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The Acidic Dissociation Constants of Glucose, Mannitol and Sorbitol, as Measured by Means of the Hydrogen Electrode and the Glass Electrode at 0° and 18° C.

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The subject of the present investigation has been a determination of the acidic strength of glucose, mannitol and sorbitol at 0° C. Simultaneously I took the opportunity to determine also the dissociation constants at 18° C.

The acid qualities of the sugars were first observed by Kullgren[1]

$$\text{ROH} = \text{RO}^- + \text{H}^+ \qquad (1)$$

where ROH represents the sugar and RO^- the saccharate ion; in 1898 he was able to show that sucrose diminishes the velocity of the saponification of ethyl acetate, and that consequently sucrose is to a certain extent able to neutralize hydroxyl ions

$$\text{ROH} + \text{OH}^- = \text{RO}^- + \text{H}_2\text{O} \qquad (2)$$

It should be noted that Madsen[2] in 1901 determined the equilibrium constant of reaction (2) for glucose.

In 1912 Michaelis and Rona[3], determining the pH in solutions of sodium hydroxide and alcohols such as glycerol and mannitol, observed that these, too, will neutralize hydroxyl ions, though to a considerably lesser degree; *i. e.* these, too, are acids, though extremely weak ones. For the determination of the value of the dissociation constants were used not only the two methods mentioned above, but also determination of electrical conductivity and freezing point depression[4–6] of solutions of sodium hydroxide and alcohols. These methods may also supply information on the consumption of hydroxyl ions, since the conductivity of OH^- is greater than that of the alcoholate ion, and since two dissolved molecules by neutralization are converted to one as may be seen from equation (2).

The values of the acidic dissociation constants for glucose, mannitol and sorbitol reported in the literature are, however, diverging to no small extent.

THE PRINCIPLE OF THE CALCULATION

The equilibrium constant of reaction (1) is

$$\frac{a_{\mathrm{RO}^-} \cdot a_{\mathrm{H}^+}}{a_{\mathrm{ROH}}} = K_S$$

which, the activity coefficient of the non-electrolyte ROH being fixed at 1, may be converted to

$$\frac{a_{\mathrm{RO}^-} \cdot a_{\mathrm{H}^+}}{c_{\mathrm{ROH}}} = K''_S$$

Furthermore, in solutions of equal ionic strength the activity coefficient of the monovalent ion RO^- will be approximately equal to that of OH^-, *i. e.*

$$\frac{c_{\mathrm{RO}^-} \cdot f_{\mathrm{OH}^-} \cdot a_{\mathrm{H}^+}}{c_{\mathrm{ROH}}} = K'_S$$

Finally, according to (2):

$$c_{\mathrm{ROH}} = c_{\text{total alcohol}} - c_{\mathrm{RO}^-}$$

$$c_{\mathrm{RO}^-} = c_{\text{total sodium hydroxide}} - c_{\mathrm{OH}^-}$$

c_{OH^-} being calculated from $a_{\mathrm{H}^+} \,.\, c_{\mathrm{OH}^-} \cdot f_{\mathrm{OH}^-} = K_{\mathrm{H_2O}}$.

The problem has thus been reduced to that of determining a_{H^+} and f_{OH^-} in solutions of NaOH and ROH of known concentrations.

a_{H^+} was measured electrometrically, by means of the hydrogen electrode as well as by means of the glass electrode. To determine f_{OH^-}, *e. g.* of a solution of the ionic strength 0.05, pa_{H} was determined electrometrically in a pure 0.05 *M* solution of NaOH. As in such a solution c_{OH^-} is known, f_{OH^-} may be calculated directly from the equation

$$a_{\mathrm{H}^+} \cdot c_{\mathrm{OH}^-} \cdot f_{\mathrm{OH}^-} = K_{\mathrm{H_2O}}$$

$K_{\mathrm{H_2O}}$ having been fixed at $10^{-14{,}93}$ and $10^{-14{,}22}$, respectively.

EXPERIMENTAL

As already mentioned the determinations were carried out by means of a hydrogen electrode as well as a glass electrode. The hydrogen ion activity of the solutions was determined by means of the hydrogen electrode by measuring the electromotive force of the following cells:

$$\text{I. Hg} \mid \text{HgCl } 0.1\ M \text{ KCl} \mid 3.5\ M \text{ KCl} \mid \text{NaOH} \mid \text{H}_2\text{Pt}$$

$$\text{II. Hg} \mid \text{HgCl } 0.1\ M \text{ KCl} \mid 3.5\ M \text{ KCl} \mid \text{NaOH} + \text{ROH} \mid \text{H}_2\text{Pt}$$

The hydrogen electrodes were platinized platinum electrodes, saturated with hydrogen of atmospheric pressure from a hydrogen flask. The hydrogen was bubbled through pyrogallol-potassium hydroxide, through water, and finally through a test solution.

The potentials measured were converted to those at 760 mm hydrogen pressure by adding, the quantity

$$E_{\text{Bar.}} = \frac{RT}{2F \cdot \log e} \log \frac{760}{B-p}$$

B = barometric height, p = water vapour pressure, $p_{0^\circ\text{C}} = 4.6$ mm Hg, $p_{18^\circ\text{C}} = 15.5$ mm Hg.

The potentials thus converted to one atmosphere of hydrogen pressure are presented as E_{760}.

The electrode vessels were of the shape indicated in Fig. 1 and were placed in a mixture of crushed ice and water for the experiments carried out at 0°C, and in a water thermostat for those carried out at 18° C.

The reference electrodes used were 0.1 M calomel electrodes, made according to the directions of Gjaldbæk [8]. The electrodes were controlled frequently against a 3.5 M calomel electrode. During the period of experiments they showed a constant potential of 0.0832 * volt against this electrode at 18° C.

For the liquid junction was used 3.5 M potassium chloride. The experimental arrangement as well as the preparation of the interface between the liquids were as stated by Bjerrum and Unmack [7].

The determinations of the potentials were carried out by means of a compensation apparatus from Hartmann and Braun and a galvanometer (N. C. Jensen). The standard cell used was a normal Weston cell.

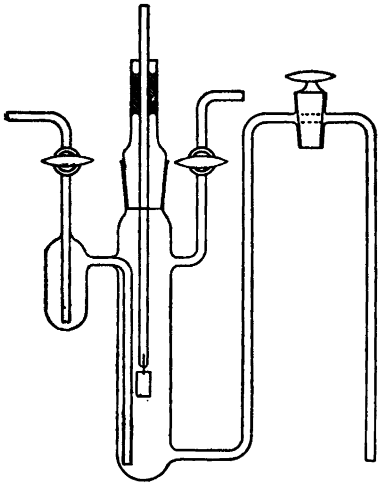

Fig. 1. The shape of electrode vessels.

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* J. K. Gjaldbæk indicates for 18°C: 0.08313.

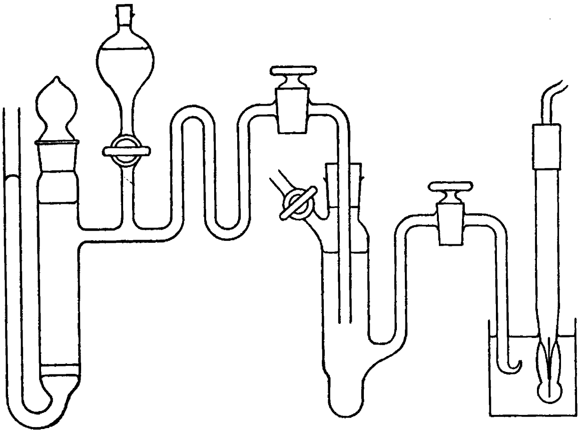

Fig. 2. The arrangement for the measurements by the glass electrode.

By means of the glass electrode the hydrogen ion activity was determined by measuring the electromotive force for the following cells:

I. Hg | HgCl 0.1 *M* KCl | 3.5 *M* KCl | NaOH | glass electrode Tp.E.

II. Hg | HgCl 0.1 *M* KCl | 3.5 *M* KCl | NaOH + ROH | glass electrode Tp.E

The arrangement for the experiments is indicated in Fig. 2, and was placed in an air thermostat at 0° and 18° C. The glass electrode was a Beckmann glass electrode [9] "Type E": a glass electrode made from a special kind of glass not giving the deflection of the potential in basic solution found by ordinary glass electrodes. The determinations of the potentials with the glass electrode were carried out by means of the potentiometer "Radiometer Tp. PHM3h".

The solutions used were prepared by the mixing of adequate amounts of carbonate-free 0.1 *M* NaOH and 0.5 *M* solutions of glucose, mannitol and sorbitol, respectively, and water. Carbon dioxide-free water was used in the preparation of all solutions.

The glucose used was "Dextropur", Corn Products Co. Ltd., Copenhagen. Upon analysis it was found to contain 91.2 % glucose and 8.8 % water, thus corresponding very closely $C_6H_{12}O_6$, H_2O.

The mannitol was *d*-mannitol Pfanstiehl Chemical Co., as well as mannitol The British Drug Houses Ltd. Both products were stated to be pure, and melted at 166—167° C. In the experiments they gave identical results. The melting point of mannitol is indicated to be 166° C.

The sorbitol was *d*-sorbitol Atlas Powder Co.*, stated to be of great purity. The melting point, indicated to be 97.7° C for the stable form, was determined to be 96—97° C.

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* The sorbitol used was supplied through the generosity of the Atlas Powder Company, Wilmington 99, Del., U. S. A.

RESULTS

pa_H may be calculated from the potential of a hydrogen electrode against a 0.1 M calomel electrode by means of the following equation

$$\frac{(E-E_o)\,F\log e}{RT} = -\log a_{H^+} = pa_H$$

E being E_{760} corrected for the diffusion potential. E_0 is the potential of a normal hydrogen electrode ($a_{H^+} = 1$ and $p_{H_2} = 760$ mm) against a 0.1 M calomel electrode. For the calculations were used the values of E_0 given by Bjerrum and Unmack [7]: 0.3351 volts at 0° C. and 0.3360 volts at 18° C. $\frac{RT}{F\log e} = 0.0542$ at 0° C. and 0.0577 at 18° C.

The results of the measurements in pure solutions of sodium hydroxide are presented in Tables 1 and 2.

In the first column are listed the concentrations of NaOH in moles per liter. E_{760} signifies the mean value of the experimental values of E_{760}. In column 3

Table 1. Hg | HgCl 0.1 mol. KCl | 3.5 mol. KCl | NaOH | H_2Pt at 0° C.

c_{NaOH}	$E_{760\,m}$		E_D	E	E_{Gm}		pa_H	f_{OH^-}
0.05	1.0676	8; 0.0005 1.0672; 1.0688	0.0017	1.0693	0.4233	4; 0.0009 0.4220; 0.4240	13.55	0.83
0.03	1.0563	7; 0.0003 1.0557; 1.0566	0.0012	1.0575	0.4154	2; 0.0009 0.4147; 0.4160	13.33	0.83
0.02	1.0483	10; 0.0009 1.0464; 1.0494	0.0008	1.0491	0.4061	2; 0.0008 0.4055; 0.4066	13.17	0.87
0.015	1.0428	5; 0.0005 1.0434; 1.0422	0.0005	1.0433	0.3996	2; 0.0009 0.3990; 0.4002	13.07	0.91
0.05 M glycine 0,05 M NaOH	0.9832	2; 0.0006 0.9828; 0.9836	0.0002	0.9834	0.3459	2; 0.0005 0.3454; 0.3464	11.96	
0,03 M borate 0.04 M NaOH	0.8901	2; 0.0002 0.8899; 0.8902	?	0.8901	0.2530	12; 0.0011 0.2518; 0.2553	10.24	

Table 2. $Hg \mid HgCl\ 0.1\ mol.\ KCl \mid 3.5\ mol.\ KCl \mid NaOH \mid H_2Pt$ *at 18° C.*

c_{NaOH}	$E_{760\ m}$		E_D	E	E_{Gm}		pa_H	f_{OH^-}
0.05	1.0750	10; 0.0004 1.0746; 1.0758	0.0016	1.0766	0.4306	4; 0.0005 0.4311; 0.4300	12.84	0.83
0.03	1.0635	7; 0.0003 1.0632; 1.0639	0.0011	1.0646	0.4192	5; 0.0008 0.4179; 0.4200	12.63	0.85
0.02	1.0541	16; 0.0005 1.0527; 1.0550	0.0008	1.0549	0.4099	8; 0.0006 0.4091; 0.4108	12.46	0.87
0.015	1.0473	7; 0.0002 1.0472; 1.0476	0.0005	1.0478	0.4037	4; 0.0001 0.4036; 0.4038	12.34	0.88
0.05 *M* glycine 0.05 *M* NaOH	0.9905	1; 0.9905;	0.0003	0.9908	0.3460	1; 0.3460;	11.35	
0.03 *M* borate 0.04 *M* NaOH	0.9133	8; 0.0004 0.9130; 0.9142	?	0.9133	0.2700	11; 0.0010 0.2688; 0.2713	10.01	
0.0153 +0.1 *M* KCl	0.9576 + 0.0875	Michaelis, Rona (17°–19° C.)	0.0005	1.0456		$pK_{H_2O} = 14.22$	12.30	0.78
0.0150 +0.1 *M* KCl	0.9554 + 0.0875		0.0005	1.0434			12.26	0.73
0.095	0.7545 + 0.3360	Urban, Shaffer 17° C.	0.0011	1.0916		$pK_{H_2O} = 14.26$	13.13	0.78
0.190	0.7700 + 0.3360		0.0023	1.1083			13.43	0.78

are indicated the number of determinations, the mean error of single determinations, and the highest and the lowest potential measured. E_D signifies the correction for the two diffusion potentials of the cell, calculated from Henderson's formula. The potential: sample solution | 3.5 *M* KCl was calculated in the manner of Bjerrum and Unmack [7] from the expression

$$\frac{RT}{F \log e}\left(-1.81 - \sum \frac{uc}{m} + \sum \frac{vc'}{m'}\right)\left(\frac{\log 302 - \log\ (\Sigma uc + \Sigma vc')}{302 - (\Sigma uc + \Sigma vc')}\right)$$

Table 3. $Hg \mid HgCl\ 0.1\ mol.KCl \mid 3.5\ mol.KCl \mid NaOH + glucose \mid H_2Pt$ *at* 0° *C.*

c_{NaOH}	$c_{glucose}$	$E_{760\ m}$		E_{Gm}		pa_H	pa_H G.	c_{OH^-}	c_{RO^-}	c_{ROH}	pK'-glucose	
0.05	0.2	1.0014	3; 0.0001 1.0013; 1.0014	0.3634	2; 0.0008 0.3628; 0.3639	12.29	12.34	0.0025	0.0475	0.1525	12.87	12.88
0.03	0.2	0.9872	2; 0.0001 0.9871; 0.9873	0.3505	2; 0.0007 0.3500; 0.3510	12.03	12.09	0.0013	0.0287	0.1713	12.88	
0.02	0.2	0.9769	4; 0.0002 0.9767; 0.9771	0.3389	2; 0.0017 0.3376; 0.3401	11.84	11.87	0.0009	0.0191	0.1809	12.88	
0.015	0.2	0.9703	3; 0.0006 0.9698; 0.9709	0.3319	2; 0.0013 0.3310; 0.3328	11.72	11.74	0.0005	0.0145	0.1855	12.87	
0.05	0.1	1.0257	6; 0.0007 1.0251; 1.0269	0.3853	2; 0.0003 0.3850; 0.3855	12.74	12.76	0.0076	0.0424	0.0576	12.95	12.93
0.03	0.1	1.0085	4; 0.0005 1.0080; 1.0089	0.3691	2; 0.0003 0.3689; 0.3693	12.42	12.45	0.0035	0.0265	0.0735	12.95	
0.02	0.1	0.9963	4; 0.0004 0.9960; 0.9968	0.3573	2; 0.0008 0.3567; 0.3578	12.20	12.22	0.0022	0.0178	0.0822	12.92	
0.015	0.1	0.9884	2; 0.0001 0.9883; 0.9885	0.3495	2; 0.0019 0.3481; 0.3508	12.05	12.07	0.0013	0.0137	0.0863	12.89	
0.05	0.05	1.0474	6; 0.0007 1.0463; 1.0481	0.4050	2; 0.0008 0.4044; 0.4055	13.14	13.14	0.0193	0.0307	0.0193	13.02	12.97
0.03	0.05	1.0274	2; 0.0002 1.0272; 1.0275	0.3873	2; 0.0010 0.3866; 0.3880	12.77	12.80	0.0081	0.0219	0.0281	12.96	
0.02	0.05	1.0151	5; 0.0003 1.0147; 1.0155	0.3749	2; 0.0010 0.3741; 0.3756	12.55	12.57	0.0048	0.0152	0.0348	12.97	
0.015	0.05	1.0056	2; 0.0001 1.0055; 1.0057	0.3660	2; 0.0016 0.3649; 0.3671	12.37	12.39	0.0029	0.0121	0.0379	12.91	

Mean 12.92

Table 4. $Hg \mid HgCl_2\ 0.1\ mol.KCl \mid 3.5\ mol.KCl \mid NaOH + glucose \mid H_2Pt$ *at 18° C.*

NaOH	$c_{glucose}$	$E_{760\,m}$		E_{Gm}		pa_H	pa_H G.	c_{OH^-}	c_{RO^-}	c_{ROH}	pK'-glucose	
).05	0.2	1.0154	5; 0.0008 1.0146; 1.0164	0.3739	2; 0.0001 0.3738; 0.3740	11.77	11.83	0.0040	0.0460	0.1540	12.38	12.40
).03	0.2	1.0013	4; 0.0004 1.0009; 1.0015	0.3586	2; 0.0001 0.3585; 0.3586	11.53	11.56	0.0021	0.0279	0.1721	12.40	
).02	0.2	0.9911	5; 0.0007 0.9900; 0.9918	0.3474	3; 0.0006 0.3470; 0.3479	11.35	11.36	0.0015	0.0185	0.1815	12.40	
).015	0.2	0.9839	3; 0.0002 0.9837; 0.9841	0.3404	2; 0.0000 0.3404	11.23	11.24	0.0011	0.0139	0.1861	12.41	
).05	0.1	1.0375	4; 0.0006 1.0368; 1.0381	0.3930	2; 0.0006 0.3925; 0.3934	12.16	12.17	0.0102	0.0398	0.0602	12.42	12.44
).03	0.1	1.0217	4; 0.0003 1.0214; 1.0220	0.3776	2; 0.0001 0.3775; 0.3777	11.88	11.90	0.0052	0.0248	0.0752	12.44	
).02	0.1	1.0103	3; 0.0001 1.0102; 1.0104	0.3656	2; 0.0001 0.3655; 0.3657	11.69	11.69	0.0034	0.0166	0.0834	12.45	
).015	0.1	1.0023	2; 0.0002 1.0021; 1.0024	0.3575	2; 0.0003 0.3573; 0.3578	11.55	11.54	0.0024	0.0126	0.0874	12.44	
).05	0.05	1.0560	5; 0.0007 1.0553; 1.0569	0.4107	2; 0.0001 0.4106; 0.4107	12.48	12.48	0.0217	0.0283	0.0217	12.45	12.46
).03	0.05	1.0392	6; 0.0007 1.0385; 1.0401	0.3933	3; 0.0005 0.3928; 0.3938	12.19	12.18	0.0107	0.0193	0.0307	12.47	
).02	0.05	1.0264	3; 0.0002 1.0262; 1.0266	0.3821	2; 0.0004 0.3818; 0.3823	11.97	11.98	0.0064	0.0136	0.0364	12.46	
).015	0.05	1.0180	2; 0.0002 1.0179; 1.0181	0.3731	2; 0.0001 0.3730; 0.3732	11.82	11.82	0.0045	0.0105	0.0395	12.46	

Mean 12.43

0.0153 +0.1 M KCl	1.0	0.8338 + 0.0875	Michaelis, Rona 17°–19° C.	10.14		0.0000	0.0153	0.9847	12.05	
0.0153 +0.1 M KCl	0.5	0.8627 + 0.0875		10.64		0.0003	0.0150	0.4850	12.26	
0.0153 +0.1 M KCl	0.2	0.8868 + 0.0875		11.06		0.0008	0.0145	0.1855	12.28	
0.0153 +0.1 M KCl	0.1	0.9090 + 0.0875		11.45		0.0021	0.0132	0.0868	12.38	
0.095	0.2	0.7019 + 0.3360	Urban, Shaffer 17° C.	12.21		0.0114	0.0836	0.1164	12.47	
0.190	0.2	0.7358 + 0.3360		12.80		0.0449	0.1451	0.0549	12.49	

where c is the number of gram-equivalents of a cation, m its valency, u its equivalent conductivity. c', m', and v, are the corresponding quantities for an anion. The equivalent conductivities needed were obtained from Landolt Börnstein: *Physikalisch Chemische Tabellen,* 1105, 5. Auflage (1923).

E_{Gm} is the mean value of the potential as measured by means of the glass electrode. Column 7 is analogous to column 3. pa_H in column 8 was calculated from the measurements with the hydrogen electrode. In the last column are listed the f_{OH^-} values. In the tables are further presented measurements with hydrogen electrode and glass electrode in a glycine buffer and a borate buffer. All of the pa_H-values listed in tables 1 and 2 were used for adjusting the glass electrode (Fig. 3)

In Tables 3—8 are given the results of the measurements in solutions of NaOH + ROH.

In columns 1 and 2 are listed the concentrations of NaOH and ROH, respectively, in the initial solutions. Columns 3—6 are analogous to the corresponding columns of the Tables 1 and 2.

The pa_H-values of column 7 originate from the hydrogen electrode measurements and have been calculated directly from E_{760}, a possible diffusion potential having been discarded. To ascertain the order of magnitude of the

Table 5. Hg | HgCl 0.1 mol.KCl | 3.5 mol.KCl | NaOH + mannitol | H_2Pt at 0° C.

c_{NaOH}	c_{mannit}	$E_{760\,m}$		E_{Gm}		pa_H	pa_H G.	c_{OH^-}	c_{RO^-}	c_{ROH}	pK'-mannitol
0.05	0.2	1.0523	8; 0.0006 1.0514; 1.0531	0.4091	3; 0.0008 0.4085; 0.4101	13.23	13.25	0.0239	0.0261	0.1739	14.13
0.02	0.2	1.0308	6; 0.0005 1.0302; 1.0316	0.3905	3; 0.0130 0.3880; 0.3905	12.84	12.86	0.0093	0.0107	0.1893	14.15
0.015	0.2	1.0238	6; 0.0006 1.0229; 1.0244	0.3829	3; 0.0011 0.3817; 0.3840	12.71	12.72	0.0064	0.0086	0.1914	14.10
0.05	0.1	1.0584	6; 0.0006 1.0579; 1.0595	0.4158	3; 0.0009 0.4149; 0.4166	13.35	13.35	0.0314	0.0186	0.0814	14.07
0.02	0.1	1.0385	8; 0.0009 1.0373; 1.0393	0.3966	3; 0.0009 0.3960; 0.3976	12.98	12.98	0.0129	0.0071	0.0929	14.16
0.015	0.1	1.0323	7; 0.0011 1.0304; 1.0340	0.3899	3; 0.0010 0.3888; 0.3907	12.87	12.86	0.0094	0.0056	0.0944	14.13
0.05	0.05	1.0626	6; 0.0005 1.0620; 1.0633	0.4197	3; 0.0010 0.4191; 0.4209	13.42	13.43	0.0370	0.0130	0.0370	13.96
0.02	0.05	1.0425	8; 0.0011 1.0410; 1.0437	0.4011	3; 0.0006 0.4005; 0.4017	13.05	13.06	0.0152	0.0048	0.0452	14.09
0.015	0.05	1.0365	7; 0.0007 1.0355; 1.0374	0.3948	3; 0.0012 0.3935; 0.3955	12.94	12.95	0.0110	0.0040	0.0460	14.04

Mean 14.09

error thus committed, the potentials were determined for some of the solutions with 3.5 *M* KCl, and subsequently with 1.75 *M* KCl, as liquid junction. Provided the diffusion potential against 1.75 *M* KCl is twice the one against 3.5 *M* KCl, we have, according to Bjerrum[10]:

$$E_{corr} = E_{3,5} - \varDelta E$$

$$\varDelta E = E_{1,75} - E_{3,5}$$

Table 6. Hg | HgCl 0.1 mol.KCl | 3.5 mol.KCl | NaOH + mannitol | H_2Pt *at 18° C.*

c_{NaOH}	c_{mannit}	$E_{760\,m}$		E_{Gm}		pa_H	pa_HG.	c_{OH^-}	c_{RO^-}	c_{ROH}	p*K*'-mannitol
0.05	0.2	1.0608	2; 0.0001 1.0607; 1.0609	0.4162	2; 0.0011 0.4154; 0.4169	12.56	12.58	0.0261	0.0239	0.1761	13.51
0.02	0.2	1.0388	2; 0.0000 1.0388; 1.0388	0.3948	2; 0.0011 0.3940; 0.3956	12.18	12.20	0.0105	0.0095	0.1905	13.54
0.015	0.2	1.0316	2; 0.0001 1.0315; 1.0316	0.3881	2; 0.0010 0.3874; 0.3888	12.06	12.09	0.0078	0.0072	0.1928	13.55
0.05	0.1	1.0673	2; 0.0000 1.0673; 1.0673	0.4224	2; 0.0014 0.4214; 0.4233	12.67	12.70	0.0337	0.0163	0.0837	13.46
0.02	0.1	1.0455	2; 0.0001 1.0454; 1.0455	0.4017	2; 0.0010 0.4010; 0.4024	12.30	12.31	0.0138	0.0062	0.0938	13.54
0.015	0.1	1.0386	2; 0.0002 1.0384; 1.0387	0.3949	2; 0.0013 0.3940; 0.3958	12.18	12.21	0.0103	0.0047	0.0953	13.55
0.05	0.05	1.0707	2; 0.0004 1.0704; 1.0709	0.4260	2; 0.0014 0.4250; 0.4270	12.73	12.76	0.0388	0.0112	0.0388	13.35
0.02	0.05	1.0496	2; 0.0001 1.0495; 1.0497	0.4057	2; 0.0011 0.4049; 0.4065	12.37	12.39	0.0162	0.0038	0.0462	13.52
0.015	0.05	1.0425	2; 0.0001 1.0424; 1.0426	0.3989	2; 0.0016 0.3978; 0.4000	12.24	12.28	0.0119	0.0031	0.0469	13.48

Mean 13.50

0.015 +0.1 *M* KCl	0.2	0.9400 + 0.0875	Michaelis, Rona 17°–19° C.			11.94		0.0071	0.0079	0.1921	13.46
0.015 +0.1 *M* KCl	0.1	0.9470 + 0.0875				12.06		0.0094	0.0056	0.0944	13.42
0.015 +0.1 *M* KCl	0.05	0.9505 + 0.0875				12.12		0.0108	0.0042	0.0458	13.29

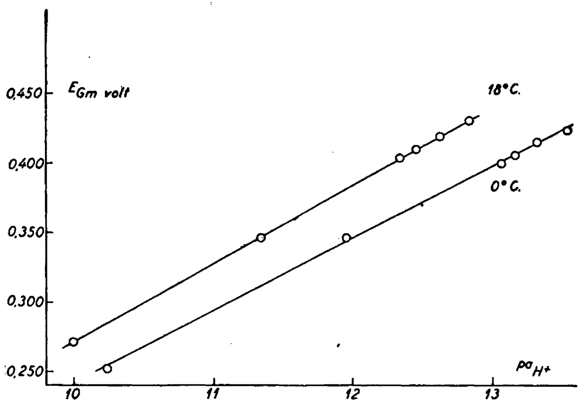

Fig. 3. Plot of the electromotive force as measured by the glass electrode in pure solutions of sodium hydroxide and buffer solutions against pa_H.

Table 7. Hg | HgCl 0.1 mol. KCl | 3.5 mol. KCl | NaOH + sorbitol | H_2Pt at 0° C.

c_{NaOH}	c_{sorbit}	$E_{760\,m}$		E_{Gm}		pa_H	pa_H G.	c_{OH^-}	c_{RO^-}	c_{ROH}	$pK'_{sorbitol}$
0.05	0.2	1.0539	4; 0.0005 1.0534; 1.0544	0.4126	2; 0.0006 0.4122; 0.4130	13.26	13.29	0.0255	0.0245	0.1755	14.19
0.02	0.2	1.0320	4; 0.0009 1.0311; 1.0328	0.3924	2; 0.0002 0.3922; 0.3925	12.86	12.90	0.0098	0.0102	0.1898	14.19
0.05	0.1	1.0597	4; 0.0005 1.0592; 1.0603	0.4190	2; 0.0001 0.4189; 0.4190	13.37	13.42	0.0329	0.0171	0.0829	14.14
0.02	0.1	1.0387	4; 0.0002 1.0384; 1.0389	0.3989	2; 0.0008 0.3983; 0.3994	12.98	13.03	0.0129	0.0071	0.0929	14.16
0.05	0.05	1.0629	4; 0.0005 1.0625; 1.0636	0.4224	2; 0.0004 0.4221; 0.4226	13.43	13.48	0.0378	0.0122	0.0378	14.01
0.02	0.05	1.0433	4; 0.0004 1.0428; 1.0439	0.4029	2; 0.0006 0.4025; 0.4033	13.07	13.10	0.0159	0.0041	0.0459	14.17

Mean 14.14

Table 8. $Hg \mid HgCl\ 0.1\ mol.\ KCl \mid 3.5\ mol.\ KCl \mid NaOH + sorbitol \mid H_2Pt$ *at 18° C.*

c_{NaOH}	c_{sorbit}	$E_{760\,m}$		E_{Gm}		pa_H	pa_H G.	c_{OH^-}	c_{RO^-}	c_{ROH}	$pK'_{sorbitol}$
0.05	0.2	1.0618	2; 0.0005 1.0614; 1.0621	0.4187	2; 0.0001 0.4186; 0.4188	12.58	12.63	0.0273	0.0227	0.1773	13.56
0.02	0.2	1.0408	2; 0.0001 1.0407; 1.0408	0.3968	2; 0.0006 0.3964; 0.3972	12.21	12.24	0.0113	0.0087	0.1913	13.62
0.05	0.1	1.0684	3; 0.0003 1.0683; 1.0685	0.4246	3; 0.0003 0.4244; 0.4248	12.69	12.73	0.0353	0.0147	0.0853	13.53
0.02	0.1	1.0470	2; 0.0001 1.0469; 1.0470	0.4029	2; 0.0008 0.4023; 0.4035	12.32	12.35	0.0145	0.0055	0.0945	13.62
0.05	0.05	1.0718	2; 0.0001 1.0717; 1.0718	0.4274	2; 0.0006 0.4270; 0.4278	12.75	12.79	0.0406	0.0094	0.0406	13.47
0.02	0.05	1.0504	2; 0.0002 1.0502; 1.0505	0.4067	2; 0.0006 0.4063; 0.4071	12.38	12.41	0.0167	0.0033	0.0467	13.59
										Mean	13.57
0.0153 +0.1 M KCl	0.2	0.9430 + 0.0875	Michaelis, Rona 17°–19° C.			12.03		0.0082	0.0071	0.1929	13.58
0.0153 +0.1 M KCl	0.1	0.9495 + 0.0875				12.15		0.0108	0.0045	0.0955	13.59

where $E_{1.75}$ and $E_{3.5}$ are equal to E_{760m} measured with 1.75 M KCl and, respectively, 3.5 M KCl as liquid junction. The correction obtained in this way appeared to be of the same order of magnitude as was the correction calculated from Henderson's formula into which was introduced the activity of free hydroxyl ions as calculated from the uncorrected potential E_{760m}.

Concerning the experiments with the glucose, the corrections were insignificant owing to the neutralization of the greater part of the sodium hydroxide.

As for the experiments with mannitol and sorbitol the corrections were somewhat greater, amounting to about 0.0005 volts, but could still be discarded provided the accuracy desired did not exceed 0.001 volts on each potential.

The pa_H-values of column 8 originate from the glass electrode measurements, and were read from Fig. 3 on the basis of the E_{Gm} values of column 5. In column 9 are given the concentrations of free hydroxyl ions, c_{OH^-}. In column 10 is listed c_{RO^-}, and in column 11 c_{ROH}. In the last column is listed pK', calculated from the mass action expression.

By comparison of the pa_H-values of the columns 7 and 8 it is found that they agree well in most cases; in a few cases they differ as much as 0.06 units of pa_H, but the deviations may be ascribed to experimental errors. From the data it may be estimated that the hydrogen of the hydrogen electrode has exhibited no reducing effect on either aldehyde or alcohol-groups.

The following mean values were calculated from the pK'-values:

	0° C.	18° C.
Glucose	12.92	12.43
Mannitol	14.09	13.50
Sorbitol	14.14	13.57

It should be noted, however, that a slight increase of the pK'-values occurs with increasing dilution of the solutions, particularly in the case of glucose.

COMPARISON WITH PREVIOUS RESULTS

In some of the earlier works on the determination on K_S on the basis of hydrogen electrode measurements of the hydrogen ion concentration in solutions of sodium hydroxide and, respectively, glucose, mannitol, and sorbitol, sufficient data are reported to allow for a recalculation of pK' according to the method employed by me. This applies to the works of Michaelis and Rona[3], and of Urban and Schaffer[11], both of which were carried out at about 18° C.

Michaelis and Rona in their summary state the pK of glucose, mannitol and sorbitol, as 12.18, 13.47 and 13.62, respectively. Urban and Schaffer indicate for glucose pK 12.34. The recalculated values, too, are listed in the tables 3 to 8 for comparison with the values found in the present investigation.

SUMMARY

The acidic dissociation constants for glucose, mannitol and sorbitol at 0° and 18° C. were determined by measuring the pa_H in solutions of these substances added NaOH. The measurements were carried out by means of the

hydrogen electrode as well as the glass electrode, the two kinds of electrodes giving practically identical results.

The following mean values were calculated for the pK'-values:

	0° C.	18° C.
Glucose	12.92	12.43
Mannitol	14.09	13.50
Sorbitol	14.14	13.57

It should be noted, however, that a slight increase of the pK'-values occurs with increasing dilution of the solutions, particularly in the case of glucose.

The experimental material, on the basis of which Michaelis and Rona, and Urban and Schaffer, calculated their pK-values at about 18° C for glucose, mannitol and sorbitol, was used by me for the calculation of pK' according to the method employed in the present work. The recalculated values and those of my own agree reasonably well.

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