CONSTANTS OF THE QUARTZ-WEDGE SACCHARIMETER AND THE SPECIFIC ROTATION OF SUCROSE

I. THE CONSTANTS FOR THE 26-GRAM NORMAL WEIGHT

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I. INTRODUCTION

1. PRELIMINARY

One of the most important factors in the development of the sugar industry in the last few years has been the increased accuracy in the testing of sugars and sugar products. The same period has also seen an augmented use of the saccharimeter[1] as an instrument of precision for general scientific research. It is therefore important that all questions regarding the accuracy of the fundamental constants of sugar polarimetry[1] as well as any uncertainty regarding the basis of standardization be eliminated.

In the development of apparatus for the analysis of sugars the necessity for rapidity and simplicity has resulted in these factors being given consideration almost commensurate with that of accuracy. Thus, sugar-testing polariscopes are so designed that the reading of the scale gives the percentage of sucrose directly. This has been attained in the following way:

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[1] Sugar in common with a large class of other substances alters or "rotates" the plane of vibration of plane-polarized light by an amount almost exactly proportional to its concentration. This property has been utilized for the exact analysis of these substances in instruments called saccharimeters and polarimeters.

Let the rotation, for plane-polarized light, of a 100 cc solution containing M grams of sucrose be ϕ. If a second solution contain M grams of an impure sugar in 100 cc, its rotation will be ϕ'. Let p be the per cent of sucrose in the impure sugar. Since the concentration of the first solution is M, the concentration of the second solution is $\frac{p\,M}{100}$. If we assume that the rotation of a sugar solution is proportional to its concentration, we have $p = \frac{100\,\phi'}{\phi}$. Hence, if ϕ be assumed 100 and the scale on which the rotation is measured be so marked when the first solution is read, the reading of the second solution gives directly the percentage of sugar present. Usage has designated M as the normal weight and the first solution as the normal solution. If M be a fixed value, ϕ is the rotation of the normal solution, and since it fixes the 100° S (see p. 71) point of the saccharimeter, its value in circular degrees for monochromatic light is a fundamental constant.

In practice it has long been found advantageous to control the reading of the scale by the use of the unchanging quartz plate, thereby obviating the difficult measurement with the normal sugar solution. The normal quartz plate may be defined as that plate which has the same rotation on the saccharimeter as the normal solution. It must read 100 on the quartz-wedge scale. In determining the value of a plate, however, it is desirable to take advantage of the high precision afforded by the polarimeter in which monochromatic light is used. It thus becomes necessary to know accurately the rotation in circular degrees of the normal quartz plate for the wave length of the monochromatic light source. This value is known as the *conversion factor*, because the value of any plate in terms of the normal sugar solution may be obtained directly by dividing its rotation in circular degrees by the $\frac{\textit{conversion factor}}{100}$. The value, once it is established, becomes the permanent record of the series of measurements which establish the 100° point of the saccharimeter. The accurate determination of the conversion factor is thus of great importance; and the necessity, for scientific and industrial purposes, that there be agreement on the magnitude of this constant by the different governments is apparent.

2. THE VENTZKE SCALE

Uncertainty regarding the exact basis of standardization has existed from the beginning of the development of methods for sugar testing. Ventzke[2] early proposed as the normal sugar solution one which should have at 17°5 a specific gravity of 1.100 referred to water at 17°5. This solution contains in 100 cc 26.048 g of sugar, weighed in air with brass weights. Subsequently the Mohr flask (100 Mohr = 100.234 cc) displaced the 100-cc flask and saccharimeter scales were graduated accordingly. Most of the instruments now in use are thus graduated according to the following definitions: The normal sugar solution[3] contains 26.048 g of sucrose, weighed in air with brass weights, in 100 Mohr cc at 17°5 C. This is polarized at 17°5 C in a 20-cm tube, the quartz wedges of the saccharimeter being at 17°5 C. Schönrock[4] determined the conversion factor for $\lambda = 5892.5$ Å[5] and obtained the value

$$100^\circ V = 34\overset{\circ}{.}68 \pm 0\overset{\circ}{.}02 \text{ at } 17\overset{\circ}{.}5 \text{ C or}$$
$$100^\circ V = 34\overset{\circ}{.}69 \text{ at } 20^\circ \text{ C.} \qquad (1)$$

This measurement has never been made at the Bureau of Standards.

3. SCALE OF THE INTERNATIONAL SUGAR COMMISSION

Because of the confusion resulting from the use of the Mohr flask, and the inconvenience of a temperature of 17°5 C, the International Sugar Commission in 1900[6] adopted the following rational basis of standardization which has been generally applied by makers of saccharimeters:

(1) In general, all sugar tests shall be made at 20° C.

(2) The graduation of the saccharimeter shall be made at 20° C. Twenty-six grams of pure sugar, dissolved in water, and the volume made up to 100 metric cubic centimeters, or during the period of transition 26.048 g of pure sugar in 100 Mohr cubic centimeters, all weighings to be made in air with brass weights,

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[2] Ventzke, Prakt. Chem., **25**, p. 84 (1842); **28**, p. 111 (1843).

[3] Landolt, Optische Drehungs-vermögen, p. 335 (1898).

[4] Schönrock, Zs. Instrk., **16**, p. 242 (1896).

[5] The Ängstrom unit (Å) which is commonly used in designating the wave-length of light is one ten-thousandth of a millimeter (10^{-4} mm).

[6] Zs. Ver. Zuckerind., **50**, I, p. 357 (1900); Wiechmann's Sugar Analysis, 3d ed., p. 222 (1914).

the completion of the volume and the polarization to be made at 20° C on an instrument graduated at 20° C, should give an indication of 100 on the scale of the saccharimeter.

(3) Preparation of pure sugar: Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol; the sugar is carefully spun in a small centrifugal machine and washed in the latter with absolute alcohol. The sugar thus obtained is redissolved in water, the saturated solution again precipitated with alcohol and washed as above. The product of the second crop of crystals is dried between blotting paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The method of the international commission was early adopted by this Bureau as the official method. Saccharimeters designed for 26.048 g in 100 Mohr cc at 17°.5 C merely need to be controlled by a quartz plate standardized for 26 g in 100 cc at 20° in order that they may give polarizations nearly identical with saccharimeters designed for the new scale.

4. THE HERZFELD-SCHÖNROCK INVESTIGATION

The change in the basis of standardization made necessary a revision of the 100° point and a new determination of the conversion factor to replace the old value, 100° Ventzke[7] = 34°.69 circular degrees at 20° C. The investigations were made by Herzfeld[8] and his coworkers, in the Institut für Zucker-Industrie, and Schönrock[9] of the Physikalisch-Technische Reichsanstalt.

Ten quartz plates having rotations approximately equal to the normal plate were examined at the Reichsanstalt for optical purity, plane parallelism, and axis error. The rotation values in circular degrees for spectrally purified sodium light ($\lambda = 5892.5$ Å) were also determined at the Reichsanstalt. The rotation values

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[7] Inasmuch as the word Ventzke in the expression 100° Ventzke or 100° V has become indissolubly linked with the older scale and thus conveys a definite idea of the values pertaining to that scale, its use has been confined to that scale at this Bureau. For the scale adopted by the international commission the word "sugar" has been adopted in order to avoid confusion; the term "100° sugar" or "100° S" corresponding for the new scale to the older term "100° Ventzke" or "100° V." It is hoped that this usage will become general. When not otherwise designated the circular degree is meant.

[8] Zs. Ver. Zuckerind., 50, II, p. 826 (1900).

[9] Zs. Ver. Zuckerind., 54, II, p. 521 (1904).

in sugar degrees were measured at the Institut für Zucker-Industrie in conformity with the definition of the new sugar scale. The source of light was a Welsbach gas mantle. The radiation was filtered through a layer of a 6 per cent potassium bichromate solution 15 mm thick before it entered the polarizing system. The results of the investigation are summarized by Schönrock[10] in Table 1, where v is rotation in sugar degrees, α, rotation in circular degrees, and u, rotation of the normal plate in circular degrees: $u = \frac{100\alpha}{v}$ and $v' = \frac{100\alpha}{34.657}$

TABLE 1

Summary of Herzfeld-Schönrock Measurements

Plate No.	v in sugar degrees	α^{20} in circular degrees	u^{00} in circular degrees	v' in sugar degrees	$v-v'$ in sugar degrees
1	2	3	4	5	6
1 99	99.72	34.529	34.626	99.63	+0.09
2 99	96.97	33.577	34.626	96.88	+0.09
3 99	98.43	34.114	34.658	98.43	0.00
4 99	96.85	33.575	34.667	96.88	−0.03
5 99	100.97	35.035	34.698	101.09	−0.12
6 99	100.00	34.683	34.683	100.08	−0.08
7 99	99.99	34.640	34.643	99.95	+0.04
8 99	100.00	34.654	34.654	99.99	+0.01
9 99	99.97	34.638	34.648	99.95	+0.02
10 99	100.05	34.680	34.663	100.07	−0.02

Mean 34.657 E (10) = ±0.023.

The data show that

$$100^\circ \text{ sugar} = 34\overset{\circ}{.}657 \pm 0\overset{\circ}{.}023 \ (\lambda = 5892.5 \text{ Å}) \text{ at } 20^\circ \text{ C.} \qquad (2)$$

which by definition is the rotation of the normal quartz plate. It will, however, be observed that the variations in the values of u are considerably larger than should be expected, the maximum deviation from the mean being $0\overset{\circ}{.}041$. Only a small part of each of these differences is to be sought in the values of α, and we are forced to conclude that considerable errors probably exist in the values of v. In fact, Schönrock[11] states that errors of $0\overset{\circ}{.}10$ S are possible.

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[10] Loc. cit., p. 523.

[11] Loc. cit., p. 524.

5. PURPOSE AND OUTLINE OF THE PRESENT INVESTIGATION

For some years it has been noted at this Bureau that the normal sugar solution, prepared from samples, both of cane and of beet origin, issued by the Institut für Zucker-Industrie, reads less than 100° S on the saccharimeter scale. Because of this fact and of the necessity of the Bureau making careful scrutiny of the values of fundamental constants used in its standardizations, the following investigation was undertaken. Owing to the absence of a more accurate value, and the desirability of a uniform procedure among the different standardizing institutions, $34^\circ 657$ has thus far been accepted by the Bureau as the value of the conversion factor.

The value of the conversion factor determined by Herzfeld and Schönrock, as stated above, is for spectrally purified sodium light, the optical center of gravity of D_1 and D_2 being taken as 5892.5 Å. It is to be regretted that they did not measure the rotation of the normal solution in circular degrees. It has been shown[12] by one of us that the so-called yellow-green line, $\lambda = 5461$ Å of the mercury spectrum possesses marked advantages over $\lambda = 5892.5$ Å as the standard light source for polarimetric work. It is more stable, has a greater intensity, and is far easier to obtain pure at the high intensity required We have therefore utilized this mercury line as the fundamental source upon which all our measurements are either directly or indirectly based. With this source it is far easier to measure with high precision the rotation of quartz plates and of the difficultly prepared normal solutions. A smaller number of determinations is required and the labor of maintaining constant temperatures, preparation of materials, etc., is reduced. It is then possible to utilize accurately determined ratios to obtain the rotations for other light sources. Thus we have determined the conversion factor for $\lambda = 5461$ Å, and since the ratio, $\frac{\phi_{\lambda=5892.5\text{ Å}}}{\phi_{\lambda=5461.\text{ Å}}}$, where ϕ is the rotation of quartz, has been accurately measured at this Bureau, we may obtain the value of the conversion factor in terms of $\lambda = 5892.5$ Å, as well as calculate it by using the sodium values of the quartz plates. We have likewise

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[12] Bates, Bull. Bur. Standards 2, p. 239, Reprint No. 34 (1906).

determined a similar ratio for sucrose and thus obtained the rotation of the normal solution for $\lambda = 5892.5$ Å.

A survey of the literature shows the large amount of work that has been done by different investigators upon the specific rotation, as compared with the other optical constants of sucrose, and the agreement between the different values found is such that we can assume the specific rotation to be known with considerable accuracy. Having determined the rotation of the normal solution for $\lambda = 5892.5$Å we have calculated the specific rotation and thus obtained a direct comparison of our work on the 100° S point with previous investigations on the specific rotation. We have also made many other experiments and with the aid of the data secured we have been able to secure values for a number of other important constants.

In carrying out this work we have devoted much effort to securing sucrose of as high a degree of purity as possible. Previous methods for the preparation of chemically pure sucrose have consisted almost exclusively of some mode of precipitation from aqueous solution by alcohol. While these methods, if great care in manipulation is taken and if the substance is not permitted to remain long in hot solution, are capable of yielding material of high purity, it seemed advisable in undertaking a study of the purification to utilize as great a variety of methods of preparation as possible.

The method of purification which has been of such importance in industrial sugar work, but which has been practically overlooked as a means of preparing the chemically pure substance, is that of crystallization from pure aqueous solution. As this method has proved a most economical one, both in respect to time and material, we have used it as our main reliance in preparing sucrose for the manifold uses of the Bureau of Standards.

II. PREPARATION OF MATERIALS

1. ACCESSORY MATERIALS

(*a*) WATER.—For the preliminary operations of purification once-distilled water was used; for the more careful work the water was redistilled after the addition of a small quantity of alkali and potassium permanganate. The first third of the distillate was rejected.

(*b*) ETHYL ALCOHOL.—Commercial grain alcohol was redistilled after the addition of caustic alkali. The first and final fourths of the distillate were rejected. For the more careful work the selected portion was redistilled and the middle fraction again selected. No attempt was made to eliminate moisture. The product answered the requirements of the present work if it was free from acids and if it evaporated without residue. The aldehyde content was too small to be made evident by the caustic alkali or silver nitrate tests.

(*c*) METHYL ALCOHOL.—The impure material was shaken with lime and distilled. The first and last fifths of the distillate were rejected. The middle portion was again distilled from lime and only the middle third utilized for experiment.

2. CRYSTALLIZATION OF SUCROSE FROM AQUEOUS SOLUTION

Through the courtesy of Dr. F. G. Wiechmann a quantity of the purest cane sugar of commerce was obtained. It was dissolved in distilled water to form a 40–50 per cent solution. This solution in addition to solid insoluble impurities contained suspended albumenoid material which had escaped clarification in the refining process. This material in the main passed through filter paper and was not entirely removed even after recrystallization. To remove it the dilute sugar solution was shaken thoroughly with a quantity of "alumina cream" which had been washed free from dissolved substances. It was then poured on large folded filters of hardened filter paper. The filtrate was brilliant in appearance and entirely free from suspended material.

The boiling of the solution to the required supersaturation was accomplished in the vacuum boiling apparatus, which is shown diagrammatically in Fig. 1. The entire assembly, with the exception of the aluminum vessel *B* and condensing coils *C*, is of glass, and with the exception of the small asbestos filter the sirup never comes in contact with any other substance. The evacuating is done by a pump connected at *D*. The solution is placed in the flask *A*, and the entire system evacuated up to the cock *E*. This cock is then carefully opened and the solution slowly driven through the asbestos filter into the boiling flask *F*, capacity 13 liters. Here it is warmed by the water bath, and the temperature of the sirup noted on the thermometer *G*. In order to obtain any desired boiling point it is only necessary to regulate the pressure. The degree of the vacuum is indicated by the mercury gauges *H H*. The efficiency of the assembly is such that sirup is rapidly brought to the desired concentration of about 80 per cent at a temperature below 32° C. This is made possible by the high efficiency of the condensing system and by having all joints carefully ground to a fit. The stop cocks are

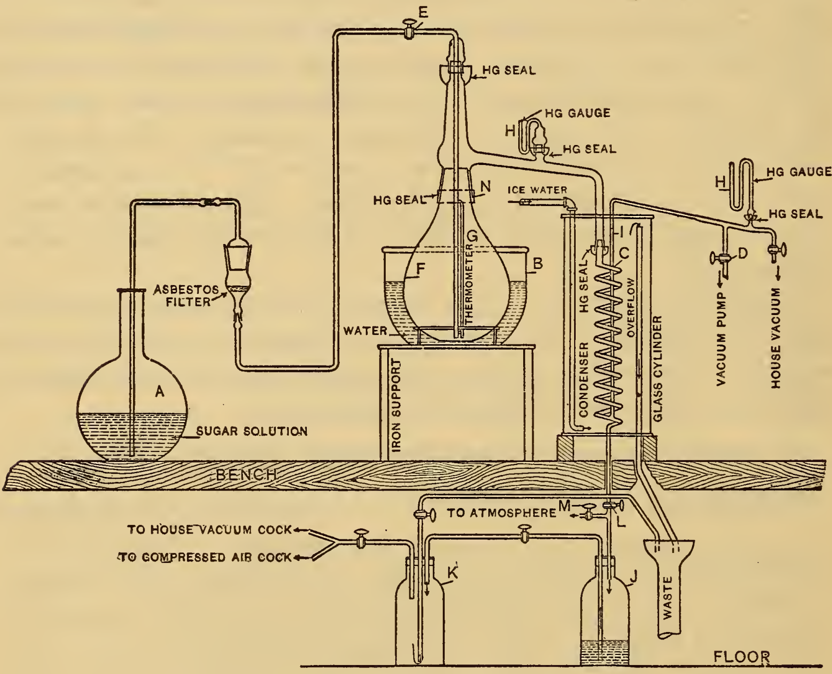

Fig. 1.—*Vacuum apparatus for concentrating sirups*

lubricated with water or sugar sirup. As rapidly as the vapors condense they pass into the vessel *J*, and subsequently by closing the cock *L* and opening *M* are expelled into *K*, from which the liquid is eventually driven into the waste.

The question of size of crystals is of the first importance. In general the smaller the crystals the less the included mother liquor. When the solution in the boiling flask *F* has reached the desired concentration, the vacuum is broken at *N* and the solution poured out to crystallize. Crystallization does not begin in these pure solutions until they are seeded with a few fine crystals of sugar. This is done after the solution is removed from the boiling flask. Two methods of crystallization were used. In the first the concentrated solution is transferred to a precipitation jar. It is then carefully stirred with a glass rod provided with a glass shield. This procedure gives satisfactory results so far as the size of crystals is concerned, but it is laborious. In the second the liquid is transferred to a crystallizer consisting of a glass flask or bottle held securely in a hardwood box mounted on bearings and driven by an electric motor. After standing overnight, the crystal mass is poured on a centrifuge and thoroughly drained of mother liquor.

After considerable experimenting with ordinary laboratory centrifuges, including the construction of three baskets in the Bureau of Standards shops, it was found that an especially designed centrifuge was necessary for the present work. A cross section of the one finally utilized is shown in Fig. 2. This centrifuge was built for this work by the International Instrument Co. of Cambridge, Mass., and has met all requirements. Its height over all is 2 feet, and it requires but 4 square feet of floor space. All surfaces with which either the crystals or the mother liquor can come in contact are silver or nickel plated. The basket is carried on the end of the vertical shaft of a three-fourths horsepower motor. It has an inside diameter of 9½ inches and is capable of carrying 10 pounds of sugar. The heavy cover is held in place by a number of set screws *A A* and may be readily detached in order to facilitate the removal of the centrifuged material. The lining to be satisfactory must retain very small crystals, permit of free drainage of the mother liquor, and be able to stand the severe strains incidental to high speeds. No single lining is available that will meet all these requirements. The built-up lining used consisted of two layers, the outer one being the regular copper centrifuge lining with elongated conical holes, and the inner of 200-mesh brass gauze. Both linings are silver plated. The small space between the lid and the frame is closed by stretching a rubber band tightly around the whole machine. When the centrifuge is in operation with the hinged lid *C* closed,

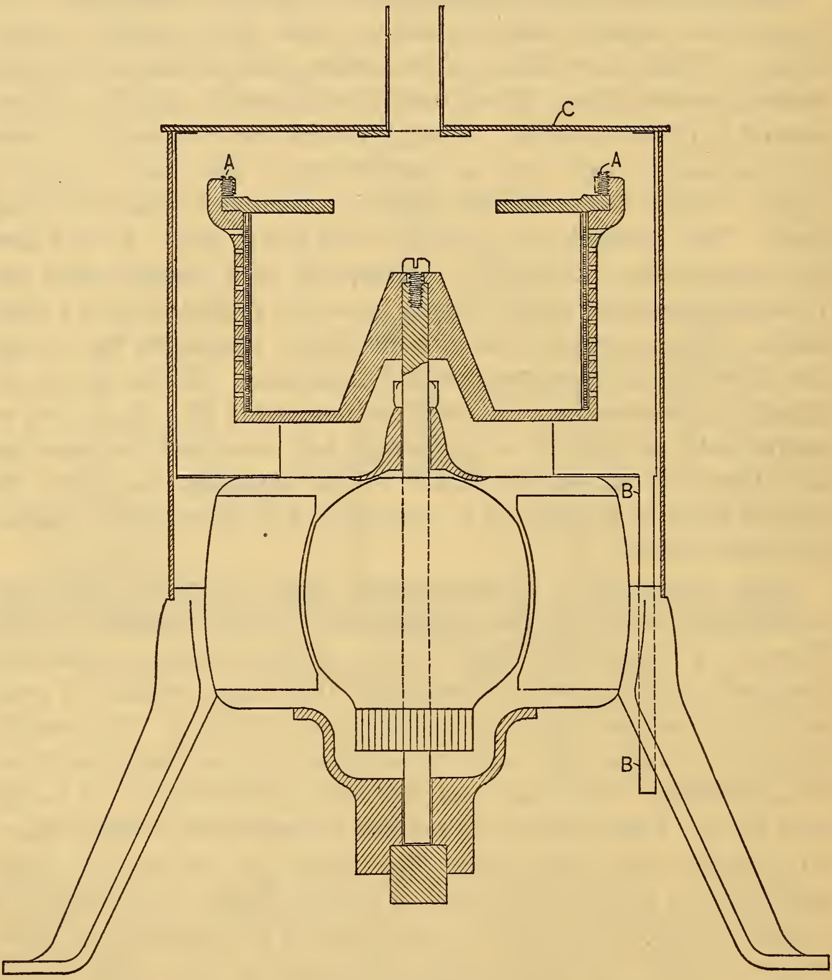

Fig. 2.—*Centrifuge*

the contents of the basket as well as the mother liquor are safe from contamination by the air of the room. The speed of rotation of the basket is controlled by a rheostat in series with the motor. In order to secure a proper distribution of the crystals and insure smooth running of the basket, the crystal mass is introduced while the machine is stationary or running at very low speed. The speed is gradually increased as the mother liquor runs off. Any desired number of revolutions per minute may be obtained up to 3000. After a thorough draining on the centrifuge the crystals are washed several times with pure redistilled alcohol, and finally placed to dry on a plate of glass carefully protected from dust.

With but little variation from this procedure a large number of samples were prepared and a study of the progress of the purification was made. What success in purification we attained, the following arguments are intended to show: If we assume that a given sample of sugar is contaminated by all sorts of impurities, these would be grouped in the following classes: (*a*) Soluble inorganic salts; (*b*) organic substances which reduce alkaline copper, such as invert sugar; (*c*) organic substances, possibly allied to sucrose, which do not reduce copper; and (*d*) moisture.

3. DETERMINATION OF ASH

Inorganic impurities are made evident by a determination of the ash. Inasmuch as most samples, after two recrystallizations, showed less than 0.1 mg of ash remaining from a 5 g sample, it was concluded that inorganic impurities were satisfactorily removed by this method of recrystallization.

4. ELIMINATION OF REDUCING SUBSTANCES

In the estimation of the small quantity of reducing sugar remaining after recrystallization, it was found to be impossible to make use of any of the published empirical tables, since these are based upon an assumed purity of the sucrose used in computing the tables, whereas the degree of purity of the sucrose is the problem to be solved. A few experiments served to show that the standard methods, in which are employed the various modifications of Fehling's solution with its large quantity of free caustic alkali, gave but little clue to the amount of reducing substances present. As an example, an experiment with the Soxhlet solution, according to the method of Herzfeld, yielded for a 10 g sample of the sucrose approximately 37 mg of copper, while a "sensitivity" experiment, i. e., an experiment in which a definite known quantity of invert sugar was added to the 10 g sample of recrystallized sucrose, showed that under these conditions 0.01 per cent, or 1 mg, of invert sugar caused an increase of precipitation of 2.5 mg of copper. Therefore, in interpreting the former analysis, we concluded that there were reducing substances present to the extent of 0.01 per cent $\times \frac{37}{2.5}$, or 0.15 per cent, in terms of invert sugar. The explanation of the apparently unfavorable result is that under these conditions sucrose is itself a substance having a slight reducing action.

Much more suitable for the present investigation, because of their slighter destructive action upon sucrose, are the solutions in which no free caustic alkali is used, but in which the latter is replaced by alkaline carbonates. Such, for example, are the Ost solution and a large number of others.[13] The Ost solution caused a precipitate of 10 mg of Cu_2O. The solution proposed by Striegler[14] caused a precipitate of about 7 mg, while an added impurity of 1 mg of invert sugar caused an increased precipitation of 3.2 mg of Cu_2O. This latter solution, because of its relatively slight destructive action upon sucrose and its high sensibility toward invert sugar in minute quantities, was deemed suitable for studying the progress of the purification. It contains in a liter 150 g $KHCO_3$, 101.4 g K_2CO_3, and 6.928 g of $CuSO_4.5H_2O$. Although particularly advantageous for the purpose in hand, this solution is not generally serviceable on account of its lack of stability on long standing. For an analysis 50 cc of the copper solution was brought to boiling and ebullition continued for one minute, then a 10 g sample of the sugar in a 50 cc solution was added and boiled for five minutes. At the end of this period the reaction was stopped by the addition of 100 cc of cold, recently boiled, water. The precipitate was filtered and weighed as Cu_2O. The weighing as cuprous oxide is justifiable when dealing with pure products. With this solution and method we made a study

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[13] v. Lippmann, Die Chemie der Zuckerarten, I, p. 606 (1904).

[14] Ibid.

of the efficiency of the recrystallization, at each point determining the comparative purity of the sample with respect to that of the previous crystallization. A supply of granulated sugar was dissolved, clarified, boiled, and recrystallized in the manner described. The original sample caused a precipitation of 20 mg of Cu_2O; the recrystallized sample precipitated but 9 mg. A second recrystallization reduced the copper precipitate to 6.8 mg, while a third recrystallization failed to produce any further decrease in the reducing sugar. This precipitate of 6.5 to 7.0 mg proved to be a minimum quantity, for no sample which we prepared, utilizing all the precautions suggested by accumulated experience, produced a further diminution in reducing power.

A sample of these crystals which precipitated 6.8 mg was dissolved and boiled in the vacuum apparatus in the usual manner, and at the end of the boiling, before crystals had formed, an analysis was made. Since 6.9 mg of Cu_2O were obtained, it was ascertained that no increase of reducing sugar content occurred during the solution and boiling. After crystallization and centrifuging, the crystals caused 6.7 mg of Cu_2O to precipitate, and a sample of the mother liquor containing 10 g of sucrose gave exactly the same precipitate.

From these experiments the conclusion was reached that, with respect to reducing substances, further recrystallization after the second could effect no improvement. Either a constant quantity of reducing sugar was present, distributing itself in a constant ratio between crystals and mother liquor, or sucrose itself effected the slight reduction of copper.

To test the latter point, analyses were made with other alkaline copper solutions in which the concentration of hydroxyl ion was diminished. The most satisfactory results were obtained with a modification of the Soldaini [15] reagent. The solution used contained in a liter slightly less than 300 g of $KHCO_3$, to which was added 1 g of copper sulphate crystals. The time of boiling was shortened to two minutes. The sample of sugar was dissolved in a 50 cc flask, from which it was poured into the copper reagent and the flask rinsed with 10 cc of water. The precipitate was finely divided, but was easily collected on a closely packed asbestos

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[15] v. Lippmann, Die Chemie der Zuckerarten, I, p. 606 (1904).

mat, or better, on a Gooch-Munroe-Nebauer crucible. An average of 13 determinations showed that a highly purified sample of sucrose produced a precipitate of 1.1 mg of Cu_2O. An average of 8 determinations, in which 0.01 per cent, or 1 mg of invert sugar, had been added, showed that 0.01 per cent of invert sugar caused an excess of precipitation of 1.9 mg. Therefore, from these analyses, it was concluded that the purified substance contained reducing substance not in excess of $1.1/1.9 \times 0.01$ per cent, or 0.006 per cent.

It seemed possible that even the small quantity of cuprous oxide precipitated under these conditions might, at least in part, be due to the action of sucrose itself. Since 0.006 per cent of invert sugar would be an optical impurity of nearly 0.01 per cent, it was deemed expedient to investigate the reactions involved in the analysis for reducing substances. Acting on the theory that there are two distinct reactions involved, the one the action of invert sugar or similar substances on the alkaline copper solution, the other the action of sucrose itself on the copper solution, we sought to ascertain if the two reactions had different velocities. For this purpose, the analysis was conducted in the same manner as before, with the single exception that the time of boiling of the mixed sample and copper solution was varied by whole minute periods from two to six minutes. The second column in Table 2 represents the weight of precipitate obtained with the purest sample of sucrose. The third column represents that obtained with the sucrose plus 1 milligram of invert sugar. Each figure in the table represents the mean of several determinations.

TABLE 2

Showing velocities of reaction of copper solution with sucrose and invert sugar

Time of boiling, in minutes	Precipitate obtained with pure sucrose	Precipitate obtained, sucrose+0.01 per cent of invert sugar	Precipitate caused by invert sugar alone—difference of columns 3 and 2
	mg	mg	mg
2	1.1	3.4	2.3
3	2.0	3.9	1.9
4	2.6	4.8	2.2
5	2.9	5.1	2.2
6	3.7	5.9	2.2

Let it be observed that the action of sucrose is progressive and practically linear with the time. The fourth column, obtained by subtracting column 2 from column 3, represents the reaction of the invert sugar upon the copper solution and it is at once seen that a distinct difference exists between the reaction of invert sugar, which is precipitated completely before the expiration of two minutes boiling, and that of the sample in question, which shows a progressive reaction. We must therefore conclude that the 1.1 mg of Cu_2O is caused in great part by sucrose itself.

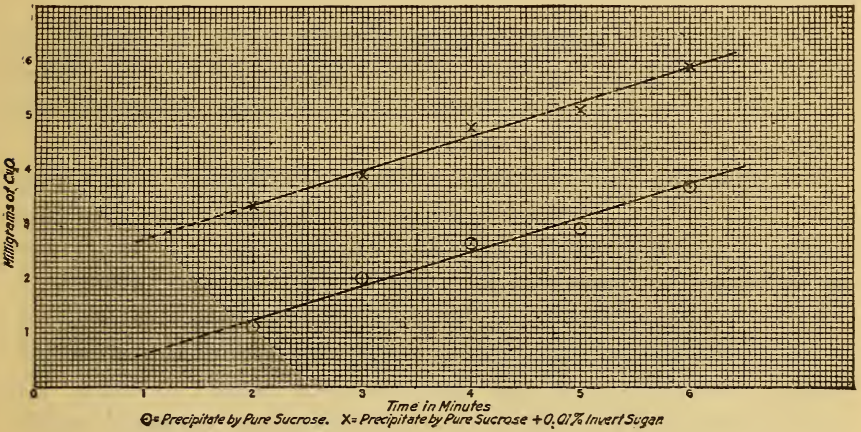

FIG. 3.—*Effect of duration of boiling upon weight of cuprous oxide*

If the velocity curves of the sucrose and of the sucrose invert sugar mixture be plotted as in Fig. 3, and both curves be produced to cut the axis at zero time, we find that the sucrose curve cuts it at approximately the origin, while the sucrose plus invert sugar curve intersects it at the point representing a weight of Cu_2O equivalent to the invert sugar added. This construction is permissible because the invert sugar reaction is complete before two minutes have elapsed and we may consider it for the purposes of this argument as instantaneous, or rather, we may say that these experimental results would be the same if it were instantaneous. If, therefore, any reducing substance other than sucrose itself is present, it is of the order of 0.001 per cent and entirely negligible.

5. STUDY OF CARAMEL FORMATION

The elimination of the last traces of moisture from the sugar necessitated a thorough knowledge of the effect of a high temperature on dry sucrose. It is well known that slightly above the melting point sugar passes rapidly into one of the varieties of caramel. Even far below the melting point the change occurs slowly and even at 100° C discoloration can be observed after several hours. By means of the reaction of caramel with the alkaline copper solution, minute changes could be observed quantitatively.

The analysis for caramel was conducted in the same manner as for other reducing substances. On account of the lack of precise knowledge concerning the constitution of caramel the results are expressed in terms of invert sugar.

In conducting an experiment a sample of sugar was thoroughly mixed and divided into two portions. One portion was kept in a stoppered container at the laboratory temperature, the other was subjected to the temperature at which it was desired to measure the rate of decomposition. When the desired time had elapsed two 10 g portions of the heated sample and two of the unheated sample were taken and all four analyzed simultaneously. At each temperature successive tests were made at increasing intervals of time in order to observe the course of the reaction. For the relatively small extent of the decomposition investigated, the velocity was approximately constant. The period of heating was continued until the decomposition was sufficient in amount to render the determination of velocity sufficiently accurate.

Table 3 gives in summary the results of these experiments. At each temperature is given the length of time necessary to effect a decomposition equivalent to 0.01 per cent of invert sugar. This decomposition depends somewhat upon the size of the crystals and these data apply only to the very fine particles used in this investigation.

TABLE 3

Length of Time at each Temperature Required to form Caramel Equivalent to 0.01 Per Cent Invert Sugar

Temperature, °C	100°	79.5	66.6	50.0	39.0
Time in hours required to form caramel equivalent to 0.01 per cent invert sugar	0.015	0.57	10.9	107.0	476

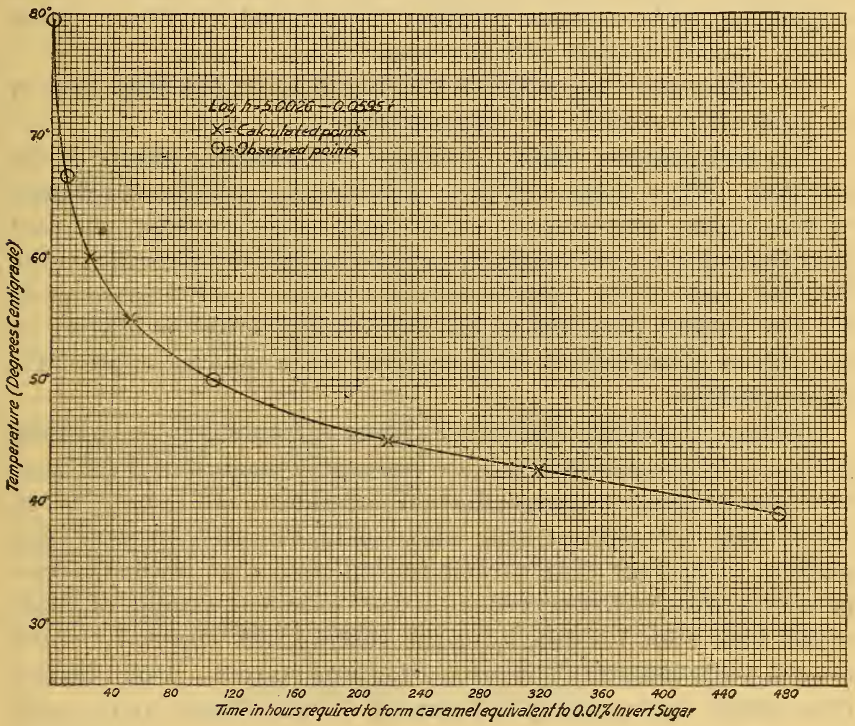

FIG. 4.—*Velocities of caramel formation at various temperatures*

It may be seen that the caramelization reaction occurs at much lower temperatures than is commonly supposed and it is unquestionably one of the factors in the determination of moisture in saccharine products. The data in Table 3 are shown graphically in Fig. 4.

This decomposition varies considerably with altered conditions. The same crystals at the same temperature but in a vacuum decompose at a much lower velocity. Furthermore, an increase in the size of the crystals exercises a considerable influence upon the reaction. Three samples, consisting of the finely pulverized crystals of our own preparation, a quantity of ordinary granulated sugar, and a number of crystals of Kahlbaum's rock candy, were heated until some decomposition had occurred. The powdered sample increased its reducing power by 5.4 mg of copper, the granulated sugar, and the rock candy by 1.2 mg and 1.3 mg, respectively. In aqueous solution the caramel reaction is much slower than is the case with dry sugar.[16]

The effect upon the rotation was found to be less than that of an equivalent quantity of invert sugar.

This investigation was not intended to reveal the nature of the reaction. That it was the same in kind as the caramel reaction of the higher temperatures would seem to follow from the fact that the curve is continuous up to 100°, at which temperature the familiar color of the caramel can be observed. It was adequate for the present purposes to ascertain what period of heating at any given temperature was required to cause an appreciable decomposition.

Another interesting feature which the extrapolated curve shows is that at temperatures which are frequently reached in the laboratory the process of caramelization continues. It is only below 20° C that it is safe to keep sugar of high purity for very long periods. The fact that caramelization occurs at ordinary temperatures was first observed in a very excellent sample of sugar which had been furnished by the Institut für Zucker-Industrie several years before this investigation was started. Upon testing this sample for reducing substances, it was found to be quite inferior, but the high reducing power was later recognized to be due to caramel formation. The low polarization of this material also indicated the presence of impurity. (See experiment No. 17, Table 4.) This same phenomenon has been observed in many of our own purest samples of sucrose. For our own purposes, then, it was necessary to have comparatively fresh samples of sugar.

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[16] Aulard, Orig. Comm. VIII Int. Cong. Appl. Chem., 25, p. 493 (1912).

TABLE 4

Preliminary Series of Saccharimeter Measurements at 20° C on Approximately Normal Sugar Solutions on the Herzfeld-Schönrock Scale

Experiment number	Weight sugar (air, brass weights)	Weight solution (air, brass weights)	Sugar by weight in vacuo	Density, K.N.E.K. table	Volume of solution—		Average rotation of solution on two saccharimeters	Rotation of normal solution
					Computed from weight and density	By flask mark		
	g	g	Per cent		cc	cc	Degrees sugar	Degrees sugar
7	25.975	108.943	23.835	1.09822	99.293	99.284	100.48	99.86
8	25.673	108.823	23.584	1.09707	99.288	99.284	99.29	99.87
9	27.156	109.857	24.712	1.10223	99.761	99.757	104.57	99.89
10	25.840	109.928	23.499	1.09669			98.97	99.92
11	25.958	109.820	23.629	1.09728			99.58	99.92
12	23.978	101.429	23.633	1.09730	92.522	92.518	99.55	99.88
13	32.833	142.196	23.084	1.09480	129.996	130.001	97.06	99.92
14	26.073	109.804	23.737	1.09777			100.03	99.89
15	24.016	101.443	23.667	1.09745	92.522	92.518	99.67	99.86
16	24.000	99.127	24.204	1.09990			102.20	99.87
17	26.053	109.883	23.702	1.09770			99.79	[a] 99.78
18	25.999	109.925	23.644	1.09735			99.62	99.89
19	23.970	101.425	23.625	1.09726	92.521	92.518	99.51	99.86
20	34.251	143.003	23.966	1.09882	130.142	130.138	101.09	99.87
21	24.560	101.649	24.154	1.09967	92.522	92.521	101.92	99.83
22	23.987	101.431	23.642	1.09734	92.519	92.518	99.60	99.89
23	25.974	109.340	23.748	1.09782	99.691	99.687	100.04	99.83
24	26.588	110.108	24.139	1.09961			101.85	99.83
35	26.105	108.395	24.075	1.09931			101.60	99.87
Average								99.875
Mean scale correction								.024
Corrected average								99.90

[a] Not included in the average. (See p. 86.)

6. ELIMINATION OF MOISTURE

In order to prepare the sugar for the final weighing before polarization it was necessary to eliminate the final traces of moisture. The period of time at each temperature during which it was possible to heat the substance without causing decomposition was definitely established by the caramelization experiments. In these operations a wide margin of safety was adopted.

For a preliminary preparation and drying, the air-dried crystals were ground in an agate mortar, the pestle of which was equipped with a dust shield. In some cases the material was transferred to a crystallizing dish and placed in a vacuum desiccator over quicklime. In other instances it was introduced directly into the weighed volumetric flask and the total weight observed. Flask and sugar were then subjected to the final drying operations and the diminution of weight closely followed. It was evident from early experiments either that the residual moisture was present only in very small quantities or that it was held with great tenacity. To test this point a variety of experiments were performed, of which the following are typical:

(1) The flask containing the sample was placed in a large glass tube 70 mm in diameter fitted with a large, perfectly matched glass grinding which was lubricated with a rubber-vaseline stopcock grease. The drying agent was placed in a porcelain boat. The tube was then connected with a vacuum pump and McLeod gauge and the air exhausted until a residual pressure of 0.01 mm to 0.0001 mm of mercury was reached. The drying agent consisted usually of a quantity of calcium chloride or calcium oxide which had been recently ignited in an electric muffle furnace. Calcium oxide was used for drying all the samples used in the final series of measurements. Simultaneously with the pumping, the sample was heated uniformly by an electric oven to a temperature of 50° to 70° C. The latter temperature was never maintained for a period greater than two hours. The results of these experiments were invariably the same. The air-dried and pulverized sample lost in weight about 0.01 or 0.02 per cent at the first drying operation, provided the conditions favorable to elimination of moisture were sufficiently thorough. For this preliminary drying the sample was usually exposed to the drying agent for 24 hours or more at a pressure of 0.01 mm or less and a temperature of 50° C. Nevertheless, the rule followed in every case was to repeat the operation with more thorough procedure until a constant weight was obtained. This second operation was carried out at a higher temperature (with care to avoid caramel formation) or for an increased length of time or at higher vacuum. The air admitted to break the vacuum was passed through a drying train, consisting of H_2SO_4, P_2O_5, and CaO. The connection to the drying train was made by breaking the tip of the capillary

of the drying tube inside a short piece of clean rubber pressure tubing. The results of this second operation were uniformly the same. In no case was a loss of weight greater than one-half milligram or 0.002 per cent found, and in the great majority of instances identical weighings were obtained after the first and second drying operations.

This experiment was carried out repeatedly during the preliminary series of measurements. In two instances phosphorous pentoxide was used as a drying agent, but it produced no further desiccation than freshly ignited calcium oxide.

In order to be certain that the small diameter of the neck of the volumetric flask did not act as a deterrent to the passage of water vapor at the high vacuum, the same experiment was tried with the sugar contained in a shallow porcelain boat. The boat was pushed into a weighing bottle and stoppered before removing from the dry air of the tube. The results of this experiment were similar to the others.

(2) A sample which had been subjected to the usual preliminary drying in a porcelain boat was further treated by exposure to a stream of air dried by successively passing H_2SO_4, P_2O_5, and CaO. In the meantime it was subjected to a temperature of 70° for two hours, and 80° for one-half hour. A weighing bottle was also placed in the tube in such a way that the boat could be pushed into it and the stopper inserted while in contact with dry air. This experiment produced no further desiccation beyond the simple exposure to high vacuum and quicklime.

(3) A sample which had been introduced into a long, narrow volumetric flask and dried for 48 hours over lime was weighed and placed in a glass tube, together with freshly ignited quicklime. The tube was drawn down and sealed to the glass parts of the mercury pump. A portion of the connecting tubing dipped into carbonic acid snow during the evacuation. When a vacuum of 0.0001 mm was registered by the McLeod gauge the tube was sealed off. This was allowed to stand for a period of five months during an interruption of the work. Dry air was then admitted by breaking the tip of the capillary, while inside a piece of clean rubber tubing connected with the drying train. The

stopper was inserted while in the dry air by the action of a magnetic field on a small iron rod, which was sealed in a glass frame and which in turn held the stopper centered.

This long period of drying produced no further desiccation. The polarization of the sugar is recorded in experiment 25 of the final series.

(4) Finally a sample, which had been placed in a long, narrow flask and dried to a constant weight, was inserted in a glass tube, together with fresh quicklime, and the tube drawn down and sealed to the glass portions of a Gaede rotary mercury pump. A portion of the connecting tube dipped into liquid air to remove the mercury vapor. The sample of sugar was heated to 50° C, and was subjected to the highest vacuum which the Gaede pump would produce. This, as indicated on the McLeod gauge, was better than 0.0001 mm, and probably represented the absolute pressure, since mercury vapor was now absent from the tube containing the sugar. After some hours the tube was sealed off and allowed to remain over night. The sample suffered no loss of weight.

Water may be present in a sample, either as surface moisture existing as a film or as included mother liquor. In the first case the quantity would depend on the fineness of the crystals. It would be, moreover, the only moisture removed by the drying agent. The included moisture could hardly be expected to rupture the crystal and escape. The method of crystallization in motion and the fineness of the crystals would almost preclude the possibility of any considerable amount of included mother liquor. The following experiment corroborates this conclusion. A sample was selected in which for some reason the crystals had developed to considerable size—as large as a fine sample of granulated sugar. This was dried without pulverizing, and its polarization determined. Another portion of the same sample was then pulverized extremely fine, dried, and polarized. These two samples yielded nearly identical polarizations. (See experiments Nos. 20 and 22.) We concluded, therefore, that even when the crystals were large enough to be visible no considerable quantity of solution was included. Much less, then, is the probability when the crystals are extremely fine and are further reduced by grinding. This conclusion would be invalidated if the liberated mother liquor were exactly compensated by increased surface moisture. This latter possibility, in view of our various drying experiments, seems remote.

The accumulated evidence of all desiccation experiments led us to the conclusion that the very simple expedient of drying sugar by means of a vacuum of one-thousandth of a millimeter of Hg over freshly ignited quicklime leaves residual moisture in amount small enough to be negligible. To corroborate this conclusion it remained to apply direct tests for the presence of moisture. Two sensitive tests were applied.

E. C. McKelvy, of this Bureau, has used the critical solution temperature [17] of an alcohol-oil mixture as a criterion for the absence of moisture, and has shown that the same method is applicable to the detection of moisture in a third substance.[18] The presence of 1 per cent of water in alcohol causes a rise in the critical solution temperature of 16 whole degrees. Since a change of a few hundredths of a degree can be detected, the method offers a means of identifying a small quantity of water in a sample of alcohol. In order to test a third substance for moisture, it is necessary to digest it with a sample of dry alcohol, whose critical solution temperature with a given oil has been already determined in blank, and then to apply the test to the alcohol after the digestion. This test involves the assumption that any moisture on the third substance distributes itself between the dry alcohol and the substance. From the digestion flask the alcohol is distilled and subjected to the solution temperature test. Since ethyl-alcohol water mixtures show a minimum boiling point at 96 per cent by weight of alcohol,[19] the first portions of the distillate will be richer in water than the remaining portions if the amount of moisture in question is small. The latter should then take more moisture from the substance to keep the same distribution ratio. Consequently a great portion of the moisture should appear in the alcohol distillate. A comparison of the critical solution temperature of the distillate with the original alcohol should show at least

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[17] Bull. Bur. Standards, **9**, p. 328 (1913).

[18] Science, **38**, p. 711 (1914).

[19] Noyes and Warfel, J. Am. Chem. Soc., **23**, p. 467 (1901).

qualitatively the presence of moisture. This experiment was very carefully carried out on a sample of dried sugar by Mr. McKelvy and practically negative results obtained. It is a pleasure to thank Mr. McKelvy for this work.

E. R. Weaver, of this Bureau, has described [20] a test for a minute quantity of moisture. This test consists of the generation of acetylene by a reaction of the moisture with calcium carbide. The acetylene is allowed to react with an ammoniacal solution of cuprous chloride to form copper carbide.

The sample of sugar dried in the usual way was placed in a glass apparatus consisting essentially of three parallel test tubes sealed in a triangle at their tops. A quantity of dry ether was poured on the sugar and after a few minutes digestion was distilled into the second test tube which contained calcium carbide. It was then distilled into the third tube whence it was poured directly into the cuprous chloride solution. The results were entirely negative. To another portion of sugar the dry ether was added and fragments of carbide were placed directly in contact with the sugar. After some shaking the ether was distilled and poured into the cuprous chloride solution. Again the results were negative. About 10 g of sugar were used in the latter experiment. The method is capable of detecting 0.1 mg of moisture. One milligram of water gives a very deep color. The quantity of moisture on the sugar must then have been of the order of one-thousandth of 1 per cent. We are glad to express our indebtedness to Mr. Weaver for this experiment.

7. PURIFICATION BY PRECIPITATION WITH ALCOHOL

The dilute solution was prepared in the manner described above. It was filtered and boiled in the vacuum apparatus until the desired concentration was reached. This concentration was usually about 70 per cent with occasional variations above and below depending upon the alcohol used for the precipitation. An equal volume of alcohol was added and the whole rotated in the crystallizer over night or until crystallization was complete. This procedure has the advantage of permitting very complete

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[20] J. Am. Chem. Soc. 35, p. 1310 (1913); 36, p. 2462 (1914); Bull. Bur. Standards 13, p. 27 (1916).

clarification and filtration while in dilute solution and of avoiding the hot saturated solution which is difficult to filter and dangerous to the sucrose.

8. FRACTIONAL CRYSTALLIZATION

The method of purification by crystallization from aqueous solution permits the utilization of the mother liquor. In many instances this was simply boiled down in a vacuum and another lot of crystals obtained. The opportunity that this method affords for a fractional crystallization for the elimination of impurities of class *c* (see p. 79) is of great importance in the present investigation.

About 18 kg of granulated sugar (designated fraction 1) was recrystallized in the manner previously described. The new crystals (fraction 3) were recrystallized. The twice-crystallized portion was called fraction 6 and its mother liquor fraction 5. The first mother liquor (fraction 2) was reboiled and recrystallized. The crystals being the lesser soluble portion of the more soluble part of the original substance were presumably of similar composition to fraction 5, since the latter was the more soluble portion of the less soluble part of the original substance. These crystals were consequently combined with fraction 5 and the whole recrystallized. The new crystals formed a portion of fraction 9 and the new mother liquor became a portion of fraction 8. The fractionation is illustrated in Fig. 5. Each number represents a fraction. Those inside the diagram indicate a combination of the previously obtained crystals and mother liquor. The unnumbered ends of lines extending from the left of the figure indicate that the respective mother liquors were rejected. Impurities of lesser solubility than sucrose tend to concentrate at the right side of the diagram, those of greater solubility at the left side. Unfortunately, owing to interruptions in the work, several fractions were allowed to remain in solution for long periods of time and consequently suffered some inversion. When the work was resumed, the crystallization was continued until the invert sugar was in the extreme fraction. It was found necessary to reject several fractions which otherwise could have been utilized for test. Nevertheless, the careful measurements of fractions 30–b, 31–b, 32–a, 27, and 21 indicate that the impurities in the original sample appear only in the mother liquors. Among these impurities must have been any raffinose which may have been present. The fact that this substance is present to such an extent in beet molasses would make it seem probable that recrystallization from water would remove it. If it had still persisted in the crystals, it should have concentrated itself in some fraction after so many fractionations. The essential identity of the various fractions tested indicates the absence of this and similar substances from the recrystallized sucrose.

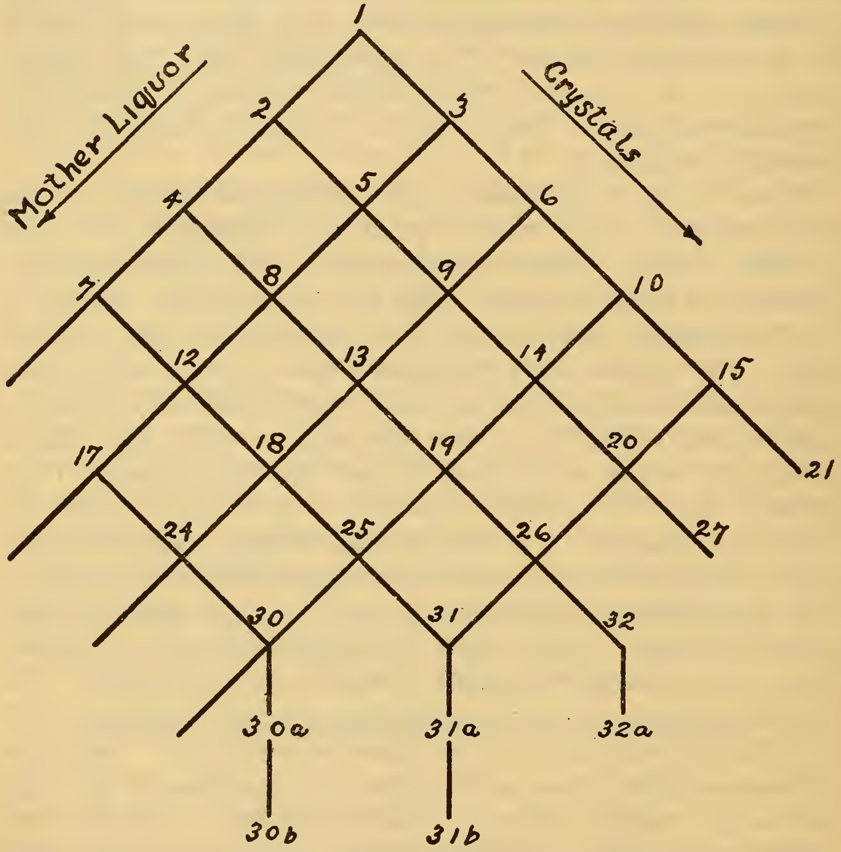

Fig. 5.—*Diagrammatic representation of fractional crystallization*

Fractions 30, 31, and 32 required one or two recrystallizations to remove small quantities of invert sugar.

9. PRELIMINARY POLARIZATION OF PURIFIED SAMPLES

The measurements recorded in the preliminary series, Table 4, were all made with samples of sugar which had undergone at least two recrystallizations. Experiments 7 to 13 were made with various samples prepared from the refined sugar of commerce. Many of the samples were obtained by recrystallization of the mother liquors. In experiments 14 and 15 the samples were precipitated by alcohol. In No. 16 the sugar was prepared from European raw-beet sugar which in the crude state polarized about 95° S. This was purged with water, clarified with alumina cream, and several times recrystallized. In experiment 17 the sugar supplied by the Institut für Zucker-Industrie was used. It has been shown on page 86 that this contained a considerable quantity of reducing substance and consequently its rotation was not included in calculating the average. Experiments 19 and 21 were made upon fraction No. 15 of the fractionally crystallized sugar described on page 93. Experiment 22 was a measurement of fraction No. 20. Experiments 20 and 22 were made upon fraction 21 and experiment 24 upon fraction 27. In experiment 35 the final purification of the sample consisted of a precipitation with purified methyl alcohol. This reagent was used because of its well-known solvent effect upon raffinose and because it offered a further variation of procedure. The result was not included in the final series because the polariscopic readings were taken by only one observer.

The preliminary measurements were continued until the procedure was entirely satisfactory. In each experiment the zero points and rotation values were observed and the averaged rotation corrected for concentration by the method described on page 115. The scale correction is obtained from Table 8. The Julius Peters instrument was not used in the preliminary series. It will be observed that the value 99°.90 S for the reading of the normal solution on the Herzfeld-Schönrock scale serves to corroborate the value obtained in the final series.

A paper describing the preliminary series of measurements in substantially the form here presented was read before the Eighth International Congress of Applied Chemistry [21] at New York in 1912. It resulted in the appointment of a subcommittee to report upon the advisability of adopting the new standard.

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[21] Orig. Comm. Eighth Int. Cong. Appl. Chem. 25, p. 517 (1912).

10. DESCRIPTION AND DESIGNATION OF SAMPLES USED IN FINAL SERIES

It is of importance to ascertain whether the alcohol used could have a harmful effect upon the sucrose. Such an effect could conceivably occur by actual combination of alcohol with sucrose to form an unknown substance which could have a very different rotary power from sucrose. Although in the absence of a catalyzer this possibility was remote, yet it seemed advisable to investigate the question. In the method which has been our main reliance, alcohol was used only in the final washing of the crystals. In the method prescribed by the international committee on uniform sugar analysis the sugar is precipitated in hot solution by alcohol. Samples A and B were prepared by methods offering the greatest possible contrast as far as the use of alcohol is concerned. To prepare sample A a quantity of sugar collected from miscellaneous samples, which had been previously twice recrystallized was recrystallized from aqueous solution in the usual manner and washed with pure water while on the centrifuge. No alcohol was allowed to come in contact with the sugar during its final preparation. During the air-drying the substance was frequently stirred to prevent the formation of cakes. A test with the copper solution showed the absence of reducing substances.

For the preparation of sample B the mother liquor from sample A was warmed with more pure sugar to form a sirup of about 70 per cent concentration. To this sirup an equal volume of pure alcohol was added and the mixture kept at a temperature of 50° C to 70° C for about 48 hours. The whole was then allowed to cool and crystallize while in continuous motion. The crystals were centrifuged and washed with alcohol. It was desired by this experiment in contrast to sample A to exaggerate any effect that might be due to the presence of alcohol. A preliminary measurement, experiment 18, showed that the sample possessed the same rotary power as the other material, and it was consequently used in the final series.

Sample C was prepared by recrystallization of the unused portion of sample A. The new crystals were washed with alcohol.

The remaining samples used in the final series were taken from the fractionated sugar, the preparation of which was described on page 93.

III. APPARATUS AND MANIPULATION

1. THE VOLUMETRIC FLASKS

A number of volumetric flasks, Fig. 6, were made for the purposes of this investigation from Jena normal 16$^{\mathrm{III}}$ glass. In the construction of these flasks no attempt was made to adjust them to exactly 100 cc, but rather attention was paid to placing the graduation mark at the most advantageous position on the neck.

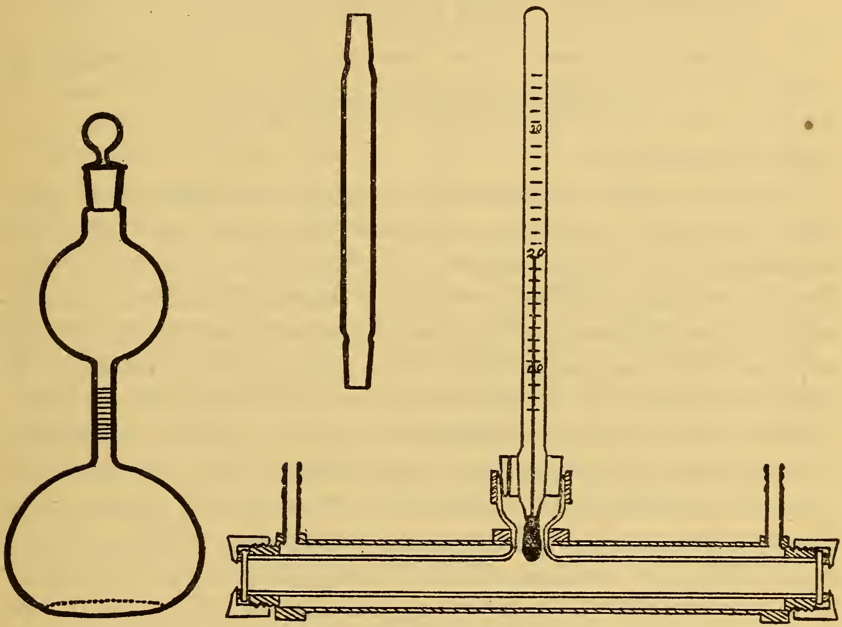

FIG. 6.—*Volumetric flask, polariscope tube, and glass connection used in conveying solution to tube*

The diameter of the neck at the graduated portion was from 5 to 7 mm. Above the graduation the neck was blown out into a bulb of about 30-cc content and at the upper end was fitted with a grinding. In two instances the necks were provided with a series of 10 graduations 0.02 cc apart. With suitable precautions the volume could be estimated to the tenth part of one of these divisions.

The flasks were calibrated by filling at 20°00 C with distilled water which was freed from dissolved air by boiling in a vacuum.

Before the final adjustment the neck of the flask above the meniscus was dried by a stream of filtered air. The temperature was adjusted by immersing the flasks in the water of a thermostat which remained constant within 0°01. The conditions for adjusting the volume of the water in the volumetric flasks were so favorable that it was found possible to reproduce the weight of contained water to 0.002 g.

2. DETERMINATION OF THE CONCENTRATION OF SOLUTIONS

In the determination of the concentration of the solutions for polarization two methods were used, both of which in many instances were applied to the same solution in order to obtain corroborative values.

The first method consisted of weighing the sugar in the flask and making the solution up to the graduation mark after the temperature had been adjusted. If, as in the two above-mentioned instances, the flask possessed a series of graduation marks, instead of a single one, the volume of solution was carefully read off to the tenth of one division. In making up sugar solutions the same procedure was followed as for the calibration of the flasks.

The second method of determining the concentration consisted of computing the percentage concentration and calculating the volume by dividing the total weight of solution in vacuo by the density of solution, the latter being obtained by reference to the density tables of the Kaiserliche Normal-Eichungs-Kommission.[22]

These two methods of determining the volume of solution checked in every instance but two to 0.005 cc or better. When the two methods were used the mean of the two determinations was taken as the volume of the solution.

It was observed that the more favorable the conditions were for making the solutions to volume, the more closely the volumetric and gravimetric methods agreed. The conditions which were subject to variation were temperature and condition of the meniscus. This agreement led us to place increasing confidence in the density tables, and in many instances the solutions were made up by the gravimetric method alone.

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[22] Plato, Wiss. Abh. der Kais. Normal-Eichungs-Kommission, **2**, p. 153 (1900). Circular Bur. Standards, **19**, p. 26 (1914)

In determining the correction for buoyancy of air for the preliminary series the value of the average density 0.0012 was assumed. For the final series the air density was determined from the temperature and barometer readings. The widest probable variations from 0.0012 would have affected the weight of the sugar or solution by a negligible quantity. For the density of dried pulverized sugar the value 1.59 was used. This is approximately the mean of the determinations of a large number of observers as well as the rounded-off figure given by Plato [23] and his coworkers.

3. PREPARATION FOR POLARIZATION

To perform a polarization a quantity of sugar, approximately 26 g, was transferred to a weighed flask and the flask again weighed after standing in the balance case. Sugar and flask were then subjected to the various drying operations previously described until assurance was had that a constant weight had been attained. Water was then added, the sugar dissolved, and the neck of the flask carefully washed down. The flask was nearly filled and the resulting solution boiled in a vacuum until the evolution of dissolved air ceased. Loss by spattering was carefully avoided. The flask and solution were then placed in the thermostat and, when a temperature of 20° had been attained, were adjusted to volume. Before weighing, the temperature of the solution was changed to approximately that of the balance case. The flask was wiped with a slightly damp cloth and allowed to remain an hour before its weight was recorded.

The solution was then carefully mixed by continually spilling into the portion of the neck enlarged for that purpose, and finally poured into the polariscope tubes. This process was carried out by means of a glass tube, Fig. 6, with grindings at both ends, one of which fitted the volumetric flasks and the other the grindings of the polariscope tubes. In this way the transfer to the tubes was accomplished without evaporation and consequent concentration of the solution. The grinding of the polariscope tube was then tightly stoppered with a glass stopper or with a thermometer.

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[23] v. Lippmann, Die Chemie der Zuckerarten, II, p. 1067 (1904).

4. WEIGHTS AND THERMOMETERS

The weights used were tested by the division of weights and measures of this Bureau by comparison with the official standards. All weighings were made by the method of substitution, a flask of similar size and shape serving for a counterpoise.

The thermometers were tested by the division of thermometry of this Bureau.

5. POLARISCOPES AND THERMOSTATS

(*a*) THE POLARIMETER.—One instrument for absolute rotation and three saccharimeters were used. The former is a special polariscope built to order for the Bureau of Standards by Franz Schmidt & Haensch. It is capable of a wide range of adjustment. The massive base rests on a three-point support and is accurately machined to permit of varying the distance between the polarizing and analyzing systems. The nicol prisms are of superior quality. The large nicol of the Lippich half-shade polarizing system is of the Glan-Thompson type and has an available opening of 14 mm. The perfection of the prisms, combined with the large apertures, make possible a high degree of sensitivity even with a 200 mm tube of solution in the instrument. The circular silver scale of the analyzing system is graduated directly to tenths of a circular degree and by means of observing microscopes reads directly to 0°001. The microscopes are 180° apart, thereby correcting for any eccentricity of the circle.

An air bath with dimensions of 60 cm by 40 cm by 55 cm was placed between the polarizing and analyzing systems and mounted on separate supports to eliminate the possibility of disturbing the adjustments of the polariscope by opening and closing the door. The trough of the instrument passed through the end walls of the thermostat without touching them. There was thus a complete separation of thermostat and polariscope.

The thermostat was cooled below 20° C by ice water circulating through a copper coil and then heated to 20° C. The heating was accomplished by a wire coil wound on a separate frame with the same dimensions as the inside of the bath. The direction of the windings was such that any magnetic field produced was at right angles to the path of the light. Careful tests failed to show the slightest magnetic rotation of the plane of polarization. The heating current was regulated by means of a toluene coil, a relay and a mercury contact interrupter. The temperature was controlled more closely than 0°.05 C.

(*b*) THE LARGE THERMOSTAT.—The saccharimeter readings were made in a large thermostat with a content of about 15 cubic meters. The temperature regulation was very similar in principle to that already described above in connection with the polarimeter for absolute measurements. The air was chilled below 20° C by a brine coil. In order to obtain effective regulation at 20° C a thermostatic heater of 800 watts capacity was required. The capacity and regulation left little to be desired. With two observers in the thermostat the maximum variations were about 0°.3 C.

(*c*) THE SACCHARIMETERS.—Three different makes of saccharimeters were used in order to eliminate the possibility of some peculiarity of the instrument construction affecting the measurements. They were a Bates type Fric, a Schmidt & Haensch, and a Julius Peters. Two instruments were used in each experiment, one of which was always the Bates type Fric.

The Bates type has been fully described [24] by one of us. It is sufficient for our purpose to note that the instrument used was a 200 mm double quartz-wedge compensating saccharimeter with transparent glass scales which could be read directly to 0°.01 S. It was equipped with a thermometer graduated in fifths of a degree, which gave the temperature of the wedges. The optical system is shown diagrammatically in Fig. 7. This saccharimeter was inclosed in a wooden thermostat insulated with asbestos. The method of automatic temperature control was similar to that used on the thermostat described above in connection with the large polarimeter for absolute measurements. The maximum temperature variations were generally a few hundredths of a degree. In order to manipulate the quartz wedges the milled head was removed from the horizontal rod which shifted the wedges and replaced by a long shaft which passed through the wall of the thermostat. The outside end of the shaft was fitted with a lever, about 10 cm long, in order to secure the slow movement of the wedges necessary to utilize the high sensibility of the instrument.

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[24] Bates, Bull. Bur. Standards, 4, p. 461 (1908).

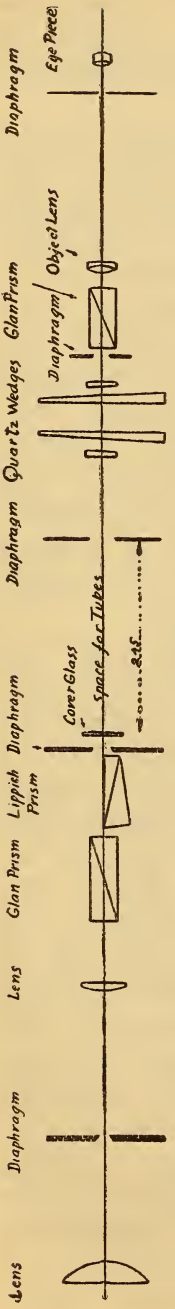

FIG. 7.—*Optical system of the Bates-Fric saccharimeter*

FIG. 8.—*Optical system of the Schmidt & Haensch saccharimeter*

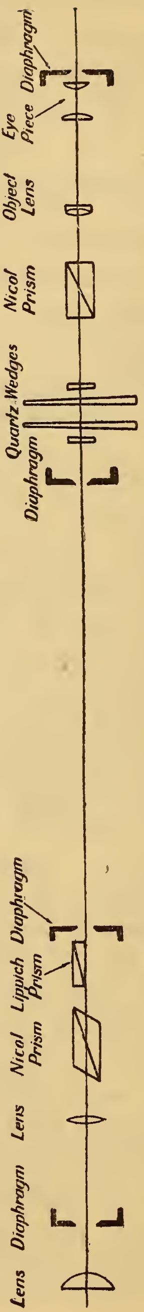

FIG. 9.—*Optical system of the Peters saccharimeter*

The Schmidt & Haensch saccharimeter was a modern instrument and an excellent example of the work of that firm. It had a double quartz-wedge compensation and a small but sensitive half-shadow field. The half-shadow angle of the Lippich polarizing system was about 6°. This saccharimeter accommodated tubes up to 600 mm in length. As it was not equipped with a thermometer giving the temperature of the wedges a hole was made in the metal case containing the analyzing system and a thermometer inserted with the bulb in proximity to the wedges. The arrangement of the optical system is shown in Fig. 8. The nickelin scales, being illuminated by reflected light, had a broad black line between verniers and scales. This fact, together with the width and irregular edges of the rulings, made it impossible to read the scales with an accuracy corresponding to that with which the settings could be made. The difficulty was overcome by resorting to the more laborious method of the micrometer microscope. The regular scale telescope of the saccharimeter was replaced by a microscope equipped with parallel cross hairs and rotating drum. The graduations on the drum were of a magnitude such that one division corresponded to a shift of the cross hairs of about 0°.01 S. In order to decrease the movement of the wedges corresponding to a given movement of the observer's hand a lever was attached perpendicular to the vertical drive rod which moved the wedges.

The Peters saccharimeter was an excellent instrument built for tubes up to 200 mm in length. It had a large and sensitive field. The Lippich polarizer had a half-shadow angle of about 6°. The optical system is shown diagrammatically in Fig. 9. The instrument was equipped with a thermometer giving the temperature of the wedges. The same difficulty was encountered in reading the nickelin scales as in the Schmidt & Haensch saccharimeter. It was overcome in the same way by the use of a suitable micrometer microscope. An additional lever was also found necessary in order to obtain a smaller movement of the quartz wedge. The instrument was tested on the basis of standardization adopted by the International Sugar Commission, at the Institut für Zucker-Industrie. The certificate showed that eight points on the positive wedge were checked against sugar solutions with a maximum error of 0°02 S, the 87°5 S and the 100° S points showing zero corrections.

6. LIGHT SOURCES

Two spectrum lines were utilized for the measurement of the rotations in circular degrees, namely, $\lambda = 5461$ Å and $\lambda = 5892.5$ Å. The former is the so-called "yellow-green" line of incandescent mercury vapor. Its many advantages for polarimetric work have already been described by one of us.[25] The lamps used were of quartz. These were fitted with special air-cooling apparatus, which permitted their operation at the high current densities necessary to give the desired intensity. The source $\lambda = 5892.5$ Å was obtained from the two sodium lines D_1 and D_2 by heating fused Na_2CO_3 in an oxyhydrogen flame. Both of these sources were carefully purified by means of an improved type of dispersive system which will be described by one of us in a subsequent paper. The purification secured was so perfect that with intensities sufficiently high to permit the use of a half-shadow angle of 3° for reading the solutions the field of the instrument was well illuminated and uniform in color.

The white light source used in the saccharimeter measurements was the same as that employed in the original Herzfeld-Schönrock research previously referred to and which gave the relation 100° S = 34°657 for the value of the conversion factor. The light from a Welsbach mantle (Auerlicht) was passed through a 15 mm thickness of a 6 per cent solution of potassium bichromate before it entered the instrument. This method of modifying the character of the light was officially adopted by the International Congress for Uniform Methods of Sugar Analysis at the New York meeting [26] in September, 1912.

7. QUARTZ CONTROL PLATES

Two quartz plates, designated Nos. 1 and 3, were used throughout the measurements. Both are of excellent quality, optically homogeneous, nearly plane parallel and are primary standards of

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[25] Bates, Bull. Bur. Standards, **2**, p. 239 (1906).

[26] Bryan, Am. Sugar Ind., Nov. 1912, p. 62. Zs. Ver. Zuckerind. **63**, I, p. 29 (1913); Int. Sug. J., **15**, p. 8 (1913).

the Bureau of Standards. They have been tested at this Bureau, and at the Physikalisch-Technische Reichsanstalt, and in addition plate 1 has been tested at the Institut für Zucker-Industrie. A summarized statement of the values of the physical constants of these plates in our possession at the beginning of the research is given in Table 5. All the values given in sugar degrees are on the basis of standardization adopted by the International Sugar Commission. The values in the column headed "calculated" were obtained by using the Herzfeld-Schönrock conversion factor and the accepted value of the rotation in circular degrees. All rotation values are for 20°.

TABLE 5

Physical Constants of Quartz Control Plates

Plate	Diameter	Axis error in degrees, P. T. R.	Rotation in circular degrees				Rotation in sugar degrees	
			λ=5892.5Å, B. S.	λ=5892.5Å, P. T. R.	λ=5892.5Å accepted value [27]	λ=5461Å, B. S.	Calculated	Inst. Zuck. Ind.
	mm							
1	15.6	0.052	34.597_8	34.596	34.596_9	40.662_6	99.827	99.82
3	16.0	0.037	34.629_2	34.626	34.627_6	40.697_3	99.915	....

[27] Bates, Bull. Bur. Standards, 2, p. 239 (1906).

In order to utilize the high sensibility of the large polarimeter it is necessary to take unusual precautions to insure that the axis of each polariscope tube and quartz plate be parallel to the axis of the optical system of the instrument. A simple calculation shows that in order to produce an increase of 0°001 in the rotation angle between the axis of tube or plate and that of the instrument must be about 27 minutes. The eyepiece of the observing telescope was replaced with a Gauss ocular and the trough adjusted until the axes coincided within approximately 15 minutes. The maximum possible error due to this source was therefore of the order of 0°0005.

8. POLARISCOPE TUBES

The polariscope tubes used were all of glass, similar in design and 200 mm in length. Preliminary experiments with 400 mm tubes read on the large polarimeter demonstrated the desirability of using the shorter tube. Two of the saccharimeters would not take the 400 mm tubes and it was advantageous in each experiment to read the same tube on both saccharimeter and polarimeter. In addition the short tube is easier to handle, it is not so difficult to keep the temperature of the liquid uniform throughout, and the definition of the polariscope field is considerably better.

All the tubes, Fig. 6, were of the water-jacketed type. Owing to the fact that air-bath thermostats were used it was unnecessary to flow water through the metal jacket to maintain the temperature of the tube at 20°. A side tube with a 10 mm opening extended into the tube proper. The flared outer end of the side tube carried a glass stopper through which a thermometer, fitted to the stopper by a ground joint, extended into the body of the solution. A capillary opening in the stopper eliminated any undue pressure on the cover glasses and consequent danger of double refraction. The cover glasses were carefully selected and were fairly free from internal strains. Inasmuch as the measurements were all made at one temperature, practically no difficulty was experienced in preventing leakage around the cover glasses. No adhesive or cement was necessary to prevent evaporation. The lengths (Table 6) were determined by D. R. Miller of the division of weights and measures. Inasmuch as the rotation measurements necessarily extended over a considerable period of time, the lengths were redetermined after an interval of about one year. Both determinations were in good agreement. The values accepted were each the average of two series of observations, one series being taken on the rim and the other with the cover glasses in place.

TABLE 6

Lengths of Polarization Tubes, with Corrections for Normal Solution

Tube number	Length in millimeters at 20° C	Corrections in degrees sugar	Corrections in circular degrees λ=5461 Å
8819A	199.945±.005	+0.028	+0.011
8819B	199.952±.005	+ .024	+ .010
7294A	199.984±.005	+ .008	+ .003
5797A	200.025±.005	− .013	− .005

9. ROTATION PRODUCED BY POLARISCOPE TUBES FILLED WITH WATER

Any change in the general appearance of a photometric field is likely to cause a difference between the settings before and after the change. The magnitude of this difference varies with the individual. It is thus of great importance in measuring the absolute rotation of a substance to insure that no change in the appearance of the field occurs between the determination of the zero point and the tube reading. The apparent total rotation of a tube of solution may thus consist of the rotation due to the active solution plus or minus a small apparent rotation due to the changed appearance of the field. The latter may be due to a number of causes, among which may be mentioned slight double refractions, lens effects, etc. Obviously the most effective method of elimination is to determine the zero point with the tube filled with the inactive solvent. Owing to the fact that it was necessary to have the tubes dry before filling with solution it was impracticable to do this. An investigation was therefore made of the change in the zero point by a tube filled with distilled water. In many instances after the observations on the sugar solutions had been made the tubes were thoroughly cleansed without removing the cover glasses, filled with distilled water, and read. A series of experiments on two tubes is given in Table 7.

TABLE 7

Rotation by Tubes Filled with Water

Tube 7294A	Tube 8819A
Degrees	Degrees
−0.0015	−0.0002
−0.0020	0.0000
−0.0043	+0.0001
+0.0003	−0.0013
−0.0013	−0.0009
....	−0.0023
0.0000	0.0000
Av. −0.0015	Av. −0.0007

In the measurements on the normal solutions the zero point was determined without the use of the tube, and from an inspection of the data in Table 7 it is very questionable whether any increase in the accuracy of our measurements could be made by a zero correction obtained by reading the tube filled with water. We have therefore in the present investigation assumed that the total rotations measured were due solely to the sucrose.

IV. OBSERVATIONS AND COMPUTATIONS

1. SACCHARIMETER VALUES OF QUARTZ CONTROL PLATES

In order to determine the agreement among the three saccharimeters and the average deviation from the Herzfeld-Schönrock values, as well as for use in the calculations in the present investigation, a series of plate readings were made. The data are summarized in Table 8. Each value is the average of two series of readings by independent observers. In taking the readings the procedure was to make six settings on the zero point followed by six settings on the plate and four on the zero. The agreement between the average values for the three different makes of instruments is very satisfactory, and is an excellent illustration of the degree of perfection attained in the modern saccharimeter. From Table 5 the sodium values of plates 1 and 3 are 34°597 and 34°628, respectively. Since the Herzfeld-Schönrock value gives 0°34657 = 1° S, we obtain 99°827 S for the value of plate 1 and 99°915 S for plate 3. From Table 8 the grand average for plate 1 is $99^\circ80_5$ S and $99^\circ88_2$ S for plate 3. The average difference between the observed and the theoretical values is thus $0^\circ02_7$ S. It is therefore evident that these modern saccharimeters give an average reading which is $0^\circ02_7$ S lower than they should if accurately standardized on the Herzfeld-Schönrock value so as to conform to the basis of the International Sugar Commission. A similar calculation using the old equation,[28] 0°3469 = 1°, shows these saccharimeters give an average reading which is $0^\circ06_7$ S higher than the Ventzke basis of standardization.

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[28] Landolt, Das Optische Drehungsvermögen 2 Auflage, p. 337 (1898).

TABLE 8

Saccharimeter Readings on Quartz Plates

Plate 1 (Herzfeld-Schönrock value= 99°827 S)			Plate 3 (Herzfeld-Schönrock value= 99°915 S)		
Bates-Fric	Schmidt & Haensch	Peters	Bates-Fric	Schmidt & Haensch	Peters
99°82	99°81	99°81	99°91	99°96	99°88
.85	.81	.80	.89	.84	.87
.81	.80	.81	.88	.86	.88
.82	.81	.79	.89	.88	.88
.80	.79	.79	.89	.84	.86
.78	.82	....	.86	.87	....
.77	.82	....	.86	.88	....
.82	.80	....	.88	.94	....
.82	.82	....	.88	.89	....
.78	.82	....	.93	.88	....
.81	.80	....	.91	.88	....
.79	....	....	.86	....	....
.81	....	....	....	....	....
Av. 99°80$_6$	99°80$_9$	99°80$_0$	99°88$_7$	99°88$_4$	99°87$_4$

Grand average for plate 1	99°80$_5$
Grand average for plate 3	99°88$_2$
Average instrument error, Bates-Fric	0°02$_4$ S
Average instrument error, Schmidt & Haensch	0°02$_4$
Average instrument error, Peters	0°03$_4$
Average	0°02$_7$

2. $\frac{\phi^{20}_{\lambda=5892.5\ \text{Å}}}{\phi^{20}_{\lambda=5461\ \text{Å}}}$ FOR THE NORMAL SUCROSE SOLUTION

The ratio of the rotations of quartz for λ = 5461 Å and λ = 5892.5Å being known with a high degree of precision it is desirable for use in the present investigation as well as for other purposes to establish a similar ratio for sucrose. Since the constant to be determined is a ratio it is unnecessary to prepare exactly normal solutions for the experiments, although the solutions used were very nearly normal. The sucrose was taken from a selected sample of known purity. Seven complete experiments were made. Two tubes, described above, were measured in each experiment, a complete set of observations being taken by two independent observers. Since it is of great importance to maintain the physical condition of the tubes constant throughout each experiment the temperature was carefully controlled at 20° C and the observations completed on the same day they were begun. In addition the light sources were so arranged that the shifting from one to the other was made with but little loss of time, thus eliminating the possibility of a change in the condition of the solution. Ten zero point and ten tube settings were made by each observer for each light source. The data are summarized in Table 9. We have therefore

$$\frac{\phi^{20}_{\lambda=5892.5\,\text{Å}}}{\phi^{20}_{\lambda=5461\,\text{Å}}}=0.84922 \qquad (3)$$

TABLE 9

Value of $\frac{\phi^{20}_{\lambda=5892.5\,\text{Å}}}{\phi^{20}_{\lambda=5461\,\text{Å}}}$ for Sucrose

Experiment	$\varphi^{20}_{\lambda=5461\,\text{Å}}$, circular degrees	$\varphi^{20}_{\lambda=5892.5\,\text{Å}}$, circular degrees	$\frac{\varphi^{20}_{\lambda=5892.5\,\text{Å}}}{\varphi^{20}_{\lambda=5461\,\text{Å}}}$
1	40.7772	34.6349	0.84937
2	40.7761	34.6239	.84912
3	40.7860	34.6357	.84921
4	40.5044	34.3975	.84923
5	40.5207	34.4073	.84913
6	40.9978	34.8163	.84922
7	41.0110	34.8297	.84928
Average			.84922±.00002

Subsequent to the determination of the similar ratio for quartz made by one of us, a redetermination of this constant was made with the assistance of Francis P. Phelps, on the apparatus used in the present research and the value 0.85076 was obtained, the original determination giving 0.85094. Taking the average of these we obtain

$$\frac{\phi^{20}_{\lambda=5892.5\,\text{Å}}}{\phi^{20}_{\lambda=5461\,\text{Å}}}=0.85085 \qquad (4)$$

We thus have 0.00163 as the difference between 0.85085 and the above value for sucrose. The quantity 0.00163 is due to the difference between the rotary dispersion curves of quartz and sucrose in this portion of the spectrum, thereby producing color effects in the field of the quartz-compensating saccharimeter when a white light source is used and necessitating the adoption of the potassium bichromate filter.

3. CORRECTIONS FOR TEMPERATURE

The temperature corrections in polarimetric work are unusually complicated. In precision measurements it is therefore desirable to keep all corrections as small as possible. Fortunately the standardization temperature of 20° C being practically room temperature, greatly facilitates this. The specific rotation coefficient for quartz is 0.000136. The linear coefficients of expansion parallel and perpendicular to the optic axis and for the nickelin scales used on quartz wedges are 0.000007, 0.000013, and 0.000018, respectively. Thus the total temperature coefficient for the ordinary saccharimeter is

$$0.000136+0.000007-0.000013+0.000018=0.000148 \qquad (5)$$

If the scale be of glass, 0.000008 must be substituted for 0.000018 and the right-hand member of (5) becomes 0.000138. Since the effect of the expansion coefficient 0.000148 is to lower the reading of the scale with an increase of temperature, the apparent polarization of any substance is lower than it should be and the reading at 20° (S_{20}) is given by the following:

$$S_{20}=S_t+S_t\,0.000148\,(t-20) \qquad (6)$$

When a quartz control plate is read in a saccharimeter this effect is not completely compensated. The temperature coefficient of the plate is

$$0.000136+0.000007=0.000143 \qquad (7)$$

The reading (W_{20}) of the plate is then

$$W_{20}=W_t+W_t\,0.000005\,(t-20) \qquad (8)$$

where t is the temperature of the wedges. The correction given by (8) changes sign if the scale be of glass.

When a normal sucrose solution is polarized in a glass tube the linear expansion coefficient of the tube is 0.000008. The temperature coefficient of the specific rotation at 20° C for the normal sucrose solution ($p = 23.701$) has been given by Schönrock as 0.000184. The expansion coefficient of the solution is 0.000285. The temperature coefficient for tube and solution is thus

$$-0.000008 + 0.000184 + 0.000285 = 0.000461 \tag{9}$$

and the reading of the solution at 20° C (R_{20}) is given by

$$R_{20} = R_t + R_t \, 0.000461 \, (t - 20) \tag{10}$$

4. DETERMINATION OF THE READING OF THE NORMAL SOLUTION ON THE HERZFELD-SCHÖNROCK SCALE

In order to check the accuracy of the Herzfeld-Schönrock scale 10 complete experiments, numbers 25 to 34, inclusive, were made in the final series of measurements. Two 200-mm tubes of solution were used in each experiment, with the exception of number 26, in which one tube was lost. The solutions were prepared as described above. The fact that no attempt was made to prepare accurately normal solutions was of advantage in that the observers could be in no degree prejudiced by a foreknowledge of what the instrument reading should be. Only after the experimental work was completed and the correction for the concentration applied was the reading of the normal solution known. If the Herzfeld-Schönrock values for the international commission's basis of standardization are correct, then our solutions, when corrected for concentration, should read 100° S on the saccharimeter within the limits of the experimental error.

The data describing the solutions used in the final series of measurements are given in Table 10. In each experiment the solutions were made up to volume and all observations completed on the same day. Each of the two tubes was read by two observers on two saccharimeters. When the tubes were first placed in a thermostat they were allowed to remain at least two hours before reading, in order to bring solution and air to the same temperature. In experiments 25 and 26 no plate readings were taken. Not less than six zero-point settings were made, followed by not less than six tube settings and four more zero-point settings. The second tube was then read, and finally not less than six additional zero-point settings made. In experiments 27 to 34, inclusive, the zero points were not read. Instead six readings were taken on plate 1, followed by eight readings on a tube of solution, six readings on plate 3, and eight on the second tube of solution. The temperatures of the air bath, the solution, and the wedges were taken at the beginning and end of each set of six or eight observations. A complete record was thus secured of the temperature conditions throughout each experiment. Owing to the excellence of the thermostats, we were able to make our measurements at a practically constant temperature, which seldom differed from 20° C by more than 0°.2 C. The corrections to be applied were therefore small.

In the present investigation all solutions were made up to volume at 20° C. In order to obtain the rotation on the saccharimeter, it is then necessary to correct the reading for the temperature difference between 20° C and the solution temperature and 20° C and the quartz-wedge temperature. The instrument correction was obtained from (6) (*t* being the temperature of the wedges) and seldom exceeded 0°.003 S. No distinction was made between the corrections for glass and nickel in scales. Similarly, in reading the quartz plates, equation (8) was ignored owing to the fact that the correction was negligible. The correction for the solution is given by (10). The magnitude of this correction rarely exceeded 0°.01 S.

The agreement between the readings of the individual observers for the final series of measurements is shown in Table 11. While it is true that all difference in color between the two halves of the field of a saccharimeter is not eliminated by the use of the bichromate cell, yet the elimination must be fairly complete as indicated by the agreement between the readings. This is in accord with the results obtained by Schönrock[29] who has made an investigation of this important point.

The saccharimeter readings for the normal solutions are given in Table 12. In experiments 25 and 26 the rotation is the difference between the zero point and the tube reading after adding the scale correction from Table 4. In the remaining experiments

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[29] Loc. cit.

TABLE 10

Data on the Preparation of the Solutions

Experiment	Designation	Weight of sugar (air, brass weights)	Weight of solution (air, brass weights)	Sugar by weight in vacuo	Density, K.N.E.K. tables	Volume of solution	
						Computed from weights and density	By flask mark
1	2	3	4	5	6	7	8
		g	g	Per cent		cc	cc
25	Fraction 27	24.370_8	101.570	23.986_6	1.09891	92.514	92.518
26	Fraction 27	26.207_2	109.497	23.926_1	1.09863	99.761	99.750
27	Fraction 27	34.052_3	142.665	23.861_0	1.09834	130.010	130.012
28	Sample C	24.029_2	101.546	23.655_7	1.09741	...	...
29	Fraction 30	23.856_3	101.381	23.523_3	1.09680	92.518	92.520
30	Fraction 32	34.018_3	142.636	23.841_9	1.09825	130.000	129.997
31	Fraction 31	24.181_1	101.496	23.817_0	1.09814	...	...
32	Fraction 31	26.003_3	109.533	23.732_4	1.09775	...	...
33	Sample A	34.326_1	143.045	23.988_7	1.09892	...	...
34	Sample B	25.881_3	109.610	23.604_5	1.09717	...	...

TABLE 11

Agreement Between Individual Observers with Use of Bichromate Light Filter

Experiment	Bates-Fric		Schmidt & Haensch		Peters	
	Observer A	Observer B	Observer A	Observer B	Observer A	Observer B
	Degrees	Degrees	Degrees	Degrees	Degrees	Degrees
25	99.908	99.891	...	99.903	...	...
26	99.916	99.902	99.852	99.852	...	...
27	99.872	99.874	99.870	99.905	...	...
28	99.874	99.883	[a] 99.912	99.894	...	...
29	99.893	99.872	...	...	99.859	99.854
30	99.920	99.937	...	...	99.890	99.928
31	99.863	99.884	...	...	99.885	99.909
32	99.901	99.898	...	...	99.965	99.884
33	99.896	99.907	...	...	99.915	99.887
34	99.905	99.896	...	...	99.878	99.900
Mean.	99.895	99.895	99.876	99.889	99.899	99.894

[a] Solution observed in only one polariscope tube.

TABLE 12

Reading of the Normal Solution on the Saccharimeter

Experiment	Average rotation of solution for two saccharimeters, degrees sugar	Rotation of normal solution on the saccharimeter, degrees sugar			
		Bates-Fric	Schmidt & Haensch	Peters	Average
1	9	10	11	12	13
25	101.19_2	99.90_0	99.90_3		99.90_2
26	100.89_6	99.90_9	99.85_2		99.88_0
27	100.61_4	99.87_5	99.88_9		99.88_2
28	99.68_7	99.88_1	99.90_5		99.89_3
29	99.04_4	99.88_5		99.85_8	99.87_0
30	100.56_0	99.93_0		99.91_1	99.92_1
31	100.41_8	99.87_6		99.89_9	99.88_8
32	100.05_1	99.90_2		99.92_7	99.91_4
33	101.23_2	99.90_4		99.90_3	99.90_4
34	99.43_8	99.90_3		99.89_1	99.89_7
Average		$99^\circ.89_7$S	$99^\circ.88_7$S	$99^\circ.89_2$S	$99^\circ.89_5$S

the total instrument correction, including the zero-point error, is found by subtracting the Herzfeld-Schönrock values of plates 1 and 3 from the readings of these plates in each experiment. The value obtained when this correction is added to the tube reading gives the actual reading of that tube on the Herzfeld-Schönrock scale. This method, which is much used in polarimetric measurements when a plate of known value can be used to eliminate errors due to instrument and light source, obviates the necessity of reading the zero point. It also eliminates as far as possible the question of any error due to a change in the instrument correction.

The final correction to be applied to the tube reading is that for concentration. Inasmuch as we may assume that the rotation is directly proportional to the concentration we have

$$R=\frac{CR'}{C'} \qquad (11)$$

where R and C are the rotation and concentration of the normal solution and R' and C' the rotation and concentration of a near normal solution. From the definition of the normal solution C is 26 grams, and as all weighings were corrected to vacuo it becomes 26.0159. R' is the observed saccharimeter reading.

$$\text{Obviously } C' = 100\,\frac{\text{Weight of sugar in vacuo}}{\text{Volume of solution.}}$$

$$= 100\,\frac{\text{Weight of sugar in vacuo} \times \text{density of solution}}{\text{Weight of solution in vacuo.}}$$

We thus have

$$R = 0.260159\,\frac{R'\ (\text{Weight of solution in vacuo})}{(\text{Density of solution})\ (\text{Weight of sugar in vacuo})} \qquad (12)$$

Equation (12) was applied to the rotation of each tube as measured by each observer, giving four values for the rotation of normal solution on each saccharimeter in each experiment. The rotations given in columns 10, 11, and 12, Table 12, are the averages of these four values. Column 9 shows the rotations actually measured. The values in column 13 show the rotation of the normal solution on the Herzfeld-Schönrock scale for each experiment. It will be observed that the agreement of the determinations for the different saccharimeters as well as that between the individual experiments is very satisfactory and that in no instance did the rotation of a normal solution even approximate 100° S. The average of column 13 is $99\overset{\circ}{.}89_5$ S. We therefore conclude that the Herzfeld-Schönrock scale is in error by $0\overset{\circ}{.}10_5$ S; and that the ordinary saccharimeter, inasmuch as its wedges are calibrated to that scale, gives readings for polarizations in the neighborhood of 100° S that are $0\overset{\circ}{.}10_5$ S too low.[30]

5. THE ABSOLUTE ROTATION OF THE NORMAL SOLUTION FOR THE MERCURY LINE, $\lambda=5461$ Å

On the same day that each of the saccharimeter measurements given in Table 12 was made the solutions were read in the large polarimeter to obtain the rotation of the normal solution for the polarimetric standard light source, the so-called yellow-green line

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[30] Subsequent to the presentation of our preliminary paper at the Eighth International Congress of Applied Chemistry, Walker checked our value for the reading of the normal solution on the saccharimeter. (See Sugar, 17, No. 2, p. 47 (1915). He prepared sucrose by the alcohol method and obtained $99\overset{\circ}{.}88$ S. He also read a standard sample issued by the Bureau of Standards and obtained $99\overset{\circ}{.}90$ S. It is important to note that a careful experimenter with average laboratory facilities obtains results in agreement with the value given in Table 12.

of incandescent mercury vapor, $\lambda = 5461$ Å. When the tubes were placed in the instrument ample time was allowed for the solution to come to the temperature of the thermostat. This was done because the thermometer in the solution was not read. Instead the temperature of the air in the immediate vicinity of the tube was taken.

TABLE 13

Rotation of Normal Solution for $\lambda = 5461$ Å

Experiment No.	Rotation $\lambda = 5461$ Å	Experiment No.	Rotation $\lambda = 5461$ Å
	Degrees		Degrees
25	40.757	31	40.749
26	40.770	32	40.769
27	40.761	33	40.771
28	40.763	34	40.767
29	40.751		
30	40.773	Average	40.763

Each of the two tubes was read by two observers. Each observer made not less than six readings on the zero point, alternating with right and left eyes. The temperature was then taken and not less than six readings made on the tube of solution, temperature taken, and not less than six zero-point readings made. Temperature was then taken and the second tube read. Temperature was again taken and six additional zero-point readings made. The scale readings were equally divided between the two reading telescopes, 180° apart, in order to correct for any eccentricity of the circle. In general, the zero-point readings immediately preceding and following the tube readings were taken to determine the zero point for that tube. The effect of any possible shift in the zero point such as might arise from a change in the illuminating system is thus eliminated. In making the corrections for the temperatures of the solutions (24) was used. The temperature of the thermostat was maintained so nearly at 20° that the magnitude of the correction was seldom 0°002. The results of the measurements are given in Table 13. In the development of polarimetric measurements at the Bureau of Standards a number of different methods of purification for intense monochromatic sources have been experimented with. The two systems finally adopted show a small unexplainable difference in the rotations obtained. We have therefore made a correction of 0°004 to the rotations actually measured so that our values are what we would have obtained had the solutions been measured with both dispersive systems. The rotation of the normal solution, column 2, correcting for concentration, was obtained from (12). Taking the average value for the 10 experiments we obtain

$$\begin{aligned}&\text{Normal sugar solution} = 100^\circ \text{ sugar} = \\ &\quad 40^\circ\!.763\ (\lambda = 5461\ \text{Å}) \text{ at } 20^\circ\ \text{C}\end{aligned} \tag{13}$$

6. THE ABSOLUTE ROTATION OF THE NORMAL SOLUTION FOR THE SODIUM LINES, λ=5892.5 Å

In Table 9 the ratio of the rotations of the near-normal sucrose solution for λ = 5892.5 Å and λ = 5461 Å is shown to be 0.84922. The rotation of the normal solution for λ = 5461 Å being 40°763 we have

$$\begin{aligned}\text{Normal sugar solution} &= 100^\circ \text{ sugar} = 40^\circ\!.763 \times 0.84922 \\ &= 34^\circ\!.616_7\ (\lambda = 5892.5\ \text{Å}) \text{ at } 20^\circ\ \text{C}\end{aligned} \tag{14}$$

as the absolute rotation of the normal solution for the sodium lines.

7. DETERMINATION OF THE CONVERSION FACTOR

The value of the conversion factor has been determined by two methods of calculation, both of which are wholly independent of the data obtained by previous investigators. In both methods the tubes of solution are used to make an independent calibration of the wedges of the saccharimeters in each experiment. Inasmuch as the same fundamental data are used in each procedure, the object in determining the conversion factor by two methods is to secure a positive check on the final value for each experiment.

From the definition of the conversion factor previously given we have

$$\text{Conversion factor} = \frac{100 \text{ rotation of plate in circular degrees}}{\text{Rotation of plate on true saccharimeter scale}} \tag{15}$$

Since the rotations of plates 1 and 3 in circular degrees are known from Table 5, it is only necessary to determine the rotation of the plates on the true saccharimeter scale as determined by our normal solutions.

The first method is the more direct of the two. The conversion factor is calculated for each experiment entirely from the data secured during that experiment. This has been accomplished by calculating directly the correction which must be applied to the saccharimeter reading in order that the normal solution shall read 100° S on that scale. All the errors involved in the instrument error, such as zero and scale errors, are automatically eliminated. The correction for each experiment is thus obtained, which must be applied to the quartz-plate readings taken during the experiment to find the values of the plates on the true scale. The latter must be known in order to calculate the conversion factor. We have therefore

$$100^\circ\text{ S (true scale)} = (\text{Reading of solution} \pm \text{instrument correction})\ (\text{concentration factor}) \qquad (16)$$

or

$$\text{Instrument correction}^{31} = \text{Reading of solution} - \frac{100}{\text{Concentration factor}} \qquad (17)$$

In this method advantage is taken of the fact that the true scale and the Herzfeld-Schönrock scale differ by only 0°.1 S at the 100° points. It thus becomes possible to use quartz plates whose sugar values differ to a considerable degree from that of the true normal quartz plate without appreciable error due to the difference in the units of the two scales. Plate 3, with a value of 99°.915 on the Herzfeld-Schönrock scale is very nearly a normal plate for the true scale, and plate 1, with a value of 99°.827 differs by less than 0°.1 S from a true normal plate. The maximum possible error in the value of the rotation of plate 1 on the true scale is therefore of the order of 0°.0001 S and is negligible. The instrument correction given by (17) is applied to the quartz-plate readings secured in each experiment to obtain the values of the plates on the true saccharimeter scale. The conversion factor is then calculated from (15).

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[31] Instrument correction here includes zero displacement as well as the errors in the scale graduation.

In the second method the scale readings on plates 1 and 3 in each experiment are averaged. The difference between this value and the averages for the two saccharimeters used, given in Table 8, gives the zero correction. The correction is applied to the tube readings giving the observed rotation of the solution. The correction for concentration is then made by equation (12) which gives the rotation of the normal solution. This value would have been 100° S on a true scale. We have, therefore, using the observed plate rotation from Table 8,

Rotation of plate on true scale

$$=\frac{100\ (\text{Observed rotation of plate})}{(\text{Reading of normal solution})} \qquad (18)$$

The conversion factor is then calculated from (15).

Although the procedure in this method differs from that indicated in the preceding and a zero-point correction is necessary, it should be noted that any possible error in the determination of the zero point due to the use of the plate values from Table 8, can not enter into the value for the plate rotation on the true scale. Obviously from (18) the desired value is a ratio. Since any error made in determining the zero point is present in both the numerator and the denominator of (18), it is not essential to know the plate readings from Table 8 to an accuracy greater than will affect the value of the sixth figure in the ratio. In this method as well as in the first method no accurate determination of the zero point is essential and the number of saccharimeter readings in each experiment necessary to the determination of the conversion factor is reduced to the minimum.

The values of the conversion factor by the first method are given in Table 14. The procedure indicated above for that method was modified in using the data from experiments 25 and 26. Since the zero was directly determined the scale correction was calculated by using the instrument correction from (17), and added to the plate values from Table 8 in order to obtain the reading of the plates on the true scale. The accuracy of the values from experiments 25 and 26 are dependent on a series of saccharimeter plate readings extending over a period of some months. Thus, the agreement between experiments 25 and 26 and the remainder of the series is an excellent illustration of the reliability of the modern saccharimeter over considerable intervals of time. The values obtained by Method II are identical with those given in Table 14 and are therefore omitted.

The average of column 5 in Table 14 is $34\overset{\circ}{.}620_1$ and the corresponding value calculated by Method II is $34\overset{\circ}{.}620_2$. The final average value is therefore $34\overset{\circ}{.}620_2$, and we have

$$\text{Normal quartz plate} = 100^\circ\ \text{S} = 34\overset{\circ}{.}620\ (\lambda = 5892.5\ \text{Å})\ \text{at}\ 20^\circ\ \text{C} \tag{19}$$

$$1^\circ\ \text{S} = 0\overset{\circ}{.}34620\ (\lambda = 5892.5\ \text{Å})\ \text{at}\ 20^\circ\ \text{C} \tag{20}$$

$$2\overset{\circ}{.}8885_0\ \text{S} = 1^\circ\ (\lambda = 5892.5\ \text{Å}) \tag{21}$$

TABLE 14

Determination of Conversion Factor by Method I

Experiment	Average reading of solution on saccharimeters, sugar degrees	Conversion factor (circular degrees)					
		λ=5892.5 Å			λ=5461 Å		
		Plate 1	Plate 3	Average	Plate 1	Plate 3	Average
1	2	3	4	5	6	7	8
25	101.31	34.620_1	34.623_8	34.622_3	40.690_3	40.694_6	40.692_5
26	101.09	$.614_3$	$.617_1$	$.615_7$	$.683_4$	686_6	$.685_0$
27	100.91	$.605_2$	$.622_4$	$.613_8$	$.672_7$	$.691_8$	$.682_4$
28	100.02	$.617_0$	$.617_9$	$.617_5$	$.686_5$	$.686_5$	$.686_5$
29	101.68	$.608_5$	$.616_9$	$.612_7$	$.677_6$	$.685_3$	$.681_5$
30	103.20	$.626_3$	$.629_7$	$.628_0$	$.697_5$	$.700_3$	$.698_9$
31	103.05	$.620_4$	$.618_3$	$.619_4$	$.690_3$	$.686_9$	$.688_6$
32	102.72	$.619_8$	$.634_9$	$.627_3$	$.689_8$	$.706_4$	$.698_1$
33	103.92	$.625_0$	$.621_7$	$.623_4$	695_9	$.691_0$	$.693_5$
34	102.13	$.621_1$	$.621_7$	$.621_3$	$.691_4$	$.691_0$	$.691_2$
Average				$34.620_1 \pm 0.0012$			$40.689_8 \pm 0.0013$

The average of column 8 in Table 14 is $40\overset{\circ}{.}689_8$ and the corresponding value calculated by method II is $40\overset{\circ}{.}689_9$. The final average value is therefore $40\overset{\circ}{.}689_9$ and we have

$$\text{Normal quartz plate} = 100^\circ\ \text{S} = 40\overset{\circ}{.}690\ (\lambda = 5461\ \text{Å})\ \text{at}\ 20^\circ\ \text{C} \tag{22}$$

$$1^\circ\ \text{S} = 0\overset{\circ}{.}40690\ (\lambda = 5461\ \text{Å})\ \text{at}\ 20^\circ\ \text{C} \tag{23}$$

$$2\overset{\circ}{.}4576_1\ \text{S} = 1^\circ\ (\lambda = 5461\ \text{Å}) \tag{24}$$

8. DIFFERENCE IN CIRCULAR DEGREES BETWEEN THE NORMAL QUARTZ PLATE AND THE NORMAL SOLUTION

The rotation of the normal solution for sodium light is, from equation (14), 34°617, and of the normal quartz plate is 34°620 from (19). The rotation of the plate thus differs by only 0°003 from that of the solution, and no great error would have been made had previous investigators used the rotation of the normal solution for sodium light as the conversion factor. This condition no longer holds when $\lambda = 5461$ Å is used for the absolute rotations. From (13) the rotation of the normal solution for that source is 40°763, and from (20) 40°690 for the plate. The rotation of the solution is thus 0°073 larger than the plate. These differences being of opposite sign indicate that the rotary dispersion curves of the normal solution and normal plate, at 20° C, have a point in common. A calculation based on the above data and using the ordinary dispersion formulæ for quartz and sucrose fixes the crossing point at approximately $\lambda = 0.585\ \mu$. The normal quartz plate might thus be defined as one which has the same rotation in circular degrees as the normal sugar solution for $\lambda = 0.585\ \mu$. We do not consider it safe, however, to lay too much stress on this definition. The rotation difference of 0°003 is of nearly the same magnitude as the experimental error of the measurements. The question of the actual crossing can be settled only by making an accurate experimental determination of the curves.

9. CALCULATED DIFFERENCE IN SUGAR DEGREES, FOR NORMAL SOLUTION, BETWEEN WHITE LIGHT WITH BICHROMATE FILTER AND $\lambda = 5892.5$ Å

Owing to the difference in the rotation dispersion curves of sugar and quartz it is obvious that, although by definition the normal solution and plate both read 100° S on the saccharimeter with white light and bichromate filter, they may not have the same rotation when the light source is $\lambda = 5892.5$ Å. In that event the setting of the instrument for the normal solution must be changed to secure a match. From (14) and (19) this change amounts to −0°003 or using (21) −0°009 S. The normal solution will therefore read 99°99 S for $\lambda = 5892.5$ Å. The work of previous investigators indicates that the saccharimeter reading for sodium light is slightly higher than 100° S. Schönrock,[32] after a careful experimental determination, gives 100°03 S as the reading of the normal solution for sodium light.

10. ROTATION DIFFERENCE, IN SUGAR DEGREES, FOR NORMAL SOLUTION BETWEEN $\lambda=5461$ Å AND $\lambda=5892.5$ Å

Owing to the constantly increasing use of the source $\lambda = 5461$ Å it is important to know the reading of the normal solution on the saccharimeter with this source as compared with sodium and white light. We know from (14) that when the normal solution is read in the saccharimeter with sodium light the rotation of the plane of polarization is 34°617. This value is therefore the negative rotation of that thickness of the quartz plate which compensates when the wedge is shifted to give a match. If the source is changed to $\lambda = 5461$ Å the rotation of the solution is 40°763 from (13), and that of the plate, using (4), is

$$\frac{34^\circ 617}{0.85085} = 40^\circ 685 \tag{25}$$

The rotation of the plate is now 0°078 less than that of the solution. This difference, using (24) is 0°192 S and the thickness of the compensating plate must be increased by shifting the wedge that amount. We have therefore

$$\text{Saccharimeter reading}_{\lambda=5461\,\text{Å}} - \text{saccharimeter reading}_{\lambda=5892.5\,\text{Å}} = 0^\circ 19_2\ \text{S} \tag{26}$$

Since the reading of the normal solution for $\lambda = 5892.5$ Å is 99°99 S the reading for $\lambda = 5461$ Å is 100°18 S.

The results of an experimental study of this difference is given in Table 15. The readings were taken by two independent observers. The sodium and mercury light sources were purified spectroscopically; and the apparatus was so arranged that the shift from one light source to the other could be quickly made. The average difference obtained was 0°185 S. This value is in agreement with the calculated value of 0°192 S. Schönrock [33] as the result of an experimental determination gives 0°117 S for the right-hand member of (26); whereas by calculation, using the ratios for sugar and quartz for the two wave lengths, he obtains 0°188 S.

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[32] Schönrock Zs. Ver. Zuckerind., 54, p. 552 (1904).

[33] Loc. cit.

TABLE 15

Rotation Difference, Normal Solution, for Na and Hg Sources

$\phi_{\lambda=5461\,Å} - \phi_{\lambda=5892.5\,Å}$. Difference in sugar degrees]

Saccharimeter 1	Saccharimeter 2
0.14	0.25
.19	.22
.11	.25
.17	.19
.11	.23
.16	.18
Av. .15	.22

Grand average, both saccharimeters, 0.18$_5$.

11. THICKNESS OF THE NORMAL QUARTZ PLATE

Inasmuch as we have found the value of the conversion factor, in the rotation of the normal quartz plate, to be 34°620 for λ = 5892.5 Å and 40°690 for λ = 5461 Å, the old value of 1.5958 mm for the thickness of the normal plate is no longer applicable. Gumlich[34] as the result of a painstaking investigation, found the rotation of 1 mm of quartz for λ = 5892.5 Å, the light, travelling parallel to the optic axis, to be 21°7182 ± 0.0005 at 20° C. Recently Lowry[35] has made a number of measurements on the rotation of quartz and finds at 20° C 21°7283 per mm for sodium light, and 25°5371 per mm for λ = 5461 Å. The values of the thickness of the normal plate calculated from the above data are given in Table 16. The agreement between the second and third values in column 4 is very satisfactory in view of the fact that two independent values of the rotation per mm are used. The agreement between Gumlich's and Lowry's values for sodium light is not satisfactory.

TABLE 16

Thickness of the Normal Quartz Plate in Millimeters

Wave length of light source 1	Rotation of normal plate 2	Rotation of 1 mm of quartz at 20° C; light parallel to optic axis 3	Thickness of normal plate 4
			mm
5892.5 Å	34°620 (Bates & Jackson)	21°7182 (Gumlich)	1.5940
5892.5 Å	34°620 (Bates & Jackson)	21°7283 (Lowry)	1.5934
5461. Å	40°690 (Bates & Jackson)	25°5371 (Lowry)	1.5934

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[34] E. Gumlich, Wiss. Abh. der Physikalisch-Technischen Reichsanstalt, 2, p. 201 (1895); Zs. Instrk., p. 97 (1896).

[35] Lowry, Phil. Trans., 212, p. 288 (1912–13).

12. THE SPECIFIC ROTATION OF SUCROSE

The rotation of the normal solution for $\lambda = 5892.5$ Å is $34^\circ\!.617$ from (14) and for $\lambda = 5461$ Å is $40^\circ\!.763$ from (13). Since this solution contains 26.016 g of sugar, weighed in vacuo, in 100 cc, at 20° C, we have

$$\left[\alpha\right]^{20}_{\lambda=5892.5\text{ Å}} = \frac{100 \times 34.617}{2 \times 26.016} = 66^\circ\!.529 \qquad (27)$$

and

$$\left[\alpha\right]^{20}_{\lambda=5461.\text{ Å}} = \frac{100 \times 40.763}{2 \times 26.016} = 78^\circ\!.342 \qquad (28)$$

Of all the polarimetric constants relating to the sugars none have received the thorough study by numerous investigators that has been given to the specific rotation of sucrose. The formulæ of Tollens[36] and of Nasini and Villavecchia[37] giving the values at different concentrations, have been generally accepted as the most accurate. Landolt[38] has combined the two giving

$$\left[\alpha\right]^{20}_{\lambda=5892.5\text{ Å}} = 66.435 + 0.00870\,C - 0.000235\,C^2 \quad (C = 0 \text{ to } 65) \qquad (29)$$

where C is the number of grams per 100 cc of solution.

Taking $C = 26.016$ we obtain from (29)

$$\left[\alpha\right]^{20}_{\lambda=5892.5\text{ Å}} = 66^\circ\!.502 \qquad (30)$$

It will be observed that this value agrees fairly well with that given by (27), the difference being $0^\circ\!.027$. However, the agreement is not as good as it should be. In view of the recent refinements in polarimetric measurement, we are of the opinion that $66^\circ\!.529$ is very nearly correct and must be considered as more nearly representing the true value of the specific rotation than $66^\circ\!.502$. It is interesting to note that the formula of Tollens gives the value $66^\circ\!.518$.

The value $66^\circ\!.529$ is obviously of about the same order of accuracy as the new conversion factor $34^\circ\!.620$ given by (19), and the identical normal solutions were used in the determination of

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[36] Ber., **10**, p. 1403 (1877).

[37] Public de lab. chim. delle gabelle Rome, p. 47 (1891).

[38] "Das optische Drehungsvermögen," p. 420 (1898).

each. If the specific rotation be calculated from the Herzfeld-Schönrock conversion factor 34°.657, the value obtained, when compared with 66°.502 from (30), should give a direct check on the relative accuracy of the two conversion factors, 34°.657 and 34°.620. Our value of 99°.89$_5$ S for the reading of the normal solution on the Herzfeld-Schönrock scale will thus be either proved or disproved.

Schönrock[39] has calculated the specific rotation by using 34°.657. Taking that value and his saccharimeter reading, 100°.03 S, for the normal solution, for $\lambda = 5892.5$ Å, he finds the rotation of the normal solution to be 34°.667. By using the same method as that indicated for (27), he obtains 66°.627 for the specific rotation; and calls attention to the fact that it is about 0°.13 too large. This error is of such magnitude that even with no additional experimental data such as has been given in the present paper, it is evident that the value of 34°.657 for the conversion factor, is too high. His value of 66°.627 for the specific rotation is of course dependent not only on 34°.657, but also on 100°.03 S, and it is possible that the latter is in error, as is indicated by our corresponding value 99°.99 S. In order to eliminate this possibility, we have calculated the specific rotation, using 34°.620 and 100°.03, and find 66°.555 for the specific rotation. The agreement between 66°.555 and the accepted value, 66°.502, is much better than 66°.627 and 66°.502. The discrepancy must be attributed for the greater part to the fact that the Herzfeld-Schönrock conversion factor is too large. We therefore consider that the value 99°.89$_5$ S for the reading of the normal solution on the Herzfeld-Schönrock scale is corroborated; and conclude that the available auxiliary data establishes the accuracy of the value 34°.620, for the conversion factor, within reasonable limits.

We desire to take this opportunity to acknowledge our indebtedness to F. P. Phelps, who assisted in making computations and observations, and to C. F. Snyder, who performed many of the crystallizations.

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[39] Zs. Ver. Zuckerind., 54, p. 553 (1904).

V. SUMMARY

1. Sucrose has been purified by concentrating aqueous solutions in vacuum below 35° C and crystallizing while in motion. For this work new apparatus has been devised.

2. It has been shown that reducing sugars are eliminated from the crystals by the above method. While no sample was found which failed to give a precipitate of cuprous oxide, it has been shown by the use of copper solutions of varying composition, and by a study of the reaction velocities of sucrose and of invert sugar, that sucrose itself was the cause of the precipitation.

3. The velocities of caramel formation at various temperatures have been determined; and the permissible time of heating plotted as a function of temperature. These data have been applied to the drying operations.

4. It has been shown that moisture can be eliminated from finely divided sugar by heating in a vacuum to 50° C for a few hours. This conclusion has been verified by a series of experiments at high vacuum extending over a long period of time. The absence of moisture has been shown by two direct qualitative tests.

5. A quantity of sugar has been fractionally crystallized and the various factions found to be identical in properties.

6. The ratios of the rotations of quartz and sugar for $\lambda = 5461$ Å and $\lambda = 5892.5$ Å have been determined. For quartz

$$\frac{\phi_{\lambda=5892.5\,\text{Å}}}{\phi_{\lambda=5461\,\text{Å}}} = 0.85085;$$

and for sugar

$$\frac{\phi_{\lambda=5892.5\,\text{Å}}}{\phi_{\lambda=5461\,\text{Å}}} = 0.84922$$

7. The reading of the normal sugar solution on the Herzfeld-Schönrock scale has been shown to be $99\overset{\circ}{.}89_5$ S.

8. The absolute rotation of the normal sugar solution has been determined with the following results:

Normal sugar solution $= 100° = 34\overset{\circ}{.}617$ ($\lambda = 5892.5$ Å) at 20° C
Normal sugar solution $= 100° = 40\overset{\circ}{.}763$ ($\lambda = 5461$ Å) at 20° C

9. The conversion factor has been determined for two monochromatic sources with the following results:

Normal quartz plate = 100° S = 34°620 (λ = 5892.5 Å) at 20° C
2°8885 S = 1° (λ = 5892.5 Å)
Normal quartz plate = 100° S = 40°690 (λ = 5461 Å) at 20° C
2°4576 S = 1° (λ = 5461 Å)

10. The difference between the rotations of the normal quartz plate and the normal solution for λ = 5892.5 Å, has been found to be 0°003, and for λ = 5461 Å, 0°073. These values indicate that the rotary dispersion curves of plate and solution cross at about λ = 0.585μ. The reading of the normal solution on the true saccharimeter scale with the source λ = 5892.5 Å, has been calculated to be 99°99 S.

11. The difference in rotation in sugar degrees, for the normal solution on the saccharimeter, for the sources λ = 5461 Å and λ = 5892.5 Å, has been calculated from the absolute rotations, with the following result:

$$\text{Saccharimeter reading}_{(\lambda=5461\text{ Å})} - \text{Saccharimeter reading}_{(\lambda=5892.5\text{ Å})} = 0°19_2 \text{ S.}$$

An independent experimental determination has been made of this difference and the value 0°18$_5$ obtained.

12. The thickness of the normal quartz plate has been calculated and the values 1.5934 mm and 1.5940 mm obtained.

13. The specific rotations of sugar for the normal solution for λ = 5892.5 Å and λ = 5461 Å have been calculated from the absolute rotations with the following results:

$$\left[\alpha\right]^{20}_{\lambda=5892.5\text{ Å}} = 66°529$$

$$\left[\alpha\right]^{20}_{\lambda=5461\text{ Å}} = 78°342$$

14. The agreement between the accepted value, 66°502, for the specific rotation and 66°529, in contrast to the disagreement between 66°502 and the specific rotation 66°627 from the Herzfeld-Schönrock conversion factor, has been shown to corroborate the new value, 34°620 (λ = 5892.5 Å), for the conversion factor.

WASHINGTON, September 30, 1915.