solution and the 80 cc solution, was intermediate between the curves of 20 and 60, and 60 and 100 respectively. Moreover, the determination of the liberated iodine is so easily made, that we possess in this method a convenient form of actinometry, lending itself readily to various practical applications. The chlorine-hydrogen method of Draper, which received at the hands of Bunsen and Roscoe, the various instrumental refinements essential to accurate quantitative results, requires a corresponding complexity of apparatus and nicety of manipulation, and is therefore carried into execution with difficulty by the working chemist. The method just described needs little or no apparatus beyond that essential to any well-equipped laboratory.

VI.—On the Influence of Variations of Temperature on the Deviation of Polarized Light by Solutions of Inverted Sugar.

By P. CASAMAJOR.

Received February 18, 1879.

The researches, of which I propose to give an account in this paper, were suggested by an interesting communication of Dr. Ricketts to this Society, which was presented at our last meeting.

Dr. Ricketts found that the temperature at which the deviation of a solution of inverted sugar becomes 0 is not 90° C., as given by some authors, but 92°, or rather 91°.7 C. From this Dr. Ricketts concluded, that if a solution of commercial sugar is inverted in the ordinary way, if, originally, the two constituents of the sugar were cane sugar and inverted sugar, after inversion there must only remain inverted sugar, and, if we bring this solution in the saccharometer tube to have the temperature of 92° C., the indication of the saccharometer scale must be 0.

As the inversion of sugar solutions in testing sugars is now almost entirely neglected, it struck me that the introduction of this subject before this Society was of great importance, as it is likely to excite inquiry in this direction, and must lead to interesting discussions which will throw much light on a ground which has not recently been explored. I hope the following remarks may be considered as a contribution to this important subject.

To enable me to present in a clear light, the results I have reached, it becomes necessary to bring before you some theoretical points relating to the inversion of sugar solutions.

It is to Mitscherlich that we owe the observation that the deviating power of solutions of inverted sugar on polarized light, varies with the temperature. It is, however, to Clerget that we owe a careful study of the subject. As far back as 1849, he published in the *Annales de Physique et de Chimie* (Vol. xxvi, 3d series, p. 175) a process for rectifying errors in tests of commercial sugars by Soleil's saccharometer, by taking into account the deviation caused by a solution of inverted sugar, obtained by heating with hydro-chloric acid a sugar solution, previously tested without inversion. In this communication, however, Clerget does not enter into theoretical considerations. He directs that sugar solutions shall be inverted by heating them with 10 per cent. of their volume of concentrated hydro-chloric acid, up to a temperature of 68° C., taking about 10 minutes in the operation. As soon as this temperature is reached, the solution is to be cooled down to some temperature between 10° and 35° C., as the table he gives for correction is calculated for temperatures between these limits, which, he says, "answer for all occasions which may present themselves in "Europe, as well as in the Colonies."

When Clerget proposed this new plan for making sugar analysis more correct, the subject of testing sugars was not a new one with him, for it is to him that we owe the idea of using Soleil's polarimeter as a special instrument for analyzing sugar, and, as far back as 1845, he had published, in the *Bulletin de la Societe d'Encouragement*, an account of Soleil's saccharometer. In his paper in the *Annales de Physique et de Chimie*, he gives no theoretical reasons for the new process. For the theory of the correction of the direct test of the saccharometer, by taking into account the test after inversion, I am indebted to some formulas in Mandlebluh's Guide (*Leitfaden zur Untersuchung der Verschiedenen Zuckerarten*, *Brunn*, 1867, p. 56). This theory I will now proceed to lay before you.

You are aware that commercial sugars contain, besides pure cane, sugar, a variety of substances, of which many exert deviating effects on a ray of polarized light. Among these is inverted sugar, which may be an immediate substance or a mixture of dextrose and lævulose. This latter supposition was advanced by Dubrunfaut, but has never been demonstrated in a satisfactory manner, although it would take volumes to collect what has been written about it, and is being written about it every day.

The other bodies which accompany cane sugar have not been studied in such a way as to throw light on their nature, with the exception of aconitic acid, isolated by Dr. Behr, who gave an interesting account of his researches, in a paper read before this Society two years ago.

A point of great importance, in connection with the analysis of sugar by optical methods, is that the impurities which are generally present, are in such a condition that they seem to exert no effect on polarized light. The proof of this is to be found in the fact that with most sugars, particularly if the saccharometric test is above 90 per cent., the result, after the correction for inversion, is the same as given by the direct test. As many of the impurities reduce the alkaline solution of tartrate of copper, they are comprised under the head of *inactive glucose*, concerning the nature of which there are many unsatisfactory doctrines.

To explain how the direct test by the saccharometer may be corrected by subsequently inverting the solution on which this direct test was made, let us suppose that we have, in the first instance, a deviation, D. We may suppose that this deviation is the resultant of the following:

$+ C$, deviation due to the cane sugar.
$- i$ " " " inverted sugar.
$+ h$ " " " one or more substances, besides cane sugar, which turn the plane of polarization to the right.
$- g$, deviation due to one or more snbstances, besides inverted sugar, which turn the plane of polarization to the left.

Then we may suppose that $C - i + h - g = D$.

In this equation the only known quantity is D, but what we want to know is C. To find this quantity we make use of this fact, that if the solution under examination is heated with 10 per cent. of hydro-chloric acid, the whole of the cane sugar will be converted into inverted sugar, while the other substances will not suffer any change. From some experiments which I made with artificial mixtures analogous, as far as I could judge, to those which constitute the impurities of commercial sugars, I am led to believe that by heating with concentrated acid, a certain change takes place in the deviating power of the impurities of commercial sugars. This change is, however, very slight, and, as the impurities are in small quantities when compared to the cane sugar, the changes they suffer may be neglected, and we may suppose that, with the exception of the conversion of cane sugar into inverted sugar, no change takes place in the other constituents of the commercial sugar from the treatment with hydro-chloric acid.

After this action of hydro-chloric acid, aided by heat, has taken place, the solution is examined again in the saccharometer, and, after making a deduction for the volume of acid added, we will obtain a deviation d. This deviation, in ordinary sugars, will take place on the negative side of the scale. We may suppose that it is the resultant of the same elements that made up deviation D, with the exception of the quantity C, now represented by the deviation due to the inversion of the cane sugar originally present. This quantity we will call — I, and we shall have $-I - i + h - g = d$. If now we wish to eliminate the quantities i, h and g, we may easily do so by subtracting the second equation from the first, and we shall have: $C + I = D - d$.

By a series of experiments, Clerget established the relation between C and the corresponding value of I. This relation varies with the temperature, but we may suppose that the observation, after inversion, is taken at 28° C., at which a quantity of cane sugar which, before inversion, gives a deviation of 100 to the right, will show for the corresponding inverted sugar 30 to the left or — 30. At this temperature $C + I$ becomes $1.3 \times C = D - d$. As d is a negative quantity, the algebraic subtraction is equivalent to an arithmetical addition, whence we draw the rule that at 28° C., the true quantity of sugar C, is equal to the sum of the two deviations divided by 1.3, as $C = \frac{D - d}{1.3}$ This number 1.3 corresponds, as we have said, to 28° C. We may, in the next place, inqnire: What are the corresponding numbers for other degrees of temperature? This brings us to the consideration of Clerget's table. For temperatures between 10° and 35° C., Clerget determined these numbers, and, on consulting his table, we find that, for a quantity of cane sugar equal to 100, we must take for the quantity D — d at 10° C., the sum 139, and that for every degree C. above 10°, up to 35°, the number representing the arithmetical sum of the deviations is equal to 139 minus one-half the difference between the number representing the temperature and 10°. Thus for 20°, we have $20 - 10 = 10$ and $139 - \frac{10}{2} = 134$; for 28°, we have $28 - 10 = 18$ and $139 - \frac{18}{2} = 130$; for 35°, we have $35 - 10 = 25$, and $139 - \frac{25}{2} = 126.5$, etc.

If the same law should hold good below 10°, we must, to 139, add $\frac{1}{2}$ for every degree below 10°, and this leads us to establish that at 0°, the number corresponding to D — d would be $139 + 5 = 144$. As this number 144 is one of great importance, allow me to recall to your attention, that it means that if we have a solution of pure sugar which will produce a deviation of 100 divisions on the positive side of the saccharometer scale, if this solution is inverted by heating with 10 per cent. of hydro-chloric acid, this inverted solution, if tested at the temperature of 0° C., will, after making the correction for the quantity of acid added, produce a deviation of 44 on the negative side of the scale.

If we now suppose that the law which Clerget found for temperatures between 10° and 35°, holds good for all other temperatures, we may easily obtain the deviation to the left of the same solution of inverted sugar at any temperature, by subtracting from 44 one-half the number expressing this temperature in degrees Centigrade. Thus we shall have for 10°, $d = -(44 - 5) = -39$; for 20°, $d = -(44 - 10) = -34$; for 28°, $d = -(44 - 14) = -30$, and for any temperature t, $d = -(44 - \frac{t}{2})$.

If now, we draw a series of parallel equidistant lines, intersected by another series of lines, also parallel and equidistant, perpendicular to the first, we may take on the horizontal base line or line of the abscisses, a space between two lines corresponding to 1°C., and we may suppose that the space between two lines of the other series corresponds to a division of the negative side of the saccharometer scale. If now, on every vertical line, starting from the base line, we take a length proportional to the numbers given by the equation, $d = -(44 - \frac{t}{2})$, and if we connect the extreme points of all these lengths by a line, we will find that it is a right line, because the equation, $d = -(44 - \frac{t}{2}) = -44 + \frac{t}{2}$, is equivalent to the equation of the right line, $y = a + bx$, in which $d = y$, $a = -44$, $b = \frac{1}{2}$ and $x = t$.

If now, we take again our equation, $d = -44 + \frac{t}{2}$, we will find that, if the law it expresses holds good to the end, the temperature at which the deviation becomes 0 is 88° C.

The announcement that it was at 92° that d became equal to 0, led me to think, at first, that, possibly, the law that I had deduced from Clerget's table was not correct. It is true that the temperatures given by Clerget only extend from 10° to 35° C., but, between these limits, the law which governs the deviations of inverted sugar as affected by temperature, as deduced from his table, is represented by a right line. This I considered as an important fact, because I do not remember a single instance in which a law is expressed by a rigorous right line, between limits that are sufficiently distant, in which this right line is not continued throughout. Having, then, very serious doubts about the accuracy of Clerget's table, I started to discover what the true law was.

For this purpose I prepared pure sugar, by taking the best cut loaf sugar and soaking it in 95 per cent. alcohol for several hours, taking the sugar out, letting the pieces drain, and drying them by hot air.

This sugar, tested before inversion, gave exactly 100 by the saccharometer. The solution, after the direct test, was inverted and tried again in the saccharometer at several degrees of temperature. After making a great many tests at various temperatures, I was forced to the conclusion that, not only is Clerget's table correct for temperatures between 10° and 35° C., but that the law represented by $d = -44 + \frac{t}{2}$ held good even beyond 88° C., at which temperature the deviation is equal to 0.

To enable an observer to seize at a glance the results I have obtained, I took a large sheet of cross-section paper divided very accurately into inches and tenths of an inch. On the line of the abscisses, I took for every degree Centigrade a space equal to $\frac{2}{10}$ of an inch, and, on the line of the ordinates, I took for every division on the negative scale of the saccharometer, $\frac{4}{10}$ of an inch. I then drew a right line, connecting the point representing -44 of the Saccharometer scale with the point representing 88° Centigrade. This right line represents the law expressed by the formula $d = -44 + \frac{t}{2}$. Afterwards I plotted on this sheet 68 observations made at temperatures varying from 14° C. to 92° C. The result of this operation was that, out of 68 dots, 10 were entirely erratic, 18 were exactly on the line, and the remaining dots were so close that their distance from the line could be explained by an error of $\frac{1}{4}$ of a division in the observation of the saccharometer. In explanation of these results, I may state that the dots which I have called erratic were due to observations made on turbid solutions, or while the temperature was fluctuating. Observations made under such circumstances cannot be expected to be accurate. The other observations were made under conditions infinitely more trying to the eyes than those under which ordinary saccharometric tests are made. When the temperature fluctuates in the least during an observation, the disc of double quartz becomes distinctly elliptical, and, at times, the line of separation between the two quartz plates swerves alternately to the right and to the left.*

To obtain the different temperatures required for these experiments, I had to alter a saccharometer so as to interpose a water bath between the two optical portions in a manner similar to that adopted by Dr. Ricketts. At the bottom of this water bath is an opening, communicating with the interior of a closed tube, three inches long, projecting at a right angle. To the closed end of this tube a Bunsen burner was applied when the water bath was to be heated. In this water bath I placed the tube containing the solution of inverted sugar. This tube is made of thin brass, and is closed at each end by a glass plate, held by a screw cap in the ordinary way. In the middle of this tube a portion was cut off, two inches long, and as wide as the diameter of the tube. Over the opening thus formed was soldered a projection, as shown in figures 1 and 2 at A. At first I used a tube with a cylindrical projection, of the same diameter as the tube itself, for the introduction of a thermometer to ascertain the temperature of the liquid in the tube, in the manner adopted for Clerget's thick glass tube. I think that the plan represented in fig. 1 and fig. 2 is preferable, as it allows the operator to agitate the solution by moving the thermometer backwards and forwards in the tube. A great advan-

FIG. 1

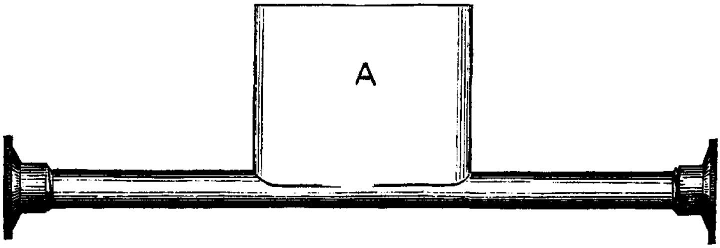
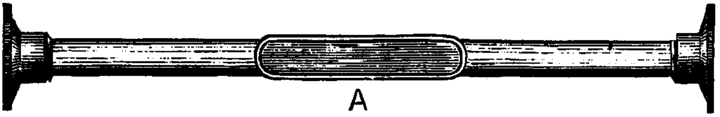


FIG. 2



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*The sheet on which these dots are plotted was shown to the American Chemical Society. I have not thought it necessary to have it engraved, as the explanation given in the text makes the subject sufficiently clear.

tage obtained by having a projection of this shape is that the liquid in the projection does not rise or fall perceptibly when the thermometer is taken in or out. If the vertical projection has a small section, whenever a thermometer is placed in it the liquid rises in this projection, and a portion may be high enough to stand above the level of the water bath. Under these circumstances, this portion of the liquid gets cooler than the portion in the horizontal rube, and, if the bulb of the thermometer is longer than the diameter of the horizontal tube, the temperature indicated will be too low. Too much care cannot be taken in observing these minutiae, as otherwise accurate results cannot be obtained. Even with the greatest care, it is impossible to avoid errors in the observation of solutions whose temperature does not remain constant. In this connection I may be allowed to express the opinion that it was due to the want of a tube like the one represented in fig. 1 and fig. 2 that Dr. Ricketts was led to take 92° as the temperature at which d becomes equal to 0. I have repeatedly found at 92° that the deviation is on the positive side of the scale, ranging from 1.4 to 2, according as the observation was more or less accurately made. In his experiments, Dr. Ricketts did not take the temperature of the liquid in his tube, but that of his water bath. As his tube was made of glass, about one-eighth of an inch thick, we must suppose that the temperature of the liquid in the tube was different from that of the water bath, and that the difference between the two temperatures must depend on the rate of heating the water bath, *i. e.*, on the size of the flame.

I have mentioned that a thermometer with a long bulb may be the cause of serious errors; so may a thermometer whose movements are too sluggish. In the thermometer that I have used, the bulb was very short; the mercury column was very fine, so as to respond very quickly to slight variations of temperature. These thermometers have 40° C. on a scale six inches long. One goes from 0° to 40°, the next from 30° to 70°, and the third from 60° to 100°. Particular attention was paid in these experiments to keeping the water bath in continued agitation immediately before taking an optical observation, and while the observation was being made. The thermometer in the brass tube was also kept moving backwards and forwards for some time before looking through the tube. Unless these things are done, there is no certainty that the temperature observed is that of the liquid in the tube.

If, as I am convinced in this case, from the numerous experiments I have made, observations on solutions of inverted sugar, taken at any temperature, are as reliable as those made at any other temperature, there can be no utility in heating the solution by the interposition of a water bath. Taking observations at the temperature at which the deviation is equal to 0, merely saves the trouble of dividing $D - d$ by $144 - \frac{t}{2}$, and it is not certainly worth while to go out of our way for this purpose. The most convenient plan for making observations on solutions of inverted sugar is to follow the directions of Clerget, which are the following :

A sugar solution is placed in the ordinary way in the saccharometer, and the saccharometric test, D, is noted down. To a portion of this solution, say 50 cubic centimeters, are added 5 cubic centimeters of concentrated hydro-chloric acid. These are mixed by shaking up the graduated flask, and the flask is placed in a water bath and heated to 68° C., taking about 10 minutes in raising the temperature. This solution is afterwards immediately cooled to a temperature between 10° and 35° C. We then place it in a thick glass tube, provided with a vertical tubulure for the insertion of a thermometer to show the temperature of the liquid at the moment of observation. This tube is made 22 centimeters long, instead of 20 centimeters, so as to compensate for the addition of $\frac{1}{10}$ of hydro-chloric acid. If the temperature, at the time of the observation, is t, and the deviation to the negative side is d, we take the algebraic difference of the two readings, $D - d$, which is the arithmetical sum. To find the correct quantity of cane sugar C, from these observations, we must remember that for 100 per cent. of sugar, $D - d = 144 - \frac{t}{2}$, therefore, $\frac{C}{D - d} = \frac{100}{144 - \frac{t}{2}}$ and

$$C = \frac{(D - d) \times 100}{144 - \frac{t}{2}}$$ [*]

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[*] Since this paper was read before the American Chemical Society, Dr. Behr has kindly called my attention to a paper of Dr. Tuchschmid in Scheibler's *Zeitschrift* for 1870, p. 649. After a series of elaborate experiments, Dr. Tuchschmid concluded that Clerget's table was very reliable. He investigated the law of this table between 4° and 41°.8 C. Instead of the formula given above, he found

$$R = \frac{100\ S}{144.16035 - 0.50578\ T};$$ R corresponds to C, S to $D - d$.

This formula leads to 87°.3 C. as the temperature at which the deviation becomes 0. The law of $d = -44.16035 + 0.50578\ T$ is also represented by a right line. As to the results given by this formula, as compared with the one I have given, they may be judged by the following :

Degrees C.	Tuchschmid.	Clerget.
10°	139.1	139
25°	131.747	131.5
35°	126.458	126.5
40°	123.875	124

If we have Clerget's table, we may, instead of making this calculation, follow the practical directions at the head of the table.

Instead of inverting by heating to 68° C., and then cooling down rapidly, it is advised by some authors that the solution be maintained at 70° for at at least 15 minutes I can say, after doing both things repeatedly, that, in the second case, the solution is no better inverted than in the first. Some persons think it necessary to heat at 70° for an hour. This I did not try, as I had found no advantage in heating 20 minutes longer than Clerget directs.

For solutions that are to be heated above 68° for experimental purposes, it is necessary to neutralize the hydro-chloric acid by a base, as otherwise the solution becomes very red. For this purpose the preference should be given to carbonate of soda, which gives the best results. I put enough of carbonate of soda to make the solution slightly alkaline, and afterwards make it acid with a slight excess of acetic acid. In this condition the solution may very conveniently be placed in a brass tube. For some reason which I have not been able to discover, when the hydro-chloric acid used in inversion is neutralized by magnesia, the indications of the saccharometer are always too low.

When Venteke's saccharometer is used for testing inverted sugar, we are obliged to operate on solutions of greater dilution than the normal solution containing 26 gr. .048 of sugar for 100 cc, because the negative side of the scale is very limited, reaching only to — 16 on some instruments. A solution holding 26 gr. .048 of sugar in 100 cc is tested directly. Then 50 cc of this are transferred to a beaker ; the 50 cc flask is washed out, and the wash water is added to contents of beaker, and also 10 cc of hydro-chloric acid. After the solution has been inverted and saturated with carbonate of soda, if necessary, the whole is put in a 100 cc flask, and enough water is added so that the whole solution at 15° C. shall occupy 100 cc. The result of the test, after inversion, has then to be multiplied by 2.

I will conclude by giving from my books a series, 28 consecutive tests of raw and refined sugars. In the second column I give the direct test, before inversion ; in the third column, the correct test, as afforded by inversion. In a fourth column I have given the copper test for glucose, when I happened to have it. These glucose tests show that the substances which reduce the alkaline tartrate of copper are, for the most part, without action on polarized light.

Designation of Sugar.	Saccharometric Test (before inversion).	Corrected by Inversion.	Glucose, Copper Test.
Raw	86½	87	
"	85	86	
Refined—B	91½	92	
" —C	83	83	
Raw	77	80	
"	90½	90½	
"	91	90½	3.57
"	80	84	11.5
"	84	86½	
"	84	89	
"	75½	79	
"	79	81	
"	90	90	4.30
"	95	94½	
Refined	78	78	8.2
"	81	82	7
Raw	92	92	2.5
"	91	91	2.5
"	87	88	5
"	90½	91	2.5
"	88	87	
Manilla	82	81	7.25
"	84	82	7.92
"	83½	81	7.5
Melado	73½	74	7.5
Domestic	82½	81½	
"	85	86	
"	78½	76½	

In the case in which the test before inversion is lower than when corrected after inversion, the presence of an excess of lævo-rotary substance is indicated. When, on the contrary, the test, before inversion, is higher than after inversion, as in the case of the Manilla sugars, an excess of dextro-rotary substance is indicated. If these sugars are inverted, and the solutions of inverted sugar are tested in the saccharometer at 88° C., they would show deviations on the positive side of the scale. This, however, does not enable us to decide to what particular dextro-rotary substance the deviation is due.