

TABLE XIX.

400 Grams Solution. A = 98.

<i>t.</i>	<i>x.</i>	$\frac{1}{2A} \log \frac{A+x}{A-x}$	$\frac{1}{2At} \log \frac{A+x}{A-x}$	$\frac{1}{t(A+B)} \log \frac{A(B+x)}{B(A-x)}$
0	0
15	10.5	0.000477	0.0000317	0.0000163
45	28.0	0.001302	0.0000289	0.0000154
75	43.5	0.002114	0.0000282	0.0000155
120	61.5	0.003267	0.0000272	0.0000155
170	78.0	0.004819	0.0000283	0.0000167
215	87.0	0.006254	0.0000291	0.0000175
240	91.0	0.007303	0.0000304	0.0000185
			0.0000291	

It appears from the above tables that the constants calculated from the simple formula, with $A = B$, are somewhat more regular than those from the other. In the first experiment, with the 100 grams solution, the reaction was not complete, and the results are at best unsatisfactory. But in the others these mean values for the speed

0.0000146
 0.0000225
 0.0000291

stand to each other almost exactly in the relation 2 : 3 : 4, showing the close relation of speed to dissolved sugar. In each series the values for K are as uniform as could be expected, and show that the formula chosen represents the reaction very well.

CHICAGO, JULY 3, 1897.

THE EXACT ESTIMATION OF TOTAL CARBOHYDRATES IN ACID HYDROLYZED STARCH PRODUCTS.

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Received June 11, 1897.

THE determination of the exact amount of carbohydrates present in solutions of commercial glucose has always been conjectural, since the evaporation method, the only available means of estimation, has always caused in the residue an intermediate amount of decomposition, usually attributed to oxidation or the destructive effect of high temperature. Since, however, in acid hydrolyzed starch products, it seems certain that the component carbohydrates preserve their individuality

throughout the combinations which they may make with each other, at least so far as to have constant optical and chemical properties, as well as a constant influence on the specific gravity per unit weight of each present in solution, it is quite possible to determine the *proportional amount* of each constituent by the use of one arbitrary specific factor throughout the calculation. This has been explained in detail in several publications of O'Sullivan, Brown, Heron, Morris, and others. It is also well known that the factor used is that representing the increase in specific gravity caused by one gram of cane sugar in 100 cc. of solution.

It follows that if the specific gravity influences of the isolated carbohydrates were known it would be quite possible to predict the specific gravity factor of any hydrolyzed starch product. A year ago an attempt was made by one of us to predict these factors of the hydrolyzed starch products for all rotation between the limits of possible specific rotatory powers for the factor 386. A provisional curve was plotted from the following formula :

$$\Sigma = m\Sigma_m + g\Sigma_g + d\Sigma_d.$$

Σ being the specific gravity factor of the hydrolyzed starch product identified by its specific rotatory power ; m , g , and d , the respective percentages of maltose, dextrose, and dextrin present ; and Σ_m , Σ_g , Σ_d , their corresponding specific gravity factors.

We considered this curve a provisional one, as we were obliged to approximate the factor for dextrin from the imperfect data of O'Sullivan, Salomon, and others, taking 0.00400 as the most probable value. The factors for dextrose and maltose were those of Salomon¹ for ten per cent. solutions, 0.00381 and 0.00390, respectively. We found that the plotted values of the calculated factors, where the specific rotatory powers were expressed as abscissae, formed a *straight line joining the plots corresponding to the factors taken for pure dextrin and dextrose* at the corresponding rotation of 195° and 53.5°.

Having defined approximate theoretical values we have sought to confirm them by actual determinations of the total solids present in a number of representative solutions prepared as previously described.²

¹ *J. prakt. Chem.*, 2, 28.

² This Journal, 18, 871-872.

Much ingenious apparatus¹ has been devised for overcoming the decomposition in drying already referred to. The principles of one class is the introduction of a presumably inert atmosphere, such as coal gas or hydrogen. Another class uses a vacuum, which mitigates at the same time oxidation and influence of high temperature.

Apparently, experience places so little confidence in the advantages of any of these multifarious appliances, at least in the case of sugars, that the ordinary method of drying at about 100° till the continual loss does not exceed a given rate per hour, is that usually recommended. We therefore at first dried ten cc. each of solutions of hydrolyzed starch products on paper rolls at 105°–110° C.,² the rolls being placed in weighing beakers, and dried to practically constant weight in an oven kept at the given temperature. The results obtained were discordant, and in general lower than those of our provisional curve.

A second series of determinations were made by drying paper rolls, prepared in a similar way, in a vacuum pan, the temperature being about 40°. In breaking the vacuum, air was passed through sulphuric acid and made to enter at the bottom of the pan to avoid the descent of moist vapors. Drying by this method was exceedingly tedious, and the values obtained are much lower than given by our assumed curve, besides being discordant. They indicate the need of more heat in drying.

At this point in our work we received the important paper by Brown, Morris, and Millar,³ giving the details of an elaborate investigation of the primary carbohydrates and of the products of diastase hydrolysis. In the latter the actual values were successfully predicted by a method similar to ours, but by a somewhat more exact formula, as it took into consideration variations in the factors due to those of concentration. These investigators used the drying apparatus designed by Lobray de Bryn and Von Laent⁴ for the drying of maltose. This apparatus had worked so successfully for diastase converted solutions that we at once adopted a modification of it for our next essay. Several pieces of apparatus of the type described below (Fig. 1) were

¹ Wiley's Principles and Practice of Agricultural Analysis, Vol. 3; see also recent bulletin by the U. S. Department of Agriculture.

² Rolfe and Defren: this Journal, 18, 872.

³ J. Chem. Soc., Jan., 1897.

⁴ Rec. Trav. Chim., 1894, 13, 218.

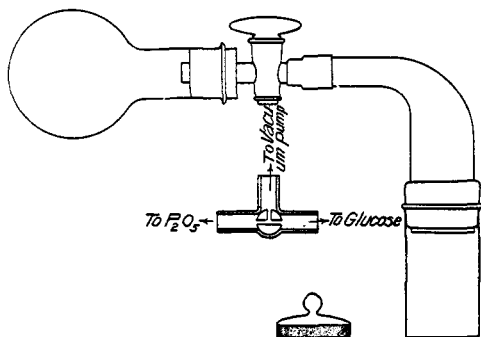


FIG. 1.—APPARATUS FOR DRYING SUGARS AND GLUCOSE SYRUPS.

improved from the stock of material available. Our apparatus is arranged so that the greater bulk of the water can be first removed without coming in contact with the phosphorus pentoxide. This avoids previous evaporation on a water-bath. The tared weighing beaker containing the solution to be evaporated is slipped on the end of the adapter, an air-tight joint being made with "bill-tie" tubing. By the three-way stop-cock, communication can be had with the vacuum pump and with a 250 cc. flask containing phosphorus pentoxide, or either can be shut off.

The method of drying is as follows: The cock is opened to the pump only, and the air exhausted to 680–690 mm. The beaker is lowered into an oil-bath and heated to about 100° till most of the water is evaporated. Communication is then made with the pentoxide flask, and the mass dried to constant weight at about 120°. For convenience, the vapor from the various pieces of apparatus were passed through a four-liter vacuum pan. This large receiver produced an almost instantaneous exhaustion when a stop-cock was opened. Complete drying usually required from eighteen to twenty-four hours. The slowness of our drying apparatus was possibly due to the contracted opening through the stop-cock, which may have prevented free circulation of vapors over the pentoxide. This drawback was the result of the necessary improvising of our apparatus from stock at hand.

The results obtained are tabulated in the following table, and

also plotted in Fig. 2. As will be seen they form a straight line

TABLE.

No. drying.	Time Hours.	Vol. of solution. cc.	$d_{15.5}$.	$\alpha_{D_{386}}$.	Weight of residue.	Factor obtained.	Factor calculated.
1	18	10	1.02835	164.2	0.7104	0.003992	0.003980
2	18	10	1.03134	160.0	0.7833	0.003999	0.003974
3	24	10	1.03657	144.8	0.9223	0.003965	0.003954
4	18	10	1.03364	141.8	0.8509	0.003954	0.003950
5	24	10	1.04212	138.7	1.0644	0.003957	0.003946
6	18	10	1.03650	136.1	0.9222	0.003953	0.003942
8	18	10	1.03701	128.0	0.9376	0.003943	0.003931
9	24	10	1.03701	128.0	0.9417	0.003930	0.003931
11	18	10	1.03841	115.7	0.9781	0.003927	0.003918
12	18	10	1.03704	111.7	0.9454	0.003918	0.003911
13	18	10	1.03704	111.7	0.9465	0.003914	0.003911
15	24	10	1.03843	104.7	0.9827	0.003910	0.003901
16	18	10	1.03545	90.5	0.9127	0.003885	0.003883
17	18	10	1.03594	81.3	0.9282	0.003883	0.003871
18	18	10	1.03549	73.4	0.9162	0.003870	0.003860
19	18	10	1.03881	70.5	1.0081	0.003850	0.003856

(The omitted numbers are those of samples which were lost by breakage, or scorching due to loss of vacuum.)

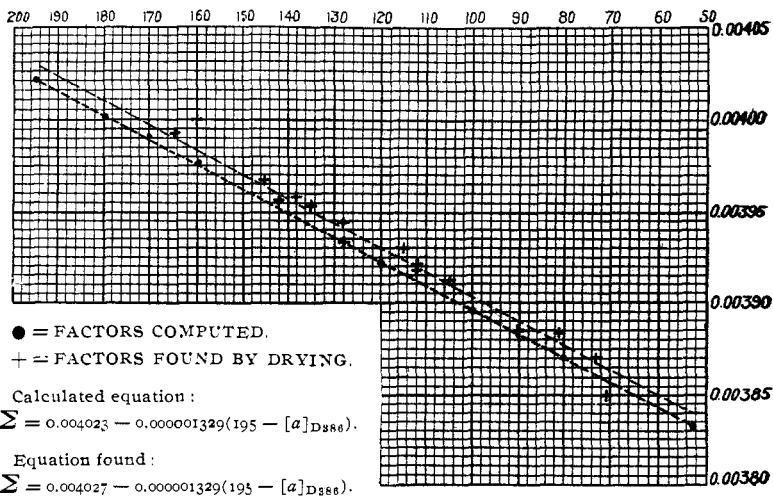


FIG. 2.—SPECIFIC GRAVITY FACTORS FOR APPROXIMATELY TEN PER CENT. SOLUTIONS OF HYDROLYZED STARCH PRODUCTS.

which is very slightly higher than the line calculated by using the revised carbohydrate value of Brown, Morris, and Millar.

The variation is very slight, as the plot is drawn on a scale by which one division represents about 0.06 per cent. of the values obtained. The two equations obtained are more nearly concordant when we take into consideration that the average of the specific gravities of the samples is about 1.0360. This would raise the calculated value 0.000003 on the scale, or a little more than one half of a division. We, therefore, have adopted as the most probable values what happens to be the mean. Our conclusion, then, is that within the concentrations expressed by the specific gravity factors, 1.035 and 1.045, we can calculate the absolute specific gravity influence of any acid hydrolyzed starch solution by the equation, $\Sigma = 0.004023 - 0.000001329(195 - [\alpha]_D)$, when the specific rotatory power (obtained by the factor 0.00386) is known. These values within the limits of concentration given are correct to less than two-tenths per cent. of their values. For commercial glucoses, the factor 0.00393, taken as a constant, is sufficiently exact for most determinations.

While this equation will now enable us to determine the exact amount of carbohydrate in solution when the specific gravity has been previously corrected for the influence of other dissolved material, the simpler computation based on the factor 0.00386 will doubtless continue in use as more convenient for those calculations where proportion of carbohydrates is alone desired.

We have also under investigation the action of heat on commercial glucoses when samples are boiled down to candies, as well as the study of certain disturbing influences on the determination of cupric reducing powers of glucoses. The results are not yet complete enough for publication.

A FURTHER COMMUNICATION ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.

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Received June 17, 1897.

DURING the past four years the writer has done a great deal of work on this method,¹ and the results obtained in this laboratory for the past two years, at least, by five analysts,

¹ Bul. 43 and 47, pp. 68-104 and 62-83, Chem. Div., U. S. Department of Agriculture; Bul. 119, North Carolina Experiment Station; and this Journal, 16 and 17, Nos. 11 and 12.