THE VELOCITY OF INVERSION OF SUCROSE AS A FUNCTION OF THE THERMODYNAMIC CONCENTRATION OF HYDROGEN ION

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In general the velocity of inversion of sucrose is a function of several variables, namely the temperature and the concentrations of hydrogen ion, undissociated acid, sucrose, added salts and non-electrolytes. Although the study of this reaction has been very extensive,[1] it must be pointed out that on account of the many variables to be considered, and the wide intervals over which each variable may be varied, the experimental data in the literature are really of such a fragmentary nature as to make it impossible to study the reaction in a critical and thorough manner.

It is the particular purpose of this investigation to study the inversion velocity as a function of the thermodynamic concentration of hydrogen ion[2] in connection with the broader purpose of testing the various theories

[1] For an admirable résumé and bibliography of the subject up until 1906, the reader is referred to R. J. Caldwell, *Brit. Assoc. Advancement Sci. Rept.*, 1906, 267–92.

[2] Following Jones and W. C. McC. Lewis, *J. Chem. Soc.*, 117, 1123 (1920), it is proposed to use this term to indicate the hydrogen-ion concentration as calculated from e.m.f. measurements. The present work in this connection is limited to experimental study only, and the term is used only in an experimental sense. Theoretical considerations along somewhat similar lines are treated by G. N. Lewis and Randall, THIS JOURNAL, 43, 1112 (1921).

that have been advanced, and to adduce evidence which will allow a study of the problem from the viewpoint of thermodynamic as well as kinetic theory.

It may not be out of place here to mention a few prominent theories regarding the relation of the hydrogen-ion concentration to the velocity of inversion of sucrose.

Ostwald[3] was the first to use the inversion of cane sugar as a means of measuring the concentration of hydrogen ion, basing his theory upon the assumption that the velocity of inversion would be directly proportional to the concentration of the latter. He found, however, that the velocity coefficients did not have the same ratio among themselves as would be expected from a calculation of their hydrogen-ion concentrations by means of conductivity ratios. Ostwald reaches the conclusion[4a] that there was only an approximate proportionality between velocity of inversion and hydrogen-ion concentration, and this proportionality was affected largely by the concentration of sucrose used.

Arrhenius[4b] states that the velocity is not strictly proportional to the concentration of hydrogen ion because the velocity can be increased by the addition of neutral salts, whereas the concentration of hydrogen ion is decreased. His premise for this decrease of hydrogen ion is embodied in his statement that since the addition of neutral salt to an acid solution lowers the degree of dissociation, the concentration of hydrogen ion must be decreased. He reaches the conclusion that as the salt itself has no inverting action upon the cane sugar, but only decreases the concentration of hydrogen ion, the accelerating influence of the salt upon the velocity of the reaction is explained by the assumption that the addition of neutral substances increases the concentration of the active cane sugar.

Palmaer,[5] reasoning from his own results as well as those of Trevor[6] states that it can be considered as soundly established that the velocity of inversion, for the region of great dilutions where the neutral salt effect has ceased, is exactly proportional to the hydrogen-ion concentration; and that earlier calculations made upon this assumption are correct. He considered that good proportionality was found to exist between the rate of inversion and the concentration of hydrogen ion for concentrations less than 0.01 M hydrochloric acid. W. A. Smith[7] arrived at practically the same conclusions as Palmaer with respect to highly dissociated acids such as hydrochloric.

Lamble and Lewis[8] in agreement with Rosanoff[9] suggest that when the catalytic effect can be examined over a sufficiently wide range, it will be found to follow an exponential law.

Without considering the various theories regarding the effect of the undissociated acid,[10] it is easily seen from the foregoing short résumé

[3] Ostwald, *J. prakt. Chem.*, **29**, 385 (1884).

[4a] Ostwald, *ibid.*, **31**, 307 (1885).

[4b] Arrhenius, *Z. physik. Chem.*, **4**, 226 (1889).

[5] Palmaer, *ibid.*, **22**, 492–501 (1897).

[6] Trevor, *ibid.*, **10**, 330 (1892).

[7] W. A. Smith, *ibid.*, **25**, 144–77 (1898).

[8] Lamble and Lewis, *J. Chem. Soc.*, **107**, 234 (1915).

[9] Rosanoff, THIS JOURNAL, **35**, 173 (1913).

[10] Some examples of the literature on this subject are: Snethlage, *Z. physik. Chem.*, **85**, 211–62 (1913); also *Z. Elektrochem.*, **20**, 202 (1914); Acree, *Am. Chem. J.*, **49**, 345–68 (1913); McBain and Coleman. *J. Chem. Soc.*, **105**, 1517 (1914).

of the conclusions of several investigators in this field that the widest divergence of opinion exists, and we must ask ourselves to what extent this divergence springs from premises which rest upon insufficient experimental evidence.

It is surprising that with one exception none of the investigators mentioned attempted a direct measurement of the concentration of hydrogen ion in the system undergoing reaction; on the contrary, the concentration of hydrogen ion was always assumed to be the same as it would be if the sucrose were absent, and its volume replaced by water.

To Jones and Lewis[11] belongs the credit of making the first direct measurement of the hydrogen-ion concentration in the reaction mixture. These investigators point out the rather remarkable fact that for a given concentration of acid the activity of the hydrogen ion, or its thermodynamic concentration, increases appreciably with increase in concentration of sucrose.

In the work mentioned above[12] the conclusion was arrived at that the velocity of inversion was proportional to the thermodynamic concentration of hydrogen ion multiplied by the water concentration.[13]

Experimental

The experimental method resolves itself into the measurement of reaction velocities on the one hand, and the thermodynamic concentration of hydrogen ion on the other. In order to define completely the various systems under consideration the masses of all components were determined or calculated from density measurements.

Apparatus.—Two water-baths were used throughout this work, one adjusted[14] at a temperature of $35°$, and controlled to within $\pm0.01°$, the other adjusted at a temperature of $25°$ and controlled within the same limits. All hydrolyses were run at $35°$, a wire rack which allowed free circulation of water being used as a support for reaction bottles with experiments extending over long periods. All e.m.f. measurements were also made at the temperature of $35°$.

For the measurement of the angular rotation a Schmidt and Haensch

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[11] Ref. 2. Attention must also be called here to the work of Harned [THIS JOURNAL, **37**, 2467 (1915)] who measured the hydrogen-ion concentration in HCl in the presence of mannitol, but who noticed no marked effect in the concentrations measured. Also note must be made of the work of Fales and Nelson, *ibid.*, **37**, 2769 (1915).

[12] Only one concentration of acid, namely 0.1 M H_2SO_4, was used in this work.

[13] $k_{bi} = \dfrac{k_{uni}}{(H_2O)\,(H^+)}$

[14] Temperature adjustment in this bath was made by means of a thermometer which had been compared with a standard Baudin thermometer and standardized at $35° \pm 0.01$ by Dr. Frederick Barry [See THIS JOURNAL, **42**, 1911 (1920)]. Temperature control in both baths was followed by the use of Beckmann thermometers.

triple-field polarimeter, sensitive to $0.01°$, was used. The light source[15] was purified sodium light from a lamp especially devised for this purpose.

Jacketed polariscope tubes, 200 mm. long, were used, the temperature being maintained at $25° \pm 0.05°$ by pumping water from the thermostat through the tube, the rate of flow being about 3.8 liters per minute. All polariscope readings were made at this temperature.

For most of the e.m.f. measurements the null method was employed, and the e.m.f. determined by means of a Leeds and Northrup potentiometer and a D'Arsonval galvanometer. The latter had a sensibility of 280 megohms, a period of 2.5 seconds, and a total resistance of 444 ohms. A Weston cell was used as a primary standard of reference. This cell had been calibrated by the U. S. Bureau of Standards and checked against other standard cells in the Department, and was found to have a value of 1.0183 volts at $20°$.

The saturated calomel electrode, described by Fales and Vosburgh,[16] and the bubbling hydrogen electrode were used throughout this work. Hydrogen electrodes and the hydrogen purification train were of the same type as described by Fales and Mudge.[17]

For concentrations of hydrogen ion less than 10^{-8}, where it was impracticable or impossible to measure the e.m.f. by the foregoing method, a ballistic galvanometer was used in conjunction with a condenser after the method of Beans and Oakes.[18] The method and apparatus as applied here were also the same as that used and described by Fales and Robertson.[19]

Measurements of Volume, Weight and Time.—For making up the various solutions preparatory to their admixture in the reaction bottle measuring flasks and burets which had been carefully calibrated at $25°$ were used; for removal and delivery of the alkali mixture or sodium carbonate employed to stop the reaction, pipets calibrated at $35°$ were used. These pipets were adjusted to deliver their respective contents as nearly as possible during the same interval of time which was about 18 seconds. All short time intervals were measured with a stop watch. Weighings for density determinations were made in pycnometers of about 20 cc. capacity. All weighings were made in air with brass weights.

Materials and Solutions. Sucrose.—The starting material was a high grade commercial sugar (Domino Cane Sugar). This was most carefully treated in the manner set forth by the U. S. Bureau of Standards[20] the method being followed in detail.

[15] Fales and Morrell, This Journal, **43**, 1629 (1921).

[16] Fales and Vosburgh, *ibid.*, **40**, 1305 (1918).

[17] Fales and Mudge, *ibid.*, **42**, 2346 (1920).

[18] Beans and Oakes, *ibid.*, **42**, 2116 (1920).

[19] Fales and Robertson (unpublished).

[20] *Bur. Standards Bull.*, **44** ("Polarimetry"), 93–99 (1918); and **268** ("The Specific Rotation of Sucrose" by Bates and Jackson), 75–79 (1916).

The specific rotation of the product obtained was found to agree with the theoretically calculated values.[21]

The solutions of sucrose were made up as required by weighing fresh samples of sugar from the stock bottle.

All of the solutions mentioned under the present caption of "Materials and Solutions" were made up at 25°, using the standard flasks and burets calibrated at that temperature.

ACIDS AND ALKALIES.—The acids used were hydrochloric and acetic. The hydrochloric acid was purified by diluting a 12 M c. p. sample with an equal volume of water, distilling and collecting the middle portion. The acetic acid was c. p. analyzed material, used as obtained. The sodium hydroxide used was prepared according to the method of Sörensen.[22]

The weaker solutions were made by dilution, using conductivity water which had a conductivity, after standing for some time in stoppered Non-sol bottles, of 1.8×10^{-6} mhos. This water was used in making up all reaction mixtures in which the total hydrogen-ion concentration was less than 10^{-2}. Reaction bottles as well as stock bottles were in all cases of Non-sol glass.

The hydrochloric acid was standardized by titration against pure sodium carbonate using methyl orange as indicator. A 0.1 M solution of sodium hydroxide was standardized against the hydrochloric acid, and used for the standardization of the acetic acid, using phenolphthalein as indicator. It was also used for the two reaction mixtures where sodium hydroxide was employed as the catalyst.

The MERCURY used in the calomel cells was purified by washing several times in nitric acid, after the method of Hildebrand,[23] filtering through a clean, dry cloth, and then distilling under reduced pressures according to the method of Hulett.[24] The potassium chloride used in the cells was a c. p. analyzed sample twice recrystallized, and fused in platinum. For the salt bridge, the potassium chloride was recrystallized, but not fused.

The CALOMEL for the cells was a c. p. analyzed sample of such quality as had been found by Fales and Mudge[17] to give satisfactory results.

Starting the Reaction.—In starting the reaction it was thought best to make use of such procedure as would enable one to determine directly the starting time for fast reactions with a greater degree of precision than has heretofore been obtained.[25] In effecting this two pipets of about

[21] Theoretical values for the specific rotation were calculated by Landolt's formula for concentrations ("Das Optische Drehungsvermögen," F. Vieweg and Son, Braünschweig, 1898, p. 420; also Browne's "Handbook of Sugar Analysis," J. Wiley and Sons, 1912, p. 177) and Andrew's formula for temperature (*Mass. Inst. Tech. Quarterly*, May, 1889, p. 367; see also Browne, *op. cit.*, p. 178). It might also be mentioned that the use of Shönrock's formula for temperature [Z. Ver. Deut. Zucker-Ind., 53, 650 (1903)] gave values identical with those obtained by Andrew's formula.

[22] Sörensen, *Biochem. Z.*, 21, 168 (1909).

[23] Hildebrand, THIS JOURNAL, 31, 933 (1909).

[24] Hulett, *Z. physik. Chem.*, 33, 611 (1900).

[25] Ostwald, Ref. 3, and others after him, counted time from the arbitrary instant of the first reading, the course of the reaction being followed in the polariscope tube. More recent investigators have taken the time at which the acid and sugar solution were mixed as the starting time. In no case has any particular precaution been taken to obtain instantaneous mixing, the method usually followed being to pour one solution into the other and shake or otherwise agitate. These methods not only introduce the possibility of error in observing the correct starting time, but also result in a loss of time, thus preventing a proper study of the reaction in its early stages.

250cc. capacity were calibrated to deliver exactly equal quantities of sugar solution and acid in the same interval of time, very nearly 33 seconds. The latter was accomplished by adjusting the bores of the tips of the pipets. The pipets were fitted with stopcocks on the upper stem, and so supported that the two liquids joined into one stream as they ran into the reaction bottle, thus avoiding the necessity of subsequent shaking or stirring. In filling the pipets, the liquids were sucked up, by means of a filter pump, from bottles which had been allowed to stand in the bath for some time, so that delivery was made at the temperature of the reaction, namely $35°$. The mean time between the moment the pipets started to deliver and the moment they finished delivering was taken as the starting time.

For the slow reactions when the concentration of hydrochloric acid was less than $0.01 M$, enough toluene to saturate the solutions was introduced into the bottles as an antiseptic agent to prevent bacterial action.

Stopping the Reaction.—For fast reactions, where the concentration of hydrochloric acid was $0.1 M$ or greater, the reaction was stopped by running 25cc. samples, withdrawn from the reaction bottle[26] in the thermostat, simultaneously with 5 cc. of alkali mixture[27] into a bulb-neck flask, calibrated to contain 30.33 cc. at $25°$.[28]

After repeated shaking the neutralized reaction mixture was cooled to $25°$, made up to the mark (30.33 cc.) and then used for polariscopic readings. In every instance the solutions were tested with litmus paper after the readings were made, and found to be neutral. For acid concentrations less than $0.1 M$, dilute solutions of sodium carbonate alone were used as the neutralizing liquid; for the alkaline reaction mixtures dil. hydrochloric acid was used.

[26] Delivery of the reaction mixture was made by pipets delivering a volume of 25 cc. at $35°$, and of the alkali mixture by pipets delivering a volume of 5 cc. at $35°$. The pipets were calibrated to deliver in the same interval of time.

[27] The alkali mixture was made up of sodium hydroxide and sodium carbonate so that 5 cc. of the solution would neutralize the acid in 25 cc. of the reaction mixture, and leave a minute amount of $NaHCO_3$ in excess. The amount of sodium hydroxide itself was such as to eliminate any possibility of an excess, which was to be avoided on account of its action upon the invert sugar. As a specific example of such a solution might be mentioned one made up to be used in connection with the reaction mixture containing $1.2 M$ acid. This particular solution contained 220 g. of sodium hydroxide, and 27.44 g. of sodium carbonate per liter of solution; calculation would show that the final solution resulting from the addition of 5 cc. of the alkali mixture to 25 cc. of the reaction mixture, at $35°$ was about $0.003 M$ with respect to sodium bicarbonate, and $0.985 M$ with respect to sodium chloride. Solutions of alkali mixtures were made up for all reaction mixtures with an acid concentration greater than $0.1 M$. They were all standardized at $25°$, but used at the temperature of $35°$.

[28] It was found that the maximum volume which resulted from the mixing of 25 cc. of the reaction mixture, and 5 cc. of the alkali mixture, at $35°$ was 30.33 cc., referred to the temperature of $25°$. Hence for convenience in manipulation and calculation a uniform total volume of 30.33 cc. was employed.

Determination of the Initial Angles of Rotation.—In determining the initial angle for fast reactions, the same original solutions were used as in the making up of the reaction mixture, but the order of addition was changed; 25 cc. of the acid was neutralized by 10 cc. of the alkali mixture; the resulting solution allowed to cool, 25 cc. of the sugar solution run in, and the whole volume made up to 60.66 cc.; portions of this were then used for the polariscopic readings. For slow reactions, that is, for mixtures containing a concentration of hydrogen ion less than 10^{-3}, the first reading, made within 90 seconds after the reaction started, was taken as the initial reading.

Determination of the Final Angle of Rotation.—The final rotations, for solutions with hydrogen-ion concentration greater than $0.001\ M$, were determined by allowing the reaction to go to completion, the rule being followed that this state was at least reached in an interval of time four to five times the interval necessary for the reaction to go to 95% of completion. In practically every case, check readings were made upon the solutions several days after removal from the bath without any appreciable change being noticed. Decomposition, however, slowly set in with the stronger acid solutions, but it may be remarked that no change was noticed with the solutions containing less than $0.6\ M$ hydrochloric acid after a period of 10 days. In the case of the solution containing the $0\ 01\ M$ hydrochloric acid the final rotation remained constant after 4 months in the bath at $35°$.

With the more dilute acid solutions final readings were made in some cases, but more dependence was laid upon the final readings obtained by the use of invertase.[29] In determining the final rotation, 0.03 cc. of invertase was introduced into the 30cc. bulb-neck flask, after which 25 cc. of the reaction mixture was added. Several samples of the same mixture were made up in this fashion and allowed to stand in the bath at $35°$ from 2 to 5 days until check readings were obtained. No correction was found necessary for the optical rotation of this particular invertase in the concentration used.

It is to be remarked here that the final rotations as determined by the above method, and for the reaction mixture containing $0.01\ M$ hydrochloric acid, which was allowed to run fully to completion, agree with each other, but do not agree with the final rotations as calculated by the formula of Ostwald[30] for $25°$, namely $a_f = a_i\ (0.44 - (0.005)t)$, where a_f and a_i, are, respectively, the final and initial rotations in angular degrees and t is the temperature in degrees C., the formula giving a greater negative rotation than that observed by experiment.

[29] This was No. 8 invertase used in the researches of Professor J. M. Nelson, and furnished through his kindness.

[30] Ostwald-Luther, "Physiko-chemische Messungen," W. Engelmann 1910, p. 529.

Polariscopic Readings.—Aside from all the usual precautions taken in making polarimetric determinations, particular care was taken to avoid strain in the glasses. This was checked by turning the tube back and forth through an angle of 180°. From 6 to 8 settings were made in each determination, and the average of these was taken as the reading; the deviation of any single observation from the average was in no case more than 0.01°. All of the readings were made during the period between the second and third hours after the reaction had been stopped, it having been previously ascertained that equilibrium was fully established during this time.

Velocity coefficients were calculated by the monomolecular formula $k = (1/t) \log (1/1 - x)$, where t is the time in seconds, x is the ratio of the angular change, which has taken place up to time t, to the total angular change, and logarithms are to the base 10. Velocity coefficients based on the "short interval" formula $k = \dfrac{1}{t_2 - t_1} \log \dfrac{1 - x_1}{1 - x_2}$ are also shown. The ratio x is really the fraction of sucrose which has been replaced by an equivalent amount of invert sugar, notwithstanding the presence of sodium chloride in the solutions upon which polarimetric determinations were made, because as shown by Vosburgh[31] the observed fraction, x, of sucrose replaced by invert sugar bears the same relation to the actual within the limits of error whether determined in solutions containing nothing but the sugars in question, or in solutions containing in addition 1 M sodium chloride or 0.02 M sodium carbonate solution, provided that the salt concentration is kept constant throughout the series of solutions.

E.m.f. Measurements.—(a) *Potentiometer Method.* The usual precautions as described by Fales and Mudge[17] were taken, sufficient time being allowed for equilibrium to be established in all cases, especial attention being paid to this factor where sucrose was present in the solutions. Precautions were taken to prevent siphoning and diffusion by carefully adjusting all levels, keeping the stopcocks closed until readings were made, care being taken at the beginning to adjust properly the cotton-wool plugs in the stem of the cell.

(b) *Ballistic Method.*—The same care and precautions as practised by Fales and Robertson[19] were exercised in these measurements. In a great many cases check measurements were made by both the potentiometer and ballistic methods.

Calculation of the Thermodynamic Concentration of Hydrogen Ion.—Fales and Vosburgh[32] recommended the use of the saturated potassium chloride calomel cell, and a saturated potassium chloride bridge or middle

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[31] Vosburgh, THIS JOURNAL, **43**, 230 (1921).

[32] Ref. 16, p. 1291.

liquid to eliminate contact potential differences, when dealing with hydrochloric acid solutions. Jones and Lewis[2] followed this recommendation in their work, making the assumption that the presence of sucrose in the acid does not affect the potential at the liquid junction, acid and salt bridge. A like course has been followed in the present work.

All thermodynamic concentrations of hydrogen ion were calculated by the use of Nernst's formula,[33] the particular form. used being $\log C_H = A - \text{Obs. e.m.f.}/RT$. In evaluating A the hydrogen-ion concentration and e.m.f. of $0.1\ M$ hydrochloric acid was used. In order to obtain the hydrogen-ion concentration of $0.1\ M$ hydrochloric acid at $35°$, the values of the equivalent conductivities of $0.1\ M$ hydrochloric acid and water were calculated by the methods of least squares from the data of Noyes.[34] The equation used in the calculations was $\Lambda_x = a + b\theta + c\theta^2$, where a is the value of Λ_x at $18°$, and $\theta = t - 18$. The value for the coefficients for Λ_0 are, respectively, $a = 379$; $b = 6.651$; $c = -0.0111$; and for $\Lambda_{0.1}$ are, respectively, $a = 350.6$; $b = 6.125$; $c = -0.01421$. Correction was made for the change in concentration from $25°$ to $35°$ by making use of the function[35] $C(\Lambda_0 - \Lambda) = K(C\Lambda)^n$, the value of the exponent n being also found by the method of least squares. The values of the coefficients are, respectively, $a = 1.45$; $b = -0.001517$; $c = 0.000008155$. Λ_0 and $\Lambda_{0.10}$ represent the values of the equivalent conductivities of water and $0.1\ M$ hydrochloric acids, respectively.

The final values obtained for the equivalent conductivities of $0.1\ M$ hydrochloric acid and for water at $35°$ were, respectively, 450.7 and 488.9, the value of the hydrogen-ion concentration in the former, therefore, being 0.09218 mols per liter.

The e.m.f. values recorded in the following table represent the average of several measurements made during the course of the reaction. In no case did the deviation from the average differ enough from the experimental error to warrant recording. In the case of the $0.01\ M$ sodium hydroxide, however, it may be mentioned that the e.m.f. values decreased appreciably during the course of the reaction but no generalization can be drawn from this fact especially since here some complicating factor may be introduced which will be noted later. With regard to the other reaction mixtures it may be definitely stated that the thermodynamic concentration of hydrogen ion remains constant during the course of the reaction, and that the environmental influence of one molecule of fructose and one molecule of dextrose, as regards this factor, is equivalent to one molecule of sucrose.

[33] Nernst, Z. physik. Chem., 4, 129 (1889).

[34] A. A. Noyes, "The Electrical Conductivity of Aqueous Solutions," Carnegie Inst. Washington, 1907, p. 137.

[36] Ref. 34, p. 140.

TABLE I
E.M.F. MEASUREMENTS
Temp. 35°

Mols per liter of HCl	(HCl + H$_2$O) Obs. e.m.f.	c_{H^+}	HCl + 0.1495 Sucrose Obs. e.m.f.	c_{H^+}	HCl + 0.2988 Sucrose Obs. e.m.f.	c_{H^+}
1.197	0.2370	1.162	0.2323	1.388	0.2284	1.607
0.8973	0.2462	0.8221	0.2411	1.0000	0.2379	1.124
0.5981	0.2570	0.5471	0.2535	0.6245	0.2509	0.6887
0.2990	0.2750	0.2777	0.2725	0.3052	0.2702	0.3334
0.09964	0.3043	0.09218	0.3020	0.1005	0.2996	0.1102
0.00997	0.3625	0.01028	0.3605	0.01109	0.3577	0.01233
0.000997	0.4220	0.001092	0.4211	0.001134	0.4210	0.001134

Mols per liter CH$_3$COOH	CH$_3$COOH + H$_2$O Obs. e.m.f.	c_{H^+}	CH$_3$COOH + 0.1495 Sucrose Obs. e.m.f.	c_{H^+}	CH$_3$COOH + 0.2988 Sucrose Obs. e.m.f.	c_{H^+}
0.03988	0.4240	0.001012	0.4225	0.001071	0.4228	0.001059
0.007976	0.4502	0.0003803	0.4502	0.0$_3$3803	0.4502	0.0$_3$3803
0.000997	0.4772	0.0001364	0.4675	0.0$_3$1965	0.4727	0.0$_3$1616
0.0000997	0.5148	0.00003307	0.5016	0.0$_4$5438	0.5046	0.0$_4$4858

Mols per liter NaOH	NaOH + H$_2$O Obs. e.m.f.	c_{H^+}	NaOH + 0.1495 Sucrose Obs. e.m.f.	c_{H^+}	NaOH + 0.2988 Sucrose Obs. e.m.f.	c_{H^+}
0.000997	0.7787	0.0$_8$1598	0.7374	0.0$_8$753	0.7205	0.0$_7$1423
0.00997	0.9291	0.0$_{11}$549	0.9034	0.0$_{10}$145	0.8834	0.0$_{10}$30

H$_2$O (Cond.) Obs. e.m.f.	c_{H^+}	H$_2$O (Cond.) + .15 M Sucrose Obs. e.m.f.	c_{H^+}	H$_2$O (Cond.) + 0.3M Sucrose Obs. e.m.f.	c_{H^+}
0.6423	0.0$_6$271	0.6469	0.0$_6$228	0.6563	0.0$_6$16

H$_2$O (ord. dist.) Obs. e.m.f.	c_{H^+}	H$_2$O (ord. dist.) + 0.15 M Sucrose Obs. e.m.f.	c_{H^+}	H$_2$O (ord. Dist.) + 0.3 M Sucrose Obs. e.m.f.	c_{H^+}
0.5682	0.0$_5$443	0.5655	0.05490	0.6352	0.0$_6$354

Discussion of Preceding Table and the Curves

As pointed out by Jones and Lewis[2] the displacement of the solvent by sucrose produces effects with regard to the change in thermodynamic concentration of hydrogen ion entirely analogous to those produced by the addition of neutral salts. As previously mentioned, however, this effect has been studied by them for only a single concentration of acid.

When examined over a wide range of concentrations it will be observed from Table I that in the case of the hydrochloric acid, displacement of the water by sucrose causes a definite increase in the thermodynamic concentration of hydrogen ion over the whole range of concentration of the acid. This effect is brought out more clearly by the accompanying graph, Fig. 1. With the acetic acid, however, increased concentration of sucrose causes a lowering of the percentage increase of hydrogen-ion concentration (Fig. 2) while in the case of pure water we actually obtain a decrease in the thermodynamic concentration of hydrogen ion when the former is

displaced by sucrose. This latter finding is somewhat analogous to that of Poma and Tanzi[36] who state that the dissociation of water is diminished in concentrated salt solution.

Displacement of water by sucrose in the sodium hydroxide solutions causes an increase in the thermodynamic concentration of hydrogen ion, although reasoning by analogy from the effect of sucrose upon acids, a decrease would be expected.

Density and Mass Calculations

The specific gravities of the acid and sugar solutions were determined at
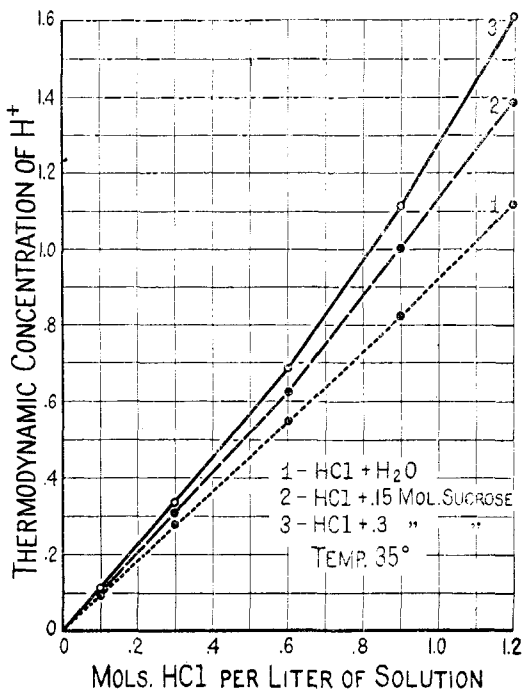
Fig. 1.
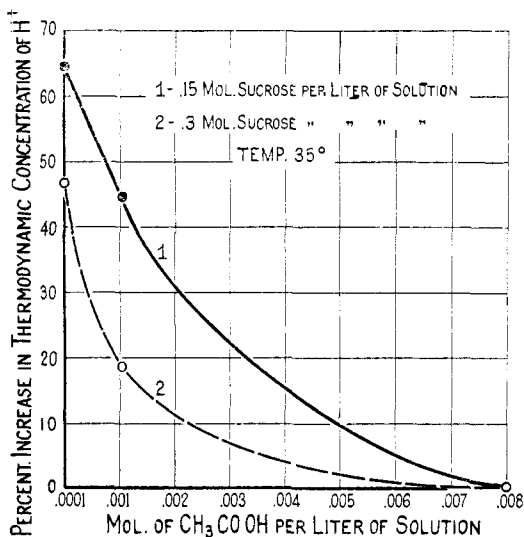
25° and 35° and those of the reaction mixtures at the latter temperature. All of the specific gravity values refer to $t°/t°$. The density values were obtained from those of the specific gravity by multiplying the latter by the weight (*in vacuo*) of 1 cc. of water at the temperature in question.

In calculating the masses of the components in the various mixtures no account was taken of the very small change in volume of the liquids when mixed; this

Fig. 2.

correction, usually amounting to from 1 to 2 parts per thousand, can be applied where desirable, as the data are given in Table II.

[36] Poma and Tanzi, *Z. physik. Chem.*, **79**, 55 (1912).

TABLE II

SPECIFIC GRAVITIES AND DENSITIES

Sucrose[a]

Mols per liter	Sp. gr. $t°/t°$		Density, $t°/4°$	
25°	25°	35°	25°	35°
0.6	1.0791	1.078	1.0759	1.0715
0.3	1.0396	1.0396	1.0365	1.0333
0.15	1.020	1.020	1.017	1.014

[a] The specific gravities of the 0.6 M and 0.3 M sucrose solutions were determined in every case where a reaction mixture was made up, the variation from ·the above values being less than 0.5 per 1000.

Hydrochloric Acid

Mols per liter	Sp. gr., $t°/t°$		Density, $t°/4°$	
25°	25°	35°	25°	35°
2.4	1.0411	1.042	1.038	1.0355
1.8	1.031	1.0310	1.028	1.0247
1.2	1.0208	1 0210	1.0177	1.0146
0.9	1.0156	1.0161	1.0125	1.0100
0.6	1.0106	1.0105	1.0076	1 0044
0.3	1.0053	1.0054	1.0023	0.9994
0.2	1.0035	1.0037	1.0005	0.99767
0.1	1.002	1.0016	0.9990	0.9956
0.02	1.0003	1.0004	0.9973	0 9944
0.002	0.9999	1.0000	0 9970	0.99405

HCl Mols per liter	HCl + 0.3 M Sucrose[b]			HCl + 0.6 M Sucrose[b]		
	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$	(Calc.)[c] Density	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$	(Calc.)[c] Density
25°		35°			35°	
2.4	1.0412	1.035	1.0344	1.0617	1.0553	1.0580
1.8	1.0366	1 0303	1.0290	1 0564	1.0500	1.0480
1.2	1.0315	1.0253	1.0250	1 0513	1.0450	1.0430
0.9						
0.6	1.0264	1.0202	1.0190	1.0466	1.0403	1.0380
0.3						
0.2	1.0230	1.0166	1.0155	1.0432	1.0370	1.0350
0.1						
0.02	1.0210	1.0147	1.0138	1.0417	1 0354	1.0330
0.002	1.0208	1.0146	1.0136	1.0407	1.0344	1.0327

[b] The captions "acid + sucrose" refer to the fact that equal volumes of the molarities indicated at 25° were mixed at 35°. The concentration of acid and sucrose in the final mixture at 35°, corrected for change in temperature, are shown in the tables referring to polarimetric measurements.

[c] The calculated values are the densities of the reaction mixtures, calculated from the specific gravities of the original components on the basis that no change in volume has occurred. Comparison of these values with the densities calculated from the observed specific gravities of the reaction mixtures will show to what extent, if any, a change in volume has occurred.

Acetic Acid

Mols per liter	Sp. gr., $t°/t°$		Density, $t°/4°$	
25°	25°	35°	25°	35°
0.08	1.0006	1.0007	0.9976	0.9947
0.016	1.0001	1.0002	0.9971	0.9942
0.002	0.9999	1.0001	0.9970	0.9941
0.0002	0.9999	1.000	0.9970	0.9940

	CH₃OOH + 0.3 M Sucrose			CH₃COOH + 0.6 M Sucrose		
Mols liter	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$ 35°	(Calc.) Density	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$ 35°	(Calc.) Density
0.08	1.0210	1.0148	1.0140	1.0410	1.0347	1.0331
0.016	1.0210	1.0150	1.0130	1.041	1.0350	1.0330
0.002	1.0210	1.0150	1.0140	1.041	1.0350	1.0330
0.0002	1.0210	1.0150	1.0140	1.041	1.0350	1.0330

Sodium Hydroxide

Mols per liter	Sp. gr., $t°/4°$		Density, $t°/4°$	
25°	25°	35°	25°	35°
0.002	1.0000	1.0000	0.9970	0.9940
0.02	1.0010	1.0011	0.9980	0.9951

	NaOH + 0.3 M Sucrose			NaOH + 0.6 M Sucrose		
Mols liter	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$ 35°	(Calc.) Density	Sp. gr., $t°/t°$ (obs.)	Density $t°/4°$ 35°	(Calc.) Density
0.002	1.0210	1.0150	1.0140	1.0410	1.0350	1.0330
0.02	1.0205	1.0143	1.0141	1.0401	1.0340	1.0330

Discussion of Results

The following table, III, and Fig. 3 sum up the results of this work as regards the velocity of inversion as a function of the thermodynamic concentration of hydrogen ion. The values of the velocity coefficients, or K_1, are the average values shown in the tables immediately following this discussion. These values were found by a system of weighting in which only those coefficients which were obtained with an experimental precision of the same order were selected for averaging. This method, however, excluded only a very few observations, and all of these were either at the very beginning or the extreme end of the reaction.

It will be observed from Table III that the velocity of inversion of sucrose, using 0.3 M sucrose, is proportional to the thermodynamic concentration of hydrogen ion, only for that range of concentration of hydrochloric acid which lies between 0.01 and 0.001 M, that is, the ratio K/c_{H^+} at these two concentrations is sensibly a constant. With the 0.15 M sucrose the proportionality here is not so good as in the former case. Palmaer[5] examined this range of concentrations at very short intervals, and obtained good proportionality between the concentration of hydrogen ion, as calculated by conductivity ratios, and the velocity of inversion. The concentration of sucrose used by him was practically 0.3 M (100 g. per liter) at a temperature of 48.18°.

TABLE III

Mols per solid liter HCl	c_H^+	K	K_i	$\dfrac{K}{c_H^-}$	$\dfrac{K_i}{c_H^+}$
			0.3M Sucrose		
1.197	1.607	0.0_3460	0.0_3496	0.0_3286	0.0_3309
0.8973	1.124	0.0_3293	0.0_3310	$0\ 0_3260$	0.0_3276
0.5981	0.6887	0.0_3182	0.0_3187	0.0_3264	0.0_3271
0.2990	0.3334	0.0_4834	0.0_4837	0.0_3250	0.0_3251
0.09964	0.1102	0.0_4252	0.0_4252	0.0_3228	0.0_3228
0.00997	0.01233	0.0_5235	0.0_5237	0.0_3190	0.0_3192
0.0_3997	0.001134	0.0_6212	0.0_6221	0.0_3187	0.0_3195
1.197	1.388	0.0_3444	0.0_3447	0.0_3319	0.0_3322
0.8973	1.000	0.0_3296	0.0_3307	0.0_3296	0.0_3307
0.5981	0.6245	0.0_3184	0.0_3188	0.0_3294	0.0_3301
0.2990	0.3052	0.0_4777	0.0_4773	0.0_3254	0.0_3254
0.09964	0.1005	0.0_4237	0.0_4235	0.0_3235	0.0_3234
0.00997	0.01109	0.0_5220	0.0_5220	0.0_3198	0.0_3198
0.0_3997	0.01134	0.0_6214	0.0_6219	0.0_3188	0.0_3193
Mols per liter CH₃COOH					
0.03988	0.001057	0.0_6178	0.0_6183	0.0_3168	0.0_3172
0.007976	0.0_33803	$0.0_7724\,-$	0.0_7717	0.0_3190	0.0_3189
0.0_3997	0.0_31616	0.0_7194	0.0_7189	0.0_3120	0.0_3117
0.0_4997	0.0_34858	0.0_9570	$0\ 0_9528$	0.0_4118	0.0_4109
0.03988	0.001071	0.0_6181	0.0_6182	0.0_3169	0.0_3166
0.007976	0.0_33803	0.0_7768	0.0_7762	$0\ 0_3201$	0.0_3200
0.0_3997	0.0_3965	$0\ 0_7225$	0.0_7243	0.0_3114	0.0_3124
0.0_4997	0.0_4544	0.0_8263	0.0_8263	0.0_4483	0.0_4489

[a] K_i in the table above represents the velocity coefficient calculated by the use of the short interval formula, $K_i = \dfrac{1}{t_2 - t_1} \log \dfrac{1 - x_1}{1 - x_2}$

For concentrations greater than 0.01 M hydrochloric acid, there is a steady increase in the ratio, which indicates that the velocity of inversion is increasing at a greater rate than the hydrogen-ion concentration. In this connection it will be noted that the ratio K/c_H^+ for the reaction mixture containing 0.6 M and 0.9 M hydrochloric acid, with both concentrations of sucrose, are sensibly constant. It must be remembered, however, that for these concentrations the velocity coefficients, calculated by the unimolecular formula, differ more among themselves than do those for the other concentrations, and that the average value of K might vary somewhat depending upon the intervals at which the observations were made.

Jones and Lewis[37] found that when the velocity coefficients calculated by the unimolecular formula were divided by the activity of the hydrogen ion, or its thermodynamic concentration, and also by the corresponding

[37] Ref. 2, 1125.

concentration of the water a constant quantity within the limit of the experimental error is obtained.

Application of this stoichiometric correction for the water to the unimolecular velocity constants reduced to unit activity of hydrogen ion, namely the ratio K/c_{H^+}, gives quantities, as we pass from one concentration of acid to another for the same concentration of sucrose, which bear about the same relation to one another as the original ratios. This is naturally to be expected since the water concentration in this work does not vary over a wide range.

Comparison of the unimolecular velocity coefficients in Table III will show that for each concentration of hydrochloric acid, with the exception of the 1.2 M, 0.3 M, 0.1 M and 0.01 M, the corresponding coefficients for both concentrations of sucrose are sensibly equal to each other. For these exceptional cases, leaving out of consideration the 1.2 M hydrochloric acid, it is found that the corresponding bimolecular coefficients, reduced to unit thermodynamic concentration of hydrogen ion, are a constant quantity for both concentrations of sucrose. This is shown below in Table IIIa.

TABLE IIIa

COMPARISON OF REDUCED BIMOLECULAR COEFFICIENTS

	c_{HCl}	c_{H_2O}	c_{H^+}	K_{uni}	K_{iuni}	K_{uni} $(c_{H_2O}) \times (c_{H^+})$ $\frac{}{(K)}$ $\frac{}{(K_i)}$	
0.3 M Sucrose	0.30	51.40	0.3334	0.04834	0.04837	0.05486	0.04500
	0.10	51.60	0.1102	0.04252	0.04252	0.05443	0.05443
	0.01	51.70	0.0123	0.05235	0.05237	0.05370	0.05370
0.15 M Sucrose	0.30	53.15	0.3052	0.04777	0.04773	0.05479	0.05479
	0.10	53.40	0.1005	0.04237	0.04235	0.05442	0.05442
	0.01	53.50	0.0111	0.05220	0.05220	0.05370	0.05370

For 0.1 M sulfuric acid, Jones and Lewis found that the bimolecular constant, as thus defined, is independent of the concentration of sucrose[38] or water, and also of the activity of the acid catalyst. As shown above, this conclusion may hold within certain limits for change in activity, or thermodynamic concentration of hydrogen ion, due to variation in the concentration of sucrose, or displacement of the water by the latter, but that the statement does not hold for changing activities, owing to changes in the concentration of the acid catalyst, is plainly evident.

With regard to the acetic acid-sucrose mixtures used here the relation between the ratios K/c_{H^+} is quite different from that obtained with the hydrochloric acid mixtures. This is somewhat to be expected for high dilutions of the acid, because here we are dealing with peculiar effects due not only to the presence of the sucrose, but also to the fact that the thermodynamic ionization of acids in high dilutions is not a simple function

[38] The concentration of sucrose was varied at close intervals from about 0.3 mol per liter to 2.0 mols per liter.

of the molecular concentration as has been believed heretofore. This is shown in this work with regard to the special cases considered, and has been shown to hold for hydrochloric, acetic, sulfuric, and phosphoric acids by Fales and Robertson.[19]

In general it can be seen from the graph, Fig. 3, upon the line representing the acetic acid portion of the curve, that the velocity coefficient decreases more rapidly than the concentration of hydrogen ion, below a concentration of 0.0004 moles per liter of the latter, and above this concentration the velocit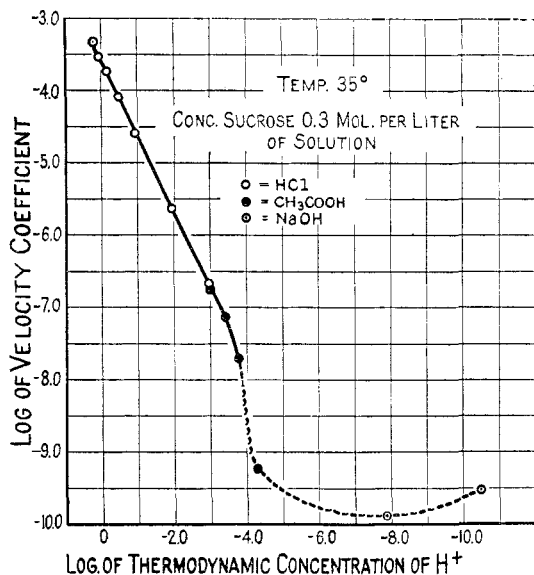y coefficient decreases less rapidly. The ratio K/c_{H^+} for the thermodynamic concentration of hydrogen ion mentioned above, which in the presence of 0.3 M sucrose corresponds to a molecular concentration of 0.008 moles per liter, is exactly equal to the same ratio for 0.01 M hydrochloric acid, namely 0.00019. This same relationship for the two ratios practically holds for the same molecular concentrations of these two acids in the presence of 0.15 M sucrose. An exact linear relationship, therefore, exists among the three points on the accompanying graph which represent the logarithms of the thermodynamic concentrations of hydrogen ion in 0.01 M and 0.001 M hydrochloric acid and 0.008 M acetic acid.

Fig. 3.

As the concentration of acetic acid is increased, however, this ratio decreases.[39] At a concentration of 0.04 M acetic acid, corresponding in the presence of 0.3 M sucrose to a thermodynamic concentration of hydrogen ion of 0.00106 mols per liter, the ratio K/c_{H^+} is 0.000168.

The decrease in thermodynamic concentration from 0.001 M hydrochloric acid to 0.04 M acetic acid is only 6.6%, whereas the decrease in velocity coefficient is 16.03%. According to Snethlage's[40] calculation from the data of Arrhenius the ratio k_m/k_h for acetic acid is 0.0058. The

[39] This is in contradiction to the theories advanced regarding the effect of the undissociated molecule, which postulate a relative increase of the velocity coefficient as the relative fraction of the undissociated portion is increased.

[40] Ref. 10, p. 235.

effect of the undissociated molecule, from this viewpoint, would then make the velocity coefficient attributed to the hydrogen ion in $0.04\ M$ acetic acid about 1.35% less than the observed velocity coefficient. If any effect can be attributed to the undissociated molecule in this case it would seem to be an anticatalytic effect. Under any circumstances there are other factors operating in the inversion process here which as yet have not been explained. From this same viewpoint, the HCl molecule is acting as a positive catalyst in acids of $0.01\ M$ or greater concentration.

TABLE IV

EXPERIMENTAL RESULTS

Concentration of Sucrose, $0.2988\ M$

Expt.	C H_2O	C HCl	Density	c_{H^+}	Obs. E.m.f.	Av. K	Av. K_i
1	50.71	1.197	1.055	1.607	0.2284	460×10^{-6}	496×10^{-6}
2	50.73	0.8973	1.050	1.124	0.2379	293×10^{-6}	310×10^{-6}
3	51.06	0.5981	1.045	0.6887	0.2509	182×10^{-6}	187×10^{-6}
4	51.38	0.2990	1.040	0.3334	0.2702	834×10^{-7}	837×10^{-7}
5	51.60	0.09964	1.037	0.1102	0.2996	252×10^{-7}	252×10^{-7}
6	51.69	9.97×10^{-3}	1.035	1.233×10^{-2}	0.3577	235×10^{-8}	237×10^{-8}
7	51.70	9.97×10^{-4}	1.034	1.34×10^{-3}	0.4210	212×10^{-9}	221×10^{-9}

		C CH$_3$COOH					
8	51.58	3.988×10^{-2}	1.035	1.059×10^{-3}	0.4228	178×10^{-9}	183×10^{-9}
9	51.68	7.976×10^{-3}	1.035	3.803×10^{-4}	0.4502	724×10^{-10}	717×10^{-10}
10	51.70	9.97×10^{-4}	1.035	1.616×10^{-3}	0.4727	194×10^{-10}	189×10^{-10}
11	51.69	9.97×10^{-5}	1.035	4.858×10^{-5}	0.5046	570×10^{-12}	528×10^{-12}

		C NaOH					
12	51.69	9.97×10^{-4}	1.035	1.423×10^{-8}	0.7205	131×10^{-12}	189×10^{-12}
13	51.70	9.97×10^{-3}	1.034	3.0×10^{-11}	0.8834	296×10^{-12}	335×10^{-12}

Concentration of Sucrose, 0.1495

		C HCl					
14	52.20	1.197	1.035	1.388	0.2323	444×10^{-6}	447×10^{-6}
15	52.51	0.8973	1.030	1.000	0.2411	296×10^{-6}	307×10^{-6}
16	52.83	0.5981	1.025	0.6245	0.2535	184×10^{-6}	188×10^{-6}
17	53.15	0.2990	1.020	0.3052	0.2725	777×10^{-7}	773×10^{-7}
18	53.37	9.964×10^{-2}	1.017	0.1005	0.3020	237×10^{-7}	235×10^{-7}
19	53.46	9.97×10^{-3}	1.015	1.109×10^{-2}	0.3605	220×10^{-8}	220×10^{-8}
20	53.47	9.97×10^{-4}	1.015	1.134×10^{-3}	0.4211	214×10^{-9}	219×10^{-9}

		C CH$_3$COOH					
21	53.36	3.988×10^{-2}	1.015	1.071×10^{-3}	0.4225	181×10^{-9}	182×10^{-9}
22	53.45	7.976×10^{-3}	1.015	3.803×10^{-4}	0.4502	768×10^{-10}	762×10^{-10}
23	53.47	9.97×10^{-4}	1.015	1.965×10^{-4}	0.4675	225×10^{-10}	243×10^{-10}
24	53.47	9.97×10^{-5}	1.015	5.438×10^{-5}	0.5016	263×10^{-11}	266×10^{-11}

		C NaOH					
25	53.47	9.97×10^{-4}	1.015	7.53×10^{-9}	0.7374	428×10^{-12}	478×10^{-12}
26	53.47	9.97×10^{-3}	1.014	1.45×10^{-11}	0.9034	757×10^{-12}	830×10^{-12}

It may be that other reactions besides the inversion process are going on in the concentrations of sodium hydroxide used in this work. The question therefore arises whether the use of the polariscope is a valid method for following such a process. Nef[41] has shown that many carbohydrates

[41] Nef, *Ann.*, **376**, 1–119 (1910).

undergo change in alkaline solution. It is significant to point out, however, that the angular change in rotation of the solution containing the 0.001 M sodium hydroxide solution, for a period of over 3 months at the temperature used here, was less than 0.3%, which is practically negligible.

Tabulation of Experimental Results

Table IV sums up the experimental results. The experiments are numbered according to their order and show the concentrations, in moles per liter of solution, of the components of the reaction mixture. In addition are shown the density of the mixture, the thermodynamic concentration of the hydrogen ion and the observed e.m.f. Following all are shown the average velocity coefficients, $K = \dfrac{1}{t} \log \dfrac{1}{1-x}$ and $K_i = \dfrac{1}{t_2-t_1} \log \dfrac{1-x_1}{1-x_2}$, or the velocity coefficients calculated by the unimolecular formulas for both the long and short time intervals.

In Table IVa are shown 4 consecutive and representative experiments to illustrate the method of procedure and calculation. These experiments give the time intervals between successive periods of the reaction; the observed angular rotation in degrees; the fraction of sucrose inverted, and both velocity coefficients calculated by the above formula.

It is to be noted that the mixtures with the more dilute acids, and with sodium hydroxide were kept at constant temperatures and studied for upwards of 4 months.

TABLE IVa

Expt. 5

$c_{sucrose} = 0.2988$ Density $= 1.037$
$c_{H2O} = 51.60$ $c_{H+} = 0.1102$
$c_{HCl} = 0.09964$ Obs. e.m.f. $= 0.2996$

Expt. 7

$c_{sucrose} = 0.2988$ Density $= 1.034$
$c_{H2O} = 51.70$ $c_{H+} = 0.00134$
$c_{HCl} = 0.000997$ Obs. e.m.f. $= 0.4210$

Time elapsed Seconds	Obs. Angle	Fraction inverted	$\dfrac{1}{t}\log\dfrac{1}{1-x}$ $K\times10^{-7}$	$\dfrac{1}{t_2-t_1}\log\dfrac{1-x_1}{1-x_2}$ $K_i\times10^{-7}$	Time elapsed Hours	Obs. Angle	Fraction inverted	$\dfrac{1}{t}\log\dfrac{1}{1-x}$ $K\times10^{-9}$	$\dfrac{1}{t_2-t_1}\log\dfrac{1-x_1}{1-x_2}$ $K_i\times10^{-9}$
Start	11.20	......	...	...	Start	11.22	......	...	...
69.00	11.09	0.0076	470	470	40.550	10.25	0.0666	205	205
1035.00	10.35	0.0582	252	235	161.616	7.70	0.2416	206	207
3113	8.87	0.1599	243	239	283.4	5.54	0.3898	206	215
4857	7.64	0.2443	252	263	402.25	3.87	0.5045	210	212
9231	5.19	0.4125	250	250	570.150	2.04	0.6301	210	211
12834	3.61	0.5209	249	246	737.616	.75	0.7186	207	197
18520	1.69	0.6527	248	246	978.4	− .64	0.8140	207	207
26320	− .16	0.7797	250	253	1213.583	−1.64	0.8826	213	235
32640	− 1.10	0.8442	247	238	1553.583	−2.51	0.9423	221	246
76969	− 3.26	0.9925	275	297	1935.533	−3.00	0.9760	232	271
	− 3.37	......	...	...		−3.35	......	...	...

Av. $= 252 \times 10^{-7}$ 252×10^{-7} Av. $= 212 \times 10^{-9}$ 221×10^{-9}

Expt. 6

$c_{sucrose} = 0.2988$ Density $= 1.035$
$c_{H_2O} = 51.69$ $c_{H^+} = 0.01233$
$c_{HCl} = 0.00997$ Obs. e.m.f. $= 0.3577$
$K \times 10^{-8}$ $K_i \times 10^{-8}$

Time elapsed Minutes	Obs. Angle	Fraction Inverted	$\dfrac{1}{t}\log\dfrac{1}{1-x}$	$\dfrac{1}{t_2-t_1}\log\dfrac{1-x_1}{1-x_2}$
Start	11.21	......	...	...
360.5	9.58	0.1120	238	238
1075.87	7.01	0.2887	229	225
1752.87	5.04	0.4241	228	226
3258.87	1.77	0.6499	233	233
3872.87	.79	0.7162	235	247
4624.37	− .07	0.7752	234	225
7161.47	− 1.87	0.8990	231	228
8307.87	− 2.38	0.9306	232	231
12673.87	− 3.15	0.9869	261	276
	− 3.34	......	...	...

Av. $= 235 \times 10^{-8}$ 237×10^{-8}

Expt. 8

$c_{sucrose} = 0.2988$ Density $= 0.135$
$c_{H_2O} = 51.58$ $c_{H^+} = 0.001059$
$c_{CH_3COOH} = 0.03988$ Obs. e.m.f. $= 0.4228$
$K \times 10^{-9}$ $K_i \times 10^{-9}$

Time elapsed Hours	Obs. Angle	Fraction Inverted	$\dfrac{1}{t}\log\dfrac{1}{1-x}$	$\dfrac{1}{t_2-t_1}\log\dfrac{1-x_1}{1-x_2}$
Start	11.22	......	...	...
40.716	10.38	0.0577	176	176
161.8	8.15	0.2107	176	177
283.6	6.25	0.3411	177	179
402.433	4.72	0.4461	177	176
570.35	2.97	0.5662	177	176
978.616	0.15	0.7598	176	175
1213.783	−0.92	0.8332	177	187
1553.716	−1.98	0.9060	183	204
1935.933	−2.61	0.9492	184	194
2243.983	−3.00	0.9760	200	294
	−3.35	......	...	...

Av. $= 178 \times 10^{-9}$ 183×10^{-9}

Discussion of the Preceding Experimental Tables

Examination of the preceding tables will show that the velocity coefficients, as calculated by the unimolecular formula, are fairly constant for each reaction, with the exception of those in which concentrated acids are used. This deviation is particularly noticeable in the case of the reactions where 0.9 M hydrochloric acid is used, the velocity coefficient rising steadily from a value of 0.000237 to 0.000337 throughout the course of the inversion.

From time to time[42] various investigators have produced results from which it appears that under certain conditions the inversion reaction is not strictly unimolecular. The above example seems to be another case of such a departure, especially in the early periods of the reaction. It therefore seems advisable that any disussion of this example should be limited to the range of the reaction where the deviation is most marked.

There is probably no doubt that the differences in the experimental method used here, and those used elsewhere would account for the failure of previous investigators to note the inconstancy of the velocity coefficient in the early periods of the inversion reaction, when high concentrations of hydrochloric acid are used.

[42] Armstrong and Caldwell, Proc. Roy. Soc., **74**, 195 (1904), obtained a regular increase in the velocity coefficient with dilute acids. On the other hand, Julius Meyer, Z. physik. Chem., **62**, 59 (1908), under similar conditions obtained a decrease in the velocity coefficients. For a discussion of the results of Armstrong and Caldwell, see Rosanoff, Clark and Sibley, This JOURNAL, **33**, 1911 (1911). Meyer's results are criticized by Hudson, ibid., **30**, 1165 (1908). F. P. Worley, J. Chem. Soc., **99**, 349 (1911), has shown that by the use of concentrated solutions of nitric acid for the inversion of sucrose, regularly increasing velocity coefficients are obtained.

It has been customary in the past to follow the course of change directly in the polarimeter tube. This usage gives rise immediately to questions which are pertinent to the present discussion. First, the time consumed in mixing the solutions, transferring the mixture to the polariscope tube, and adjusting the instrument, would be about 5 to 10 minutes,[43] even in the hands of a skilled experimenter. This would obviate a study of the reaction in the early period, where strong acids are used. Secondly, it follows directly from the first statement that a correct determination of the initial angle is impossible, under the foregoing conditions.

Rosanoff, Clark and Sibley,[44] realizing the error introduced in determining the initial angle by the foregoing method, have suggested a graphic method, by the use of which they claim that the value of the initial angle can be reliably determined. The method devised and made use of in the present work resorts neither to graphic nor arithmetical means of extrapolation, but allows the determination of the initial angle with a very high degree of precision.

In order to determine what the effect upon the velocity coefficients would be, in the case where 0.9 M hydrochloric acid (0.3 M sucrose; Expt. 2) was used, when the observations made during the first 10 minutes of the reaction are disregarded, the velocity coefficients for the remaining observations were calculated by the monomolecular formula $k = 1/t_2 - t_1 \log \dfrac{1-x_1}{1-x_2}$, this form giving the velocity coefficients between any time intervals at any stage of the reaction. The coefficients so obtained were plotted against the time, and extrapolated[45] to $t = 0°$.

The results are shown below, the velocity coefficients being multiplied by 10^6, and the time given in seconds.

Time........	0	200	600	1500	2500	4000
Vel. coef......	316	320	326	339	347	349

If the observations in the first 30 minutes are disregarded and treated according to the foregoing method, the velocity coefficients over the same range of time vary only from 340 to 350. It is perfectly obvious from the above that such methods of graphic extrapolation involve assumptions regarding the true course of the reaction in the early stages which are eliminated if the method used in this research is adopted.

Summary and Conclusions

1. The addition of sucrose to hydrochloric acid causes a definite increase in the thermodynamic concentration of hydrogen ion over the whole

[43] Lamble and Lewis, Ref. 8, report no accepted observation made in less than 7 minutes.

[44] Ref. 38, p. 1917.

[45] This method was used by F. P. Worley, Ref. 42, as well as by Rosanoff and Potter. THIS JOURNAL, 35, 253 (1913).

range of concentration of the acid.   With acetic acid a maximum increase in hydrogen-ion concentration is obtained which falls off as the concentration of sucrose is increased.   With water the thermodynamic concentration of hydrogen ion decreases upon the addition of sucrose.

2.   The addition of sucrose to solutions of sodium hydroxide seems to cause an increase in the thermodynamic concentration of hydrogen ion.

3.   The thermodynamic concentration of hydrogen ion in the system remains appreciably constant during the course of the inversion process.

4.   The velocity of inversion of sucrose by hydrochloric acid is proportional to the thermodynamic concentration of hydrogen ion only for the limited range of concentration of acid which lies between 0.01 and 0.001 mols per liter.

5.   The bimolecular velocity coefficients, reduced to unit thermodynamic concentration of hydrogen ion, are constant with changing concentrations of sucrose only for each molecular concentration of hydrochloric acid between 0.01 to 0.3 mols per liter.   These constants vary considerably for different concentrations of acid.

6.   Evidence has been adduced which shows that for acetic acid, the undissociated molecule is not a positive catalyst in the inversion process; or that there are other factors entering here which have never been considered.

7.   With strong acids, the inversion process does not seem to be strictly unimolecular, especially in the early periods of the reaction.

8.   Within the limits of the concentrations of the reactants used, no appreciable change in volume was noted when the solutions of hydrochloric acid and sucrose were mixed.

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A STUDY OF THE LUMINOUS DISCHARGE IN HYDROGEN AND IN MERCURY AND A NEW METHOD OF MEASURING IONIZATION POTENTIALS

BY GEORGE E. GIBSON AND W. ALBERT NOYES, JR.

I.   Introduction

In a previous article[1] the authors have described some experiments on the obliteration of the characteristic spectra of metals by certain gases. The sparking potentials of these gases relative to air were determined and it was found that the gases which had a marked obliterating effect also had a high sparking potential.   The method used for determining the sparking potential was, however, only roughly quantitative and the present

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[1] Gibson and Noyes, THIS JOURNAL, **43**, 1255 (1921).