Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

$$Zn + \frac{7}{A-7}(ZnSO_4 \cdot AH_2O) + Hg_2SO_4 \rightleftarrows 2\,Hg + \frac{A}{A-7}\,ZnSO_4 \cdot 7\,H_2O.$$

        liquid   solid

and

$$Zn + \frac{6}{a-6}(ZnSO_4 \cdot a\,H_2O) + Hg_2SO_4 \rightleftarrows 2\,Hg + \frac{a}{a-6}\,ZnSO_4 \cdot 6\,H_2O$$

        liquid   solid

in which A, or a, represents the number of mols. of water which accompany one molecule of $ZnSO_4$ in the saturated solution at the temperature of the cell.

3. It has been demonstrated that calculations based on the old view lead to utterly faulty results.

4. The value of E_c in the equation of GIBBS and v. HELMHOLTZ is calculated by means of the new equation. For the CLARK-normal-cell in which undissolved $ZnSO_4 \cdot 7\,H_2O$ is present the calculation gave:

at 18° C. $E_c = $ **81127** calories

whilst experimentally the value $Ec = $ **81490** calories was found or, the calculation gives as temperature-coefficient at 18° C.

                                              — **0,001207** Volt.

whilst experimentally   — **0,001235** »

was found.

For the CLARK-cell containing undissolved $ZnSO_4 \cdot 6\,H_2O$, the calculation at 15° C. gives $E_c = $ **75159** calories,

whilst experiment gives $E_c = $ **75677**   „

Amsterdam, University Chemical Laboratory,
            April 1900.

Chemistry. — *"Studies on Inversion"* (First Part). By Dr. ERNST COHEN (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

1. A few years ago (1896) it was stated by RAYMAN and ŠULC in a paper on catalytic hydration by metals [1]), that when cane-sugar is dissolved in very pure water (conductivity 0.7×10^{-6}) and exposed in platinum vessels to temperatures over 80° C. a decided inversion takes place which proceeds with a steadily increasing velocity.

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[1]) Zeitschrift für phys. Chemie **21**. 481 (1896).

From their rather extensive material I have taken the following table:

T A B L E I.

Temperature 80°.

Time (in hours).	Rotation of the solution.	k.
0	11°.56	— .—
8	11 .49	0.00025
14	11 .42	0.00029
26	10 .89	0.00076
36	9 .23	0.00203
48	4 .95	0.00523
58	0 .31	0.01032

I have calculated the velocity-constant k in the third column from the equation:

$$k = \frac{1}{t} \, l. \; \frac{A}{A - x}$$

in which A represents the initial concentration of the inverted sugar solution and x the concentration at the time t.

I have taken it for granted in that calculation that RAŸMAN and ŠULC have polarized their solutions at 25° C. Although they do not actually say so, I conclude such to be the case from a remark on p. 488 of their paper.

For the calculation of the end-rotation I have made use of the equation of HERZFELD [1]) who states that every degree of right-handed polarisation of the original solution gives (0.4266—0.005 t) degrees of left handed polarisation at the temperature $t°$.

I have now made a further investigation of the peculiar phenomenon described by RAŸMAN and ŠULC, in the laboratory of Prof. SVANTE ARRHENIUS at Stockholm to whom I wish here to express my hearty thanks for the great hospitality extended to me during my stay in Stockholm.

In the first place this article will deal with the method of working and the facts thus collected whilst in a future communication this material will be subjected to a closer calculation.

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[1]) See E. O. VON LIPPMANN, die Chemie der Zuckerarten (1895) S. 516.

2. If it be supposed that both cane-sugar and the products obtained by inversion d-glucose and d-fructose are of an acidic nature, then the qualitative action in the experiments of RAŸMAN and ŠULC may be explained by assuming that the produced invert-sugar is a stronger acid than the originally present saccharose.

It was now my object to experimentally prove in the first place the correctness of that assumption. If it is correct then it must be assumed that by the action of pure water on saccharose two (stronger) acids are formed which as their amounts increase will accelerate the inversion.

That cane-sugar behaves like an acid is shown by the researches of C. KULLGREN in ARRHENIUS' laboratory. He determined the influence exercised by different non-electrolytes on the saponification-velocity of ethyl acetate by sodium hydroxide at 20°.7 C.

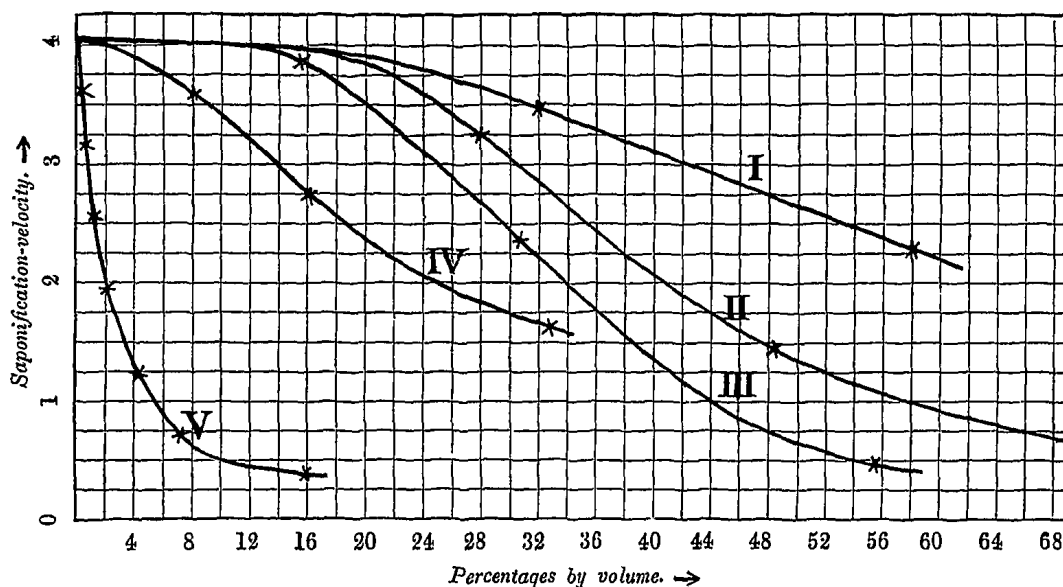His results are represented graphically in fig. 1. The abscissae

Percentages by volume. →
Fig. 1.

represent the concentrations of the added non-electrolytes (in percentage by volume).

Curve I relates to the experiments with acetone.
  ,, II   ,,   ,,   ,,   ,,   ,,   ethyl alcohol.
  ,, III   ,,   ,,   ,,   ,,   ,,   methyl alcohol.
  ,, IV   ,,   ,,   ,,   ,,   ,,   glycerol.
  ,, V   ,,   ,,   ,,   ,,   ,,   saccharose

the ordinates the saponification-velocities at 20°.7 C.

From this representation we see at once that glycerol and parti-

cularly saccharose enormously diminish the saponification velocity. Now, these are just the substances which form salts with Na OH according to the scheme:

$$C_{12} H_{22} O_{11} + Na\ OH = C_{12} H_{21} O_{11} Na + H_2O.$$
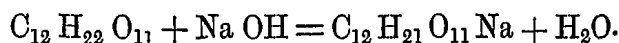
KULLGREN attributes the influence exercised by glycerol and saccharose to a chemical change in the above sense, showing plainly the acidic nature of cane-sugar.

If, on the strength of this view, the influence exercised by the addition of saccharose on the electrical conductive power of N./40 NaOH solutions is calculated, a satisfactory agreement appears to exist between the calculation and the experiment as shown by the following table taken from KULLGREN.

TABLE II.

Percentage by volume saccharose.	Relative Conductivity (at 20°.7 C.)	
	found.	calculated.
0	4.04	—
0.533	3.06	3.32
1.058	2.79	2.36
2.11	2.12	2.33
4.20	1.63	1.78
7.00	1.26	1.31
15.87	0.78	0.73

3. I have now studied the influence which cane-sugar invert-sugar, d-glucose, d-fructose and finally mannitol exercise on the saponification-velocity of N./40 ethylacetate by N./40 Na OH. 25° was chosen as the temperature of the experiments.

Mannitol was also investigated in order to show once more that substances which do not yield salts exercise an influence of a quite different kind than those who do form such compounds.

The different solutions were mixed together in the well-known manner in 100 cc. flasks made of Jena-glass which were previously steamed. In every case the concentration of the ethyl acetate and of the lye was N./40.

The flasks were suspended in a thermostat the temperature of which was constant within 0,03° (toluene-regulator and powerful stirring by means of HEINRICI hot air-motor). From time to time

(the chronometer showed a fifth of a second) 10 cc. were pipetted from the flasks and added to 10 cc. of standardised acid; the excess of acid was then titrated with $N./_{40}$ NaOH using phenolphthalein as indicator.

The standard liquids were kept in large bottles and duly protected from the carbon dioxide of the air [1]).

The preparation of lye free from CO_2 is generally done by allowing metallic sodium to liquefy under a jar in which a basin of water is placed. By following this method [2]) the preparation of, say, 1 litre of N. soda takes many days. I have, therefore, constructed a simple little apparatus which enables us to dissolve in a few hours 50 grams of sodium out of contact with the air. The apparatus may be put together by means of materials
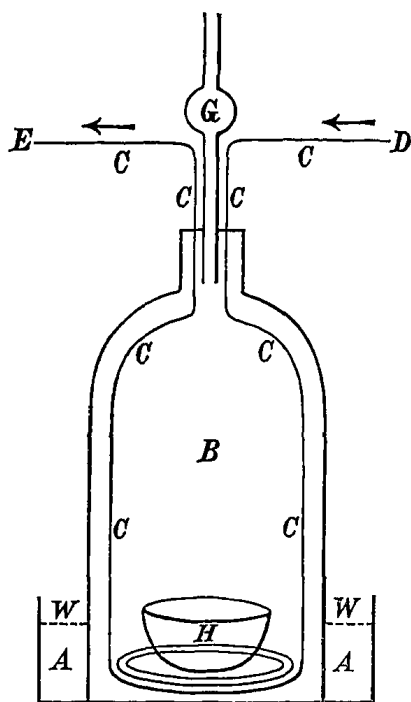
Fig. 2.

which are found in every laboratory [3]). (Fig. 2).

B is a jar (bottomless bottle) closed by a trebly-perforated cork. Through the hole in the centre passes a soda-lime tube G. Through both the other holes a thin copper tube enters (or leaves) the jar, which runs alongside the walls and is rolled circularly at the bottom (3 windings). Within the circle is placed a silver dish filled with metallic sodium cut up into small pieces. The jar with the dish is then placed into a crystallizing basin containing a little water so that the lower edge of the jar dips a few c.m. into the water. From a boiling-flask with a safety tube steam is passed through the copper tube the other end of which is connected with a water-airpump to remove condensed water.

Soon the jar gets filled with water vapour, hydrogen escapes through the soda-line tube and after a few hours, the sodium is completely liquefied and dissolved. Traces of carbon dioxide which may be present in the solution were removed by boiling the solution with a little $Ba(OH)_2$.

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[1]) Compare SPOHR, Zeitschrift für phys. Chemie 2, S. 194 (1888).

[2]) OSTWALD, Hand- und Hulfsbuch zur Ausführung physiko-chemischer Messungen, S. 281.

[3]) Compare ROSENFELD, Journ. für pract. Chemie N. F. 48 (1893) 599.

A. *Experiments with saccharose.*

4. Pure sugar candy was dissolved in water [1]), precipitated with alcohol (96 vol. proc.), washed with ether and then dried in vacuo [2]). The ethyl acetate used in these and subsequent experiments was thrice redistilled and afterwards a $N./_{10}$ solution was made of it.

I investigated the influence of $N./_5$, $N./_{10}$, $N./_{20}$, $N/_{40}$ and $N./_{80}$ sugar solutions on the saponification-velocity. These were prepared by means of $N/2^1/_2$ stock solution which was preserved with camphor to prevent fungoid growth. In these as in all subsequent experiments the solutions were always prepared quite independently of each other whilst for each solution the velocity constant was determined 5 (or more) times. The mean of the two series thus obtained will be taken as the end figure.

When calculating the constant (k), the concentration at the first observation was considered as the initial concentration, so that the influence of the first errors becomes trifling. The constant follows from the equation [3]):

$$k = \frac{C_1 - C_n}{C_1 \, C_n \, (t_n - t_1)}.$$

Before giving the results obtained on saponifying solutions to which saccharose had been added, I will first give some determinations made with purely aqueous solutions.

In all the following tables, t represents the time required for saponification in minutes, C_n the concentration of the lye (expressed in $N/_{40}$ NaOH); the third column contains the value $k\,C_1$.

TABLE III.

$N./_{40}$ ethyl acetate $+$ $N./_{40}$ NaOH

First series				Second series		
t	Cn	k C₁		t	Cn	k C₁
2	7.29	—·—		2	7 20	—·—
4	5.82	0.126		4	5.75	0 126
6	4 90	0.122	k = 6,85	6	4.81	0 124
8	4.18	0.124		9	3.90	0 121	k = 6,88
10	3 63	0.126		12	3.18	0 126
12	3.23	0.125		15	2 73	0.123
	average 0.125				average 0.124	

[1]) The water used in the experiments was distilled with particular care and freed from carbon dioxide by passing a current of air (free from CO_2) for 6 hours.

[2]) See E. O. VON LIPPMANN, die Chemie der Zuckerarten (1895), S. 59.

[3]) See VAN 'T HOFF-COHEN, Studien zur chemischen Dynamik (1896), S. 13; ARRHENIUS, Zeitschrift für phys. Chemie 1. 112 (1887).

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As the average of both series we, therefore, find $k = 6,86$ at $25°$.

By way of comparison we may put the figures of ARRHENIUS and SPOHR side by side:

ARRHENIUS[1]) found at $24°.7$ (N./$_{40}$ ethyl acetate $+$ N /$_{40}$ NaOH) 6.45 and 6.59 aver. 6.52

SPOHR [2]) found at $25°.0$ (N./$_{40}$ ethyl acetate $+$ N./$_4$, NaOH)   6.51

The found figure 6.86 at $25°.0$ agrees very well with ARRHENIUS' figure 6.52 at $24°.7$, if we consider that a difference in temperature of $0°.3$ already influences the velocity of the reaction to the extent of about 6 pCt. [3]).

T A B L E IV.

N./$_{40}$ ethyl acetate $+$ N/$_{40}$ Na OH $+$ N./$_5$ saccharose.

First serie.				Second series.			
t	Cn	kC$_1$		t	Cn	kC$_1$	
10	6.43	—		10	6.45	—	
15	5.51	0.0333		15	5.55	0.0324	
20	4.85	326	k = 2,03	20	4.90	316	k = 1,99
25	4.30	330		25	4.38	315	
35	3.58	318		35	3.53	330	
	average	0.0327			average	0.0321	

T A B L E V.

N./$_{40}$ ethyl acetate $+$ N./$_{40}$ Na OH $+$ N./$_{10}$ saccharose.

First series.				Second series.			
t	Cn	kC$_1$		t	Cn	kC$_1$	
5	6.91	—		5	6.81	—.	
10	5.45	0.0535		10	5.40	0.0525	
15	4.47	545	k = 3,14	15	4.45	530	k = 3,10
20	3.81	542		20	3.78	534	
25	3.30	547		25	3 33	522	
	average	0.0542			average	0.0528	

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[1]) ARRHENIUS, Zeitschrift für phys. Chemie J. 112 (1887).
[2]) SPOHR, ibid 2. 194 (1888).
[3]) Studien zur chemischen Dynamik S. 129.

TABLE VI.

N./$_{40}$ ethyl acetate + N./$_{40}$ NaOH + N./$_{20}$ saccharose.

First Series.				Second series.		
t	Cn	kC$_1$		t	Cn	kC$_1$
3	7.20	—		6	5.81	—
7	5.52	0.076		9	4.90	0.0619
9	4.91			13	4.02	635 k=4,32
13	4.08	764 k=4,26		17	3.43	630
17	3.48	763				
	average 0.0766				average 0.0628	

TABLE VII.

N./$_{40}$ ethyl acetate + N./$_{40}$ NaOH + N./$_{40}$ saccharose.

First series.				Second series.		
t	Cn	kC$_1$		t	Cn	kC$_1$
3	6.91	—		3	6.93	—
6	5.43	0.0908		6	5.48	0.0882
9	4.48	903 k=5,22		9	4.50	900 k=5,15
12	3.82	901		12	3.85	888
15	3.33	896		15	3.37	880
	average 0 0902				average 0.0887	

TABLE VIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ NaOH + N./$_{80}$ saccharose.

First series.				Second series.		
t	Cn	kC$_1$		t	Cn	kC$_1$
2	7.40	—		2	7 30	—
4	6.08	0.108 k=5,84		4	6.00	108 k=5,92
6	5.12	106		6	5 05	111
9	4.21	108		12	3.52	107
12	3.55	108				
	average 0.108				average 0.108	

B. *Experiments with invert-sugar.*

A N.2$^{1}/_{2}$ solution of invert-sugar was prepared by inverting a N.2$^{1}/_{2}$ solution of cane-sugar by means of a little acid at 60° C. A weighed quantity of saccharose was dissolved in a little water

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contained in a measuring flask, 20 cc. of $N./_{20}$ HNO_3 were added and the whole kept for 24 hours at 60°. The acid was then neutralized with lye and the liquid was diluted to the mark. I made sure about the completeness of the inversion by a polariscopic test.

Operating in this manner, the liquid contains but little $NaNO_3$; the presence of salts should be avoided as, according to SPOHR's experiments they exercise a great influence on the saponification-velocity of ethyl acetate by $NaOH$.

To be more sure, I inverted a second solution with a trace of oxalic acid: the figures which I obtained afterwards on saponification were identical with those given by the solution inverted with HNO_3. Both the solutions were, therefore, used in the further saponification experiments. I have studied closer an additional phenomenon which might have been of influence on the experiments where invert-sugar or d-glucose and d-fructose were used.

LOBRY DE BRUYN and ALBERDA VAN EKENSTEIN [1]) when studying the action of dilute alkalis on carbohydrates have found that d-glucose and d-fructose undergo decomposition even by dilute solutions of $NaOH$. A portion of the added $NaOH$ disappears as it gets neutralized by the organic acids which are formed. The decomposition was very plainly observable at 63° after a short time, when $N./_{50}$ $NaOH$ was used.

It, therefore, became necessary to ascertain in how far a similar secondary reaction may interfere here at 25° C. during the time my observations lasted.

For that purpose, I mixed in a flask: 50 cc. $N.2^{1}/_{2}$ invert-sugar, 25 cc. of water and 25 cc. of $N./_{10}$ $NaOH$ and kept the mixture in a thermostat at 25° C. From time to time, the alkalinity was determined by titrating 10 cc. with $N./_{40}$ acid.

After   80 minutes 0.2 cc. of $N./_{40}$ $NaOH$ were assumed.

„   250   „   0.3 cc. „ $N./_{40}$ $NaOH$ „   „

„   1320   „   1.1 cc. „ $N./_{40}$ $NaOH$ „   „

As in our case the experiments are finished within 150 minutes, the secondary action is not likely to influence the general result.

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[1]) Rec. des Trav. chim. des Pays-Bas. 14, 156, 203 (1895).

T A B L E IX.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_5$ invert-sugar.

t	C_n	kC_1	
30	7.52	—	
50	6.59	0.00705	
80	5.51	729	k = 0.379
110	4.79	712	
		average 0.00715	

T A B L E X.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{10}$ invert-sugar.

	First series				Second series.		
t	C_n	kC_1		t	C_n	kC_1	
15	7.78	—		15	7.78	—	
30	6.50	0.0131		30	6.50	0.0131	
50	5.35	129	k = 0.68	50	5.38	127	k = 0.66
73	4.35	131		75	4.39	128	
105	3.59	142		105	3 55	132	
		average 0,0133				average 0 0139	

T A B L E XI.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{20}$ invert-sugar.

	First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1	
10	7.44	—		10	7.40	—	
20	6.10	0.0219		20	6.05	0.0223	
30	5.20	215	k = 1.15	30	5.13	221	k = 1.18
45	4.28	211		45	4.21	216	
65	3.40	216		65	3.42	212	
	average 0.0215				average 0.0218		

T A B L E XII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{40}$ invert-sugar.

	First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1	
5	7.51	—		5	7.50	—	
10	6 32	0.0376		15	5.42	0.0383	
15	5.41	388	k = 2.01	20	4.78	379	k = 2.04
20	4.80	376		30	3.81	387	
30	3.90	370					
	average 0.0377					average 0.0383	

T A B L E XIII.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_{80}$ invert-sugar.

First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1
3	7.60	—		3	7.52	—
6	6.36	0.0650 $k = 3.39$		6	6.32	0.0633
9	5 48	644		9	5 42	645 $k = 3.36$
12	4.82	641		12	4.80	629
				17	4.01	625
	average 0.0644				average 0.0633	

C. *Experiments with d-glucose.*

For these experiments I made use of a preparation sold by MERCK as "Traubenzucker purissimum, wasserfrei'. By polarisation and a water determination, the article, however, appeared to contain about 6 pCt. of water.

A second preparation in beautiful crystals was kindly offered to me by Prof. RINDELL of Helsingfors. Both specimens gave the same figures in the saponification experiments and were used side by side.

T A B L E XIV.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_5$ d-glucose

First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1
15	7.32	—		15	7.32	—
30	6.07	0.0137		30	6.02	0.0143
45	5.13	142		45	5.14	142
60	4.41	146 $k = 0.79$		60	4.41	146 $k = 0.79$
80	3.72	148		80	3.72	148
110	3.05	147		110	3.05	147
	average 0.0144				average 0.0145	

T A B L E XV.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_{10}$ d-glucose.

First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1
10	7.04	—		10	7.04	—
20	5.68	0.0239		20	5.68	0.0239
30	4.70	248 $k = 1 36$		30	4.70	248
45	3.83	239		45	3.83	239 $k = 1.38$
60	3.20	240		60	3.18	242
75	2.80	233		75	2.70	247
	average 0.0240				average 0.0243	

T A B L E XVI.

N./$_{40}$ ethyl acetate + N/$_{40}$ NaOH + N./$_{20}$ d-glucose.

First series.				Second series.			
t	C$_n$	kC$_1$		t	C$_n$	kC$_1$	
5	7.39	—		5	7.32	—	
10	6.08	0.0430	k = 2,31	10	6.03	0.0427	
15	5.18	426		15	5 11	432	k = 2,32
20	4 50	428		20	4.48	422	
				25	3 98	419	
				30	3.55	424	
	average 0.0428				average 0.0425		

T A B L E XVII.

N./$_{40}$ ethyl acetate + N./$_{40}$ NaOH + N/$_{40}'$ d-glucose.

First series.				Second series.			
t	C$_n$	kC$_1$		t	C$_n$	kC$_1$	
4	6.96	—		4	6.89	—	
7	5 81	0.0659		7	5.80	0.0626	
10	5.02	644	k = 3,72	10	4.99	634	k = 3,66
13	4 40	646		13	4.40	628	
17	3.80	639		17	3.78	633	
	average 0.0647				average 0,0630		

T A B L E XVIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ NaOH + N./$_{80}$ d-glucose.

First series.				Second series.			
	C$_n$	kC$_1$		t	C$_n$	kC$_1$	
	7.02	—		3	6.92	—	
6	5 60	0.0845		6	5.52	0.0845	
9	4.61	871	k = 4 79	12	3.98	818	k = 4.79
12	4.50	839		15	3.47	828	
15	3.53	824		18	3.10	821	
18	3.13	828					
	average 0.0841				average 0.0828		

D. *Experiments with d-Fructose.*

Two specimens of this substance were in my possession. A small quantity of crystallised d-fructose from MERCK of Darmstadt and a larger quantity which Mr. ALBERDA VAN EKENSTEIN, director of the Government sugar laboratory of Amsterdam, had been kind enough to prepare and recrystallize for me. I will not neglect to express here my particular thanks for the great kindness with which Mr. ALBERDA has obliged me with this expensive preparation as this alone has rendered it possible for me to do the experiments with d-fructose on a somewhat larger scale.

Both preparations gave the same figures as will be noticed from the tables.

T A B L E XIX.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_5$ d-fructose.

First series (ALBERDA's preparation.)				Second series (MERCK's preparation.)		
t	C_n	kC_1		t	C_n	kC_1
30	6.73	—		30	6.60	—
45	5.82	0.0104		45	5.80	0.0092
60	5.21	097 $k = 0,59$		60	5.10	98 $k = 0,59$
80	4.52	098		80	4.40	100
111	3.73	099		110	3.63	102
145	3.07	104		145	3.03	102
	average	0.0100			average	0.00988

T A B L E XX.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N/_{10}$ d-fructose.

First series.				Second series.		
t	C_n	kC_1		t	C_n	kC_1
11	7.48	—		10	7.53	—
20	6.38	0.0191		20	6.38	0.0180
30	5.49	190 $k = 1,03$		33	5.44	192 $k = 1,01$
45	4.51	193		45	4.50	192
60	3.85	192		60	3.82	194
80	3.22	191		80	3.15	198
				100	2.76	192
	average	0.0192			average	0.0191

T A B L E XXI.

$N./_{40}$ ethyl acetate $+$ $N./_{40}$ NaOH $+$ $N./_{30}$ d-fructose.

First series.

t	C_n	kC_t	
5	7.68	—	
10	6.50	0.0363	
15	5 64	363	k = 1.89
20	4.92	373	

average 0.0363[1])

Second series.

t	C_n	kC_1	
5	7.60	—	
10	6.39	0 0378	
15	5.60	357	
20	4 90	367	k = 1.87
30	4.10	341	
40	3.42	349	
50	3.00	340	

average 0.0355

T A B L E XXII.

$N./_{40}$ ethyl acetate $+$ $N./_{40}$ NaOH $+$ $N./_{40}$ d-fructose.

First series.

	C_n	kC_1	
4	7.21	—	
8	5.90	0.0555	
12	5.00	552	
16	4.38	538	k = 3.02
20	3.87	539	
24	3.46	541	
28	3.13	544	

average 0.0545

Second series.

t	C_n'	kC_1	
4	7.20	—	
8	5.90	0.0550	
12	4.99	553	
16	4.33	552	k = 3.05
20	3.82	553	

average 0.0552

T A B L E XXIII.

$N./_{40}$ ethyl acetate $+$ $N./_{40}$ NaOH $+$ $N./_{80}$ d-fructose.

First series.

t	C_n	kC_1	
3	7.12	—	
9	4.87	0.0770	
12	4.22	763	k = 4,29
15	3.71	766	
20	3.11	758	
25	2.65	766	

average 0.0764

Second series.

t	C_n	kC_1	
3	7.12	—	
9	4.87	0.0770	
12	4.25	750	k = 4,24
15	3.71	766	
20	3.11	758	
25	2.71	739	

average 0.0756

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[1]) As I find in my notes that the figure 4.92 is decidedly too low I have disregarded the value 0.0373 when calculating the average.

E. *Experiments with Mannitol.*

The preparation obtained from KAHLBAUM was sharply dried and then used for making the solutions.

T A B L E XXIV.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_{5}$ mannitol.

First series.				Second series.			
t	C_n	kC_l		t	C_n	kC_l	
3	7.23	—		3	7.19	—	
9	4.68	0.0907	k = 5,13	6	5.61	0.0938	
12	3.92	938		9	4.60	938	k = 5,20
17	3.12	940		12	3.90	937	
				17	3.11	937	
	average 0.0928				average 0.0938		

T A B L E XXV.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_{10}$ mannitol.

First series.				Second series.			
t	C_n	kC_l		t	C_n	kC_l	
2	7.53	—		2	7.49	—	
4	6.19	0.109		4	6.17	0.107	
6	5.21	111	k = 5,83	6	5.20	110	k = 5,87
8	4.50	112		8	4.52	109	
11	3.80	109		11	3.70	113	
	average 0.110				average 0.110		

T A B L E XXVI.

$N./_{40}$ ethyl acetate $+ N./_{40}$ Na OH $+ N./_{20}$ mannitol.

First series.				Second series.			
t	C_n	kC_l		t	C_n	kC_l	
2	7.32	—		2	7.30	—	
4	6.01	0.109		4	5.97	0.111	
6	5.01	115	k = 6,17	6	4.99	115	k = 6,19
8	4.33	115		8	4.31	115	
10	3.80	115		10	3.81	111	
	average 0.113				average 0.113		

T A B L E   XXVII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N./$_{40}$ mannitol.

First series.				Second series.		
t	C_n	kC_t		t	C_n	kC_t
2	7.20	—		2	7.23	—
4	5.84	0.116		4	5.84	0.119
6	4.98	111 k = 6,33		6	4.98	112 k = 6,47
8	4.22	117		8	4.23	118
10	3.76	114		10	3.71	118
		average 0.114				average 0.117

T A B L E   XXVIII.

N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH + N/$_{80}$ mannitol.

| First series.				Second series.		
t	C_n	kC_t		t	C_n	kC_t
2	7.20	—		2	7.12	—
4	5.79	0.121		4	5.75	0.119
6	4.80	124 k = 6.88		6	4.80	120 k = 6.74
8	4.10	126		10	3.60	122
10	3.62	124				
		average 0.124				average 0.120

Summary of results obtained.

If we now take the mean of the figures obtained in the above tables as end-figure we get the following summary:

T A B L E   XXIX.

Saponification-velocity of N./$_{40}$ ethyl acetate + N./$_{40}$ Na OH at 25°.0 C.

In:	N./$_5$	N./$_{10}$	N./$_{20}$	N./$_{40}$	N./$_{80}$	
Water						6.86
Saccharose	2 01	3.12	4.29	5.19	5.88	
Invert-sugar	0.38	0.67	1.17	2.03	3.38	
d-Glucose	0.79	1.37	2.32	3.69	4.79	
d-Fructose	0.59	1.02	1.88	3.04	4.27	
Mannitol	5.17	5.85	6.18	6.40	6.81	

Fig. 3 gives a graphic representation of the results; the abscissae representent the concentrations and the ordinates, the velocities[1]).

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[1]) It must be observed that in fig. 1 which gives KULLGREN's results the abscissae represent percentages by volume, whilst here normalities have been used for calculation. In KULLGREN's case, this representation would have caused difficulties in connection with the great concentrations of several of the non-electrolytes used by him, in view of the scale to be used.

Fig. 3.
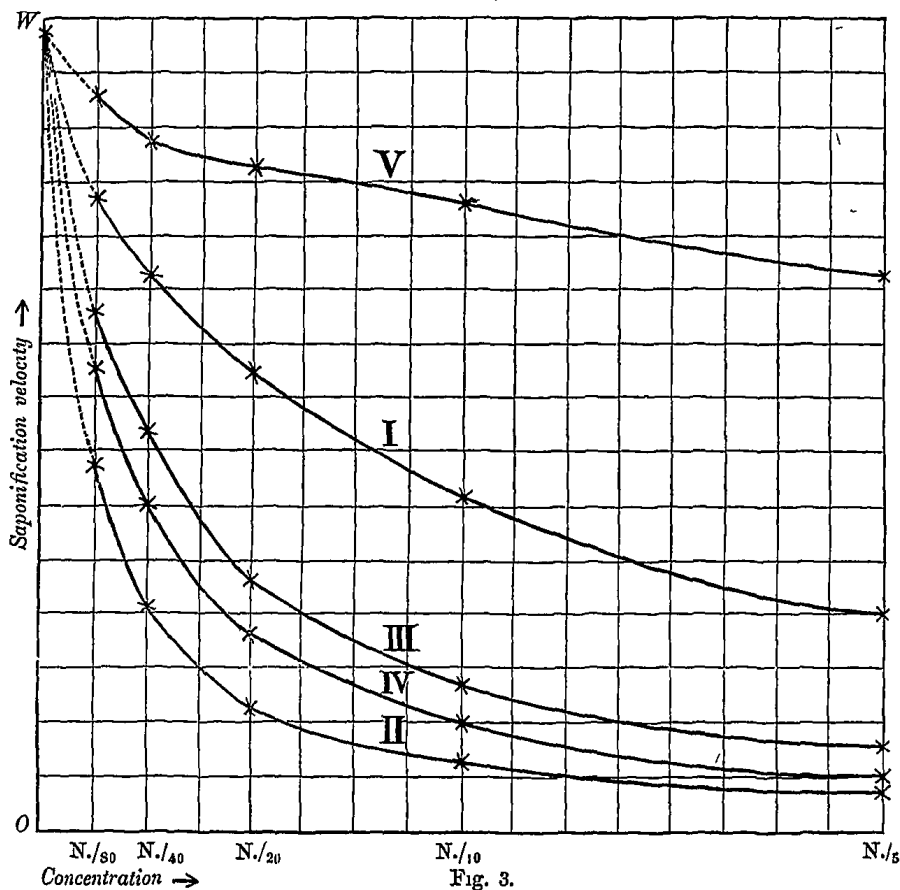
Curve   I relates to saccharose.
Curve   II   „   „ invert-sugar.
Curve III   „   „ d-glucose
Curve IV   „   „ d-fructose.
Curve   V   „   „ mannitol.

These curves must, of course, intersect in one point (W).

A glance at the figure shows at once that the saponification-velocity is considerably retarted by saccharose; still more so by invert-sugar. The result showing that the influence exercised by d-glucose and d-fructose is different, is of importance as d-fructose retards the saponification to a much larger extent than d-glucose.

Mannitol, however, exercises but little influence even in the strongest solutions and thus behaves like ethyl and methyl alcohol.

In connection with what has been said at the commencement about KULLGRENS researches, we see that saccharose, d-glucose, d-fructose and invert-sugar behave like acids. Invert-sugar is stronger than cane-sugar, d-fructose stronger than d-glucose. The remarkable behaviour of cane sugar solutions observed by RAÝMAN and ŠULC may be easily explained after these results.

In a following communication the results obtained will be sub-jected to calculation.

Stockholm, University physical Laboratory. Aug. 1899.