ON THE SPEED OF REDUCTION OF FERRIC ALUM BY SUGAR.

BY J. H. LONG.

IN two papers published last year in this Journal, I gave numerous experiments on the inversion of cane sugar solutions by various salts. In several cases certain secondary reactions were noticed, but they were not discussed at length, as they had no direct bearing on the problem in hand. Certain salts were found to invert sugar and to become reduced or otherwise changed at the same time. A good illustration of this is a mixture of ferric alum and sugar, in which inversion of the sugar and reduction of the iron salt take place rapidly on warming, and even on standing in bright sunlight through several warm days. A somewhat analogous change takes place with solutions containing chrome alum, but this was not followed in detail.

On June 4, 1896, a solution was prepared containing in 250 cc., fifty grams of pure cane sugar and ten grams of ferric alum ; this had the usual dark color. It was allowed to stand in the light two weeks. At the end of the first week the color had changed to light green, with apparent conversion of the ferric to ferrous salt. On June 18, a polarization was made, giving $\alpha = -3.85°$ in a 100 mm. tube, at 20°. A test made some days later showed the same results. This doubtless corresponds to complete reduction, as the theoretical end reading of $-4.3°$ is not reached in such a mixture, as I pointed out in my papers referred to, and possibly from an alteration of a little of the levu-

lose. The solution was found also to contain free sulphuric acid, and an approximate titration showed this to correspond in amount to what should be expected from a conversion of ferric into ferrous sulphate. It is not possible here to measure the rate of inversion, because of the dark color of the liquid, until near the end, and this was not attempted.

At first sight it appeared possible to measure the rate of reduction of the ferric salt from the change of color during the reaction, but this was not found satisfactory, even by the aid of an excellent spectro-photometer, and the conversion of the ferric salt into thiocyanate. Two reasons may be given for this; it is well known that the color of a ferric solution varies greatly with the temperature, and this alone makes an accurate observation difficult with the ordinary instruments; further, it has been shown by Krüss that no accurate relation exists, in the case of ferric thiocyanate, between concentration and extinction coefficient. My own experiment confirms this view.

As may be easily seen, the usual methods of determining ferric in the presence of ferrous salts can not be applied here, because of the presence of the great excess of organic matter, and I therefore gave up all attempts to make direct determinations. On consideration of the reaction which must take place in the reduction, however, a possible method soon presented itself, and this on trial was found to be very satisfactory. Considering the iron salt alone in the alum, the reaction is this :

$$Fe_2(SO_4)_3 + H_2O = 2FeSO_4 + H_2SO_4 + O.$$
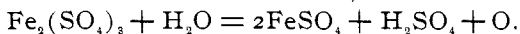
Ferrous sulphate and free sulphuric acid are formed and remain in solution, while oxygen is liberated and is absorbed in the oxidation of a part of the sugar.

The text-books are practically silent on the subject of the oxidation of sugar by heavy salts in neutral or acid solution. Even less seems to be known concerning the products of such oxidation than is known for the Fehling and similar reactions in the presence of alkali. In an experiment on the subject, the following observations were made : I dissolved fifty grams of pure cane sugar in water and mixed with it fifty grams of ferric alum in solution ; the mixture was diluted to 250 cc. and heated in a flask with a capillary stopper to 85° C. In about an hour the color of the liquid had become greenish, indicating reduc-

tion to the ferrous condition, but on longer heating the solution grew darker and became finally dark brown. During the last stage of the heating numerous gas bubbles escaped from the liquid, suggesting active decomposition. With lime water these bubbles gave a precipitate. In a second similar experiment the apparatus was arranged to permit the collection of this gas. For this purpose a sulphuric acid bulb was attached to the delivery tube from the flask, and beyond this a weighed potash bulb. After the evolution of the gas had ceased the increase of weight in the potash bulb was found to be 0.015 gram. Although this amount is not large, it is sufficient to indicate that a small portion of the sugar undergoes advanced oxidation. What the principal changes are lies outside the scope of this investigation.

If, as suggested above, a direct reduction of the ferric salt is effected, the change is one which should be easily followed by a series of electrical conductivity determinations, and this hypothesis I was soon able to confirm by simple experiments. With decomposition of the complex ferric salt into the simpler ferrous salt and free acid a marked increase in conductivity should be noticed, and that this is the case, the following experiment shows. I made up a thick syrup with ferric alum and determined its resistance in a U cell of the Kohlrausch type at 20.2°, and found it to be 406 ohms. After standing several days in January, in diffused light, I found at 20° 407.5 ohms ; that is, practically, no change. I next heated the solution through five hours to a temperature of 70° in a flask closed with a rubber stopper and long capillary tube. After cooling a new test was made, showing now a resistance of 197.2 ohms at 20°.

Another solution was made containing in 500 cc. fifty grams of sugar and 48.2 grams of pure ferric alum. The resistance of this was found to be 396.6 ohms at 20.3° in the same apparatus. A portion of this solution was allowed to stand four months exposed to the light, when a new test was made. It was then green in color, but still contained a little ferric salt. The resistance at 20° was found to be 199.5 ohms. Part of the same solution stood through the same period in a dark cupboard and at a higher mean temperature. It remained yellowish brown, and gave in the same apparatus a resistance of 323.3 ohms at 20°.

The influence of the light is very clearly indicated by the above tests.

As is well known, dilute solutions of ferric alum are not stable, even at the ordinary temperature, while relatively strong solutions decompose when heated. To follow the rate of reduction accurately, it is desirable to choose such a concentration and such a temperature that the whole change may be completed in a single working day, that is, within eight or ten hours. A mixture containing 15.0625 grams of ferric alum and 100 grams of sugar in 500 cc. was tried, but as it became turbid at 70°, after a time, was discarded. The same was found true of the solution, referred to above, containing in 500 cc. 48.2 grams of alum and fifty grams of sugar. It was found practically that the most stable solutions were those made with large amounts of ferric salt, the weight of sugar present being of far less importance. After a few trials the following solution was found to have the required stability and to satisfy all demands : Ferric alum, 120.05 grams ; sugar, 100 grams ; water to make 500 cc. This is a fourth normal solution, as it contains one molecule of alum in four liters. Many of the following experiments were made with a solution of this concentration. It was found to have a resistance of 282 ohms at 20° in the cell used throughout all the tests ; this corresponds to a molecular conductivity, $10^3 \mu = 111.4$, the factor for reduction being determined by fiftieth-normal potassium chloride and saturated sodium chloride solutions. The following table shows the variation in the value of μ with dilution :

<div align="center">TABLE I.</div>

V, liters.	$10\mu^3$.
4	111.4
8	179.5
16	248.5
32	318.0
64	388.1
128	467.5
256	567.0
512	692.3
1024	846.4
2048	1093.5

The solutions became somewhat turbid before the end of the experiments, which were conducted as rapidly as possible. The

last values show that dissociation was far from complete. When a portion of the undiluted solution was heated to 75° through five hours, it became yellowish green and completely reduced. The resistance for this was found to be 126.6 ohms, corresponding to $\mu = 248.1 \times 10^{-3}$, for the original ferric salt. On diluting the product the conductivities were found as shown in the table below, the dilution being referred to the ferric salt originally present.

TABLE II.

V, liters.	$10^3\mu$.
4	248.1
8	390.4
16	506.6
32	612.8
64	716.7
128	823.8
256	930.6
512	1037.5
1024	1141.2
2048	1244.0

The solutions remained perfectly clear throughout, and ionization appears to be more nearly complete than before. By repeating these experiments several times with fresh prepaiations of ferric alum, slightly different values were found for the original resistances and those after reduction. The limits for the first were 281.5 to 282.5, and for the last 125 to 127.

In the reduction of the ferric alum, ferrous sulphate, ammonium sulphate and free sulphuric acid are formed. I next prepared a solution of these substances in the proportions which would result from the reduction of the amount of ferric alum taken above. The solution contained:

	Grams.
Sugar	100.0
Crystallized ferrous sulphate	69.5
Ammonium sulphate	16.5
	cc.
Normal sulphuric acid	250
Water to make	500

With this solution a resistance of 125.8 ohms was found at 20.5°, which corresponds very closely to 127 ohms at 20°. Indeed, this result is much closer than one at first thought

might expect, when it is remembered that a part of the sugar suffers oxidation during the reduction of the salt. But practically the same figures were found in many subsequent trials, from which it is evident that the resistance of the sugar is not greatly changed by inversion and partial oxidation. It is probable that the products formed are but slightly dissociated. A few experiments were made to throw light on this point. A solution was prepared containing in 250 cc. 60.25 grams of ferric alum and an amount of pure dry crystallized dextrose to correspond to fifty grams of cane sugar (52.6 grams). The resistance of this at 20.5°, was found to be 279.2 ohms. The resistance of dextrose is therefore practically the same as that of cane sugar. This solution was heated to 70° through several hours, but still remained yellowish brown, and deposited finally a basic precipitate. A solution was next made containing in 250 cc. fifty grams of dextrose, fifty-five grams of ferric alum and twenty-five cc. of normal sulphuric acid. The resistance was found to be 230.5 ohms at 20.2°. A portion of the solution was heated two hours at 95°; it remained dark and deposited a slight basic precipitate. The resistance was now found to be 195.6 ohms at 20.3°, which is a relatively small change. Finally I made a solution with fifty grams of cane sugar, 60.25 grams of ferric alum and twenty-five cc. of normal sulphuric acid in 250 cc. The sugar was inverted by the acid before the alum was added, and for the mixture a resistance of 244.3 ohms at 20.2° was found. After heating to 95° through two hours, the resistance was reduced to 111 ohms at 20°, while tests showed the ferric salt to be wholly reduced. It would appear from the above that the reduction is largely due to the levulose of the inverted sugar, and this agrees with the known behavior of levulose in other reactions.

That the resistance after reduction corresponds closely to that found from mixtures of the reduction products according to the equations assumed above, was found in other cases where larger and smaller amounts of sugar were used with the given weights of the salts. This established, we have evidently a very simple means at hand for determining the speed of the reduction reaction, by determination of resistances from time to time, the results being compared with the resistances found from known mixtures

of acid, ferric and ferrous salts and ammonium sulphate. These mixtures were made to contain amounts of ferric alum, ferrous sulphate, ammonium sulphate and acid corresponding to those present at different stages in the reduction. In the following table are given the weights of the pure materials mixed, the iron salts being taken in the crystallized condition.

TABLE III.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
50	60.25	....	....	..	100	282.1
50	48.20	6.95	1.65	25	80	241.6
50	36.15	13.90	3.30	50	60	204.6
50	24.10	20.85	4.95	75	40	173.2
50	12.05	27.80	6.60	100	20	148.3
50	....	34.75	8.25	125	∞	126.6

In the last column the resistances in ohms for the several solutions are given. I have not thought it necessary to calculate the corresponding conductivities, as the direct determinations are sufficient for all comparisons to be made. By means of coordinate paper, I have plotted a curve from these values on a large scale, and from this curve the resistance of any intermediate mixture may be found with a high degree of accuracy. The form of this curve is shown in the accompanying figure at *B*. In making the above mixtures the ferric alum was dissolved in part of the water by the aid of heat; the solution was then cooled to 20°. The sugar and the other substances were then dissolved in more water, the cooled mixture was added to the ferric alum and the whole brought to 250 cc. at 20°. At this temperature the ferric alum changes very slowly, and not appreciably during the time of an experiment. The sugar in the mixtures was probably mostly in the inverted condition. Experiments with mixtures, as in the above table, were repeated several times and always practically with the same results.

The data secured in the manner described were applied to follow the speed of reduction in a solution warmed in the thermostat. I made a solution with 241 grams of ferric alum in 500 cc. at 20°, and another with 200 grams of sugar in 500 cc. These solutions were warmed to 70° and mixed. The mixture
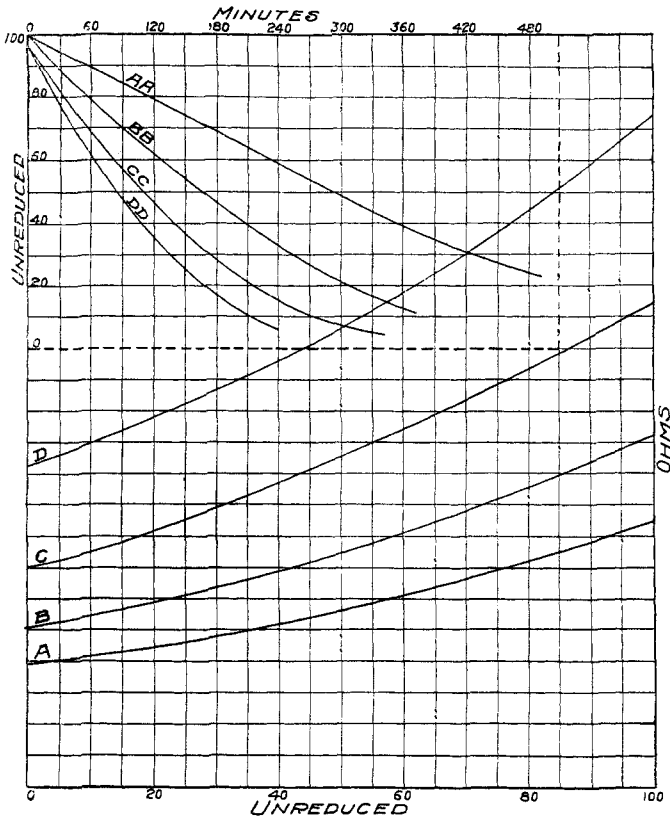
was divided among eight flasks holding over 100 cc. each. The
flasks were closed with capillary stoppers and were supported in
a frame to be immersed in the thermostat and rotated. While
being filled, the flasks were kept at a temperature of 66°, and
this was the exact temperature of the thermostat in all experi-
ments. The liquids mixed at 70° cooled to about 66° during the
filling, and after immersion in the water the flasks remained
fifteen minutes before the first one was removed for an observa-
tion; this to allow the temperature to become constant. Some
preliminary experiments were carried out at a temperature of
75°, but here it was found that the reaction was completed too
quickly for accurate observation. In another series of tests at
55° the time required to complete the tests was found to be too

long. Finally 66° was chosen as the temperature best suited to all the experiments contemplated.

In the table below the results obtained by testing the solutions from the eight flasks are given. The first column shows the time at which each flask was removed from the thermostat and quickly cooled. The second column shows the resistance found at 20°, while in the third column the amount of ferric salt remaining is expressed in per cent. for each test.

TABLE IV.

Time.	Ohms.	Unreduced.
9.00	281.4	99.5
9.30	262.9	90.5
10.00	240.6	79.3
11.00	207.9	02.5
12.00	182.5	46.8
1.00	163.6	33.0
2.00	149.6	21.6
3.00	140.4	13.5

The numbers in the third column are obtained by interpolation from the curve referred to above. When these numbers are plotted in the same manner, with the times in minutes (duration of heating) as abscissas, a very regular curve, shown at BB, is obtained. An inspection of the curve and the table is sufficient to show that the speed of the reduction decreases slowly at the start ; the law of the reduction is not immediately apparent, but this will be taken up later.

It was thought best to make other tests with larger and smaller amounts of sugar, and the results of these will be given below. As preliminary, however, I determined roughly the behavior of constant amounts of ferric alum with varying amounts of sugar, and this is shown in the following table. Five solutions of 100 cc. each were made, and these were heated three hours to 75° in the thermostat.

TABLE V.

No.	Amount of alum.	Amount of sugar.	Ratio of of alum to sugar. Mol.	Results.
1	24.1	4.275	$1 : \frac{1}{2}$	Heavy basic precipitate.
2	24.1	8.550	$1 : 1$	Slight precipitate.
3	24.1	17.10	$1 : 2$	Clear, slightly colored.
4	24.1	25.65	$1 : 3$	Clear, dark.
5	24.1	34.20	$1 : 4$	Clear, dark.

It is evident, therefore, that the proportion of sugar in the first is much too low; in the second it is slightly low, while in the others it is sufficient.

I made next solutions of 250 cc., with the amounts of sugar and salts as shown in the following table, and found the corresponding resistances given in the last column, in ohms at 20°.

TABLE VI.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
25	60.25	....	....	....	100	213.0
25	48.20	6.95	1.65	25	80	181.0
25	36.15	13.90	3.30	50	60	152.5
25	24.10	20.85	4.95	75	40	130.0
25	12.05	27.80	6.60	100	20	111.2
25	....	34.75	8.25	125	∞	96.2

A curve plotted from these figures is shown at A. This curve was used as before to calculate the proportions of ferric and ferrous salts, in mixtures undergoing reduction, from observations of resistance.

A solution for the thermostat was prepared containing in 1000 cc. 100 grams of sugar and 241 grams of ferric alum. As in the former case, the sugar and alum were dissolved separately and made up to 500 cc., mixed and distributed in the small flasks as before. The table below gives the result of the tests, the thermostat being kept at 66°, and the first flask removed at the end of fifteen minutes.

TABLE VII.

Time.	Ohms.	Unreduced.
9.00	213.6	100.0
10.30	190.4	86.0
12.00	165.0	69.5
1.00	151.3	59.0
2.00	138.8	48.5
3.00	129.4	40.0
4.00	121.5	31.6
5.00	115.5	25.5

The results of the last column are plotted and shown at AA. It will be observed that the rate of reduction is much slower here than in the former case. It was also noticed that the last

flasks removed from the thermostat were slightly turbid from partial dissociation.

Two other sets of solutions were studied. The details of the results are here given.

TABLE VIII.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
75	60.25	....	...	...	100	386.5
75	48.20	6.95	1.65	25	80	333.5
75	36.15	13.90	3.30	50	60	285.0
75	24.10	20.85	4.95	75	40	243.2
75	12.05	27.80	6.60	100	20	206.4
75	....	34.75	8.25	125	00	177.1

In curve *C* the results of the observations are found plotted. A mixture of 300 grams of sugar and 241 grams of ferric alum was made and used in the thermostat as before. The resistance found and the amount of reduction are tabulated below.

TABLE IX.

Time.	Ohms.	Unreduced.
8.30	379.1	97.4
9.30	304.4	68.5
10.15	264.8	50.5
11.00	237.3	37.0
11.45	214.7	25.0
12.30	199.8	16.0
1.15	191.2	10.0
2.00	184.4	5.5

The results of this test are plotted and shown in curve *CC*, which is very regular, without any sharp breaks.

Finally a series of concentrated solutions were made to fully test the effect of increased amounts of sugar on the speed of the reaction. It was found that 400 grams to the liter could be brought into solution with the amount of salts taken, and the table below shows the results obtained with such mixtures.

TABLE X.

For 250 cc. of Solution.

Sugar. Grams.	Ferric alum. Grams.	Ferrous sulphate. Grams.	Ammonium sulphate. Grams.	Normal sulphuric acid. cc.	Ferric salt. Per cent.	Resistance in ohms.
100	60.25	....	..	...	100	538.0
100	48.20	6.95	1.65	25	80	462.3
100	36.15	13.90	3.30	50	60	397.5
100	24.10	20.85	4.95	75	40	341.2
100	12.05	27.80	6.60	100	20	296.0
100	....	34.75	8.25	125	00	261.0

Curve D was plotted from these observations.

A corresponding mixture with 400 grams of sugar and 241 grams of ferric alum was then investigated after heating in the thermostat to 66° as before.   The results show a greater rapidity in the reduction of the ferric salt than was found in either of the other mixtures, as indicated in the following table.

TABLE XI.

Time.	Ohms.	Unreduced.
8.45	530.4	98.0
9.00	490.9	87.5
9.30	428.8	70.0
10.00	381.2	54.5
10.45	332.9	36.5
11.35	296.1	20.0
12.20	279.4	11.0
12.45	273.3	7.0

The curve DD, plotted from the figures of the last column is, like the last one, very regular.

The question now presents itself, What is the law governing the rate of reduction of ferric salt?   In all cases the amount of sugar is relatively great in proportion to that of the salt, if we take as our basis of comparison the salt and sugar which react in the well known Fehling test.   But it must be noted that the oxidation here is much less complete than it is in that case, extending probably, to a small portion of the levulose formed only.   Because of the uncertainty as to the exact nature of the reaction between the two substances taken, it would appear at first view that the rate of reduction can not be accurately expressed by a formula, but as the sugar is certainly in excess in some cases, I have calculated the speed of the reduction on the assumption that the iron salt alone undergoes a change in the reaction.   From what was shown in one of the experiments cited above, it appears probable that the invert sugar, and not the cane sugar, is the reducing agent, and, further, that from the very beginning of the reaction, enough of this is possibly present to absorb all the oxygen furnished.   It is also true that most of the invert sugar is still present at the end of the reaction. Looking upon the change, therefore, as a reaction of the first order, we have

$$\frac{dx}{dt} = K(A - x),$$

where A represents the ferric salt present at the beginning of the experiment, and x that reduced at the time, t. Therefore as $x = 0$ for $t = 0$, we have :

$$K = \frac{1}{t} \text{ nat log } \frac{A}{A - x}.$$

The calculations below are made with common logarithms, as only the relative, not the actual values are considered. Table XII gives the value of K for the weakest of the above solutions, while in the three following tables the values for the other solutions are given.

TABLE XII.

100 Grams Solution. $A = 100$.

t.	x.	$\log \frac{A}{A-x}$.	$\frac{1}{t} \log \frac{A}{A-x}$.
0	0	......	......
90	14.0	0.06550	0.00073
180	30.5	0.15802	0.00088
240	41.0	0.22915	0.00095
300	51.5	0.31426	0.00105
360	60.0	0.39794	0.00111
420	68.4	0.50031	0.00119
480	74.5	0.59346	0.00124

TABLE XIII.

200 Grams Solution. $A = 99.5$.

0	0	......	......
30	9.0	0.04117	0.00137
60	20.2	0.09855	0.00164
120	37.0	0.20194	0.00168
180	52.7	0.32757	0.00182
240	66.5	0.47931	0.00199
300	77.9	0.66337	0.00221
360	86.0	0.86745	0.00241

TABLE XIV.

300 Grams Solution. $A = 97.4$.

0	0	......	......
60	28.9	0.15287	0.00254
105	46.9	0.28527	0.00262
150	60.4	0.42036	0.00280
195	72.4	0.59162	0.00303
240	81.4	0.78444	0.00326
285	87.4	0.98856	0.00347
330	91.9	1.24820	0.00378

TABLE XV.

400 Grams Solution.   A = 98.

t.	x.	$\log \frac{A}{A-x}$	$\frac{1}{t} \log \frac{A}{A-x}$
o	o	. . . . . .	. . . . . .
15	10.5	0.04922	0.00328
45	28.0	0.14613	0.00325
75	43.5	0.25483	0.00339
120	61.5	0.42894	0.00357
170	78.0	0.69020	0.00406
215	87.0	0.94984	0.00442
240	91.0	1.14623	0.00477

A consideration of the above figures shows at once that the hypothesis regarding the nature of the reaction is not the right one, as the speed increases regularly from the beginning to the end.   In other words, the speed is an accelerated one, and the cause of this acceleration may be found in the sulphuric acid liberated as the reduction advances.   The acid liberated is proportional to the ferric salt reduced, and may be measured, therefore, by x.

It is evident also from the tables that the speed of the reaction varies with the amount of sugar in the solution, as it is almost four times as great with the 400 grams solution as with the 100 grams solution.   In any one experiment, however, this sugar amount may be considered as remaining practically constant, and a new equation expressing the speed may now be written with two terms:

$$\frac{dx}{dt} = K(B+x)(A-x),$$

in which B represents amount of sugar.

This on integration yields :

$$Kt = \frac{1}{A+B} \log \frac{B+x}{A-x} + \text{Cons.}$$

As $x = 0$ for $t = 0$, we have for the definite integral :

$$Kt = \frac{1}{A+B} \log \frac{(B+x)A}{(A-x)B}.$$

Before this formula can be used for practical calculations some numerical value must be given to B.   From preliminary tests referred to above, it appears that the sugar amount is prob-

ably a little low in the weakest solution and high in the strongest to be considered chemically equivalent to A. However, for simplicity in calculation, it may be assumed that A and B are equal, when our formula becomes :

$$K = \frac{1}{2\,At} \log \frac{A + x}{A - x}.$$

On this assumption the tables below have been calculated. For the 100 grams sugar solution the value of K for $B = 0.75\ A$ is added in the last column, and for the 400 grams solution the value for $B = 2A$.

TABLE XVI.

100 Grams Solution. $A = 100$.

t.	x.	$\frac{1}{2A} \log \frac{A+x}{A-x}$.	$\frac{1}{2At} \log \frac{A+x}{A-x}$.	$\frac{1}{t(A+B)} \log \frac{A(B+x)}{B(A-x)}$
0	0	....	....	....
90	14.0	0.000612	0.00000679	0.00000888
180	30.5	0.001385	0.00000760	0.00000969
240	41.0	0.001892	0.00000788	0.00000996
300	51.5	0.002473	0.00000824	0.00001031
360	60.0	0.003010	0.00000836	0.00001037
420	68.4	0.002632	0.00000865	0.00001064
480	74.5	0.004176	0.00000820	0.00001063
			0.00000802	

TABLE XVII.

200 Grams Solution. $A = 99.5$.

0	0	......	....
30	9.0	0.000395	0.00001319
60	20.2	0.000896	0.00001497
120	37.0	0.001704	0.00001420
180	52.7	0.002573	0.00001430
240	66.4	0.003525	0.00001469
300	77.9	0.004595	0.00001532
360	86.0	0.005718	0.00001586
			0.00001465

TABLE XVIII.

300 Grams Solution. $A = 97.4$.

0	0	....	....
60	28.9	0.001364	0.0000227
105	46.9	0.002340	0.0000223
150	60.4	0.003233	0.0000215
195	72.4	0.004271	0.0000218
240	81.4	0.005381	0.0000224
285	87.4	0.006502	0.0000228
330	91.9	0.007888	0.0000239
			0.0000225

TABLE XIX.

400 Grams Solution.   A = 98.

$t.$	$x.$	$\dfrac{1}{2A}\log\dfrac{A+x}{A-x}.$	$\dfrac{1}{2At}\log\dfrac{A+x}{A-x}.$	$\dfrac{1}{t(A+B)}\log\dfrac{A(B+x)}{B(A-x)}$
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.

BY GEO. W. ROLFE AND W. A. FAXON.

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