrated, an incorrect expression is obtained.

It is reasonable to conclude, therefore, that possibility 5 as it stands is the only satisfactory mechanism.

The two stoichiometric equations which express the inversion process are therefore:

and

It is obvious that this mechanism accounts for the fact that the hydrogen ion is necessary in order that inversion may proceed with measurable speed. There is also some evidence of a preliminary nature for the existence of an addition complex of sucrose and hydrogen ion, which it is hoped may be communicated in detail later.

The mechanism of the inversion process to which we have been led involves equations (1) and (2), and also the assumption that the hydrogen ions and the sucrose molecules are not appreciably hydrated in aqueous solution. This represents the simplest set of conditions, but the result is somewhat surprising. Sucrose is usually regarded as being heavily hydrated in solution. As already pointed out, however, such an assumption would not lead to the observed constancy of the quantity expressed in the final columns of tables IV and V.

Hydrogen-ion Activity as a Function of the Composition of the Solution.

Rosanoff (*J. Amer. Chem. Soc.*, 1913, **35**, 173) has suggested that the catalytic effect of a solvent may be expressed as an exponential function of the concentration of the solvent. A similar relation has been employed by Wilson (*ibid.*, 1920, **42**, 715) to account for the effect of neutral salts on the hydrogen ion, as determined by electrometric measurements. Wilson appears to regard the increase in concentration of the hydrogen ion in the presence of neutral salts as real. The effect, however, involves the activity, and not necessarily the concentration, of the ion. The analogy of the effect produced by the displacement of water by addition of sucrose to that produced by a neutral salt has already been mentioned.

In the conditions obtaining in the present investigation we deal with the simultaneous influence of sucrose and water, since by addition of one constituent a certain amount of the other is eliminated. Let us suppose that the activity of the hydrogen ion can be expressed by

$$[H^+] = A \cdot e^{(bR + b'W)} \quad . \quad . \quad . \quad (3)$$

where R and W are the concentrations of sucrose and water respectively in gram-molecules per litre, b and b' are the catalytic environmental constants characteristic of sucrose and water, b is a positive, whilst b' is a negative, quantity.

When there is no sucrose present, W becomes W_0 (namely, 55.55 gram-molecules per litre) and H^* becomes H^*_0 . We can thus re-write equation (3) in the form:

$$H^* = H^*_0 e^{\{bR - b'(W_0 - W)\}} \quad (3a)$$

Hence,

$$\log_e H^* = \log_e H^*_0 + bR - b'(W_0 - W) \quad (4)$$

In the present case it happens that a straight line is obtained when the concentration of sucrose is plotted against the concentration of the water. Hence we can write $W = W_0 + pR$, where p is a negative constant having the value -12.1 , the sucrose and water being expressed in gram-molecules per litre. Equation (4) can therefore be written in the present case in the form

$$\log_e H^* = \log_e H^*_0 + (b + b'p)R \quad (5)$$

or, alternatively,

$$\log_e H^* = \log_e H^*_0 + (b/p + b')(W - W_0) \quad (6)$$

Equations (5) and (6) are both linear, that is, they represent the observed behaviour of the activity of the hydrogen ion as a function of the composition of the mixture, as is shown in the figure (graphs *C* and *D*).

Hence equation (3) is justified in so far, at least, as it satisfies the above condition in the present case. From the experimental data the following mean values are obtained:

$$\begin{aligned} b - 12.1b' &= 0.47 \text{ at } 20^\circ, \\ b - 12.1b' &= 0.56 \text{ ,, } 40^\circ. \end{aligned}$$

It will be observed that equations (5) and (6), being equivalent, do not permit of a calculation of b and b' separately. Further experimental data involving a different functional relationship between the concentration of the sucrose and the water are required.

In equations (3) to (6) we have employed the most general type of formula, in which a possible catalytic effect has even been ascribed to the reactant solute, sucrose. In this connexion, there is an important consideration which has to be taken into account.

The observed unimolecular velocity-constants obtained at various temperatures are found to remain constant, within the limit of experimental error, throughout the entire course of the reaction. This is the case even when the initial concentration of sucrose is as high as 70 per cent., as is shown by the following results of duplicate experiments, which give the observed velocity-constants

obtained with 70 per cent. sucrose at 40° in the presence of *N*/10-sulphuric acid. The velocity-constant is calculated to the base *e*.

TABLE VI.

Experiment 1.		Experiment 2.	
Time in seconds.	Unimolecular velocity constant $\times 10^5$.	Time in seconds.	Unimolecular velocity constant $\times 10^5$.
0	—	0	—
780	10.82	1200	10.81
1500	11.03	1950	10.81
2100	10.98	2460	10.83
3060	11.00	3060	10.77
3900	11.03	3960	10.89
5160	11.07	4440	10.86
6420	11.11	6360	10.96
7500	10.98	6900	10.97
(55 per cent. of the sucrose decomposed.)		(53 per cent. of the sucrose decomposed.)	

The fact that the velocity-constant does not alter indicates that the activity of the hydrogen ion is likewise sensibly constant. As, however, the concentration of the sucrose has diminished by more than one half, it follows that the environmental influence of the sucrose, if any, as measured by the quantity b , must be the same as that of the dextrose and lævulose formed as a result of the inversion. If these substances are inert, it would follow that $b=0$, and that therefore the environmental catalytic term b' , characteristic of water, is -0.039 at 20° and -0.046 at 40° . The negative value indicates, of course, that the water is a negative catalyst for the process. The question of the absolute value of b will be dealt with in a later communication.

Returning to the graphs shown in the figure, it will be observed that with diminution in the concentration of water the curves for the hydrogen-ion activity at 20° and 40° are not parallel, but convergent. The same relation is exhibited by the curves for the velocity-constant shown in the same diagram, graphs *A* and *B*.

When the two sets of curves are combined, constant values for k_{bi} , as defined in the preceding section, are obtained. The relative positions of the two sets of curves afford the most direct evidence yet obtained for the conclusion that the activity of the ion completely determines the velocity of the reaction.

Summary.

(1) The velocity of inversion of sucrose in the presence of $N/10$ -sulphuric acid has been determined at 20° , 30° , 40° , and 50° , the composition of the solution being altered by gradual displacement of the water by the sucrose. The velocity-constants vary with the initial composition of the mixture.

(2) The average activities of the hydrogen ion have been determined electrometrically in the various mixtures referred to in (1) at 20° and 40° . It is shown that the alteration in the velocity-constant can be accounted for completely by (a) allowing for the stoichiometric correction for the water present, and (b) by allowing for the change in the activity of the hydrogen ions.

(3) In agreement with (2), the inversion process is shown to be bimolecular. It consists of two processes, (i) union of the non-hydrated hydrogen ion with a non-hydrated molecule of sucrose, thus, $R + H^+ = RH^+$, this process being practically instantaneous, and (ii) the actual inversion reaction, $RH^+ + H_2O = \text{dextrose} + \text{lævulose}$. It is also concluded that the hydrogen ions and the sucrose molecules are not sensibly hydrated in aqueous solution.

(4) In agreement with Rosanoff's suggestion regarding the mode

of expressing the influence of solvent catalysts, the activity of the hydrogen ion is found to be an exponential function of the concentration of sucrose and water present.

(5) It is shown that the environmental catalytic influence of a molecule of sucrose, referred to in (4), is identical in magnitude with that exerted by one molecule of dextrose together with one molecule of lævulose.

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