

Some remarks by Dr. Waller then followed, after which the second paper "On the precipitation of tannic acid as tannate of copper," by Mr. Nelson H. Darton, was read.

After some remarks and questions by Dr. Grothe the third paper, "On the water supply of N. Y. City," by Dr. E. Waller, was read.

This paper provoked a lively discussion between Drs. Endemann & Waller.

Dr. Endemann then read a paper by title "On Heptane," by F. P. Venable, Ph. D.

After which the meeting adjourned.

JAMES H. STEBBINS, JR.,
Recording Secretary.

IV ON CRYSTALLIZED ANHYDROUS GRAPE SUGAR.

DR. ARNO BEHR.

The general physical and chemical properties of crystallized anhydrous grape sugar are pretty well known, and I am only able in a few points to supplement this knowledge on this occasion. Anhydrous grape sugar in a state of purity has so far only been obtained from an alcoholic solution. Two years ago F. Soxhlet found that the best solvent for it is methylic alcohol, from which much larger and better developed crystals can be obtained than from the solution in ethylic alcohol. I have found that it can, even more easily, be prepared from a watery solution.

The principle that a crystal introduced into the supersaturated solution of the same substance induces crystallization, has long been applied to the practice of grape sugar manufacture. In order to hasten the hardening of the sugar a certain quantity of the already hardened sugar of a previous operation is stirred into the mass. But as the ordinary commercial grape sugar always contains the hydrate the crystallization so obtained is also that of the hydrate. I put the question to myself, what would happen if, instead of the hydrate, I introduced the anhydrous sugar into a concentrated solution of ordinary grape sugar. I tried the experiment and must confess that I had not much hope that anything else but crystallized hydrate would be the result, for I expected to see the anhydride transformed into the hydrate within the watery solution. I was agreeably surprised when, on the next morning, I found the glass filled with a neat crystallization of anhydrous grape sugar,

from which the liquid part could be easily drained. The few crystals of anhydride, far from being transformed into the hydrate, had induced an ample crystallization of their kind. The explanation of this fact is found in the following. In its crystalline form anhydrous grape sugar is not deliquescent even in very moist weather, and it is stable in comparatively dilute solutions of grape sugar. I have kept crystals exposed to the atmosphere of the laboratory through months and during moist weather without seeing them lose their sharp outlines and bright appearance, and I have repeatedly found the syrup drained from a crystallization of anhydrous sugar to contain as much as 26% of water.

The limits of concentration within which this crystallization can be obtained are rather wide, but in order to secure a good result the solution ought to contain from 12 to 13% of water. It is well not to allow the mass to cool rapidly or the temperature to fall much below 30° C. For, at a lower temperature, and before the remaining syrup has been diluted by the separation of the anhydrous crystals, concentrated solutions are rather viscous and this viscosity prevents a free crystallization. A good temperature is 30 to 40° C. The time within which the crystallization is completed varies between half a day and several weeks, according to the purity of the mass.

Though it is always well, in order to secure a uniform and speedy crystallization, to start it by the introduction of some crystals, yet it is possible and, for sugars of high purity, quite easy to obtain the same crystallization by simply keeping the concentrated solutions at a temperature of about 30° C for some time. Under these circumstances a crystallization of anhydrous grape sugar takes place. This behavior of grape sugar is also unexpected. Soxhlet, who, a short time ago, took patents in different countries for the refining of grape sugar by means of alcoholic liquids, and for the production of a hard crystallized grape sugar, describes one of his products expressly as the hydrate of the formula $C_6H_{12}O_6 \cdot H_2O$, yet he concentrates highly a solution of very pure grape sugar and allows it to crystallize at an elevated temperature. I have failed, under the conditions of my experiments, to obtain the hydrate. But that it is possible for the hydrate to crystallize in large and well developed crystals has been established in 1877 by Halse and Steiner, who analyzed a crystallized hydrate of grape sugar, of which some crystals weighed 4 to 5 grams, and which was readily taken for cane sugar. This grape sugar had made the voyage from England to Australia

and back and during this time had undergone the transformation.

A product which has for some time played an important part in the literature of this subject is Anthon's hard crystallized grape-sugar. As early as 1857, Anthon in Prague prepared a very pure sugar by crystallizing and pressing the hydrate; he then melted the press-cakes without addition of water, and allowed the mass to solidify in moulds.

He obtained crystalline masses which, according to his analysis, contained 4.7% of water and for which he claimed the constitution of a half hydrate of grape sugar of the formula, $2(C_6H_{12}O_6) + H_2O$. As he did not drain his crystals, he certainly had nothing but a mixture of anhydrous sugar and the hydrate, the surplus water of the hydrate having been evaporated during the melting. This has already been suggested by Stohmann in the latest German edition of Muspratt's chemistry (vi 2077).

Crystallized anhydrous grape sugar such as I have prepared it from a watery solution has the following properties. Dried at 30 to 40° C. it does not retain more than .02 per cent. of moisture; the moisture determination made at 130° C. It shows a neutral reaction, with sensitive litmus paper. It melts in a capillary tube between 141 and 145° C. It was tested in the polariscope, and showed birotation. Landolt in his book on the optical rotatory power of organic substances (Braunschweig 1879, p. 184), gives 32.68 grams as the amount of pure grape sugar, which taken instead of the normal weight of cane sugar should show 100 on the scale of a Veutze-Soleil instrument.

Mr. Lungwitz, who has made these determinations for me, found, if he rapidly dissolved this amount in cold water and immediately polarized the solution, a polarization varying between 202 and 204; if he allowed it to stand for 24 hours, 101 to 102.

This difference is mainly due to an error in Landolt's figure. This figure is calculated from an assumed specific rotation of $\alpha_D = 53.0$. This is correct only for a concentration of 10 grams of sugar in 100 cc. of solution, but for a concentration of 32.68 grams in 100 cc. α_D becomes $= 53.57$ according to Tollen's determinations. Therefore 32.68 grams ought to polarize 101.1; while the observed polarization for monorotation was 101 to 102.

These are the facts so far as they refer to chemistry, but in view of the increasing importance of grape sugar as an article of general consumption, I wish to add a few remarks with reference to the industrial application of these observations.

In the ordinary process of the manufacture of grape sugar from starch the conditions are such that the resulting product is always far from being pure grape sugar, however pure the starch from which it is derived may have been. Though a good method for the quantitative determination of starch consists in its conversion with a mineral acid and subsequent determination with Fehling's solution, yet, in practice, a smooth and complete conversion is not attainable. The reason of this difference lies in the fact that the chemist, for a complete conversion, works with a very diluted solution, while the manufacturer necessarily works with solutions of higher density. At a higher density, however, the acid seems to act on the sugar already formed, and before all the dextrine is converted into sugar, the sugar itself is partially converted into something else which constitutes an impurity in the final product. So far we know very little about the nature of these impurities of commercial grape sugar, but several chemists have asserted that the residues which remain after fermentation and distillation are more or less injurious to the human system. This subject, though, requires a more complete investigation. As the principal use of all the grape sugar produced is that which is made of it in the manufacture of fermented beverages, beer and wine, it is easy to understand the rising demand for a purer article.

Fr. Anthon has, twenty years ago, called attention to the disadvantages arising from the use of impure grape sugar in wine making, and suggested a remedy. His suggestion was to refine the ordinary grape sugar by crystallization and the use of a centrifugal machine for the removal of the liquid impurities. He modified this process in so far as he used a strong press instead of a centrifugal machine, and, according to the testimony of several chemists, really produced an article of remarkable purity. His process seems to have never been used for any length of time or on an extensive scale.

Fouchard had already, in 1853, manufactured a refined grape sugar by allowing grape sugar solutions to crystallize in barrels and then withdrawing the liquid portion through a number of holes in the bottoms of the barrels.

Though the principle of these refining processes is correct, yet there is a difficulty inherent in it which arises from the form and nature of the crystals in which the sugar solidifies. Under ordinary circumstances grape sugar crystallizes from a watery solution as the hydrate in the shape of very fine tablets which are mostly

grouped spherically. Owing to the fineness of the tablets and the capillary attraction, it is difficult to remove the impure mother-liquor sufficiently from the crystals by means of a centrifugal machine, and even with a hydraulic press high purity cannot be obtained, together with a large yield. It is different with the crystals of anhydrous grape sugar. They are of a prismatic shape, and form loose aggregations from which the syrup can be easily removed by centrifugal force, and which lend themselves to a treatment of draining and washing very similar to that of cane sugar. Under these circumstances it is possible to produce a grape sugar which compares in purity with block and granulated cane sugar. A number of applications for such an article readily suggest themselves. The confectioner, the druggist, the manufacturer of condensed milk may use it. In the preparation of certain wines it can safely take the place of cane sugar; but its principal use ought to be in the kitchen for all those preparations where utmost sweetness is not sought for. It is not so well suited for sweetening tea or coffee, though it does not quite so unfavorably compare with cane sugar as the books will have it. To obtain a moderate sweetness, equal to that produced by a given amount of cane sugar, it is not necessary to take $2\frac{1}{2}$ or 3 times as much as cane sugar, but only about $1\frac{2}{3}$ times the quantity; at least I have found it so, and some of my friends also.

V. THE WATER SUPPLY OF THE CITY OF NEW YORK.

BY E. WALLER, PH. D.

I desire, in the first place, to present the results of complete analyses of the Croton water made at different times. The various denominations of salts quoted have been given in order to literally quote the different analysts. For the three first, double columns are given, representing the results in grains per English (Imperial) gallon of 70,000 grains, and also in grains per United States gallon of 58,318 grains, the first columns in each case being the form in which the analysts have recorded their results, to judge from the context. In Nos. 4 and 5, the magnesium and calcium bicarbonate have been calculated back to mono-carbonates, and the results given in brackets. Another table of the same results, calculated to parts per 100,000, is appended.