

## ON THE INVERSION OF SUGAR BY SALTS.

By J. H. LONG.

Received December 5, 1895.

IT is a well known fact that the specific rotation of solutions of cane sugar is decreased by the presence of many neutral salts, even by sodium chloride and other salts of the alkali and earth groups. The amount of this decrease has been measured by several chemists, and recently very carefully by K. Farnsteiner,<sup>1</sup> who has noted the connection between the molecular weights of the salts dissolved with the sugar and the amount of the depression they produced. In a solution containing for each part of sugar three parts of water and 1.0036 parts of sodium chloride the specific rotation dropped from  $66.6^\circ$  to  $62.47^\circ$ . Similar effects were observed in other cases.

The extent of this depression is dependent to some degree on the temperature, but a temporary increase in temperature does not permanently alter the rotation. In illustration, a solution of pure saccharose containing in 100 cc. twenty-five grams of the sugar and ten grams of potassium nitrate gave a specific rotation of  $\alpha_D = 66.22^\circ$  at  $20^\circ$ . After heating one hour, but so as to avoid evaporation or pressure, the rotation was again determined and found to be practically the same. The solution was heated in a small flask closed with a perforated rubber stopper having a capillary glass tube in the perforation. It was possible by this means to heat the liquid to  $100^\circ$  in boiling water without risk of appreciable loss by evaporation.

On the other hand, a solution of sugar and zinc sulphate which gave a specific rotation of  $64.98^\circ$  when fresh, showed, after having been heated forty-five minutes in boiling water, as before, a specific rotation of  $36.84^\circ$ . In this case a decided inversion had taken place, as easily shown by other tests. The behavior of zinc sulphate is similar to that of a large number of other substances. Loewenthal and Lenssen<sup>2</sup> state that zinc sulphate and other neutral salts are without inverting action, but Béchamp, a little later<sup>3</sup> gave a list of these salts which are able to produce a marked inversion. The phenomenon is an inter-

<sup>1</sup> *Ber. d. chem. Ges.*, 23, 3570.

<sup>2</sup> *Jsb. Chem.*, 1863, 120, and Ostwald, *Allg. Chemie*, 2, 811.

<sup>3</sup> *Jsb. Chem.*, 1864, 573, and Gmelin, *Handbuch der Org. Chem.*, iv., 1, 691.

esting one, and one which can now be easily explained, but until quite recently the literature has been almost silent on the subject. I wish to present in what follows a few observations bearing on the question.

Over a year ago in giving instruction to a class of students in the use of the polarimeter I suggested, as an illustration of a substance for examination, not free from color, the syrup of ferrous iodide of the pharmacopeia. Instead of exhibiting a more or less marked right hand rotation, as was expected, it was found to be strongly levo-rotatory. The syrup, however, was known to be old and had been exposed to the light. As a certain practical interest attaches to the question it was decided to investigate fresh solutions.

The syrup of the pharmacopeia is made to contain in 100 cc. about 63 grams of sugar and 13.4 grams of ferrous iodide. On January 19, 1895, a liter of this solution was made according to the usual process, special care, however, being taken in the selection of the sugar and iodine employed. The liquid polarized immediately, in a 200 mm. tube, gave  $\alpha_D = 81.15^\circ$  at  $20^\circ$ . Four days later the rotation was found practically unchanged, the syrup having been kept meanwhile in the dark. A bottle holding about 100 cc. and furnished with a glass stopper was then filled with the syrup and allowed to stand until May 6th and exposed to diffused light. This portion now showed on polarization  $\alpha_D = 53.12^\circ$  in the 200 mm. tube, while the original, kept in the dark, polarized  $63.17^\circ$ . On this date, May 6th, a second portion of the original was filled into a bottle and allowed to stand in the light. It was polarized at different intervals, with results as follows, at  $20^\circ$ , in the 100 mm. tube :

July 15th	$\alpha_D$ .....	+6.66°
Aug. 24th	" .....	-4.36°
Oct. 22nd	" .....	-13.10°
Nov. 15th	" .....	-13.42°

Another portion of the original which had stood since January 19th in a small full bottle in the light gave now in the 100 mm. tube  $\alpha_D = -15.66^\circ$ . From this it appears that in the interval the saccharose had undergone complete inversion. The original rotation observed,  $81.15^\circ$ , was that of a solution in which some inversion had already taken place.

Another solution was prepared on May 9th, containing in 250 cc. 140 grams of sugar and an amount of ferrous iodide corresponding to twenty-eight grams of iodine. The syrup and iodide solution were hot when mixed. This polarized at  $20^\circ$  gave a rotation of  $33.25^\circ$  in the 100 mm. tube, which corresponds to a specific rotation of  $59.38^\circ$ . At intervals the following rotations were found from two portions of this solution, which had been poured into glass stoppered bottles and kept in the light. One bottle was full and the other not quite full.

		Full bottle.	Partly filled.
July 13th	$a_D$ .....	$18.66^\circ$	$+9.30^\circ$
Aug. 24th	" .....	$8.58^\circ$	$+3.56^\circ$
Oct. 22nd	" .....	$3.76^\circ$	$-10.16^\circ$
Nov. 15th	" .....	$2.70^\circ$	$-10.75^\circ$

It is apparent from the above that the presence of air in the bottle with the solution has a marked influence on the rapidity of inversion.

#### INFLUENCE OF TEMPERATURE.

The solution just described stood at the laboratory temperature during the time of the observations. A marked decrease in the time required for full inversion would naturally be expected by working at a higher temperature. This was shown by heating some of the last solution in boiling water during ninety minutes. The solution was contained in a flask with a capillary stopper. Before heating it had a rotation of  $33.25^\circ$  in the 100 mm. tube ; after the application of heat the reading was  $-12.75^\circ$  in the same tube. The following day the solution was reheated through three hours and polarized again, giving now  $-13.00^\circ$  at  $20^\circ$ . Heating through ninety minutes was therefore sufficient to complete the reaction, and it is evident that an inversion which at the mean laboratory temperature of  $20^\circ$ - $25^\circ$  requires months for its completion may be accomplished in less than two hours at the temperature of boiling water.

It was found later that a moderate increase of temperature does not greatly hasten the inversion ; this becomes rapid only above  $60^\circ$ .

#### INFLUENCE OF LIGHT.

It should be remarked that the inversion by heat, as well as

by long standing in the light, is accompanied by a decided loss of color. A solution of ferrous iodide exposed to the air, or protected from the air and kept in the dark, soon becomes brown from partial decomposition and separation of iodine, which is easily shown by the starch reaction. In stoppered bottles in the light, however, this decomposition is almost wholly prevented and in an already colored solution in which free iodine is shown by tests, the color is lost by exposure to the light.

Well-made undecomposed solutions of ferrous iodide are described as light green, but they may become almost as colorless as water, leaving the iron in a perfectly reduced condition. It has been found by numerous trials that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together. More will be said of this later.

The phenomena described above are not confined to ferrous iodide but are exhibited by many other salts. In fact, from theoretical considerations, they should be expected in some degree from the salts of all the so-called heavy metals, as will presently be pointed out. First, however, some actual experimental results will be given.

#### FERROUS CHLORIDE.

A solution containing in 100 cc., 50 grams of cane sugar and four and one-tenth grams of pure ferrous chloride was prepared. The ferrous salt was made by the action of an excess of iron on hydrochloric acid, and the syrup made with this and the sugar was bright green. It showed a rotation of  $32.75^\circ$  in the 100 mm. tube, or a specific rotation of  $65.50^\circ$ . After heating one hour to  $100^\circ$  the rotation was found to be  $-6.42^\circ$  in the same tube.

#### FERROUS BROMIDE.

The solution contained in 100 cc., 50 grams of saccharose and ten grams of the bromide. The latter was made by the action of bromine and water on iron, and the solution so obtained was filtered into the dissolved sugar. The rotation of the fresh mixture was found to be  $32.25^\circ$ . A portion was heated one hour to  $100^\circ$  and was then polarized, after cooling to  $20^\circ$ , giving now a rotation of  $-10.26^\circ$ .

## FERROUS SULPHATE.

The solution of 100 cc. was made with fifty grams of sugar and ten grams of pure crystallized sulphate. It was slightly cloudy and could not be polarized with the greatest accuracy, but the reading was nearly  $33^\circ$ . A portion was heated one hour away from the air. It became clear and could be easily examined in the polarimeter, showing now at  $20^\circ$  in the 100 mm. tube  $18.20^\circ$ . This decrease is much less than in the other cases, but not unexpected.

## FERROUS AMMONIUM SULPHATE.

The solution made contained in 100 cc., fifty grams of sugar and ten grams of the crystallized salt. When fresh it gave a rotation of  $33.08^\circ$ . After heating five hours to  $71^\circ$  the rotation was found to be  $27.20^\circ$ . This solution was allowed to stand in a stoppered bottle in the light and was polarized at different intervals with the following results:

July 24th	$\alpha_D$ .....	$27.20^\circ$
Aug. 24th	" .....	$20.22^\circ$
Oct. 22nd	" .....	$10.23^\circ$
Nov. 15th	" .....	$7.53^\circ$

We have here, as before, a slow rate of inversion.

## MANGANOUS CHLORIDE.

A solution was made on July 24th, containing in 100 cc. fifty grams of sugar and ten grams of the carefully purified salt with  $4H_2O$ . It gave immediately a rotation of  $32.88^\circ$ , and after heating five hours to  $71^\circ$  a rotation of  $28.16^\circ$ . From this date, July 24th, the heated portion was allowed to stand in the light at the laboratory temperature in a full bottle, and showed at intervals the following rotations, all in the 100 mm. tube, at  $20^\circ$ :

Aug. 24th	$\alpha_D$ .....	$22.20^\circ$
Oct. 22nd	" .....	$4.71^\circ$
Nov. 15th	" .....	$1.66^\circ$

After standing a short time in the light this solution became as colorless as water when observed in a clear glass bottle of four cm. diameter.

## MANGANOUS SULPHATE.

The experimental solution was made to contain in 100 cc. fifty

grams of sugar and ten grams of crystallized manganous sulphate ( $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ). The rotation was found to be  $33.16^\circ$ . On heating the solution one hour to  $100^\circ$  it became slightly decomposed and darker in color, instead of lighter as with the chloride. The decomposition product was small in amount but exceedingly fine and dark. It remained long in suspension, making an exact reading of the rotation impossible. It was about  $+7^\circ$ , however, in the 100 mm. tube. The suspended substance was probably an oxide of manganese.

#### ZINC SULPHATE.

A solution containing fifty grams of sugar and ten grams of the sulphate in 100 cc. showed when fresh a rotation of  $32.98^\circ$  for 100 mm. After heating forty-five minutes in boiling water the rotation was reduced to  $18.42^\circ$  for the same tube.

#### POTASSIUM ALUMINUM SULPHATE.

With a solution containing fifty grams of sugar and five grams of the alum in 100 cc. a rotation of  $33^\circ$  was found immediately. A portion was heated one hour in the water-bath to  $100^\circ$ , and on cooling to  $20^\circ$  was polarized again, showing now a rotation of  $-9.99$ . The heated solution became slightly cloudy, but the original remained clear through the several weeks it was kept.

#### LEAD NITRATE.

A fresh solution with 50 grams of sugar and ten grams of the salt in 100 cc. showed a rotation of  $33.13^\circ$ . A portion heated one hour to  $100^\circ$ , showed, after cooling to  $20^\circ$ , a rotation of  $-9.65^\circ$  in the same tube.

#### LEAD CHLORIDE.

Some chloride was made by precipitation of the nitrate by sodium chloride. The product was recrystallized from hot water and washed repeatedly on a filter with cold water. About two grams of the moist precipitate was mixed with fifty grams of sugar in water enough to make ninety cc. and heated until it dissolved. On cooling the volume was made to 100 cc. A part of the chloride separated. The rotation was now found to be  $23.52^\circ$ . The mixture was shaken and a portion transferred to a flask with capillary stopper, where it was heated one hour to  $100^\circ$ . After cooling the rotation was found to be  $-7.53^\circ$ .

## CADMIUM CHLORIDE.

A fresh solution with fifty grams of sugar and eight grams of the chloride in 100 cc. gave a rotation of  $32.91^\circ$ . After heating to  $100^\circ$  it was reduced to  $-9.50^\circ$ .

## MERCURIC CHLORIDE.

The original solution of fifty grams of sugar and five grams of chloride in 100 cc. gave a rotation of  $33.22^\circ$ . A portion was heated an hour to  $100^\circ$  and became turbid, depositing on cooling a fine white precipitate. The clear liquid showed a rotation of  $-10.80^\circ$ . A second portion was heated a shorter time, to the beginning of turbidity only. It was quickly cooled and polarized, showing a rotation of  $-4.82^\circ$ . By prolonged heating more of the precipitate is formed. It appears to consist of mercurous chloride only.

The salts tested above, while commonly called neutral, are those in which the base is very weak when compared with the acid. It is such salts that show in solution an acid reaction with certain indicators and the parallelism between the phenomena observed here and that of the inversion of sugar by acids naturally suggested itself. The following further test with a solution of ferrous iodide was therefore made. This solution contained in 100 cc. fifty grams of sugar and ten grams of the iodide. It polarized when fresh  $32.41^\circ$  in the 100 mm. tube. A number of small vials were nearly filled with this solution and they were heated in a thermostat through different times as shown below. The vials were made of selected glass, not readily attacked, and before use were heated some hours with hydrochloric acid. They were then washed and boiled with distilled water and dried. Before being placed in the thermostat they were closed with rubber stoppers having a capillary tube through the perforation. The upper end of this extended above the water in the thermostat. The capillary opening was sufficiently fine to prevent any appreciable evaporation of the syrup while being heated. The water in the thermostat was kept at about  $77.5^\circ$ . Vials were removed from time to time and cooled quickly so that the contents could be examined in the polarimeter. The following results were found :

Time of heating in minutes.	Observed rotation.
0	32.41 <sup>o</sup>
30	28.00 <sup>o</sup>
60	26.25 <sup>o</sup>
90	26.15 <sup>o</sup>
210	24.61 <sup>o</sup>
390	18.48 <sup>o</sup>
570	16.60 <sup>o</sup>
810	4.70 <sup>o</sup>

These figures show a rapid, but an irregular change, in the rotation with the time, but as the temperature was not maintained with great accuracy, and as some of the vials were more exposed to the light than others, greater uniformity could not be expected.

To determine whether or not the inversion proceeds according to the law of Wilhelmy, a second series of experiments was made in which the temperature was carefully regulated and in which the small vials holding the sugar solutions were wrapped in tinfoil for protection against the light. The temperature in the last series of experiments was too low to permit them to be completed in a reasonable time. It was therefore brought to 87.5° for the following tests.

The amounts of sugar and ferrous iodide were the same as before, but greater care was taken in the preparation of the solution. Several samples of high grade commercial sugar were tested, and one was selected which satisfied all requirements as to purity. For 250 cc. of solution 125 grams of this sugar is dissolved in a small quantity of water in a graduated flask by aid of heat. Then 20.5 grams of the pure iodine, sublimed with potassium iodide, is weighed out and mixed in a flask with fifty cc. of water and seven grams of pure fine iron wire. The action of the iodine on the iron begins soon and must be checked after a time by dipping the flask in cold water. Finally when the action is practically complete, as shown by the disappearance of the iodine and change of color to greenish brown, the solution is boiled to make the reduction to the ferrous condition perfect. The amount of iron taken is largely in excess of that which can combine with the iodine. The ferrous solution is now allowed to cool to 50°-60° C. and filtered into the cooled sugar



solution made as above. The last traces of iodide from the flask and paper are washed down into the syrup by aid of a little boiled and cooled water. Finally the whole volume is made up to 250 cc. by the addition of distilled water. In this manner a solution is secured which contains in 100 cc., fifty grams of saccharose and ten grams of ferrous iodide, and which is practically free from inversion. The specific rotation of the strong pure syrup is  $66.5^\circ$ ; that prepared with the iodide is  $64.82^\circ$ , as found from the mean of many closely agreeing determinations. It will be noted that this lower specific rotation is about the same as that found for the solutions of the other salts described above. The decrease in the rotation is apparently not a result of inversion.

The method of preparation of the syrup of ferrous iodide as described in the Pharmacopeia leaves a product slightly inverted because of the higher temperature of mixing the sugar and iodide solutions. When portions of the syrup made as just described are heated in boiling water an hour, in flasks with capillary stoppers to prevent evaporation, the rotation is reduced to  $-11.5^\circ$  at  $20^\circ$  for the 100 mm. tube. This value is almost identical with that calculated from the experiments of Gubbe,<sup>1</sup> *viz.*,  $-11.31^\circ$  for the rotation produced by the inversion of fifty grams of cane sugar in 100 cc. The presence of the excess of iodide seems to be without much influence on the specific rotation of the invert sugar.

In the experiments given below, the rotations were found in a 100 mm. tube at  $20^\circ$ . The reading before heating was  $32.41^\circ$ , and this is taken as the initial rotation instead of the theoretical  $33.25^\circ$ . Applying the Wilhelmy-Ostwald formula we have

$$\text{nat. log. } \frac{A}{A-x} = Ct,$$

in which  $A$  represents the total amount of sugar present and may be measured by the total change in the rotation. It is therefore  $32.41^\circ - (-11.5) = 43.91^\circ$ .  $x$  represents the amount of sugar inverted at the time  $t$ , and is measured by the decrease in rotation at that time.  $A - x$  represents the sugar remaining and the velocity of the inversion should be proportional to this.

<sup>1</sup> *Ber. d. chem. Ges.*, 1885, 2207.

The table below gives the results of a series of experiments. The solutions were warmed two minutes before the counting of the times,  $t$ , began, as this was found necessary to bring them to the proper temperature. This, of course, introduces a small error into the calculation. The values in the fourth column are obtained by the use of common logarithms.

$t$ min.	Observed rotation.	$x$	$\log. \frac{A}{A-x}$	$\frac{1}{t} \log. \frac{A}{A-x}$
30	28.50°	3.91°	0.04050	0.00135
60	24.85°	7.56°	0.08206	0.00137
120	17.80°	14.61°	0.17569	0.00146
180	13.35°	19.06°	0.24723	0.00137
240	6.32°	26.09°	0.39165	0.00163
300	4.32°	28.09°	0.44335	0.00148
420	-9.00°	41.41°	1.24461	0.00296

The results of the last column are sufficient to indicate that the inversion follows the general law shown by Wilhelmy to hold for the action of weak acids on sugar solutions. The values of  $\frac{1}{t} \log. \frac{A}{A-x}$  are not constant, but considering the conditions of the experiment, must be considered close enough until the last one is reached. The solution of the sugar is a very strong one containing fifty grams in 100 cc., and from such a degree of concentration no great regularity can be expected. The variation in the amount of water present as the saccharose becomes changed into dextrose and levulose must have some influence on the progress of the reaction, and one of the fundamental conditions of the Wilhelmy experiment is therefore not accurately observed. It has frequently been pointed out that the constant  $\frac{1}{t} \log. \frac{A}{A-x}$  may be quite irregular when calculated from tests on very strong solutions. The values are really constant only when the solvent is so greatly in excess that slight changes in it in the progress of the reaction, may be neglected. In the present case about two and five-tenths grams of water disappear in the formation of the new molecules, and this from a solution already very strong. Part of the irregularity in the constant may doubtless be explained in this manner. An accidental exposure to light during the last interval of the heating may partly account for the change in the last value.

It has been found by later experiments, some of which are still in progress, that with dilution of the solutions much more uniform results may be secured, approaching, in fact, those obtained from the action of weak acids alone.

The cause of the inversion of strong sugar solutions by these heavy salts is undoubtedly to be found in their condition of partial hydrolysis by the solvent. The acid ion in each case is a strong one, while the basic ions are all relatively weak. Indeed, it has been suggested by Walker and Aston<sup>1</sup> that the amount of hydrolysis in solutions of certain salts may be approximately measured by comparing the speed of inversion with that of known amounts of weak acids. The method can be easily applied to a large number of solutions of moderate concentration. Further investigations with special reference to ferrous salts are now in progress.

CHICAGO, DECEMBER, 1895.

## MIXED DOUBLE HALIDES OF PLATINUM AND POTASSIUM.

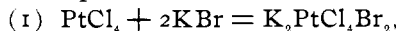
BY CHARLES H. HERTY.

Received November 16, 1895.

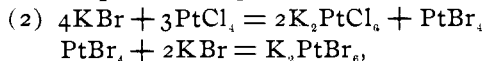
### INTRODUCTION.

BY mixing together water solutions of platinum chloride and potassium bromide in the proportion of one molecule of platinum chloride to two molecules of potassium bromide, Pitkin obtained<sup>2</sup> a compound having the composition represented by the formula  $K_2PtCl_4Br_2$ .

Two possible explanations were advanced by Pitkin,



a true chemical compound being formed, or



giving thus an isomorphous mixture of  $K_2PtCl_6$  and  $K_2PtBr_6$ . In either case the percentage of the elements remains the same. To determine which of the two explanations is correct, he resorted to fractional crystallization, and from the above solu-

<sup>1</sup> *J. Chem. Soc.*, July, 1895.

<sup>2</sup> *This Journal*, 1, 472.