[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DEPARTMENT, UNIVERSITY OF ADELAIDE]

THE UNIMOLECULARITY OF THE INVERSION PROCESS

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Many workers question the strict applicability of the unimolecular logarithmic formula to the inversion process; thus Worley[1] concludes that the unimolecular law is not followed; Armstrong and Caldwell[2] find that with weak acids in the earlier stages a linear and not a logarithmic formula is applicable; Fales and Morrell[3] claim that the unimolecular law holds in the presence of weak acids, but fails when strong acids catalyze the inversion; and so on. On the other hand Jones and Lewis,[4] Rosanoff, Clark and Sibley[5] and others find that the inversion process follows the unimolecular law within the limits of experimental error.

The author has shown[6] that the mutarotation lag may, and does, appreciably effect polarimetric determinations of the inversion coefficient, and with the help of this knowledge a very careful determination of the variation of the coefficient has been carried out.

Experimental Part

Previous workers assuming that the mutarotation lag is negligible have found the rotation at zero time by extrapolating[5] the log $(\lambda_t - \lambda_\infty)$ against time curve to $t = 0$, or else have taken the time of first reading as zero time, or again have used the short time interval formula. The inaccuracies that these methods give rise to will be pointed out later.

In this work three methods were used that allowed an accurate experimental determination of the rotation at zero time. First, weighed quantities of acid and sugar solutions were mixed at the reaction temperature while immersed in the water-bath. Samples were withdrawn from time to time, rapidly chilled to 0° and their rotations read. The rotation at zero time was obtained by separately cooling the correct weights of acid and sugar solutions to 0°, mixing them at this temperature and immediately reading the rotation. At 0° the inversion was negligibly slow and very accurate rotations could be obtained. Although the inversion is negligible at this temperature, mutarotation rearrangements can proceed steadily owing to their larger velocity constants; accordingly, each solution was further kept at 0° for an estimated time until the mutarotational equilibria were complete and the rotations were again read. The constants obtained

[1] Worley, *Trans. Chem. Soc.*, **99**, 349 (1911).

[2] Armstrong and Caldwell, *Proc. Royal Soc.*, **74**, 195 (1905).

[3] Fales and Morrell, THIS JOURNAL, **44**, 2072 (1922).

[4] Jones and Lewis, *Trans. Chem. Soc.*, **117**, 1120 (1920).

[5] Rosanoff, Clark and Sibley, THIS JOURNAL, **33**, 1911 (1911).

[6] Pennycuick, *Trans. Chem. Soc.*, **125**, 2049 (1924).

by these two methods are marked A and B, respectively, in the tables. The third method employed was essentially that of Fales and Morrell.[3] The solutions were mixed in the water-bath as described above; from time to time samples were then removed and the acid was neutralized by the quick addition of the calculated amount of sodium hydroxide solution. These were chilled to 0° and the rotations read. This method obviously allows an experimental zero time reading. The constants are marked C in the tables.

All three methods have the definite advantages that they allow an experimental zero time reading to be taken generally at leisure (great care was observed to get this reading very exactly), that all rotations can be obtained very accurately owing to the very slow inversion changes at 0°, and that all constants obtained are quite free from any mutarotation lag effect. By the ordinary methods a high experimental error is unavoidable in early readings, owing to the large changes in the rotation as the readings are being taken.

The Sugar.—The highest grade sugar was purified by precipitation from alcohol, according to the method of Kraisy.[7] The solutions were made up as required with conductivity water and no solution was used after it had been made up for more than two days.

Polarimeter Readings.—All readings were taken at 0°, in a 2dcm. tube let into a specially made, gun-metal ice boat. The boat was coated with felt and kept full of ice shavings. The polarimeter was a high grade, triple-field Schmidt and Haensch instrument, calibrated to 0.01°. In the great majority of solutions examined the change in rotation during the reading was negligible, and hence very accurate results were obtained. The following procedure was adopted. Six readings of the rotation were taken. The ends of the tube were then loosened, to test for any strain in the glass, and the windows wiped to remove any dew. Six more readings were then taken, and if the average differed from that of the first six by more than 0.01°, another six readings were taken and so on. Very few individual readings differed from the average by more than 0.02°; and in fact the majority of the readings are believed to be correct to 0.01°.

It was found that if the intensity of the sodium flame varied, a personal error of about 0.02° was introduced by an unconscious displacement of the end-point. An intense sodium flame was used throughout, from fused sodium chloride fed into an Alundum boat on a platinum triangle in a Méker flame, and the intensity was kept as constant as possible for all readings.

Starting the Reaction.—It was considered advisable, and in some cases necessary, to run each reaction in two or three sets, and therefore strictly reproducible mixtures and an accurate zero time were required. Weighed quantities (about 200 g.) of acid and sugar solutions of twice the required strength were placed in wide-necked flasks, joined at the necks, and placed in the water-bath. After 40 minutes the solutions were poured back and forward several times, the rate of mixing being facilitated by the width of the necks of the flasks. The flasks were kept immersed during the whole operation. The inversion thus receives a proper start at the correct temperature and zero time can be obtained correct to within two or three seconds. By keeping a check on the weights of the solutions mixed the same inversion can be accurately repeated, and readings from the different runs accordingly fit into the one table. This is not only advantageous but was also necessary in many cases owing to time limitations in the removal of samples. The weight check (which is obviously superior to a

[7] Kraisy, *Z. Ver. deut. Zucker-Ind.*, 1921, 785.

volume check) is further used to find the correct solutions for the zero time readings. For this purpose, the correct relative weights of much smaller quantities of solution (about 20 g.) were cooled to 0° and carefully mixed at this temperature. The rotation was then taken and is the correct rotation at zero time. Two such readings were always taken and if they differed by more than 0.01°, another pair of solutions was made up.

Chilling the Solutions.—It was very necessary—particularly when stronger acids were being used—to chill each removed sample very rapidly. A long spiral tube was surrounded with broken ice, and as each sample of about 30 or 40 cc. was removed it was immediately run through the spiral and received in a flask which was then rapidly agitated in a very cold freezing mixture until the solution reached 0°.

Final Reading.—A rough value of the infinity reading is generally obtained by heating the solution to 100° for two minutes. That this value is rough is evident from the fact that it varies with the time the solution is held at 100°, becoming *less* negative the longer it is heated. This is doubtless due to the decomposition of the invert products. Although more pronounced in strong acid solutions, the minimum is also shown by weak acids. To get the best value of λ_∞, then, the solution must not be over inverted. This matter has received some attention from Worley[1] who attempts to introduce a correction.

In this work, however, the solutions are hydrolyzed to 0.01° of complete inversion by keeping them in the bath at the temperature of the experiment for a calculated period of time. To obtain the latter, a rough value of λ_∞ is first got by heating the solution to 95° for two minutes. This is used to get the order of the velocity constant, and from this the time to 0.01° of inversion is obtained. With a little care the time can be determined to within a few minutes, and the infinity reading is thus strictly reproducible. Whether this is the true value of λ_∞ to 0.01°, is doubtful; but practically it has this advantage, the inversion being carried through at a relatively low temperature and for the minimum time, decompositions are reduced to a minimum, and such changes are not exaggerated in the infinity readings alone.

Experimental Results

TABLE I

0.02 *N* HCl + 17.1% of sucrose at 40°

Initial sucrose remaining, %	Time, min.	$k_A \times 10^6$	$k_B \times 10^6$	$k_C \times 10^6$	Av. $k \times 10^6$
97.5	19.8	576	566	579	574
95	39.71	593	576	570	579
92.4	59.35	581	581	591	584
92	63.01	593	593	...	593
90	77.5	597	595	592	595
87	101.41	591	592	596	593
78	181.61	594.7	594.7	594.9	594.8
73.4	226.3	590.3	592.6	...	591.4
66	299.01	596.9	597.3	594.0	596.1
61.3	371.35	602.3	600.2	597.3	599.9
50.7	490.2	600.8	601.8	600.0	600.9
43	608.7	600.6	601.1	600.9	600.9
32.4	811.64	603.3	602.1	601.5	602.3
21.8	1100.6	603.8	602.0	602.7	602.8
20	1152.5	603.6	604.0	...	603.8
12.6	1486.4	604.0	604	604	604
2	2696.4	603	604	604	604

TABLE II

0.099 *N* HCl + 17% of sucrose at 35°

Initial sucrose remaining, %	Time, min.	$k_A \times 10^6$	$k_B \times 10^6$	$k_C \times 10^6$	Av. $k \times 10^6$
98.0	5.97	(1660)	1540	1540	1580
96.5	9.82	1620	1600	1545	1588
92.6	21.77	1560	1570	1579	1569
89.8	29.80	1580	1570	1578	1576
85.1	44.47	1597	1592	1584	1591
80.3	59.60	1597	1591	1590	1593
74.6	79.60	1608	1601	..	1605
71.0	93.18	1609	1600	1591	1600
64.5	119.60	1601	1599	1597	1599
59.1	142.9	1604	1600	..	1602
51.6	179.7	1600	1610	1603	1604
41.1	239.8	1608	1610	1609	1609
32.8	299.8	1614	1614	1609	1612
26.1	359.7	1623	1624	1617	1621
14.1	522.9	1626	1627	..	1626
11.1	589.4	1619	1620	1615	1618
9.1	639.8	1621	1628	1620	1623

The velocity coefficients in Tables I and II above are free from mutarotation lag effects; k_A is computed using the corrected formula set out in a previous paper;[6] while the methods that yield k_B and k_C are inherently free from lag.

In the calculation of the coefficients decimal logarithms are used. All solutions contain 17.1 g. of sucrose in 100 cc. of solution, and the acid normality of the latter is set out at the head of each table. The initial columns indicate the uninverted percentage of the original sugar content at time of reading.

Cols. I and II strictly refer only to the calculations for K_A and K_B; they refer approximately to the K_C values which is quite sufficient for the purpose.

In Table III the average constants only are given.

TABLE III

Approximate % of initial sucrose remaining	0.507 *N* HCl + 17.1% of sucrose at 35°		0.905 *N* HCl + 17.1% of sucrose at 35°	
	Time, min.	Av. $k \times 10^6$	Time, min.	Av. $k \times 10^6$
96	1.97	974	...	...
93.5	2.95	977	...	...
91	4.14	979	1.90	2180
88	5.54	989	2.59	2202
87.4	5.94	997	2.71	2189
82	8.62	991	3.90	2182
80	9.80	1007	...	...
77	11.61	996	5.09	2192
71	14.83	1003	6.71	2210
60.3	21.75	1009	9.79	2230

TABLE III (*Concluded*)

Approximate % of initial sucrose remaining	0.507 *N* HCl + 17.1% of sucrose at 35°		0.905 *N* HCl + 17.1% of sucrose at 35°	
	Time, min.	Av. $k \times 10^5$	Time, min.	Av. $k \times 10^5$
54.5	25.71	1011	11.82	2226
47	30.86	1015	14.70	2233
42	36.27	1011	16.81	2225
34	45.10	1016	20.68	2234
28	54.62	1020	24.50	2254
27.3	...	...	24.99	2243
21	65.21	1017	29.73	2269
15	80.61	1023	38.6	2245
12.3	88.87	1024	40.53	2242
6.7	114.71	1021	51.46	2247
3.6	141.6	1026	61.61	2245

The results summarized in Tables I, II and III were not only obtained by three different methods as set out, but in all cases each method was carried out in two or three sets which then fitted into one whole table. The agreement among such sets and also among the different methods leaves little doubt that the coefficients obtained are the correct ones under the conditions of temperature and concentration.

Discussion

It is at once evident that the coefficient increases slightly and steadily throughout the inversion, the maximum increase over the whole range being never more than 5%. Now this increase can be very easily masked, and it is interesting to notice how many workers obtain very constant coefficients from quite simple errors.

If the log $(\lambda_t - \lambda_\infty)$-against-time curve be extrapolated to $t = 0$, as recommended by Rosanoff, Clark and Sibley,[5] the accuracy of the important value log $(\lambda_0 - \lambda_\infty)$, a value used in all subsequent calculations, depends entirely on the accurate extension of the curve. As the experimental values at early times show the greatest experimental errors (that is, lie less regularly on the curve) a certain laxity follows in drawing the curve through these points and thence to $t = 0$. Further, the very early values contain an error due to mutarotation lag as the author has pointed out, and this tends to throw them farther from the curve. It can be seen then that the extrapolated value of log $(\lambda_0 - \lambda_\infty)$ will vary with the method of extrapolation. This has important consequences, as even a very slight variation has a big effect on the calculated coefficients. In Table IV, the third column sets out the constants recalculated, using the extrapolated zero time value 1.5139 (= log 32.65), instead of the correct value 1.5133 (= log 32.60). It is seen that this slight difference has effectively hidden the steady increase. This affords another illustration of the unreliability of the method of extrapolation. It is obvious now why special attention

was paid in this work to the very accurate determination of the zero time reading.[8]

Again, many workers prefer to neglect the zero reading, and take the time of first reading as zero time. As this first reading is subject (usually) to a high experimental error, owing to the rapidly changing rotation, any variations in the coefficient have been put down to this cause. In this work there is no such exaggerated experimental error in the early readings, although of course the percentage error is necessarily high. In Table IV, the fourth and fifth columns give the recalculated coefficients, using the 10- and 20-minute readings, respectively, as zero readings. Here it is seen that the real increase becomes less pronounced the further the time of first reading is removed from zero time. The explanation of this is contained in the next paragraph.

Further, various authors have stressed the strict accuracy of the short-time interval formula, and have accordingly preferred to use it. Now on integrating the fundamental equation, $dx/dt = k(A - x)$, between the limits t_2 and t_1, and writing $(\lambda_t - \lambda_\infty) \propto (A - x)_t$, we have, $k_2t_2 - k_1t_1 = \log [(\lambda_{t_1} - \lambda_\infty)/(\lambda_{t_2} - \lambda_\infty)]$. If the unimolecular coefficient be uniformly constant, that is, $k_2 = k_1$, the short-time-interval formula follows; but if k_2 does not equal k_1 as in the action under discussion, let us write $k_2 = k_1 + s$.

It follows that

$$k_1 = \frac{\log [(\lambda_{t_1} - \lambda_\infty)/(\lambda_{t_2} - \lambda_\infty)] - st_2}{t_2 - t_1}, \text{ and } k_2 = \frac{\log [(\lambda_{t_1} - \lambda_\infty)/(\lambda_{t_2} - \lambda_\infty)] - st_1}{t_2 - t_1}$$

It is evident from inspection that if s is appreciable but neglected, then the value of $k_1 (= k_2)$ which follows is *greater than either* of the true values of k_1 and k_2. An examination shows that this effect on an increasing coefficient of the order set out in Tables I, II and III, tends to smooth over the increase. This, together with exaggeration of the experimental error, overrides any advantage which this formula may have been thought to possess. In Table IV, the sixth column gives the redetermined coefficients, using the short-time-interval formula. They show quite extreme variations which overshadow the true, steady change.

The preceding analysis and a study of Table IV explain why so many determinations show a more or less constant coefficient or at all events the lack of a steady increase. Where a very large increase has been found it can generally be traced to experimental error. For instance, Fales and Morrell,[3] using the method called C in this work, find very large increases with strong acids, for example, a 44% increase with 0.9 N hydrochloric acid, and claim that the method used lays bare an irregularity

[8] It might be pointed out here that for ordinary inversion determinations, where an approximate coefficient *only* is required, the extrapolated log $(\lambda_0 - \lambda_\infty)$ is quite sufficient.

TABLE IV

0.02 N HCl + 17.1% of sucrose at 40°

Initial sucrose remaining, %	Av., $k \times 10^6$	Redetermined coefficients			
		3	4	5	6
99	(565)	(655)	...	...	...
97.5	574	606	(560)	...	(560)
95	579	607	590	608	608
92.4	584	594	581	586	564
92	593	602	593	600	720
90	595	604	597	603	613
87	593	597	595	595	563
78	595	600	596	598	600
73.4	591	594	590	592	574
66	596	598	597	600	617
61.3	600	604	603	604	624
50.7	601	602	601	602	596
43	601	601	601	602	600
32.4	602	603	603	604	611
21.8	603	604	604	604	605
20	604	604	604	604	598
12.6	604	604	604	604	604
2	604	604	602	602	600

Col. 3. 32.65 used for $\lambda_0 - \lambda_\infty$ instead of 32.60.
Col. 4. Time of first reading (10 minutes) used as zero time.
Col. 5. Time of second reading (20 minutes) used as zero time.
Col. 6. Coefficients redetermined, using the short-time-interval formula.

and that in strong acids the action is not fundamentally unimolecular. Their method of mixing the solutions, however, allows a slight temperature fall and with rapidly inverting solutions this causes the early constants to be far too low. With slow inversions this effect is less pronounced. As Fales and Morrell's figures have been accepted in certain quarters, the author repeated the 0.905 N hydrochloric acid inversions, but mixed the solutions according to the method used by these authors and reproduced their large increases. But when the solutions were mixed while wholly immersed in the water-bath, and the temperature error was thus avoided, the large increases disappeared and the lesser increases set out in this paper were obtained. Incidentally, Fales and Morrell averaged their coefficients and made use of the average value in their subsequent work. Their coefficients with stronger acids are, therefore, too low, for example, 0.000293 for 0.9 N hydrochloric acid instead of 0.000337. The percentage increases found in this work over the last 90% of the inversion are approximately, 2, 2, 4 and 4% for 0.02 N, 0.099 N, 0.507 N and 0.905 N hydrochloric acid, respectively. The increase is greater with stronger acids but not abnormally so.

The Cause of the Increase.—The inversion is, of course, bimolecular and not unimolecular. and it is customary to write velocity = k_{bi}[sucrose]-

[water] (assuming for the time being that hydrogen-ion activity is constant during inversion). The relation $k_{bi} = k_{uni}/[H_2O]$ used by Worley[1] and Jones and Lewis[4] is not strictly correct as $[H_2O]$ varies with time. The correct relation would be obtained by integrating $dx/dt = k(A - x)(B - x)$, whence $(B - A)k_{bi} = k_{uni} - (1/t) \log (B/B - x)$, (where B is the number of initial water molecules, and x the molecules of sugar inverted). It is obvious from inspection that either equation gives a bigger increase still for the bimolecular coefficient.

An examination of the inversion process has convinced the author that the universally used relation $dx/dt = k$ [sucrose][water], where [water] represents the number of water molecules per liter, is not only misleading, but as generally applied is quite unsound.[9] The solute by the very nature of solution is always in contact with the water, the latter being a reactant as well as the solvent. As the inversion in water alone is immeasurably slow, one accepts the Arrhenius conception of active molecules, and writes the concentration of such molecules proportional to the total concentration. The hydrolysis then takes place only when an active sugar molecule is in contact with an active water molecule. Applying these ideas to the inversion of sucrose (or to any other hydrolysis for that matter) in pure water, the active water at fixed temperature may be written proportional to total water, no matter to what the activation may be due, and the active sugar proportional to total sugar. The velocity equation then assumes the usual form, $dx/dt = k'$[active sugar][active water] $= k$[total sugar][total water]. In practice, however, the inversion is invariably catalyzed by acids, and as such systems are homogeneous, we may conclude that the action is still one between active sugar and active water molecules, and that the increased velocity caused by the presence of the acid is due to the increase in concentration of active sugar or water or both. Further, it is evident that these activated molecules must be those that are most affected by the presence of the acid, that is, those that are in some sort of contact or combination with the acid or rather with the active acid agent, the hydrogen ion.

Now, if combination takes place between hydrogen ion and sugar, it will lead to a constant amount of sugar being inverted in equal intervals of time when the acid concentration is very low. Armstrong and Caldwell[2] believed that they had obtained evidence in this direction, but as the author[6] has pointed out they neglected the mutarotation lag effects which give their results quite a different meaning. In fact, we have no conclusive experimental evidence whatever, that any of the hydrogen ion is held up

[9] Since this was written the author's attention has been called to the papers of Worley [*Proc. Roy. Soc.*, **87A**, 582 (1912)] and Armstrong and Worley [*ibid.*, **87A**, 604 (1912)] where a somewhat similar conclusion is reached though from a different point of view.

in this way in any hydrolysis. On the other hand, all the evidence points very definitely to the combination of the hydrogen ion with the water to form a hydrated ion, though statistical values of the degree of hydration are as yet uncertain. As the hydrogen ion is a positive nucleus only, and as the water molecules have very active auxiliary fields, it is generally concluded that at any instant every hydrogen ion is exerting some influence on the water molecules in its neighborhood. We may imagine that such molecules are thus rendered more hydrolytically active, and in fact may be regarded as the only water molecules which are able to react with sugar molecules. We may then write the velocity of inversion proportional to the number of such active centers, that is, proportional to the hydrogen-ion concentration. In acid solution, then, the inversion velocity becomes $dx/dt = k_A[\text{sugar}][\text{initially active water}] + k_B[\text{sugar}][H^+ \cdot nH_2O]$, where k_A is the velocity constant in pure water and k_B the added constant due to catalysis. As the first term is negligibly small, we find $dx/dt = k_B[\text{sugar}][H^+ \cdot nH_2O]$. The reaction velocity is thus determined by the rate of meeting of active sugar molecules (which are probably hydrated) and hydrated hydrogen ions whose water of hydration is in a more reactive condition. No water concentration term appears in the equation, for the rest of the water acts simply as the solvent medium. Both the above factors, however, vary with change in water concentration, so that the above relation inherently contains the water factor.

It is not improbable that the water itself owes its initial hydrolytic activity to the hydrogen ion due to its self-ionization, and that the active water molecules are in all cases those associated with this ion. If this be so, then the accelerating action of acids is quite normal and by no means mysterious. The extremely low velocity of inversion in pure water is in accord with such an explanation, as is the work of Wijs[10] on the hydrolysis of methyl acetate, where it is shown that the velocity of hydrolysis by water alone is given by $k_1[OH^-] + k_2[H^+]$; as this indicates that even at such low ionic concentrations the "catalytic" effect far outweighs any other, it seems reasonable to conclude that the former is the only real hydrolytic effect. If this be so, and the active water molecules are always (and only) those that are associated with the hydrogen ions, then the velocity of sugar inversion at once becomes $dx/dt = k[\text{sugar}][H^+ \cdot nH_2O]$ for *all* inversions.

Although this conception of activated molecules might be expected to cause a displacement in the equilibrium point, such displacement is not necessarily large; for while the active hydrolyzing agent is the hydrate $H^+ \cdot nH_2O$, where n has a value as yet indefinite, the active agent in the back reaction is the hydrate $H^+ \cdot (n-1)H_2O$. This is at once evident from the equilibrium, sucrose + $H^+ \cdot nH_2O \rightleftarrows$ glucose + fructose + $H^+ \cdot (n-1)H_2O$. In the aqueous system there must be an equilibrium

[10] Wijs, *Z. physik. Chem.*, 12, 514 (1893).

between the hydrates, $H^+ \cdot nH_2O \rightleftarrows H^+ \cdot (n-1)H_2O$, which is definite for each acid system and instantaneous. On the addition of further acid, the hydrate equilibrium is displaced, probably to the right, and therefore the inversion equilibrium displaced to the left. In dilute acid solutions, where water is in large excess, such displacements would be a minimum; but in stronger acid solutions they may appreciably affect the hydrolytic equilibrium. The weight of experimental evidence is very much in favor of such a shift in the equilibrium in the presence of acids. As far back as 1890, Wehl[11] showed that inversion proceeds further with less acid than with excess, and Fischer[12] prepared isomaltose by the action of hydrochloric acid in excess on glucose. Worley[1] using weak solutions of esters, and Jones and Lapworth[13] using strong solutions, or mixtures, show that the degree of hydrolysis decreases with increase in acid concentration. These and numerous other conclusions are in entire agreement with the foregoing. By current theories it is believed that active molecules possess a certain minimum critical energy, or a certain critical increment above the average. Such molecules are more reactive or less stable than the average, and the possible nature of the activation of a water molecule by a hydrogen ion is as follows. It has been suggested by Latimer and Rodebush[14] that water molecules associate through their auxiliary fields to form coördination compounds, such as $H:\ddot{O}:\begin{matrix}\ddot{H}\\ \vert\end{matrix}\begin{matrix}H:\ddot{O}:\\ \ddot{H}\end{matrix}$. In the presence of acids we should expect an even more ready formation of the compounds, $H:\ddot{O}:\begin{matrix}\ddot{H}\\ \vert\end{matrix}H^+$, $H:\ddot{O}:\begin{matrix}\ddot{H}\\ \vert\end{matrix}H^+\begin{matrix}\vert\\ \ddot{H}\end{matrix}:\ddot{O}:H$, etc.

The formation of such hydrates results in certain changes in electronic energy levels, as is the case with all compound formation, so that such a hydrate behaves, for the period of its existence, as a positively charged unit, with a definite energy content. Now it has often been advanced (see, for example, Ghosh)[15] as an explanation of the abnormal mobility of the hydrogen ion (and also the hydroxyl ion), that the union between hydrogen ion and water may be of such an intimate nature that on decomposition one of the hydrogen atoms of water becomes the hydrogen ion, as is represented below

$$H:\ddot{O}:\begin{matrix}\ddot{H}\end{matrix} + H^+ \longrightarrow \left[H:\ddot{O}:H\right]^+ \longrightarrow H^+ + :\ddot{O}:H$$

[11] Wehl, *Ber.*, **23**, 2048 (1890).

[12] Fischer, *Ber.*, **23**, 3687 (1890).

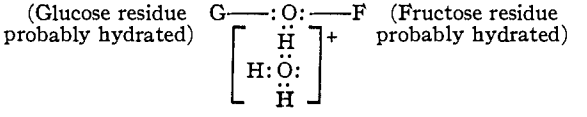
[13] Jones and Lapworth, *J. Chem. Soc.*, 99, 1427 (1911).

[14] Latimer and Rodebush, THIS JOURNAL, **42**, 1431 (1920).

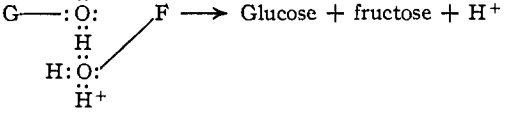
[15] Ghosh, *J. Chem. Soc.*, 113, 790 (1918).

It would thus appear that in the hydrate, the hydrogen nuclei of the original water molecule may be displaced from their normal positions, and thus be more easily removed or, in other words, the water molecule becomes more easily broken and is therefore more reactive.

To be effective, such an activated water molecule would have to meet a sugar molecule under favorable conditions as regards position, energy, content of sugar, and so on. For instance, the meeting would have to take place at the linking oxygen atom between the glucose and fructose fractions. The action would then be represented



When all conditions are favorable, a hydrogen nucleus is transferred to the sucrose oxygen, and we have



Reverting to the equation $dx/dt = k[\text{sugar}][H^+ \cdot nH_2O]$ which, it is claimed, is the complete measure of the inversion velocity, one finds it usual to represent the sugar concentration as moles of sugar per liter of solution. This is correct for very dilute solutions, but for ordinary and for stronger solutions it has been shown by Morse and Frazer,[16] Caldwell[2] and Rosanoff[17] that the active mass of the sugar is more correctly written as proportional to the osmotic pressure, and that [sugar] should then be expressed as moles of sugar per liter of water. During an inversion the water content slightly decreases, and assuming for the moment that the $[H^+ \cdot nH_2O]$ remains constant, then the velocity becomes $dx/dt = k'(A - x)/(B - x)$, where A and B represent initial number of sucrose and water molecules, respectively. Here the water term $(B - x)$ which is usually placed in the numerator, actually appears in the denominator. That this is its correct position is evident from the well-known fact, that if water be replaced by glucose, lactose, alcohol, or other non-electrolyte, keeping total sucrose constant, the inversion velocity increases, often quite remarkably.[18]

[16] Morse and Frazer, *Am. Chem. J.*, **34**, 1 (1905).

[17] Rosanoff, THIS JOURNAL, **35**, 248 (1913).

[18] It should be noticed that this rearrangement does not require any serious alteration in the equilibrium constant, as might be expected at first sight. For, writing the forward velocity

$$\frac{dx}{dt} = k' \frac{\text{mols. of sugar}}{\text{mols. of water}} \cdot [H^+ \cdot nH_2O],$$

On integrating the above equation and re-arranging, we get $k' = 1/t \cdot x + (B - A) \times 2.303\ k_{uni}$. If the coefficients from the previous tables are recalculated according to this formula, it is found that the gradual increases set out are diminished by approximately 1%.

As regards the factor $[H^+ \cdot nH_2O]$, which appears in the true velocity equation, we can only assume with our present knowledge that it is proportional to the thermodynamic concentration or the activity coefficient of the hydrogen ion. During an inversion, owing to a decrease in water content and to other environmental changes, the hydrogen-ion activity shows a slight change. Fales and Morrell[3] and Jones and Lewis[4] found no evidence of this change, but Taylor and Bomford[19] found a 7% increase in the presence of sodium chloride. Before the appearance of the latter paper, the author had taken several careful observations of the hydrogen-ion activities of two samples of each of the various solutions used in this work, one before and the other after inversion. A definite but very slight increase in activity was always shown by the inverted solution. For example, the 0.099 *N* hydrochloric acid + 17.1% of sucrose at 35° showed an average change in e.m.f. (with a normal calomel electrode) from 0.3381 before inversion to 0.3375 after inversion, and a corresponding increase in hydrogen-ion activity from 0.112 to 0.114. Stronger acid solutions showed a slightly greater increase, but as the greatest difference shown was 0.0009 of a volt, and the experimental error was of the order 0.0001 volt, the author did not care to draw any quantitative conclusions. The measurements however definitely indicate that during inversion the hydrogen-ion activity increases by from 1 to 3%, and does not appear to exceed 3% even with the stronger acid solutions.

For small changes in activity we are justified in writing velocity proportional to hydrogen-ion activity, whence the true velocity equation for

we must write the back velocity

$$\frac{dy}{dt} = k'' \frac{\text{mols. of glucose}}{\text{mols. of water}} \times \frac{\text{mols. of fructose}}{\text{mols. of water}} [H^+ \cdot (n-1)H_2O].$$

At equilibrium the mass constant is therefore given by

$$K = \frac{k''}{k'} = \frac{(\text{mols. of sugar})\ (\text{mols. of water})}{(\text{mols. of glucose})\ (\text{mols. of fructose})} \times \frac{[H^+ \cdot nH_2O]}{[H^+ \cdot (n-1)H_2O]}.$$

As has been pointed out the last fraction determines the constancy of the equilibrium constant in the presence of acids, and may itself be taken as having a constant value in dilute acid systems; hence we have

$$K' = \frac{(\text{mols. of sugar})\ (\text{mols. of water})}{(\text{mols. of glucose})\ (\text{mols. of fructose})}.$$

A similar mass constant is obtained for any ordinary hydrolysis, and the successful application of this equation to the hydrolysis of ester-water mixtures is classical. But it is very evident that the form of the constant does not at all necessitate that the numerator should be a measure of the forward velocity and the denominator of the back velocity.

[19] Taylor and Bomford, *J. Chem. Soc.*, **125**, 2016 (1924).

any particular inversion becomes $dx/dt = K$ (mols. of sucrose $\times$ mols. of water) $\times$ H^+ activity.

Both the removal of water during inversion and the corresponding increase in hydrogen-ion activity act in the same direction, causing the unimolecular coefficient to increase during the inversion. Possibly other changes play some part, but the two mentioned above are the only changes that can be estimated at present; and as their total effect is of the same order as the increases set out, it is reasonable to conclude that these changes are the chief causes of the steady increase in the unimolecular coefficient.

In order to determine whether any defects peculiar to the polarimetric method (such as changes of specific rotation during inversion) influenced the value of the coefficient, an attempt was made to follow the inversion by a freezing-point method. As the refined freezing-point methods of Adams[20] were not applicable, the ordinary method with the usual precautions as to stirring, etc., was used. It has been shown that mutarotation changes have no effect on freezing-point readings, and that therefore sucrose concentration at time t_1 can be taken as proportional to $\Delta t_1 - \Delta t_\infty$. A high degree of accuracy was aimed at, but the percentage experimental error was always very much greater than that which prevailed when the polarimetric method was used; and although an increasing coefficient was always indicated, the error quite overshadowed the order of the increase. Both methods gave approximately the same average coefficients. Some of the figures obtained by this method for the 17.1% of sucrose and 0.099 N hydrochloric acid are set out below, and compared with those obtained by the usual method.

$k \times 10^5$ (polarim.)..	158	157	158	159	160	160	161	161	162	162
$k \times 10^5$ (f. pt.).....	(174)	151	159	154	152	159	164	161	158	166

It is well known that in the presence of invertase the inversion coefficient shows a very marked increase during inversion,[21] and it is, therefore, concluded that the action is not unimolecular. The argument above, which satisfactorily accounts for the smaller increases shown by acids, cannot explain these larger increases, and the two actions (enzyme and acid catalysis) appear to be dissimilar.

Summary

The unimolecular inversion coefficient has been very carefully determined by methods in which the zero time readings are experimentally obtained.

The coefficients show a steady increase during inversion, up to about 4% with stronger acids (0.9 N hydrochloric acid).

The hydrogen-ion activity during inversion shows an increase of from 1 to 3% according to the strength of the acid.

[20] Adams, THIS JOURNAL, **37**, 481 (1915).

[21] Nelson and Vosburgh, *ibid.*, **39**, 790 (1917).

The use of the bimolecular equation, velocity = k[sugar][water] is shown to be unsound, and it is shown that the inversion velocity is best expressed by the equation, $dx/dt = k$ (sucrose molecules per molecule of water) (H^+ activity), for any particular inversion.

The decrease in water content and the increase in hydrogen-ion activity during inversion, are sufficient to explain the steady increase in the coefficients.

SOUTH AUSTRALIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY AND ENTROPY OF LEAD BROMIDE AND BROMINE

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The purpose of this investigation was to obtain a more accurate experimental value for the entropy of bromine. At the time it was undertaken the only existing data were determinations of the average specific heat[1] of solid bromine from the boiling point of liquid hydrogen to that of liquid air, and from the latter point to 190°K. Since that time Eucken's coworkers[2] have investigated the specific heat of bromine; a discussion of their results will be included.

The entropy of bromine was determined by two independent methods.

1. The specific heat of solid bromine from 14°K. to its melting point was measured and the entropy calculated from the relation,

$$S = \int_0^T \frac{C_p}{T}\,dT = \int_0^T C_p\,d\,ln\,T$$

This expression was integrated by plotting C_p against $ln\ T$ and taking the area under the curve. Existing values for the entropy of fusion and the specific heat of liquid bromine were used to obtain the entropy at 298°K.

2. In a similar manner the entropy of lead bromide was determined, and the entropy of bromine calculated using this value, the entropy of lead and the ΔS for the reaction, $Pb + Br_2 = PbBr_2$, since we have, from the third law of thermodynamics, $S_{Pb} + S_{Br_2} = S_{PbBr_2} + \Delta S$. ΔS was determined from the experimental values for the change in free energy ΔF and the change in heat content, ΔH, of the reaction employing the relation, $T\Delta S = \Delta H - \Delta F$.

Since both the substances investigated retain a large portion of their

[1] (a) Dewar, *Proc. Roy. Soc.* (London), **76**, 325 (1905). (b) Barschall, *Z. Elektrochem.*, 17, 341 (1911). (c) Koref, *Ann. Physik*, **36**, 49 (1911). (d) Estreicher and Staniewski, *Krakauer Anzeiger*, 1912, p. 834.

[2] Suhrmann and Lüde, *Z. Physik*, **29**, 71 (1924).