THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE INVERSION OF SUGAR BY SALTS.

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Received September 20, 1898.

INTRODUCTION.

THE inversion of cane-sugar by salts has been studied by Walker and Aston[1], who determined the affinity of weak organic bases by ascertaining the extent to which their hydrochlorides are decomposed by water from the speed with which solutions of these salts invert sugar. They also measured the speed with which sugar is inverted by the nitrates of lead, cadmium, aluminum, zinc, and hydrogen. The work on the inorganic salts were conducted at 80° C., the sugar solution used being about ten per cent. The results are given in Table I, the coefficient C indicating the speed of the inversion.

TABLE. I.

Nitrates.	C.	Hydrolysis per cent. in equiv. $\frac{1}{2}$ solution.
Cadmium ($\frac{n}{2}$)	0.000154	0.014
Zinc ($\frac{n}{2}$)	0.000207	0.019
Lead ($\frac{n}{2}$)	0.001590	0.015
Aluminum ($\frac{n}{2}$)	0.007700	0.700
Hydrogen ($\frac{n}{1000}$)	0.002250	....

As the speed of inversion is proportional to the concentration of the hydrogen ions present (the latter being formed by the hydrolysis of the salt) the coefficients represent roughly the relative strengths of the respective bases. In the last column of

J. Chem. Soc., London, 67, 576.

the table are the percentages of hydrolysis in equivalent half-normal solutions as deduced by comparing the values of C for the salts with that of the millinormal nitric acid solution.

J. H. Long[1] made a more extensive investigation of the inversion of sugar by inorganic salts. He pointed out that salts of the heavy metals in general have the power of inverting sugar solutions, and in some cases very rapidly, especially at an elevated temperature. He also correctly indicated that the cause of the inversion by these salts is to be found in their condition of partial hydrolysis by the solvent. Long gave special prominence to the work with ferrous salts ; in addition to these, however, he investigated the chlorides of manganese, cadmium, mercury, and lead, the sulphates of manganese, zinc, and aluminum (potassium alum), and the nitrate of lead. The coefficients expressing the rate of inversion were calculated and the percentages of hydrolyzed salt were deduced by comparing these coefficients with that obtained by employing a millinormal hydrochloric acid solution under like conditions. The temperature at which Long's systematic investigations were performed is $85°$, and the sugar solution used was of such strength that fifty grams were contained in 250 cc.

In the investigations of Walker and Aston and also in those of Long the polariscope was used exclusively to follow the progress of the inversion. This is no doubt the simplest and most accurate method to use whenever it is applicable. It is evident, however, that the polariscope cannot be used in working with colored solutions and that the accuracy of measurement with this instrument is greatly impaired when the solutions are not perfectly clear. Long cites several instances where, after prolonged heating, the solutions became somewhat colored or turbid, making their polarization difficult.

The objects of this investigation are: (1) to find a method by means of which the speed of inversion of sugar by colored salts can be determined, and (2) to compare the basicity of the metals as ascertained by the method of sugar inversion with their so-called solution tensions, as found by the measurement of the electromotive forces of galvanic chains.

The inversion of sugar is expressed by the equation :

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$
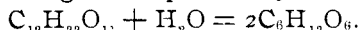
1 This Journal, 18, 120 and 693.

If the solution is not too concentrated, the change in the number of molecules of water may practically be neglected. From the equation it appears that during the process of inversion each molecule of cane-sugar is converted into two molecules. Now since the osmotic pressure exerted by a dissolved substance is proportional to the number of its molecules, it is clear that when inversion is complete the dissolved sugar will exert just double the osmotic pressure that it did in form of cane-sugar. Furthermore, by measuring the osmotic pressure from time to time during the progress of the inversion, the rate of the latter may be determined. As the methods that are known at present for the direct measurement of the osmotic pressure could not be used advantageously, it was decided to measure some physical property that is proportional to the osmotic pressure. The lowering of the freezing-point and the elevation of the boiling-point suggested themselves. Trevor and Kortright[1] have shown that by noting from time to time the boiling-point of a sugar solution to which a small quantity of acid has been added, the speed of the inversion can be determined. A few preliminary tests indicated that the boiling-point method is not well suited for studying the inversion of sugar by salts of the heavy metals, for by boiling the solution some of these salts suffer considerable reduction. The freezing-point method was consequently chosen, although less convenient of execution. Before this method was applied in the work with colored salts it was definitely ascertained that it would yield reliable results. This was done by following the progress of the inversion of several colorless solutions by both the polariscope and cryoscopic methods.

METHOD OF EXPERIMENTATION.

The following is an outline of the method of experimentation. The desired quantities of sugar and salt were weighed out and each was dissolved in a small quantity of water, generally with the aid of heat. These solutions were then thoroughly cooled and finally mixed in a graduated flask, cold water being added to fill the latter to the mark. It was found that at room temperature the inversion takes place very slowly; nevertheless no time was lost unnecessarily in transferring the solution to test-tubes, generally eight to ten in number, which were then tightly

[1] *Ztschr. phys. Chem.*, 14, 149.

stoppered with rubber stoppers or closed by fusing the ends. These tubes were then kept at a higher temperature in a thermostat, the time of their introduction into the latter was noted, and then from time to time one was taken out and quickly immersed in a bath of melting ice to cool it rapidly and thus check the reaction. Its contents were then examined with the polariscope or freezing-point apparatus or both. A few tests showed that at 0° the inversion in the solutions used was so slow that no change could be detected for hours. It was consequently not necessary to investigate each tube at once, but several could thus be collected and their contents tested in rapid succession. While this is of no particular importance in working with the polariscope, with which determinations are so easily made, it is very advantageous in employing the freezing-point method, as it admits of making the determinations more rapidly and with a greater degree of accuracy relatively. It consumes time to prepare the freezing mixture properly and to find the freezing-point of pure water on the thermometer scale. The latter operation of course must be performed each time a series of observations is made, as the reading of a Beckmann's thermometer for a fixed temperature varies from time to time, partly because changes in the barometric pressure affect the bulb, and partly because minute amounts of mercury escape from the mercury that is attached to the thread in the upper chamber to the lower part of that chamber. The mercury can often be seen in form of very fine drops condensed on the sides of the upper chamber after the thermometer has stood for a number of hours.

Crystallized cutloaf sugar of a high degree of purity was used in all the experiments. It was dried, pulverized, and thoroughly mixed. For each series of experiments 84.93 grams were weighed out and dissolved in a small amount of water in a 500 cc. flask that was carefully graduated. The cold solution containing one-fourth of a gram equivalent of the salt to be investigated was then added. The solutions were mixed and finally made up to exactly 500 cc. Thus the resulting solution was half-normal with respect to each, the sugar and the salt.[1] All the salts used were of the C. P. variety of standard makes. They were recrystallized several times to free them from any

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[1] In a few cases less concentrated solutions had to be used on account of the slight solubility of the salt.

excess of acid they might contain.   Thirty cc. of the solution
last named were introduced into each of the test-tubes, which
were twenty cm. long.   These were then quickly sealed in a hot
pointed flame.   The liquid did not change its temperature
materially during this operation.   After the supply of twenty
cm. test-tubes was exhausted, eighteen cm. ones were used ;
these could not be sealed as readily without heating the solution
somewhat, so they were tightly stoppered with rubber stoppers.

   The bath in which the tubes were placed is shown in Fig. 1.
The cylindrical outer vessel A is thirty cm. high and thirty cm.
in diameter.   It is fitted with a similarly shaped inner vessel B,
so that the distance between the sides of the two vessels is about
four cm. and that between the bottoms eight cm.   This part of
the apparatus is made of tin.   A spiral return condenser of glass
is fitted to A as indicated.   A bent glass tube D serves as a
gauge to indicate the height of the liquid in A. B contains
water in which the test-tubes are immersed.   It has a wooden
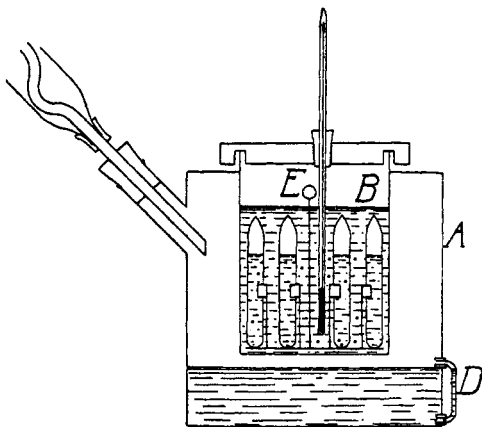

Fig. 1.

cover through which a thermometer is inserted.   The test-tubes
are held in position by wires as indicated.   These wires are sol-
dered on a disk of heavy tin provided further with a stout cen-
tral wire E, by means of which all the tubes together with the
supporting disk can be placed into the apparatus at the same
time.

   At first it was proposed to perform the experiments at about

80° C. ; but a preliminary test on copper sulphate, using alcohol in the vessel A, showed that this temperature was too high inasmuch as partial reduction of the salt to the cuprous condition and even to metallic copper occurred. After still further tests, the temperature of boiling acetone, 55.5° C. was finally chosen.

The acetone was placed in A (Fig. 1), and kept boiling by a small flame. Water of the temperature of about 65° was poured into B to such a height that when the tubes were finally introduced they were sufficiently immersed. By introducing the cold tubes into this bath of a little higher temperature than finally desired, the temperature of the whole soon became 55.5°. This did not require more than three or four minutes. The tubes were ordinary test-tubes. They were cleaned with concen· trated hydrochloric acid, washed with water, and finally thoroughly steamed according to Ostwald's[1] suggestion. A sample of the solution was always retained for making the initial determination. The time when the tubes were introduced into the bath was taken as the starting-point and placed equal to zero. This, of course, was not quite correct, as the temperature was not instantly adjusted. The error introduced was not great, however; it would show itself mainly in the first coefficient found, which would be a little too low.

The polariscope used was a triple field instrument manufactured by Schmidt & Haensch. It was of a pattern devised by Landolt.[2] All the observations were made in a twenty cm. tube at 20° C., the liquids being kept at this temperature during the time of the determination by running water of 20° C. through the jacket surrounding the observation tube.

The freezing-point apparatus was essentially of the form of that constructed by Beckmann,[3] but its dimensions were larger. The tube containing the solution and the differential thermometer had no side neck ; it was about twenty-two cm. long, and nearly five cm. in diameter. The thermometer and the stirrer[4] passed through the cork as usual, but the latter was further provided with another opening through which the freezing could be

[1] Hand· u. Hilfsbuch, p. 295.

[2] *Ber. d. chem. Ges.*, 28, 3102.

[3] Compare Ostwald's Hand· u. Hilfsbuch, p. 216.

[4] The stirrer had the usual shape, but was made entirely of glass. With an appa· ratus of the above dimensions this works very well and is much cheaper than the usual stirrer with the heavy platinum loop.

inaugurated by "vaccinating" the slightly overcooled liquid with a bit of ice. The air jacket was made of heavy tin; it was soldered to the cover of the jar, and the whole was then heavily coated with asphaltum to prevent rusting. The jar containing the freezing-mixture was an ordinary large size gravity battery jar. A Beckmann's thermometer was used. It was graduated to hundredths and the thousandths could be judged by means of a lens. Generally thirty cc. of the solution were tested. The temperature of the bath was so regulated that it was only a few tenths of a degree lower than the freezing-point of the liquid tested.

The calculation of the coefficient C expressing the speed of the reaction was made according to the well-known formula $C = \frac{1}{t} \log_{10} \frac{A}{A-x}$, in which A represents the amount of cane-sugar present at the beginning, and x the amount inverted during the time t. In working with the polariscope, A is measured by the total change in rotation observed from the beginning to the end of the reaction, and x is measured by the change in rotation during the time t. In applying the freezing-point method, A is measured by the total increase in the lowering of the freezing-point of the solution from the beginning to the end of the reaction, and x is measured by the increase in the lowering during the time t. In thus applying these methods, it is assumed that the influence of the salt present in solution on the rotation and freezing-points respectively is constant throughout the reaction. Though the action of the salt on the cane-sugar, and the invert sugar is probably slight, some interaction does seem to take place as Long[1] has already pointed out.

A half-normal solution of cane-sugar gave as an average of four series of independent experiments a lowering of the freezing-point of 1.114°. A solution that was half-normal with respect to cane-sugar, and centinormal with respect to hydrochloric acid gave a lowering of 2.248° after complete inversion had taken place. The sugar after inversion would theoretically cause the lowering to be 2.228°, consequently the difference, 0.020°, is the lowering caused by the acid. Theoretically the hydrochloric acid ought to give the lowering 0.019°; but since in centinormal

[1] This Journal, 18, 716.

solution the dissociation is nearly complete, this figure would become 0.038°. It is clear then that the above result, 2.248°, is a little too low, theoretically considered ; it was thought to be sufficient, however, to warrant adopting the figure 1.114° in future calculations as the increase of lowering of the freezing-point caused when the inversion is complete.

It is somewhat difficult at times to obtain the exact rotation of the plane of polarization of a sugar solution after complete inversion because of changes produced by prolonged heating.[1] For this reason, the calculated value found by reckoning 0.315^{02} negative rotation for every degree of initial positive rotation was used as the end-point of the reaction except when the observed value exceeded it. Thus, the most probable initial angle for the twenty cm. tube was found to be 22.60°; the end-point would consequently be 22.60° × —0.315 or —7.12°.

<div align="center">RESULTS.</div>

The experimental results will now follow in detail.

<div align="center">TABLE II.</div>

<div align="center">*Hydrochloric Acid.*</div>

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{100}$ g. mol. HCl. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.62°	....	.....
1.0	16.58	6.04	0.0983
2.0	9.92	12.70	0.1205
2.5	7.68	14.94	0.1208
3.0	5.94	16.68	0.1186
4.0	2.54	20.08	0 1215
4.5	1.42	21.20	0.1198
7.0	—2.40	25.02	0.1130
17.5	—6.90	29.52	0.1142
26.5	—7.20	29.82	.....
			0.1158

<div align="center">TABLE III.</div>

<div align="center">*Hydrochloric Acid.*</div>

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{100}$ g. mol. HCl. (Freezing-point.)

Time. hours.	Lowering.	Change.	C.
0.0	1.175	....	.....
1.0	1.393	0.218	0.0977
2.0	1.635	0.460	0.1217
2.5	1.705	0.530	0.1185
3.0	1.809	0.634	0.1296
4.0	1.912	0.737	0.1263
4.5	1.954	0.779	0.1252
7.0	2.105	0.930	0.1254
17.5	2.230	1.055	0.1028
26.5	2.247	1.072	.....

[1] Compare Long : This Journal. 18, 697.
[2] Compare Raymond and Sulc : *Ztschr. phys. Chem.*, 21, 488.

0.1147

In Table II, $-7.2°$ was taken as the end-point and in Table III, $2.247°$, for the change that had taken place in nine hours was but $0.3°$ on the polariscope scale and $0.017°$ on that of the thermometer. Considering the experimental difficulties encountered in the work the agreement of the values of C in Table III, with those in Table II, must be considered sufficient. It has been established therefore that the freezing-point method can be successfully used to determine the rate of inversion of sugar. As the amount of hydrochloric acid present was small as compared with the amount of sugar, this was an especially favorable case in which to test the reliability of the cryoscopic method in following the progress of the reaction. Further comparisons between the two methods in which salts were used to invert the sugar will be given below.

ALUMINUM SALTS.

The aluminum salts investigated are potassium alum, aluminum sulphate and chloride. The alum solution was weaker than the usual strength on account of the low solubility of the salt in the cold.

TABLE IV.
Potassium Alum.

In 1000 cc., $\frac{1}{4}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{32}$ g. mol. $K_2Al_2(SO_4)_4$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	$11.23°$	...	......
1.0	10.48	$0.75°$	$0.02260°$
2.0	9.29	1.94	0.03053
4.0	8.12	3.11	0.02551
6.5	6.35	4.88	0.02675
8.0	5.54	5.69	0.02637
41.25	−2.54	13.77	0.02815
83.5	−3.16	14.39	0.02525
∞	−3.56	14.79	......
			0.02645

TABLE V.
Potassium Alum.

In 1000 cc., $\frac{1}{4}$ mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{32}$ g. mol. $K_2Al_2(SO_4)_4$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0.0	$0.855°$	....	......
1.0	0.859(?)	$0.004°(?)$	$0.00313°(?)$
2.0	0.889	0.034	0.01368
4.0	0.925	0.070	0.01458
6.5	0.980	0.125	0.01697
8.0	1.009	0.144	0.01757
41.25	1.278	0.423	0.01502
83.5	1.327	0.472	0.01002
∞	1.412	0.557	......
			0.01464

Tables IV and V show that alum inverts sugar rapidly.[1]   The values of C in Table V, are only about half as large as those in Table IV.   It seems that a change decreasing the number of molecules in the solution must be going on in this case as time elapses; the matter was not studied further, but it deserves investigation.   The value of C in Table IV is the more reliable one.   The inversion in case of the alum solution is caused by the aluminum sulphate present, which is hydrolyzed.   It is a well-known fact that a solution obtained by mixing potassium sulphate and aluminum sulphate in molecular proportions, is the same as an equivalent solution of alum.   Table VI shows that the potassium sulphate is not the cause of the inversion, and Table VII clearly shows that the aluminum sulphate is the active agent.

TABLE VI.

Potassium Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{2}$ g. mol. K_2SO_2.   (Polariscope.)

Time, hours.	Rotation.	Change.
0.0	22.54	...
3.0	22.40	0.14
16.5	22.06	0.46
25.0	22.22	0.32

TABLE VII.

Aluminum Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{12}$ g. mol. $Al_2(SO_4)_3$.   (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.54°	....	......
3.5	16.39	6.15	0.02884
6.0	12.32	10.22	0.03058
8.0	9.91	12.63	0.03012
10.0	7.26	15.28	0.03244
14.0	4.14	18.40	0.03006
21.0	−0.26	22.80	0.03028
24.0	−1.64	24.18	0.03055
29.0	−3.10	25.64	0.02993
37.0	−4.82	27.36	0.03001
55.0	−6.44	29.98	0.02980
∞	−7.12	29.66	......
			0.03026

[1] The same was found by Long : *l. c.*

Table VII shows that the aluminum sulphate solution inverts very rapidly, a little over one-fourth as rapidly as does centi-normal hydrochloric acid (Tables II and III). As the solution used in Table VII is not equivalent to that in Table IV, the constants are not directly comparable. We should expect alum to invert less rapidly, however, than an equivalent amount of aluminum sulphate, for the presence of the potassium sulphate tends to decrease the number of hydrogen ions in the solution.[1]

TABLE VIII.

Aluminum Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{6}$ g. mol. $AlCl_3$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0	22.47°	....	......
6	6.92	15.55	0.0539
18	—1.98	24.45	0.0366
25	—4.44	26.91	0.0417
45	—6.45	28.92	0.0365
∞	—7.13	29.59	......
			———
			0.0422

The chloride was of Schuchardt's make. It was recrystallized three times. A comparison of Tables VII and VIII shows that the chloride inverts much faster than the sulphate. This is what one would be inclined to expect from the strong ionizing tendency of chlorine. (This point will come up again below.) Long found that ferrous chloride inverts much more rapidly than ferrous sulphate.

MANGANESE SALTS.

TABLE IX.

Manganous Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $MnSO_4$. (Polariscope.)

Time, hours.	Rotation.
0	21.64
5	22.12
10	22.20
15	22.34
20	22.10
25	22.50
35	22.14

[1] Long found that ferrous sulphate inverts faster than ferrous ammonium sulphate which illustrates the same point.

Table IX shows that manganous sulphate does not invert sugar appreciably at 55.5° C.   The readings obtained vary irregularly within the limits of experimental error.   At higher temperatures this salt does invert sugar, but of course very slowly (compare Long : *l. c.*).

TABLE X.

Manganous Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $MnCl_2$.   (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.79°	. . .	. . . . . .
5.5	22.72	0.07	0.000185
12.0	22.65	0.14	0.000170
24.0	22.54	0.25	0.000152
36.0	22.45	0.34	0.000138
48.0	22.23	0.56	0.000171
300 (about)	21.92	0.87	. . . . . .
∞	—7.12	29.91	. . . . . .
			0.000163

Table X shows that manganous chloride does invert slightly. Here again we see that the chloride inverts faster than the sulphate.   In working at 80° C., Long also found that manganous chloride inverts much more rapidly than does the sulphate.

ZINC SALTS.

Of the zinc salts only the sulphate was tested.   The specimen was a particularly fine one.   Table XI shows that the inversion caused by this salt at 55.5° is very slight, but little change having taken place in fifty hours.

TABLE XI.

Zinc Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $ZnSO_4$.   (Polariscope.)

Time, hours.	Rotation.
0.0	22.52°
2.0	22.38
6.0	22.38
20.66	22.42
46.0	22.02
50.0	21.96

The same solution heated in a water-bath to 100° C. gave the results in Table XII.

TABLE XII.

Zinc Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $ZnSO_4$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	21.96	....	.....
1.0	18.84	3.12	0.04929
2.0	15.00	6.96	0.05940
3.0	12.22	9.74	0.05904
4.5	3.84	18.12	0.09417
8.16	— 3.50	25.46	0.11089
∞	— 7.12	29.08	......

After three to four hours' heating the solution became colored. An acid odor was also perceptible. After three hours the values of C ran up rapidly. Long also noted an increase in the value of the coefficient at 80° C.

CADMIUM SALTS.

Cadmium sulphate inverts very slowly indeed as both the polariscopic and cryoscopic tests show (Table XIII). The inversion is practically nil.

TABLE XIII.

Cadmium Sulphate.

In 1000 cc., $\frac{1}{2}$ mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CdSO_4$. (Polariscope.)

Time, hours.	Rotation.	Freezing-point. lowering.
0.0	22.23°	1.720°
5	22.49	1.756
10	22.72	1.745
15	22.58	1.747
19	22.54	1.754
24	22.75	1.758
34	22.65	1.755
44	22.72	1.754

Cadmium chloride was tested and gave similar results, as Table 14 shows. This salt was particularly pure.

TABLE XIV.

Cadmium Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation.
0.0	22.30°
2.0	22.54
3.0	22.62
5.0	22.62
8.0	22.60
18.0	22.28
20.0	22.46
46.25	....

Another fine-looking sample of cadmium chloride of Schuchardt's manufacture was tested by both the polariscope and freezing-point methods. This salt, which was not recrystallized, yielded the results in Tables XV and XVI.

TABLE XV.

Cadmium Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol $CdCl_2$.   (Polariscope.)

Time. hours.	Rotation.	Change.	C.
0.0	21.63°	....	......
3	7.57(?)	13.06	0.08375
16	5.94	15.69	0.05430
10	—0.28	21.91	0.05793
15	—3.82	25.45	0.05612
20	—5.71	27.34	0.05474
25	—6.90	28.53	0.05576
35	—7.70	29.33	0.05346
∞	....	29.73	......

TABLE XVI.

Cadmium Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CdCl_2$.   (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0	2.872°	....	......
3	2.176(?)	....	......
6	3.584	0.712	0.07389
10	3.700	0.828	0.05916
15	3.836	0.964	0.05822
20	3.919	1.047	0.06134
25	3.960	1.098	0.07480
35	3.977	1.105	0.08390
∞	3.986	1.114	......

The values of C in Table XVI are somewhat higher and more irregular than those of Table XV. This is to be ascribed to the difficulty in working with such strong solutions by the freezing-point method. The values of C in both tables seemed abnormally high, however, and consequently the salt was recrystallized twice and then tested again, this time with the polariscope only. Table XVII gives the results found.

TABLE XVII.

Cadmium Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C
0	22.60°	....	......
4	22.12	0.48	0.00177
20	20.85	1.75	0.00132
30	20.28	2.32	0.00121
45	19.61	2.99	0.00102
70	18.75	3.85	0.00086
100	17.88	4.72	0.00075
∞	—7.13	29.73	......

The values of C in Table XVII continually decrease. They are much smaller than those in Tables XV and XVI, which shows that recrystallization further purified the salt by removing free acid that probably adhered to it. Long found a relatively very high coefficient for this salt at 80° C. He states that the salt he used was recrystallized several times, and was free from uncombined acid. As the above work shows that pure cadmium chloride inverts exceedingly slowly at 55.5° C., the inference must be drawn that the rate of inversion of sugar by this salt increases rapidly as the temperature rises. To test this inference, the same salt as was used to obtain the results in Table XIV was investigated at 100° C. Table XVIII gives the results obtained, which show that the inversion does increase enormously with the temperature.

TABLE XVIII.

Cadmium Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{2}$ g. mol. $CdCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0.0	22.54°	....	......
1.0	11.16	11.38	0.21011
1.5	7.48	15.06	0.20511
2.0	3.82	18.72	0.21645
2.5	1.30	21.24	0.21859
3.0	—0.46	23.00	0.21606
4.5	—4.80	27.34	0.24554
7.0	—6.42	28.96	0.23158
∞	—7.13	29.67	......

| | | | 0.22049 |

NICKEL SALTS.

Only one salt of nickel, the sulphate, was tested. The salt was a very pure specimen; it was recrystallized several times to free it from any excess of acid. The results in Table XIX show that the salt inverts slowly. The reaction progresses very slowly after about ten hours.

TABLE XIX.
Nickel Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $NiSO_4$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0	1.713°	...	......
1	1.728	0.015	0.00589
2.5	1.731	0.018	0.00283
4.5	1.740	0.027	0.00237
9.75	1.772	0.059	0.00243
38.5	1.765	0.052	0.00054
∞	2.827	1.114	......

COPPER SALTS.

The rate of inversion by both the sulphate and chloride of copper was determined by means of the freezing-point method. Both salts were very fine samples. The sulphate was recrystallized three times and the chloride twice. In Table XX, the values of C gradually diminish to the sixteenth hour after which they increase. This increase is due to a reduction which the salt suffers after prolonged heating even at 55.5°. The last tube taken from the bath contained a deposit of metallic copper. This explains the high value of the final coefficient C.

TABLE XX.
Copper Sulphate.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CuSO_4$. (Polariscope.)

Time, hours.	Lowering.	Change.	C.
0	1.690°	....	......
1.25	1.721	0.031	0.00973
3.25	1.744	0.054	0.00661
5.25	1.754	0.064	0.00489
8.25	1.770	0.080	0.00392
12.25	1.795	0.105	0.00351
16.25	1.860	0.170	0.00442
28.75	2.407	0.717	0.15586
∞	2.804	1.114	......

TABLE XXI.

Copper Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{4}$ g. mol. $CuSO_4$. (Freezing-point.)

Time, hours.	Lowering.	Change.	C.
0	2.446°	....	......
2	2.452	0.006	0.00118
5	2.484	0.038	0.00302
8	2.525	0.079	0.00400
12	2.595	0.149	0.00520
17	2.721	0.275	0.00726
23	2.836	0.390	0.00816
29	2.980	0.534	0.00980
45	3.365	0.919	0.01690
65	3.560	0.114	......
∞	3.560	0.114	......

In Table XXI, the values of C continually increase. This may be due to a reduction of the salt; the solution, however, remained clear from beginning to end. The inversion is complete in sixty-five hours. Comparing this table with the preceding one, it appears that the chloride inverts more slowly than the sulphate for about the first eight hours; after that, the former inverts much more rapidly. The final value of the coefficient in Table XX is, of course, abnormally high for the reason already mentioned.

MERCURY SALTS.

Of these salts only mercuric chloride was studied. The specimen used was a sublimed product. It was not recrystallized from water. Both the polariscopic and cryoscopic methods were used. The solutions became somewhat turbid toward the latter part of the reaction, probably because of a slight reduction of the salt to mercurous chloride, which separated out. This necessitated filtration of the solutions before they could be tested with the polariscope.

TABLE XXII.

Mercuric Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{8}$ g. mol. $HgCl_2$. (Polariscope.)

Time, hours.	Rotation.	Change.	C.
0	22.59°	....	......
0.5	22.38	0.21	0.00616
2	21.88	0.71	0.00525
4	21.20	1.39	0.00520
7	20.19	2.40	0.00522
12	18.57	4.02	0.00526
17	16.11	6.48	0.00628
22	14.12	8.46	0.00661
∞	—7.12	29.71	......

| | | | 0.00572 |

TABLE XXIII.

Mercuric Chloride.

In 1000 cc., $\frac{1}{2}$ g. mol. $C_{12}H_{22}O_{11}$ plus $\frac{1}{8}$ g. mol. $HgCl_2$. (Freezing-point).

Time. Hours.	Lowering.	Change.	C.
0	1.293	....	......
0.5	1.295	0.002	0.00158
2	1.323	0.030	0.00593
4	1.338	0.045	0.00448
7	1.376	0.083	0.00481
12	1.432	0.139	0.00482
17	1.519	0.226	0.00579
22	1.603	0.310	0.00644
32	1.674	0.381	0.00568
∞	2.407	1.114	......
			0.00542

The first coefficient in Table XXIII is very low. The experimental error in this case is, of course, relatively very great, since the increase of the lowering in half an hour is so small. No reliance whatever can be put on this first coefficient, and it has not been taken into consideration in the average. A comparison of the coefficients of Tables XXII and XXIII shows again the usefulness of the cryoscopic method in tracing the process of inversion, in spite of the many difficulties that are met in applying the method.

FERRIC SALTS.

Ferric potassium alum and ferric ammonium alum were tested, but the salts soon suffered reduction. A precipitate formed in these solutions in less than an hour and continued to increase rapidly. The sugar was speedily inverted as a few freezing-point tests showed.

AMMONIUM SALTS.

The effect of ammonium sulphate was studied at 55.5° and at 100°. No appreciable inversion took place at either temperature, although the mixture was kept at 55.5° for about sixty-seven hours. At 100° the solution turned brown after five hours' heating and, as it was being investigated with the polariscope, no more readings were made after that time. Ammonium chloride was tested only at the lower temperature. The readings showed

that after heating for eighty hours a change of only 0.1° in rota·
tion had taken place. Even this might have been error of
observation.

In Table XXIV are collected the coefficients of inversion at
55.5° C. for solutions that are half-normal with respect to sugar
and half-normal (equivalent) with respect to the salt. Those
marked with an asterisk (*) are only rough averages, since the
coefficients in the series are not constant. In the last column is
given the degree of hydrolysis deduced by comparing the speed
of inversion of the salt with that of centinormal hydrochloric
acid under the same conditions. The comparison is only very
rough at best.

TABLE XXIV.

Salt.	C.	Hydrolysis per cent. in equivalent half-normal solution.
Aluminum sulphate	0.03026	0.52
Aluminum chloride	0.0422	0.73
Manganese sulphate	....	....
Manganese chloride	0.00016	0.003
Zinc sulphate	....	....
Cadmium sulphate	....	....
Cadmium chloride	0.0014*	0.024
Nickel sulphate	0.00281*	0.048
Copper sulphate	0.00551*	0.095
Copper chloride	0.00694*	0.12
Mercuric chloride $\left(\frac{n}{4}\right)$	0.00572	0.2
Hydrogen chloride $\left(\frac{n}{100}\right)$	0.1158	....

Theoretical Considerations.

The hydrolytic decomposition of a salt may be expressed by
the general equation:

$$MA + H_2O = MOH + HA,$$
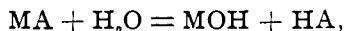
in which M represents the metal and A the acid radical. If the
metal has several valences, correspondingly more molecules of
water enter into the reaction. The more dilute the solution is,
the greater is the extent of the hydrolysis. If for the sake of
simplicity we assume the solution to be so dilute that the elec-
trolytic dissociation of the salt is practically complete, the reac-
tion takes the form:

$$\overset{+}{M}, \overset{-}{A} + H_2O = MOH + \overset{+}{H}, \overset{-}{A}.$$
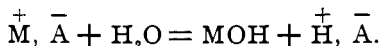
From this it appears that A remains in the ionic condition throughout. There must, of course, be present an equal number of cations in order to preserve the electrical neutrality of the solution. These cations are mainly those of the metal (if the salt is but slightly hydrolyzed), but there are also present hydrogen ions formed as indicated by the equation. The compound MOH, the hydroxide of the metal, is probably held in solution in colloidal form, in which case its molecules are polymerized. In stronger solutions this hydroxide may unite with undissociated molecules of the salt to form a basic compound, which would gradually be broken upon further dilution. In general then at any stage of dilution a solution of a salt of a heavy metal contains (1) a certain number of undissociated molecules of the salt, (2) the anions of the electrolytically dissociated molecules, (3) ions of the metal plus hydrogen ions together chemically equivalent to the anions, (4) molecules of colloidal hydroxide of the metal or of a basic salt equivalent to the hydrogen ions. At each stage of dilution an equilibrium between these various classes of molecules establishes itself.

The acid radical A becoming ionized, forces positive ions to form. If the metal is such that it readily passes into the ionic condition (*e. g.*, the alkalies and alkaline earths), practically the only positive ions in the solution are those of the metal, and the solution has a neutral reaction and does not invert sugar; but if the metal assumes the ionic state less readily (*e. g.*, the heavy metals), the ions of the metal form up to a certain extent only, the rest of the necessary positive ions being supplied by the water, which is decomposed, yielding hydrogen ions and an hydroxyl residue that forms either a colloidal hydroxide of the metal or a basic salt, as already pointed out. It is clear that if the metal readily enters into such colloidal or basic combinations the formation of hydrogen ions will be aided thereby. In a solution of a ferric salt, the deepening of the color on further dilution indicates the presence of the colloidal hydroxide or very basic salt, whereas the acid reaction, the high electrical conductivity, the power to invert sugar, etc., indicate the presence of hydrogen ions. In solutions of other salts, the presence of the colloidal or basic compound is generally not as readily detected, either because it is less abundant or because it is color-

less, and hence is less easily discovered. Colloidal hydroxides of some of the metals are well known, of others such substances are not known; but nearly all of the heavy metals form basic salts with more or less readiness. In most solutions the amount of such colloidal or basic compounds is small, the hydrolysis generally being less than one per cent. and but seldom exceeding three per cent.

For equivalent strengths of solutions the relative extent of the hydrolysis of salts of the same anion is determined by the readiness with which the various metals pass into the ionic state and the ease with which they form basic or colloidal compounds. The tendency that the metals have to pass from the metallic to the ionic condition is expressed by the so-called electrolytic solution tensions of the metals. These have been calculated from the differences of potential existing between the metals and normal solutions of their salts.[1] Since the passing of a metal from the metallic to the ionic state is not identical with the formation of cations from a salt after the latter is once formed, we should not expect to find a simple relation between the solution tensions of the metals and the degree to which their salts are hydrolyzed. Leaving out of consideration the tendency of the metal to enter colloidal or basic combinations, it might be expected, however, that the order in which the salts of the heavy metals of the same anion invert sugar be the same as that in the table of their solution tensions. This is in general found to be the case. According to Neumann[2] the order of the metals in the table of their solution tensions is: Aluminum, manganese, zinc, cadmium, iron, nickel, lead, copper, mercury.[3] Taking the results of Walker and Aston as given above and arranging the metals in the order in which their nitrates invert sugar, beginning with the one causing least inversion, we have: Cadmium, zinc, lead, aluminum. Here aluminum is last instead of first, and the order of cadmium and zinc is the reverse of that in the electrochemical series given above. A consideration of Long's results gives the order: Manganese, zinc, iron, aluminum for the sulfates, and manganese, iron, lead,[4] cadmium for

[1] Compare Neumann: *Ztschr. phys. Chem.*, 14, 223 and 229; also Le Blanc's Elektrochemie, pp. 183 and 185.
[2] *Loc. cit.*
[3] Only those metals whose salts have been investigated as to their sugar-inverting power are here given.
[4] Taken from the nitrate.

the chlorides. According to the present investigation the order for the sulphates is: Nickel, copper, aluminum, the sulphates of manganese, zinc and cadmium having caused practically no inversion at 55.5°. The order for the chlorides is: Manganese, cadmium, copper, mercury, aluminum. While it is apparent that the order is, in general, similar to that in the electro-chemical series, it is clear that aluminum is a striking exception, its salts being the most hydrolyzed of those tested instead of the least. According to Walker and Aston and also according to Long, the position of cadmium is lower in the series than it should be. The present work indicates that the inversion by cadmium chloride is especially influenced by temperature, and as the electrochemical series was determined at room temperature and the inversion was carried out at high temperatures, this might account for the abnormal position of cadmium. It remains to consider the relatively high degree of hydrolysis of aluminum salts. The metal, like iron in the ferric state, forms a colloidal hydroxide. According to the above considerations, this tendency of aluminum would aid the hydrolytic decomposition of its salts. The freezing-point results on alum solutions, indicating that a diminution of the number of molecules in solution occurs, deserves further study in this connection.

The results of Long, and also those contained in the foregoing tables, show that chlorides invert faster than sulphates. The explanation lies in the fact that chlorine has a greater tendency to pass into the ionic state than has SO_4. Hence in the solutions of the chlorides the number of anions is relatively greater and consequently the number of cations is also greater, resulting in an increase of the number of hydrogen ions and consequently more rapid inversion.

Summary.

The main results of this investigation may be summed up briefly as follows :

1. The freezing-point method may be successfully employed in determining the speed of the inversion of sugar.

2. When the metals are arranged in a series according to the speed with which their salts of the same acid radical invert sugar, it appears that the order is similar to that of the electro·

chemical series. Aluminum forms a notable exception. In spite of the high position of this metal in the electrochemical series, its salts invert sugar more rapidly than those of any other metal thus far tested.

3. Chlorides invert sugar more rapidly than sulphates, because the ionizing tendency of chlorine is greater than that of the sulphuric radical.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE CASE SCHOOL OF APPLIED SCIENCE, NO. 32.]

SODIUM ALUMINATE AS A MEANS FOR THE REMOVAL OF LIME AND SUSPENDED MATTER FROM WATER FOR USE IN BOILERS.[1]

BY CHARLES F. MABERY AND EDWIN B. BALTZLEY.

THROUGHOUT the section of country including Northern Pennsylvania, Ohio, and farther west, in districts removed from the lake or the large rivers, the only sources of water in seasons of drought are deep wells. Since the water from these wells contains large quantities of lime salts, there are serious difficulties in the way of procuring water suitable for use in steam boilers, especially in locomotive boilers. Even such water as that from Lake Erie or the rivers, deposit scale to such an extent as to occasion extreme inconvenience. In stationary boilers, the deposition of scale may be avoided at least in part by using some of the many so-called scale preventatives, if the boiler is in charge of an intelligent engineer.

The inconvenience of boiler scale, the additional cost in fuel, the injury to the boiler, and the danger are features of this question familiar to all who have charge of boilers. The large masses of scale withdrawn from boilers in which hard or turbid water is used, are not surprising when the great quantities of water evaporated in boilers under high pressures are taken into consideration.

The wide variations in the composition of boiler scale are de-

[1] The work described in this paper formed the subject of a thesis for the degree of Bachelor of Science.