path, but this much is given in order that the practical value of these reactions and methods may be put to the test.

UNIVERSITY OF MT. ALLISON COLLEGE,
SACKVII N. B.

AN ANALYTICAL INVESTIGATION OF THE HYDROLYSIS OF STARCH BY ACIDS.

BY GEO. W. ROLFE AND GEO. DEFREN.

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FEW problems of commercial analysis have been so complicated and so discouraging as that of the determination of the components of starch conversion products. The well-known schemes of commercial analysis of worts and similar products of the action of diastase are based on the assumption that but two simple compounds are formed from the starch—maltose and dextrin. In the case of glucose syrups and starch sugars, which are the results of acid hydrolysis, it is known that the reaction proceeds farther as dextrose is formed from the maltose and dextrin.

Musculus and Gruber[1] decided that these reactions went on together so that except at the very beginning or final stage of hydrolysis all of these compounds must be present in solution.

The analysis of acid-converted starch products must therefore take into consideration the presence of the third compound, dextrose.

Much doubt, however, has been thrown on the accuracy of such analyses, as during the past twenty years the researches of O'Sullivan, Brown, Heron, Morris, Bondonneau, Herzfeld, Musculus, Bruckner, Fischer, and other distinguished investigators, have shown that not only the simple compounds referred to can be isolated from starch products but also many others of quite distinct optical and chemical properties. Space will not permit a review of this work, which is in many points conflicting. The recent conclusion of Lintner and Düll is that the following compounds result from hydrolysis :[2]

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[1] *Bull. Soc. Chim.*, 2, 30.

[2] *Ber. d. chem. Ges.*, 28, 1522-1531.

Hydrolysis with oxalic acid.	With diastase.
Amylodextrin	Amylodextrin
Erythrodextrin I	Erythrodextrin I
“ IIα	......
“ IIβ	......
Achroodextrin I	Achroodextrin I
“ II	“ II
Isomaltose	Isomaltose
Dextrose	Maltose

Others, as Brown and Morris,[1] deny the existence of the isomaltose of Fischer and Lintner and Düll, and mention another compound, maltodextrin, an intermediate between dextrin and maltose.

In 1885 Brown and Morris[2] discovered the remarkable law that at any stage of the conversion of starch by diastase, the total product, in its optical properties and relation to Fehling solution, behaved exactly as if made up of two components only, maltose and dextrin, so that it was possible by taking the rotatory power to calculate at once the cupric reducing power if the total carbohydrates were known. This law indicated that, however complicated the bodies isolated, they could be considered as existing in solution as two simple compounds, and did much to establish the validity of the principles of the usual commercial analyses of beer-worts and similar products.

The method of analysis of glucose syrups and starch sugars implies the assumption of a similar law, but the proof that this law actually exists under varying conditions of hydrolysis apparently has not been worked out.[3]

Our investigations have been made, first, to determine whether there was any simple constant relation between the optical rotation and the cupric reducing powers of starch products hydrolyzed under different conditions; and, secondly, whether any laws could be found affecting the three simple bodies assumed to be formed and determined by the usual methods of analysis.

Incidentally we have collected some data as to the speed of hydrolysis, influence of carbohydrates on specific gravity of

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[1] *J. Chem. Soc.*, No. 393. Aug., 1895.

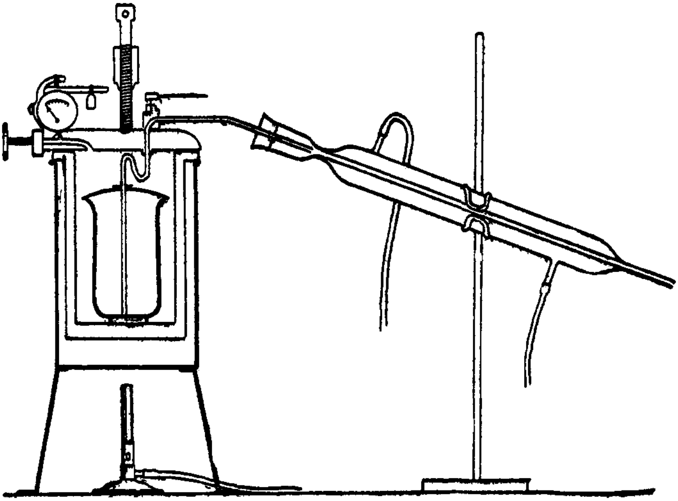
[2] *Ann. Chem.* (Liebig), 231, 131.

[3] A very complete bibliography of the original publications on the carbohydrates is in *Tollen's Handbuch der Kohlenhydrate*, Vol. 1, *1888*, 331-360; Vol. II, *1895*, 368-398.

solutions, and some looking to the adoption of a more rapid and accurate method of determining cupric reducing power by Fehling solution.

The latter data are included in a separate paper. The work on specific gravities is not yet sufficiently complete for publication.

An autoclave of the usual construction was modified in the following manner: The thermometer tube was taken out and in its place was attached a specially constructed valve, by means of which liquor cooking in a beaker in the interior could be removed at any time during the progress of the experiment. This superheated liquor was prevented from vaporizing by passing through a condenser. Excessive condensation into the beaker was prevented in large part by a well fitting lead cap. The illustration sufficiently explains the apparatus.



In most of the work about 100 grams of a good quality of commercial corn starch[1] was mixed with a liter of water con-

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[1] An analysis of this starch by the usual commercial methods gave:

	Per cent.
Starch	89.15
Oil	0.14
Ash	0.12
Albuminoid	0.42
Water	10.21
	100.04

taining the hydrolyzing acid. Samples of from fifty to seventy-five cc. of the liquor were removed at different stages of the conversion and immediately shaken up with a few grams of marble dust. Two drops of tenth normal sodium hydroxide solution were then added to the sample, which was cooled and filtered. This method of neutralization, except in cases of very low converted samples, gave an absolutely clear filtrate, the filtration being exceedingly rapid, and the removal of the albuminoids being practically complete. Low-converted products often required to be heated with aluminum hydroxide before filtering.

The samples were tested as follows:

(1) For specific gravity by Westphal Balance, corrected to a temperature of 15.5° C.

(2) Specific rotatory power ($[\alpha]_D$) by a Schmidt and Haensch half-shade saccharimeter.

(3) Cupric reducing power by means of Fehling solution.

Total Solids—Total solids were calculated from the specific gravity of the solution by the factor 0.00386, which was taken to represent the influence of one gram of the mixed carbohydrates in 100 cc. of solution. Corrections were made when necessary for the influence of other substances in solution, not carbohydrates. This factor 386 is practically that of Balling and Brix and has been found exact for approximately ten per cent. solutions of cane sugar, and the balance of evidence seems to be that it is correct for starch products.

We have made several determinations of this factor by drying ten cc. of solution on rolls of dried paper at a temperature of 100–105° C. Our results point to the constancy of this factor 386 even in solutions of low rotatory power, but are not yet complete enough to establish the value for all rotations.

Therefore, in this work we have adopted the expedient used by Brown and Morris, and others, and calculated all optical and copper reduction constants on the assumption that all three carbohydrates in solution affect the specific gravity like cane sugar when the concentration is approximately ten per cent. Even if subsequent investigations show that this view is not exactly correct, the relative values of the constant will not be appreciably affected nor the truth of the laws as set forth.

To illustrate this method of calculation of constants we give the following from our own determinations:

Ten grams of dextrose dissolved in 100 cc. of water gave a rotation of 30.70° on the Schmidt and Haensch saccharimeter. This gives $[\alpha]_D$ as 52.8.[1] As the increase in specific gravity per gram of crystallized dextrose in 100 cc. is 0.00381, $[\alpha]_{D386}$ is 53.5.

9.751 grams of crystallized maltose anhydride in 100 cc. of water gave a rotation of 76.40. This gives an absolute specific rotatory power of 136.6. The specific gravity factor of maltose being 0.00390, $[\alpha]_{D386}$ is 135.2°. No exact figure is known for the influence of crystallized dextrin on the specific gravity of its solution. O'Sullivan gives 0.00385, and the balance of evidence seems to favor this. Hence 195 is probably correct for $[\alpha]_{D386}$.[2]

In like manner the values for K have been reduced to a dextrose with the factor 386.

Specific Rotatory Power.—All readings were made as nearly as possible at a temperature of 20° C. in 200 mm. tubes, the mean of several readings being taken. Corrections for zero-error were made frequently, and the instrument was carefully screened by glass plates from the heat of the lamps. Comparisons were made with a Laurent polariscope to determine the value of the division in terms of angular degrees for sodium light, the accuracy of the quartz wedges having being verified previously. With standard quartz plates the usual factor 0.346 was obtained, but solutions of commercial glucose of approximately ten per cent. gave the figure 0.344, which agrees with the recent work of Rimbach[3] and other investigators. We have taken, therefore, the latter factor in our calculation.

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[1] Precautions against bi-rotation were taken in both examples cited.

[2] Brown and Hearn; *Ann. Chem.* (Liebig), 199, 190–243.

[3] *Ber. d. chem. Ges.*, 27, 2282.

TABLE A.

COMPARISON OF SCHMIDT AND HAENSCH HALF-SHADE SACCHARIMETER WITH THAT OF LAURENT POLARISCOPE READING IN ANGULAR DEGREES.

	S. and H. saccharimeter. (Using bat-wing burner and lens.)			Laurent polariscope. (Sodium flame.)			
Test.	Reading.	Zero error.	Corrected reading.	Reading.	Zero error.	Corrected reading.	Factor.
(t = 20—22)							
Quartz A	62.965	0.300	62.665	21° 40′	0	21.666°	0.3457
"	62.800	0.150	62.650	21° 40′	0	21.666°	0.3458
"	62.970	0.290	62.680	21° 40.2′	0.6′	21.660°	0.3458
"	62.836	0.130	62.706	21° 40.7′	c.6′	21.666°	0.3455
Glucose A...	77.510	0.277	77.233	26° 35′	0	26.582°	0.3442
" B ...	76.355	0.150	76.205	26° 15.3′	0	26.254°	0.3445
" B ...	76.355	0.150	76.205	26° 14′	0	26.233°	0.3442
" C ...	76.535	0.150	76.385	26° 18′	0	26.300°	0.3443
" D...	76.110	0.130	75.980	26° 10.3′	0.6′	26.162°	0.3443
(t = 25)							
Hydrolized starch products E.	92.73[1]	00	92.73	31° 56′	−1′	31.95°	0.3445
F.	24.84	00	24.84	8° 32′	—1′	8.55°	0.3442

Cupric Reducing Power.—Our method is practically that of O'Sullivan, first published in 1876. The copper is weighed as the oxide. We have found this method exact and rapid. An analytical investigation of this process has been made by one of us and given in detail in a separate paper.

Plotted Results.—To show the relationship of the copper-reducing power, and the specific rotatory power of the products formed during the progress of the hydrolysis of the starch, we have plotted our results, taking as abscissae the decreasing values of the rotatory power, from the amylodextrin stage (195°) to that of dextrose ($[\alpha]_{D386} = 53.5^\circ$), and as ordinates the cupric reducing power (K_{386}) taking that of an equivalent weight of dextrose as 100.[2] [See Plate A.]

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[1] Using Welsbach burner.

[2] Data given in Table B.

TABLE B.

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes Cooking.	grams starch.	Atmospheric pressure.	Acid.		Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading.	Copper oxide.	$[\alpha]_D$ 386.	K 386.
					Kind.								
8*a*	2	30	110	2	HCl	$\frac{n}{10}$	10	990	1.0456	98.0	0.1552	142.7	0.4747
	3	45							1.0394	59.3	0.2103	99.95	0.7480
	4	75							1.0374	41.5	0.2275	73.67	0.8537
	5	135							1.0367	32.9	0.2480	59.53	0.9283
10	1	15	110	2	HCl	$\frac{n}{10}$	10	990	1.0199	57.3	0.0060	191.30	0.0412
	2	45							1.0320	84.8	0.0366	176.0	0.1567
	3	75							1.0348	80.7	0.0923	154.0	0.3652
	4	100							1.0315	67.6	0.1026	142.5	0.4523
	5	130							1.0315	60.8	0.1258	128.1	0.5584
	6	160							1.0318	54.6	0.1368	114.0	0.5993
	7	190							1.0318	49.4	0.1594	103.1	0.6995
	8	220							1.0318	44.7	0.1781	93.95	0.7827
	9	250							1.0323	42.2	0.1848	86.66	0.8000
	10	280							1.0323	38.4	0.1940	78.94	0.8407
11	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0414	89.55	0.1290	143.6	0.4434
	2	30							1.0417	55.95	0.2320	89.10	0.7825
	3	45							1.0419	41.0	0.2747	64.98	0.9230
	4	60							1.0414	36.0	0.2837	57.75	0.9663
	5	75							1.0412	33.0	0.2830	53.19	0.9685
	6	90							1.0406	32.5	0.2763	53.16	0.9590
13	1	15	110	2	HCl	$\frac{n}{10}$	100	900	1.0394	103.2	0.0056	174.0	0.1958
	2	45							1.0384	75.7	0.1500	129.9	0.5405
	3	60							1.0380	61.1	0.1898	105.7	0.6988
	4	90							1.0380	45.5	0.2339	79.50	0.8646
	5	120							1.0375		0.2448	67.75	0.9175
14	2	22½	110	2	HCl	$\frac{n}{10}$	100	900	1.0379	97.8	0.0661	167.4	0.2415
	3	35							1.0384	85.9	0.1095	148.6	0.3964
	4	52½							1.0370	64.75	0.1664	116.2	0.6279
	5	75							1.0374	50.80	0.2040	90.20	0.7640

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid.		Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K 386.
					Kind.								
	6	105							1.0374	39.60	0.2281	70.31	0.8561
	7	135							1.0374	34.95	0.2493	62.34	0.9367
15	2	30	110	2	HCl	$\frac{n}{10}$	1000		1.0371	88.1	0.0890	157.7	0.3329
	3	60							1.0337	67.05	0.1247	132.1	0.5146
	4	90							1.0337	56.50	0.1551	111.4	0.6421
	5	120							1.0337	46.00	0.1863	90.65	0.7727
16	1	25	110	2	HCl	$\frac{n}{10}$	1000		1.0327	79.90	0.0679	162.3	0.2877
	2	40							1.0393	81.40	0.1395	137.5	0.4946
	3	50							1.0380	70.60	0.1617	123.4	0.5936
	4	75							1.0380	57.00	0.1994	99.61	0.7348
17	1	15	55	2	HCl	$\frac{n}{10}$	25	475	1.0360	105.5	0.0173	188.5	0.0643
	2	23							1.0341	92.9	0.0344	180.9	0.1393
	3	33							1.0343	88.1	0.0539	170.6	0.2173
	4	42							1.0352	86.2	0.0751	162.7	0.2963
	5	50							1.0308	79.5	0.0828	157.0	0.3396
18	1	75	60	2	HCl	$\frac{n}{10}$	50	450	1.0422	74.7	0.1892	117.6	0.6273
	2	90							1.0423	68.0	0.2100	106.8	0.6958
	3	110							1.0428	60.3	0.2369	93.56	0.7796
	4	120							1.0428	52.6	0.2587	81.62	0 8507
	5	135							1.0429	49.2	0.2676	76.05	0.8720
19	1	15	60	2	HCl	$\frac{n}{10}$	50	450	1.0383	105.0	0.0329	182.1	0.1186
	2	30							1.0374	87.0	0.0975	154.5	0.3619
	3	40							1.0374	66.2	0.1337	117.6	0.6255
	4	130							1.0359	39.8	0.2272	73.62	0.8882
	5	150							1.0326	34.8	0.2093	70.89	0.8997
20	1	45	60	2	$H_2C_2O_4$	$\frac{n}{10}$	50	450	1.0327	87.2	0.0396	177.1	0.1673
	2	90							1.0301	71.2	0.0766	157.7	0.3526
	3	120							1.0318	65.8	0.1125	135.5	0.4917
21	2	60	60	2	$H_2C_2O_4$	$\frac{n}{10}$	100	400	1.0352	75.9	0.1145	143.2	0.4523

HYDROLYSIS OF STARCH. EXPERIMENTAL DATA.

Run.	No. of sample.	Minutes cooking.	grams starch.	Atmospheric pressure.	Acid.		Amount cc.	Water cc.	Sp. gr. 15.5.	Sacch. reading	Copper oxide.	$[\alpha]_D$ 386.	K_{386}.
					Kind.								
	3	75							1.0359	71.6	0.1350	132.4	0.5237
	4	105							1.0355	64.0	0.1577	119.8	0.6200
24	1	30	65	2	HCl	$\frac{n}{10}$	100	400	1.0440	88.2	0.1651	133.1	0.5236
	3	60							1.0371	38.1	2x(0.1211)	68.19	0.9080
	4	75							1.0376	33.95	2x(0.1319)	59.95	0.9745
	5	90							1.0406	34.7	2x(0.1388)	56.75	0.9526
25	1	45	65	2	$H_2C_2O_4$	$\frac{n}{10}$	200	300	1.0414	99.7	0.0966	159.9	0.3240
	2	90							1.0448	85.6	0.1799	126.9	0.5611
	3	135							1.0452	67.0	2x(0.1265)	98.42	0.7791
	4	180							1.0458	55.3	2x(0.1401)	80.17	0.8525
	5	225							1.0455	47.7	2x(0.1483)	69.61	0.9088
26	1	30	65	2	H_2SO_4	$\frac{n}{10}$	100	400	1.0447	110.9	0.0869	164.7	0.2760
	2	62							1.0466	89.3	2x(0.0821)	127.3	0.5480
	3	90							1.0478	74.2	2x(0.1227)	103.[illegible]	0.7144
	4	120							1.0500	63.1	2x(0.1475)	83.79	0.8206
	5	150							1.0525	56.4	2x(0.1614)	70.96	0.8848
27	1	10	60	4	HCl	$\frac{n}{10}$	50	450	1.0430	95.2	0.1281	147.0	0.4144
	2	20							1.0430	60.85	2x(0.1196)	93.97	0.7738
	3	30							1.0430	42.7	2x(0.1414)	65.94	0.9162
	4	45							1.0430	35.3	2x(0.1466)	54.51	0.9506
	5	60							1.0430	34.8	2x(0.1533)	53.70	0.9968
33	1	10	60	4	HCl	$\frac{n}{10}$	100	400	1.0426	60.8	0.2351	94.77	0.7754
	2	15							1.0426	41.4	0.2833	64.54	0.9378
	3	20							1.0423	35.4	0.2919	55.58	0.9736
34	1	10	60	3	HCl	$\frac{n}{10}$	200	300	1.0435	56.4	0.2532	86.10	0.8143
35	1	90	60	1	HCl	$\frac{n}{10}$	100	400	1.0381	87.6	0.0992	152.7	0.3616
	2	180							1.0391	66.5	0.1887	112.9	0.6751
	3	225							1.0403	49.5	0.2525	81.56	0.8831
39	2	90	60	4	HCl	$\frac{n}{10}$	50	450	1.0384	39.7	0.2621	53.01	0.9607
	3	120							1.0378	30.4	0.2628	53.40	0.9779

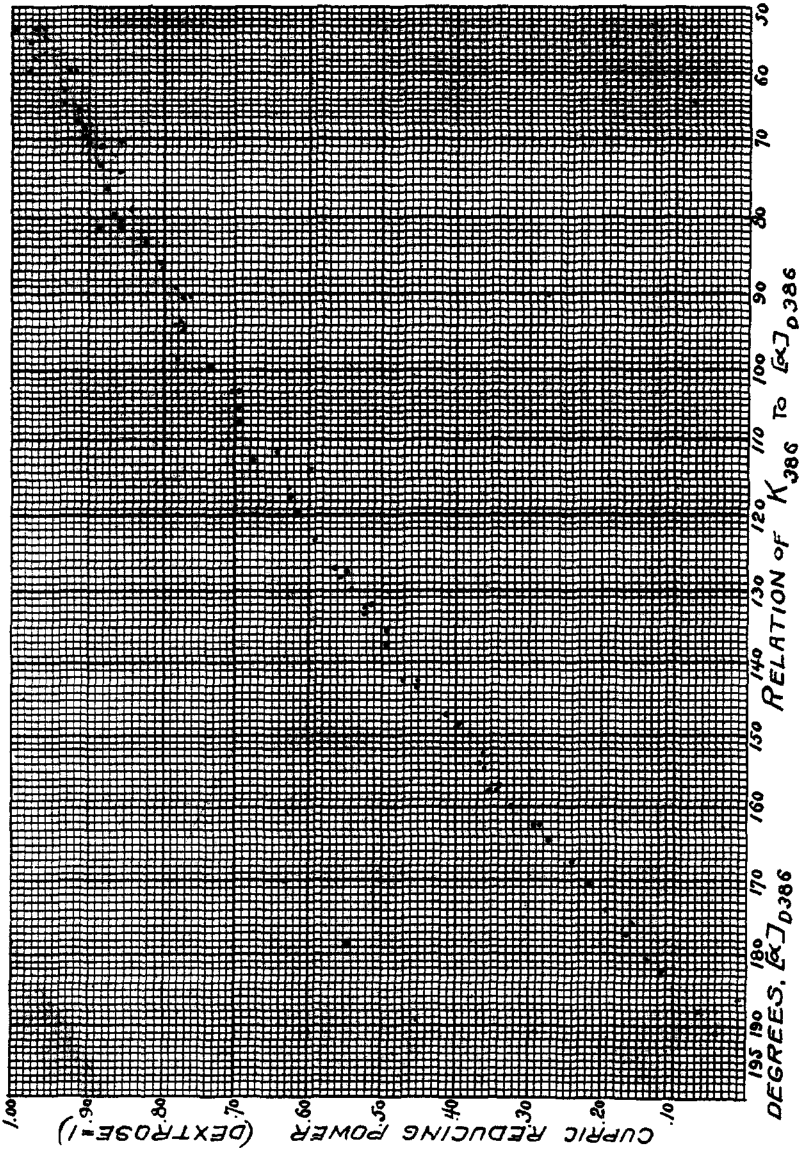
RELATION OF K_{386} TO $[\alpha]_{D386}$
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
195
DEGREES. $[\alpha]_{D386}$
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
CUPRIC REDUCING POWER (DEXTROSE=1)

PLATE A.

The results point to the remarkable fact that the cupric reducing power of the total product bears a constant relation to the specific rotatory power, even when the starch is hydrolyzed under widely varying conditions. Hence, given the one, the value of the other can be calculated. To a rotation of about 90°, the plotted results outline with extraordinary exactness the arc of a circle, the equation of which is

$$x^2 + y^2 + 468x - 646y + 1580 = 0,$$

which exactly intercepts the "zero" and "hundred" points at 195 and 53.5, respectively. The upper part of the curve is not so well defined, the results showing more discrepancy at the high conversion stages. This may be due to some decomposition and the formation of "reversion" products as stated by Wohl,[1] Maercker, Ost, and others. Wohl's figures show the maximum amount of dextrose possible to be 92.7 per cent. of the theoretical quantity. Others give ninety-six to ninety-seven per cent., the missing dextrose being supposed to be converted into dextrin-like bodies identical with those variously described as "gallisin," "isomaltose," etc. We have experimented but little along this line, having made but one hydrolysis with this special object, using $\frac{N}{100}$ hydrochloric acid at four atmospheres pressure, with the following results:

Time of cooking.	$[\alpha]_D$.
60 minutes	55.24
90 "	53.09
120 "	53.40
150 "	54.42

While several of our own results at the low rotations show a cupric reducing power of only about ninety-six per cent. of that of pure dextrose, we do not think that we are justified in arriving at any definite conclusion with the data at hand.

That the solutions begin to color considerably at rotations beyond 90° is, moreover, a strong indication of such decomposition. On the other hand, this accounts for much of the discrepancy of the plot at this part of the curve, as it is exceedingly difficult to get accurate readings on the saccharimeter of these highly colored solutions. Obviously, too, slight errors in the

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[1] *Ber. d. chem. Ges.*, **23**, 2101.

readings affect the calculations of the rotatory power the most at these lowest rotations.

Quite as noteworthy are the curves[1] plotted by taking the values of maltose, dextrin, and dextrose as computed for every

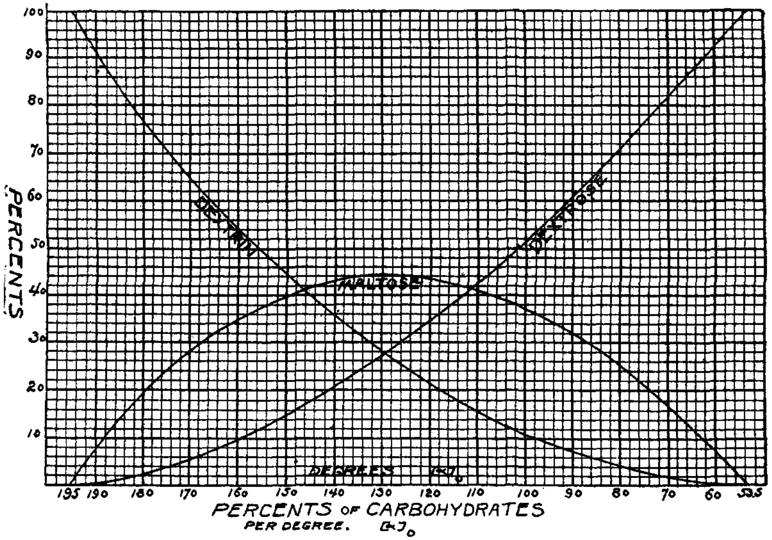

PLATE B.

five degrees of rotation from the values of K, as given by this curve.

In this work we have figured constants for solids estimated from the specific gravities of solutions by the factor, 386, and calculated percentages by the well-known equations:

$$g + m + d = 1.00$$

$$g + 0.61m = K$$

$$195d + 135.2m + 53.5g = \alpha$$

Where g is per cent. dextrose,
m is per cent. maltose,
and d is per cent. dextrin.

$$\text{Hence, } m = \frac{d + 141.5K - 195}{27.82}$$

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[1] See plate B.

Examining these curves we see that the dextrin starting from the maximum of 100 per cent. gradually falls to zero near the rotation corresponding to dextrose, while the maltose gradually rises, reaches a maximum percentage of 44.1 at about 129° rotation, corresponding to the usual state of conversion of commercial glucose, and then falls, disappearing at 53.5°. The dextrose, on the contrary, steadily mounts to 100 per cent. It will be noted, too, that at the point of maximum maltose the dextrin and dextrose, as shown by the intersection of the curves, are present in equal quantity.

Tests with phenylhydrazin acetate show the presence of the dextrose distinctly at about 185°, and we had hoped to prove the gradual rise of the dextrose percentage by means of the dextrosazon. While copious precipitates of this beautiful compound were obtained, any attempt of ours to isolate it in anything like quantitative amounts proved a failure, even in solutions containing a known amount of pure dextrose. We hope to take this up more fully in a later investigation.

We have also calculated a table (Table C) from the curves giving the value of maltose, dextrose, and dextrin within one-tenth per cent. for successive stages of acid hydrolysis represented by each degree of rotation between 195 and 53.5. This table, calculated for the factor 386, makes no allowance for possible decomposition of high-converted products.

TABLE C.

CALCULATED VALUES OF CUPRIC REDUCING POWERS AND PARTS OF MALTOSE, DEXTROSE AND DEXTRIN PER UNIT OF CARBOHYDRATE FOR EACH DEGREE OF ROTATION OF A NORMALLY HYDROLYZED STARCH SOLUTION.

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
195	0.000	0.000	0.000	1.000
194	0.011	0.017	0.001	0.982
193	0.022	0.033	0.001	0.966
192	0.032	0.048	0.002	0.950
191	0.041	0.063	0.002	0.935
190	0.051	0.079	0.003	0.918
189	0.061	0.094	0.004	0.902
188	0.071	0.110	0.005	0.885
187	0.081	0.123	0.007	0.870

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
186	0.090	0.135	0.009	0.856
185	0.100	0.147	0.010	0.843
184	0.109	0.160	0.013	0.827
183	0.118	0.171	0.016	0.813
182	0.127	0.182	0.019	0.799
181	0.137	0.192	0.022	0.786
180	0.146	0.203	0.025	0.772
179	0.155	0.212	0.028	0.760
178	0.164	0.222	0.031	0.747
177	0.173	0.231	0.034	0.735
176	0.182	0.240	0.037	0.723
175	0.191	0.250	0.040	0.710
174	0.199	0.257	0.043	0.700
173	0.207	0.265	0.047	0.688
172	0.216	0.273	0.050	0.677
171	0.224	0.280	0.054	0.666
170	0.233	0.287	0.058	0.655
169	0.242	0.294	0.062	0.644
168	0.251	0.301	0.066	0.633
167	0.259	0.307	0.071	0.622
166	0.267	0.314	0.075	0.611
165	0.275	0.320	0.080	0.600
164	0.283	0.326	0.084	0.590
163	0.292	0.332	0.089	0.579
162	0.300	0.338	0.093	0.569
161	0.308	0.344	0.098	0.558
160	0.316	0.349	0.103	0.548
159	0.324	0.356	0.107	0.537
158	0.332	0.362	0.111	0.527
157	0.340	0.369	0.115	0.516
156	0.348	0.373	0.121	0.506
155	0.356	0.378	0.126	0.496
154	0.365	0.383	0.130	0.487
153	0.373	0.388	0.135	0.477
152	0.381	0.392	0.141	0.467
151	0.389	0.397	0.146	0.457
150	0.397	0.401	0.153	0.446
149	0.404	0.405	0.157	0.438
148	0.412	0.408	0.163	0.429
147	0.419	0.412	0.164	0.420
146	0.427	0.415	0.174	0.411
145	0.435	0.415	0.182	0.403
144	0.442	0.421	0.186	0.393
143	0.450	0.423	0.192	0.385

$[\alpha]^{20}_{D\,386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
142	0.458	0.425	0.199	0.376
141	0.465	0.427	0.205	0.368
140	0.473	0.428	0.212	0.360
139	0.481	0.431	0.217	0.352
138	0.488	0.432	0.224	0.344
137	0.496	0.434	0.231	0.335
136	0.503	0.436	0.237	0.327
135	0.510	0.437	0.243	0.320
134	0.517	0.438	0.249	0.313
133	0.524	0.439	0.256	0.305
132	0.531	0.439	0.263	0.298
131	0.538	0.440	0.270	0.290
130	0.546	0.440	0.277	0.283
129	0.553	0.441	0.284	0.275
128	0.560	0.441	0.291	0.268
127	0.567	0.440	0.298	0.262
126	0.574	0.440	0.305	0.255
125	0.580	0.439	0.313	0.248
124	0.588	0.438	0.320	0.242
123	0.595	0.438	0.327	0.235
122	0.602	0.437	0.335	0.228
121	0.608	0.436	0.343	0.221
120	0.614	0.435	0.350	0.215
119	0.621	0.433	0.358	0.209
118	0.628	0.431	0.366	0.203
117	0.635	0.429	0.374	0.197
116	0.642	0.428	0.381	0.191
115	0.649	0.425	0.390	0.185
114	0.656	0.422	0.398	0.180
113	0.663	0.420	0.408	0.174
112	0.669	0.417	0.414	0.169
111	0.675	0.414	0.423	0.164
110	0.681	0.408	0.432	0.160
109	0.687	0.407	0.439	0.154
108	0.694	0.403	0.448	0.149
107	0.700	0.400	0.456	0.144
106	0.707	0.396	0.465	0.139
105	0.713	0.392	0.474	0.134
104	0.719	0.387	0.483	0.130
103	0.725	0.383	0.492	0.125
102	0.732	0.379	0.500	0.121
101	0.738	0.375	0.508	0.117
100	0.744	0.370	0.518	0.112
99	0.750	0.366	0.527	0.107

$[\alpha]^{20}_{D386}$.	K_{386}.	M_{386}.	g_{386}.	d_{386}.
98	0.757	0.361	0.537	0.102
97	0.763	0.356	0.546	0.098
96	0.769	0.350	0.556	0.094
95	0.775	0.345	0.565	0.090
94	0.781	0.341	0.574	0.085
93	0.787	0.336	0.583	0.081
92	0.793	0.331	0.592	0.077
91	0.799	0.326	0.601	0.073
90	0.805	0.320	0.610	0.070
89	0.810	0.314	0.620	0.066
88	0.816	0.308	0.629	0.063
87	0.822	0.302	0.638	0.060
86	0.828	0.295	0.649	0.056
85	0.834	0.288	0.658	0.054
84	0.839	0.282	0.667	0.051
83	0.844	0.275	0.677	0.048
82	0.850	0.267	0.688	0.045
81	0.856	0.259	0.698	0.043
80	0.862	0.251	0.709	0.040
79	0.867	0.243	0.719	0.038
78	0.872	0.234	0.730	0.036
77	0.878	0.225	0.741	0.034
76	0.884	0.217	0.751	0.032
75	0.889	0.208	0.762	0.030
74	0.895	0.200	0.772	0.028
73	0.901	0.191	0.783	0.026
72	0.906	0.182	0.794	0.024
71	0.911	0.173	0.805	0.022
70	0.916	0.163	0.817	0.020
69	0.921	0.153	0.828	0.019
68	0.926	0.143	0.839	0.018
67	0.932	0.134	0.850	0.016
66	0.937	0.125	0.861	0.014
65	0.942	0.115	0.872	0.013
64	0.947	0.105	0.883	0.012
63	0.952	0.095	0.895	0.010
62	0.957	0.085	0.906	0.009
61	0.962	0.075	0.917	0.008
60	0.967	0.065	0.927	0.008
59	0.972	0.055	0.938	0.007
58	0.977	0.045	0.949	0.006
57	0.982	0.035	0.960	0.005
56	0.987	0.025	0.971	0.004
55	0.992	0.015	0.982	0.003
54	0.997	0.005	0.993	0.002
53.5	1.000	0.000	1.000	0.000

It would seem obvious that we are now prepared to determine whether a sample of glucose is a product of one hydrolysis or is a mixture of two separately converted products, by comparison of the actual analytical results with those calculated from the rotatory power.

For testing this method we have made a few analyses of commercial glucoses obtained in open market.

In the manufacture of glucose syrup all the starch is not hydrolyzed under strictly the same conditions, as the factory practice is to pump the starch into the converter, which is under steam pressure and already contains the hydrolyzing acid. As the filling of a converter takes about one-third of the total time of cooking, it is clear that there is a radical difference in the time of hydrolysis of different portions of starch. Nevertheless, we have found that samples known to have been made under these conditions conform to the laws of our curve, and the evidence seems strong that those which depart widely from these conditions are mechanical mixtures.

The following determinations of four samples of commercial glucose giving the cupric reducing power as found and as calculated for the corresponding rotation will illustrate the method :

	Sample.	α_{D386}.	K_{386} (obtained).	K_{386} (calculated).
I.	C. Pope Co. (J)·····	131.1	0.566	0.537
II.	C. Pope Co. (M)····	125.4	0.578	0.578
III.	Rockford Co ·······	141.9	0.454	0.457
IV.	Chicago Co··········	137.2	0.505	0.495

Evidently II and III are normally hydrolyzed. IV is possibly a mixture, while I is undoubtedly so. As this latter is a sample of jelly goods which in factory practice are often made by mixing two lots, our conclusion is strengthened.

From the results as a whole we have concluded that the evidence is strong, (1) that in any homogeneous acid-converted starch product, irrespective of the conditions of hydrolysis, the specific rotatory power always represents the same chemical composition.

(2) That but three simple carbohydrates,[1] possible in molecular aggregates, exist in the solution of a starch product hydrolyzed by acids.

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[1] Leaving out of consideration the possible small amounts of products formed by reversion.

DETERMINATION OF THE CONVERSION OF COMMERCIAL GLUCOSE.

In the manufacture of glucose it is obviously essential to have a rapid means of determining the degree of conversion of the starch during the cooking process. The usual factory practice is to control the conversion by means of iodine color tests. These tests are usually made by adding a definite number of drops of standard iodine solution to a test-tube of the cooled glucose liquor. The tint at which the conversion is considered complete varies in general practice from that corresponding to $[\alpha]_D = 128$ to $[\alpha]_D = 135$, the variation being even greater in some cases, depending on the ideas of the manufacturer and the grade of goods desired.

By daily practice workmen become quite expert in making these iodine tints, which are usually carried out by crude methods and read off without comparison with any standard. Nevertheless, the product, when examined by more refined laboratory processes, shows wide variations from day to day, which does not appear surprising when we examine into the errors of such color tests.

Assuming that the test is carried out under uniform conditions of concentration and proportion of reagent to liquor to be tested, which is by no means always the case, the other conditions affecting the color are (1) temperature, (2) turbidity, and (3) illumination.

Uniform temperature can be obtained easily by some simple cooling device as a stream of running water.

The acid converter liquors are always turbid when tested, as filtration in this rapid testing is impracticable. The turbidity, however, is fairly constant. It is the third condition, that of illumination, which is constantly variable and which gives rise to the greatest error. This source of error can be largely eliminated by the use of a comparison standard, prepared of the same volume as that used in the color test and hermetically sealed in a glass tube of the standard size used in testing. Mixtures of solutions of iron salts with finely pulverized glass giving the requisite turbidity when shaken, can be easily made to exactly match the iodine tint, and will preserve their intensity indefinitely. When properly adjusted by means of polariscopic tests such standards have served well to fix the point of conversion within narrow limits and have done much to insure a uniform product.

It is of course important that these should be in the hands of the chemist or superintendent of the works, a much more exact means of testing the degree of conversion. This is most naturally accomplished by determining the specific rotatory power.

We have arranged a table for quickly calculating specific rotatory power, and found it so useful that we venture to publish it. The following simple calculation will sufficiently explain the principles on which the table has been worked out:

TABLE D.

TABLE FOR DETERMINING SPECIFIC ROTATORY POWER OF SOLUTIONS OF 7.50°–10° BRIX BY READING OF VENTZKE SACCHARIMETER.

Brix.	Sp. gr.	W = gram per 100 cc.	Log $\frac{17.20}{W}$.	Brix.	Sp. gr.	W = gram per 100 cc.	Log $\left(\frac{17.20}{W}\right)$.
7.50	1.0298	7.724	0.3477	8.80	1.0352	9.110	0.2760
7.55	1.0300	7.777	0.3447	8.85	1.0354	9.163	0.2735
7.60	1.0302	7.829	0.3418	8.90	1.0356	9.217	0.2709
7.65	1.0304	7.883	0.3388	8.95	1.0358	9.270	0.2684
7.70	1.0306	7.936	0.3359	9.00	1.0360	9.324	0.2657
7.75	1.0308	7.989	0.3330	9.05	1.0362	9.378	0.2634
7.80	1.0310	8.042	0,3301	9.10	1.0364	9.430	0.2610
7.85	1.0312	8.096	0.3272	9.15	1.0366	9.484	0.2585
7.90	1.0315	8.149	0.3244	9.20	1.0368	9.538	0.2560
7.95	1.0317	8.202	0.3216	9.25	1.0370	9.592	0.2536
8.00	1.0319	8.255	0.3187	9.30	1.0372	9.646	0.2510
8.05	1.0321	8.308	0.3160	9.35	1.0374	9.690	0.2488
8.10	1.0323	8.361	0.3132	9.40	1.0376	9.753	0.2464
8.15	1.0325	0.415	0.3104	9.45	1.0378	9.807	0.2440
8.20	1.0327	8.468	0.3077	9.50	1.0381	9.862	0.2415
8.25	1.0329	8.522	0.3050	9.55	1.0383	9.916	0.2391
8.30	1.0331	8.575	0.3022	9.60	1.0385	9.970	0.2368
8.35	1.0333	8.629	0.2995	9.65	1.0387	10.023	0.2346
8.40	1.0335	8.682	0.2969	9.70	1.0389	10.077	0.2323
8.45	1.0337	8.735	0.2943	9.75	1.0391	10.130	0.2300
8.50	1.0339	8.788	0.2916	9.80	1.0393	10.185	0.2277
8.55	1.0341	8.842	0.2889	9.85	1.0395	10.239	0.2252
8.60	1.0343	8.895	0.2864	9.90	1.0397	10.293	0.2231
8.65	1.0345	8.949	0.2838	9.95	1.0399	10.347	0.2207
8.70	1.0347	9.002	0.2812	10.00	1.0401	10.401	0.2185
8.75	1.0350	9.056	0.2786				

Taking the usual formula for the specific rotatory power, $\alpha = \frac{av}{lw}$, where a is the angle of rotation of the solution of w

gram of the active substance in v cc. of water observed through a column l decimeters long. If we make $a = \alpha$ it is plain w is the weight of substance under standard conditions which will give a direct reading of the specific rotatory power without calculation. In an instrument reading in angular degrees under the usual conditions of $v = 100$ and $l = 2$, w is therefore 50 g.

If a is the reading of a saccharimeter with the Ventzke scale, $w = 50 \times 0.344 = 17.20$, and the specific rotatory power of any solution of known concentration of an optically active substance will be $\frac{17.2a}{w}$. The easiest way of finding the concentration of glucose solutions with sufficient exactness for this work is by the Brix (or Balling) hydrometer, as this instrument is now made of great accuracy.

Brix hydrometers are carried in regular stock of the larger houses dealing in chemical apparatus for brewers and sugar manufacturers, with scales having a range of about five degrees and easily read to 0.05 per cent. Thermometers are attached having corrections for temperature marked on the scale. Concentrations of about ten per cent. are most convenient for polarizing; hence a spindle will be needed reading from five to ten per cent.

The method of determining rotatory powers is as follows: The glucose is diluted to an approximately ten per cent. solution. An exact Brix (or Balling) reading is taken, corrected for standard temperature and the solution polarized in a 200 mm. tube in any saccharimeter with the Ventzke scale. The logarithm of the factor $\frac{17.20}{w}$ corresponding to the Brix reading is then found in the table. Therefore, the calculation which is, $\log\,[\alpha]_D = \log\left(\frac{17.20}{w}\right) + \log\,a$, simply requires finding the logarithm of the saccharimeter reading and the number corresponding to the sum of this and the logarithm given in the table. This number is the required specific rotatory power.[1]

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[1] Obviously a table made on the scheme of the well-known Schmitz table for cane-sugar syrups would do away with all calculation. Such a table is, however, rather bulky for insertion here.

Thus a solution of 7.85 Brix having a reading of 51.7°, Ventzke has the rotatory power of its anhydrous carbohydrates determined as follows:

By the table, the corresponding logarithmic factor is 0.3272.

$$\begin{array}{ll} \text{Log } 51.7 = & 1.7135 \\ \text{Factor} & \underline{0.3272} \\ & 2.0407 = \log 109.8 \end{array}$$

which is the required rotatory power.

In this calculation no correction is made for ash, which, as a rule, does not affect the results appreciably.

The errors due to the slight variations in the concentration of the solutions used and changes in the temperature of the laboratory are too small to be taken into consideration in factory work or in general commercial analysis. The method in practice is quite as rapid as the "quotient of purity" determination of cane-sugar syrups. We suggest that this, or some similar scheme, be uniformly used for expressing the results of all polarimetric investigations of honeys, syrups, and similar indeterminate mixtures of carbohydrates met with in commercial analysis, instead of merely giving the polarizations, or the specific rotatory powers referred to the weights of the sample. The advantages are obvious. Such analytical results would be close approximations to the exact specific rotatory powers of the mixed anhydrous carbohydrates, and would be convenient of interpretation by inspection as being directly comparable on what is for all practical purposes an absolute standard and the one used in all strictly scientific work of the kind.

THE SPEED OF THE HYDROLYSIS OF STARCH BY ACIDS.[1]

The laws of the speed of hydrolysis of the carbohydrates with the exception of that of cane-sugar have been but little studied. Solomon[2] has collected some data on the action of various acids at boiling temperature. Welhelmy[3] showed in the case of the catalytic action of hydrochloric acid on cane-sugar that if the

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[1] We are greatly indebted to Prof. A. A. Noyes, of this department, for valuable aid in calculating the results of this work on speed of hydrolysis.

[2] *J. prakt. Chem.*, (2), 28.

[3] *Ber. d. chem. Ges.*, 18, 2211.

amount of acid and the temperature remained constant the rate of the inversion at any specified moment is proportional to the amount of unchanged sugar present at that moment.

That is, if A_0 represent the amount of sugar originally present, x the amount of this sugar changed over in any period of time, t, and c the reaction-constant, we have $\frac{dx}{dt} = c\ (A_0 - x)$.

The relative values of the constant, c, of the various acids in their action on cane-sugar have been determined by several observers, notably Ostwald,[1] who has compared, by means of their constants, the relative effect of chemically equivalent quantities of a large number of acids, taking the constant of hydrochloric acid as a standard with the arbitrary value of 100.

Recent work shows that acids act on salicin,[2] one of the glucosides, in a manner analogous to that of cane-sugar, the speed of hydrolysis of this body by the different acids bearing the same relation to hydrochloric acid.

The observations noted above suggested the possibility that in the hydrolysis of starch the acids would show the same proportional speed of reaction. This is an especially interesting problem because the starch molecule is exceedingly complicated, the molecular weight being undoubtedly very high. Starch hydrolysis, however, must be considered as somewhat different from that of cane-sugar or salicin. While these are easily soluble in cold water, starch is totally insoluble at ordinary room temperature. On the other hand, amylodextrin, the product of decomposition of starch by boiling water, is somewhat soluble in cold water, its solubility increasing with rise of temperature.

As by the customary procedure in determining speed of hydrolysis, it would be necessary to ascertain the exact moment when all the starch has been converted into the soluble form, a point not conveniently determined, we have adopted a method of measurement, based on the following principles:

The conversion products of starch, with the possible exception of those of very high rotatory power, are easily soluble in water, and can be looked upon as mixtures of maltose, dextrose and dextrin.

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[1] *J. prakt. Chem.*, *1884*, 401.

[2] Noyes and Hall: *Ztschr. phys. Chem.*, *1895*, 240.

The starch first changes to amylodextrin. The hydrolysis then proceeds by successive stages through the so-called maltodextrin, maltose, and dextrose. "Reversion," so-called, may take place to some extent, a small amount of the dextrose forming dextrin-like bodies, "gallisin," "isomaltose," etc., but this point is not considered in this work. The dextrin may therefore be looked upon as the original substance hydrolyzed, and maltose and dextrose as successive products of the reaction.

Further, we have shown that whatever the condition of hydrolysis by acids, the specific rotatory power of any conversion product corresponds to a definite chemical composition, tables for determining which we have constructed.

Thus, for instance, a conversion product of 160° has been proved to contain 54.8 per cent. dextrin, the remainder being maltose and dextrose.

Hence, the time of taking any sample after the contents of the autoclave has acquired constant temperature, which requires about ten minutes, can be taken as the initial point for determining speed of hydrolysis, and all subsequent samples referred to this, as it is obvious that in any sample we can ascertain the dextrin unacted upon at that stage of the hydrolysis. The same holds true of maltose.

We have to deal with two reactions, the first being the hydrolysis of dextrin to maltose.

If A_0 is the amount of dextrin at the initial point taken, $A_0 - x$, the amount remaining at any time, t, and c the constant depending on conditions of hydrolysis we get, $\frac{dx}{dt} = c\,(A_0 - x)$.

This, on integrating, gives $\log \frac{A_0}{A - x} = ct$, or $\frac{1}{t} \log \frac{A_0}{A_0 - x} = c$, which is the general equation of a first-order reaction. The second decomposition is that in which maltose is hydrolyzed to dextrose, and is peculiar in so far as it proceeds simultaneously with that by which the maltose is formed. As a result of the hydrolysis of the dextrin the maltose increases rapidly to a maximum of 44.1 per cent. at a rotation of 129°.

It then gradually diminishes, while the dextrose percentage always increases.

Consequently, the equation expressing accurately the rate of change in the total amount of maltose present is quite complicated, and we have therefore used an approximate formula, which is sufficiently exact for the work in hand. The formula is derived from the exact differential equation

$$\frac{dD}{dt} = c_2 M,$$

which states that the amount of dextrose formed at each moment is proportional to the amount of maltose present by replacing the differential quantities by finite differences, which in applications of the formula must of course be taken small. In the place of M the average amount of maltose present during the interval of time considered is also substituted. That is, if M_1 and M_2 are the amounts of maltose present at the time, t_1 and t_2, and D_1 and D_2 the amounts of dextrose present at these same times, and c_2 is the reaction constant, we get as a result of the above mentioned substitutions :

$$D_2 - D_1 = c_2 \frac{M_1 + M_2}{2} (t_2 - t_2),$$

or,

$$\left(\frac{1}{t_2 - t_1}\right) \left(\frac{D_2 - D_1}{\frac{M_1 + M_2}{2}}\right) = c_2.$$

The results are contained in the following tables :

TABLE E.

SPEED OF HYDROLYSIS OF STARCH.

Time t. (minutes)	$[\alpha]^{20}_{D_{386}}$	$A_0 - x$.	$\log \frac{A_0}{A_0 - x}$	C_1.	$\frac{D_2 - D_1}{\frac{m_1 + m_2}{2}}$	C_2.
Hydrochloric acid : 0.02 normal ; at 2 A $T = 135°$ C.						
$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 161$; $A_0 = 55.8$.						
10	137	35.5	0.2216	0.02216	0.3581	0.0358
20	118	20.3	0.4391	0.02196	0.3118	0.0312
30	100	11.2	0.6784	0.02261	0.3790	0.0379
40	88	6.3	0.9684	0.02421	0.3274	0.0327
50	76	3.2	1.2415	0.02483	0.4638	0.0464
60	69	1.9	1.4678	0.02446	0.4162	0.0416
70	64	1.2	1.6674	0.02382	0.4264	0.0426
	$C_1 = 0.02344$.				$C_2 = 0.0373$.	

Sulphuric acid : 0.02 normal ; at 2 A $T = 135^\circ$ C.

$t_0 = 20$; $[\alpha]^{20}_{\mathrm{D}\,386} = 177^\circ$; $A_0 = 73.5$.

10	163	57.9	0.1036	0.01036	0.1954	0.0195
20	152	46.7	0.2248	0.01124	0.1436	0.0144
30	140	36.0	0.3100	0.01033	0.1703	0.0170
40	129	27.5	0.4270	0.01068	0.1678	0.0168
60	109	15.4	0.6788	0.01131	0.3656	0.0188
80	90	7.0	1.0212	0.01277	0.4700	0.0235
100	77	3.4	1.3348	0.01335	0.4809	0.0240
120	66	1.4	1.7202	0.01434	0.6915	0.0346

$C_1 = 0.0118$. $C_2 = 0.0211$.

Oxalic acid : 0.04 normal ; at 2 A $T = 135^\circ$ C.

$t_0 = 20$; $[\alpha]^{20}_{\mathrm{D}\,386} = 180^\circ$; $A_0 = 77.2$.

20	157	51.6	0.1750	0.00875	0.3147	0.0157
40	137	33.5	0.3626	0.00907	0.2890	0.0145
60	120	21.5	0.5552	0.00925	0.2738	0.0137
80	106	13.9	0.7446	0.00931	0.2762	0.0138
100	93	8.1	0.9791	0.00979	0.3224	0.0161
120	82	4.5	1.2344	0.00029	0.3426	0.0171
140	73	2.6	1.4726	0.01052	0.4149	0.0207

$C_1 = 0.00957$. $C_2 = 0.0159$.

Sulphurous acid : 0.02 normal ; at 2 A $T = 135^\circ$ C.

$t_0 = 50$; $[\alpha]^{20}_{\mathrm{D}\,386} = 187^\circ$; $A_0 = 87$.

50	179	76.0	0.0587	0.00117	0.1254	0.00251
100	172	67.7	0.1089	0.00109	0.0907	0.00181
150	165	60.0	0.1613	0.00108	0.1012	0.00202
200	159	53.7	0.2095	0.00105	0.0799	0.00159
250	151	45.7	0.2796	0.00112	0.1036	0.00207
300	144	39.3	0.3451	0.00115	0.0978	0.00196
350	137	33.5	0.4145	0.00119	0.1053	0.00211
400	131	29.0	0.4773	0.00119	0.0893	0.00179

$C_1 = 0.00113$. $C_2 = 0.00198$.

Acetic acid : 0.5 normal ; at 2 A $T = 135^\circ$ C.

$t_0 = 50$; $[\alpha]^{20}_{\mathrm{D}\,386} = 170^\circ$; $A_0 = 65.5$.

50	143	38.5	0.2307	0.00461	0.3775	0.00755
100	121	22.1	0.4718	0.00472	0.3516	0.00703
150	103	12.5	0.7193	0.00480	0.3643	0.00729
200	86	5.6	1.0680	0.00534	0.4638	0.00928
250	74	2.8	1.3690	0.00548	0.4969	0.00994

$C_1 = 0.00449$. $C_2 = 0.00822$.

Hydrochloric acid : 0.01 normal ; at 1 A $T = 121^\circ$ C.

$t_0 = 40$; $[\alpha]^{20}_{\mathrm{D}\,386} = 183^\circ$; $A_0 = 81.3$.

40	168	63.3	0.1087	0.00272	0.2118	0.00529
70	158	52.7	0.1883	0.00269	0.1358	0.00453
100	149	43.8	0.2686	0.00269	0.1199	0.00400
140	137	33.5	0.3851	0.00275	0.1764	0.00441
180	126	25.5	0.5036	0.00280	0.1693	0.00423
200	120	21.5	0.5777	0.00289	0.1028	0.00514
250	107	14.4	0.7517	0.00301	0.2539	0.00508

$C_1 = 0.00279$. $C_2 = 0.00467$.

Hydrochloric acid: 0.01 normal; at 2 A $T = 135°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 176°$; $A_0 = 72.3$.

10	162	56.9	0.1040	0.0104	0.1937	0.0194
20	148	42.9	0.2266	0.0113	0.1877	0.0188
40	128	26.8	0.4310	0.0108	0.3015	0.0151
60	110	16.0	0.6550	0.0109	0.3259	0.0163
80	93	8.1	0.9506	0.0119	0.4102	0.0205
100	81	4.3	1.2256	0.0123	0.3830	0.0182
120	70	2.0	1.5581	0.0130	0.4479	0.0294

$C_1 = 0.0115$. $C_2 = 0.0187$.

Hydrochloric acid: 0.01 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3979	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640

$C_1 = 0.0314$. $C_2 = 0.00548$.

Hydrochloric acid: 0.01 normal; at 4 A $T = 153°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 147°$; $A_0 = 42.0$.

5	117	19.7	0.3287	0.0657	0.4900	0.0980
10	96	9.4	0.6501	0.0650	0.4671	0.0934
15	79	3.8	1.0434	0.0696	0.5443	0.1088
20	68	1.8	1.3679	0.0684	0.6060	0.1212
25	61	0.85	1.6938	0.0678	0.7157	0.1431
30	57	0.5	1.9242	0.0641	0.7818	0.1564

$C_1 = 0.0668$. $C_2 = 0.1202$.

Hydrochloric acid: 0.04 normal; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 150°$; $A_0 = 44.7$.

3	115	18.5	0.3831	0.1277	0.5736	0.1912
5	95	9.0	0.6961	0.1392	0.4541	0.2270
7	80	4.0	1.0481	0.1497	0.4833	0.2416
10	66	1.4	1.5042	0.1504	0.8083	0.2694
13	58	0.6	1.8721	0.1440	1.0350	0.3450
15	66	0.4	2.0482	0.1365	0.6285	0.3143

$C_1 = 0.1413$. $C_2 = 0.2648$.

Hydrochloric acid: 0.02 normal; at 3 A $T = 145°$ C.

$t_0 = 10$; $[\alpha]^{20}_{D_{386}} = 148°$; $A_0 = 42.9$.

5	116	19.1	0.3515	0.0703	0.5246	0.1029
10	96	9.4	0.6594	0.0659	0.4478	0.0896
15	80	4.0	1.0304	0.0687	0.5075	0.1015
20	69	1.9	1.3537	0.0677	0.5889	0.1178
25	61	0.85	1.7031	0.0681	0.7739	0.1548
30	56	0.45	1.9793	0.0660	1.0800	0.2160

$C_1 = 0.0678$. $C_2 = 0.1304$.

Hydrochloric acid : 0.01 normal; at 3 A $T = 145°$ C.

$t_0 = 5$; $[\alpha]^{20}_{D_{386}} = 174°$; $A_0 = 70$.

5	158	52.7	0.1233	0.0247	0.2766	0.0553
10	140	36.0	0.2888	0.0289	0.2528	0.0506
15	125	24.8	0.4506	0.0300	0.2351	0.0470
20	110	16.0	0.6410	0.0321	0.2756	0.0551
30	88	6.3	1.0458	0.0349	0.5544	0.0554
40	74	2.8	1.3974	0.0350	0.5630	0.0563
50	65	1.3	1.7212	0.0344	0.6349	0.0640

$C_1 = 0.0314$. $C_2 = 0.0548$.

Hydrochloric acid : 0.005 normal; at 3 A $T = 145°$ C.

$t_0 = 20$; $[\alpha]^{20}_{D_{386}} = 172°$; $A_0 = 67.7$.

20	142	37.6	0.2554	0.0128	0.4270	0.0214
40	113	17.4	0.5901	0.0148	0.4900	0.0245
60	91	7.3	0.9673	0.0161	0.5226	0.0261
80	77	3.4	1.2991	0.0162	0.5082	0.0254
100	66	1.4	1.6845	0.0168	0.7429	0.0371
120	59	0.7	1.9855	0.0165	0.8172	0.0409

$C_1 = 0.0155$. $C_2 = 0.0279$.

At the head of each table are given data as to the concentration and nature of the acid, the temperature corresponding to the steam pressure given in atmospheres and $[\alpha]^{20}_{D_{386}}$ at the initial time period t_0 with the corresponding value of A_0. Time values are expressed in minutes, and the constants c_1 for the hydrolysis of dextrin, c_2 for that of maltose, are calculated according to the formulas given above.

The results show that the constants in general are satisfactory, and that therefore the reaction like the sucrose inversion follows the law of the first order. It will also be seen that the values c_1 are much more uniform than those of c_2, which is to be expected since c_1 is absolute and c_2 only approximate. Deviations of c_1 may be fairly ascribed to variations in temperature which, though slight, are significant, owing to the high temperature coefficient of the reaction.

The dextrin values in Table C are consequently correct within the limits of error of analysis. It will be seen that the values of c_2 are much more constant in those determinations in which t is larger and the values of $[\alpha]_D$ decrease slowly. This was to be expected from the conditions of the approximate formula given above for the decomposition of maltose, these requiring that the amount of substance changed in a period of time must be small. The question of reversion may possibly have some influence on the values of c_2 but as yet we are not prepared to express ourselves definitely on this subject.

The relative effects are shown in the following table: Table I shows the influence on the speed of hydrolysis of various acids at the same temperature, 135° C.

Table II shows the influence of temperature on the speed of hydrolysis when the same amount of acid is used.

Table III gives the influence of varying amounts of acid.

The mean value of constants are given in column II. Column III gives the relative value of the constants referred to that of $\frac{1}{100}N$ hydrochloric acid at 135° taken as 100. Column IV gives the velocity constants determined by Ostwald[1] for cane-sugar inversion by the same acids at half-normal concentration.

TABLE I.

Acid.	Concentration.	II.	III.	IV.
Hydrochloric	0.02 N	0.02344	100	100
Sulphuric	0.02 N	0.0118	50.35	53.6
Oxalic	0.04 N	0.00957	40.83	....
(“)	(0.02 N)	(0.00479)	(20.42)	18.6
Sulphurous	0.02 N	0.00113	4.82	....
Acetic	0.5 N	0.00499	21.29	....
(“)	(0.02 N)	0.00020	0.8	0.4

TABLE II.

Acid.	Concentration.	Temp.	I.	II.
Hydrochloric	0.01 N	121	0.00279	11.91
“	0.01 N	134	0.0115	49.07
“	0.01 N	145	0.0314	13.40
“	0.01 N	153	0.0668	28.50

TABLE III.

Acid.	Concentration.	II.	III.
Hydrochloric	0.04 N	0.1413	602.9
“	0.02 N	0.0678	289.3
“	0.01 N	0.0314	134.0
“	0.005 N	0.0155	66.13

It is seen that the corresponding numbers of columns III and IV agree fairly well. The relative influence of the various acids upon the hydrolysis of starch, sucrose and salicin are therefore nearly identical. It should be noted however that the chemical activity of hydrochloric acid on starch, as in the case of salicin

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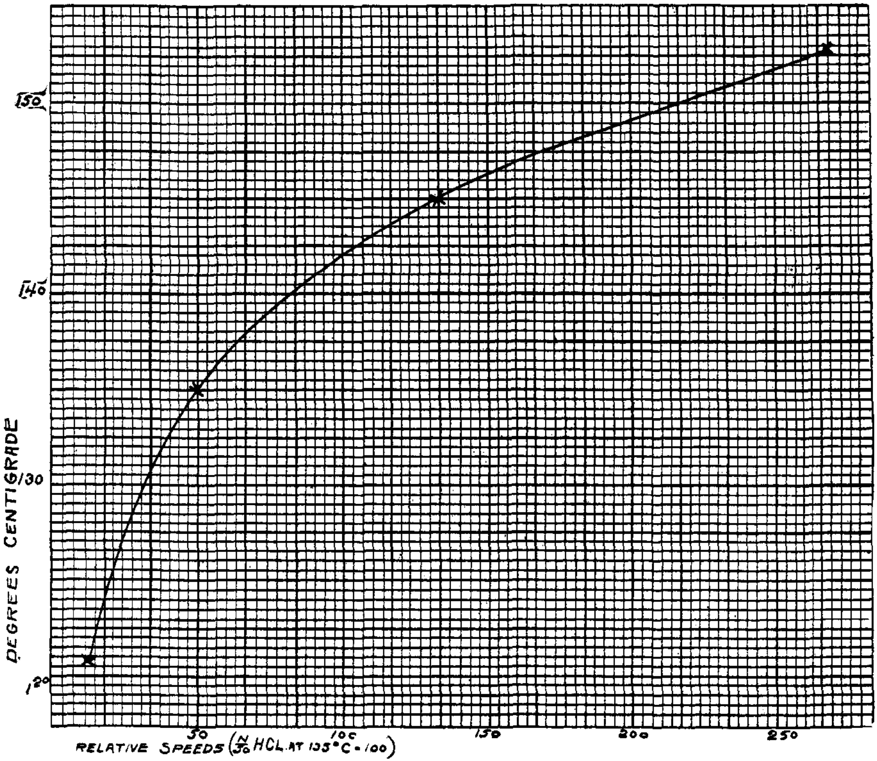
[1] *Loc. cit.*

and cane-sugar, increases in a greater ratio than the concentration, while the electrical conductivity increases more slowly.

The influence of temperature can be explained graphically by a curve approximating a parabola.



INFLUENCE OF TEMPERATURE

PLATE I.

Plate II shows the influence of the various acids.

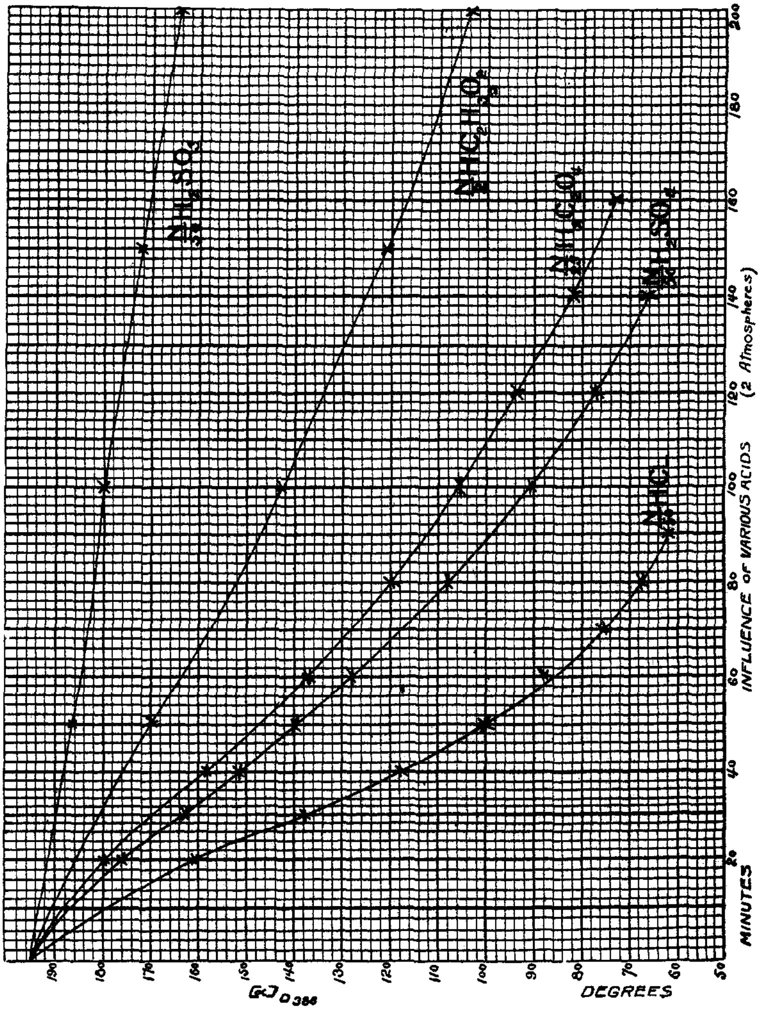


PLATE II.

Plate III shows the influence of the concentration, or amount of acid used.

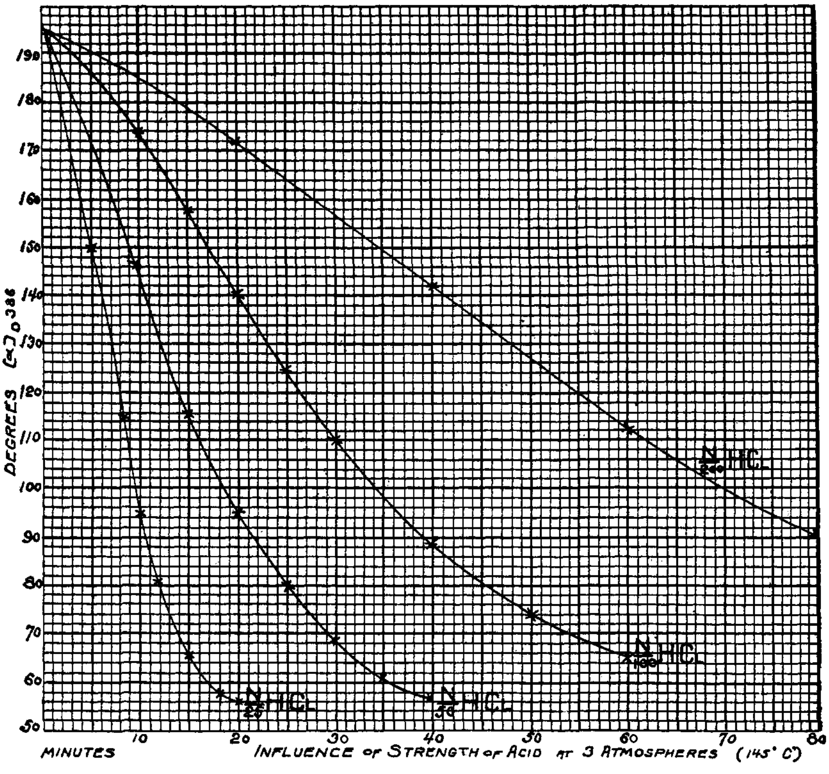


PLATE III.

Plate IV shows the relative curves due to temperature.

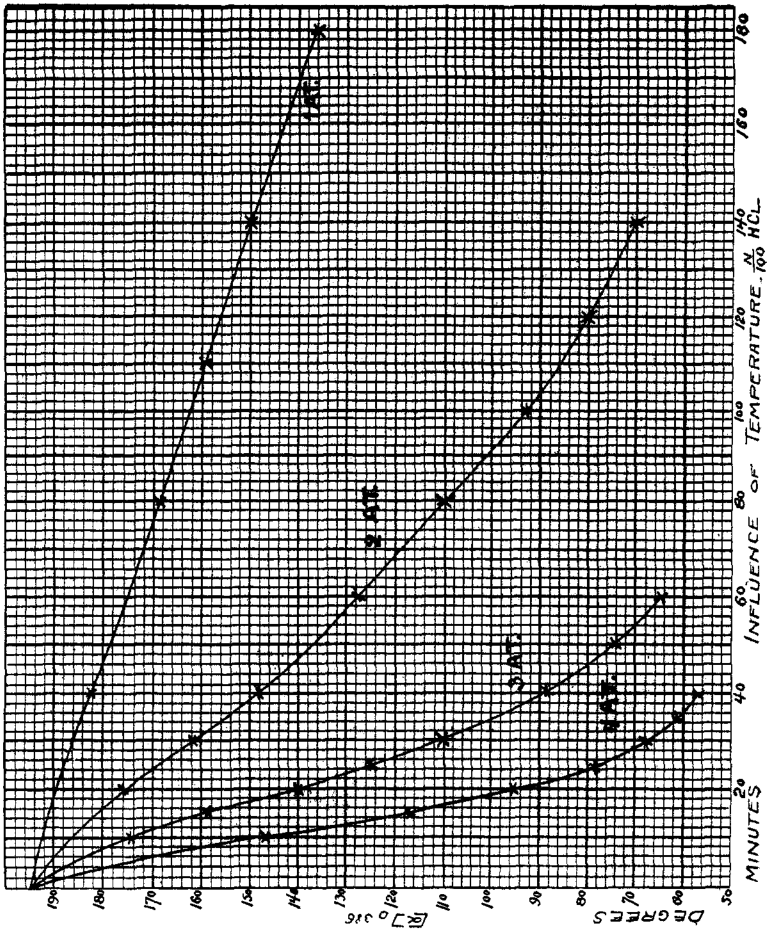


PLATE IV.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.