LXV. INFLUENCE OF GLUCOSE, ALCOHOL AND CARBON DIOXIDE AT BAROMETRIC PRESSURE ON THE p_H VALUES OF PHOSPHATE AND BICARBONATE SOLUTIONS, DETERMINED BY MEANS OF HYDROQUINHYDRONE ELECTRODES.

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I. INTRODUCTION.

LIQUIDS in the state of fermentation are generally saturated with CO_2 . The determination of the p_H of such liquids, therefore, presents certain difficulties, though the liquids have a rather heavy buffer effect and well defined p_H values.

As a matter of fact, hydrogen electrodes cannot be used for the determination of p_H in liquids saturated with CO_2 at a pressure of one atmosphere, and if colorimetric methods are used, special care must be taken to keep the liquids saturated with CO_2 during the measurements.

On the other hand, it seemed possible that the quinhydrone electrode [Biilmann, 1921, 1923] would be suitable for the determination of p_H in liquids saturated with CO_2 , as this electrode acts as a hydrogen electrode with a very feeble hydrogen pressure. For our purpose it will be sufficient to remember that the quinhydrone acts as a hydrogen electrode, in which hydrogen and platinum black are substituted by quinhydrone and bright platinum. The quinhydrone dissolves in water and dissociates into quinol, $\text{C}_6\text{H}_4\text{O}_2\text{H}_2$, and quinone, $\text{C}_6\text{H}_4\text{O}_2$. Quinol acts as hydrogen by the reaction

which substitutes the reaction

in the hydrogen electrode.

The inverse reaction

also takes place. It corresponds to the reaction

produced in the hydrogen electrode by the catalytic action of the platinum black.

In dilute solutions the potential of the quinhydrone electrode is a linear function of the p_H value, similar to that of the potential of the hydrogen electrode. At higher concentrations the influence of the solutes on the activities of quinol and quinone, formed in equimolar concentrations by the dissociation of quinhydrone, may have a certain influence on the potential, because the reversible reaction in the cell is a transformation of *dissolved* quinol into *dissolved* quinone and *vice versa*, so that the potential does not in this case depend exclusively on p_H . This influence also interferes with our experiments, which deal with solutions containing up to 10 % glucose, but it is eliminated in the quino-quinhydrone electrode and the hydroquinhydrone electrode, described by Biilmann and Lund [1923]. For our purpose, we have only to mention that in the hydroquinhydrone electrode the liquid under examination is *saturated* both with quinol and with quinhydrone, and consequently, as shown in the quoted papers, the electrode reaction is here a transformation of *solid* quinol into *solid* quinhydrone. As the liquid is kept saturated with both these substances, their activities are constant, and this is why the relation between the potential and p_H is linear and independent of the concentration of other substances dissolved in the liquid.

Our experiments revealed a specific influence of glucose on the platinum plates of the electrodes, when the simple quinhydrone electrode was used. This interesting phenomenon is treated in Section VII. For the study of the influence of glucose and alcohol on the p_H values of buffer solutions and of the determination of p_H in solutions saturated with CO_2 , we used the hydroquinhydrone electrode.

First of all we established, by means of phosphate buffer solutions, that the electrodes are reproduced with well-defined and stable potentials. By these experiments we arrived at a comparison electrode of the same type and almost the same p_H as the other electrodes examined, which gives our determinations the advantage that the measured cells have either no liquid junction potentials at all or only very feeble liquid junction potentials, and that the determinations do not depend on determinations of potentials between the comparison (standard) electrodes and other electrodes, but directly on the thermodynamical equation

$$p_H = p_{H_1} - \frac{\pi}{0.0001983 \times T},$$

in which p_H is the p_H value of the examined liquid, p_{H_1} that of the standard electrode, and π indicates how much the potential of the examined electrode is higher than that of the standard electrode. Consequently, the higher the observed potential, the more acid the examined liquid, and the lower the p_H value.

II. STANDARD HYDROQUINHYDRONE ELECTRODE.

TEST OF METHOD.

The electrolyte of the standard electrode is a mixture of equal volumes of $1/15\ M\ Na_2HPO_4$ and $1/15\ M\ KH_2PO_4$. By direct measurement its p_H value was found to be 6.79.

For the electrodes were used vessels as described by Biilmann and Lund [1923] and shown in Fig. 1. 10 cc. phosphate solution shaken with a pulverised mixture of 1 g. quinol and 0.1 g. quinhydrone were put in the vessel, and the platinum spiral was placed in the narrow part of the vessel. The electrode was left in the thermostat at 18° and measured against another electrode of the same kind, next day against a newly prepared electrode and so on. The two electrodes were joined by means of a $3.5\ M\ KCl$ bridge. The results are shown in Table I.

Fig. 1.

Table I.

Days	$\Delta\pi$	Δp_H
0	-0.00002	+0.003
1	+0.00040	-0.007
2	-0.00024	+0.004
4	-0.00005	+0.001

It is seen from the table that the changes in potential correspond to changes Δp_H which during the first 4 days are quite negligible.

Further we examined the reproducibility and steadiness of similar electrodes containing 10 g. glucose in 100 cc. Table II shows the potentials of two such electrodes measured against the phosphate standard electrode at 18° .

Table II.

(+) $1/15\ M$ phosphate, p_H 6.79 + glucose, 10 g. in 100 cc. | $3.5\ M\ KCl$ | $1/15\ M$ phosphate, p_H 6.79 (-)

Minutes	Volt	
	I	II
0	+0.0077	+0.0079
10	+0.0074	+0.0078
30	—	+0.0078
35	+0.0074	—
65	—	+0.0078
70	+0.0075	—
1020	—	+0.0075
1080	+0.0073	—

The figures show that the maximum difference between the potentials of the two glucose-phosphate electrodes, namely between 0.0079 for electrode II at time 0 and 0.0073 for electrode I at time 1080, corresponds to less than 0.01 in the p_H value.

The reproducibility and stability of the hydroquinhydrone electrodes in a glucose-phosphate solution therefore proved to be very good.

III. INFLUENCE OF GLUCOSE ON p_H OF PHOSPHATE MIXTURE.

The figures in Table II show that glucose has an influence on the p_H value of the phosphate mixture. We therefore examined the influence of different concentrations of glucose on the phosphate mixture. The mixtures were prepared from stock solutions of primary and secondary phosphate in double concentrations ($2/15 M$), carbon dioxide-free water being used. Table III shows the results obtained with mixtures in which the concentration of glucose varied from 10 g. in 100 cc. to $1/32$ of this value. The measurements were carried out at 18° and 25° , and the potentials recorded in the table are corrected for liquid junction potentials by means of $3.5 M$ and $1.75 M$ KCl. The corrections were between 0.0005 and 0.0000 volt. (It is because of this correction that the value for 10 g. glucose in Table III is higher than the corresponding value in Table II, where it is given without correction.)

Table III.

(+) $1/15 M$ phosphate, p_H 6.79 + glucose KCl $1/15 M$ phosphate, p_H 6.79 (-)				
	18°		25°	
g. glucose in 100 cc.	π	Δp_H	π	Δp_H
10	+0.0081	-0.140	+0.0081	-0.137
5	+0.0042	-0.073	+0.0043	-0.071
2.5	+0.0024	-0.042	+0.0023	-0.039
1.25	+0.0017	-0.029	+0.0017	-0.029
0.625	+0.0012	-0.021	+0.0012	-0.020
0.3125	+0.0008	-0.014	+0.0009	-0.015

We first observe that the electrodes *with* glucose are positive to the electrodes *without* glucose, which means that *glucose makes the mixture more acid*. The influence Δp_H is not negligible. The acidity of glucose itself is so feeble that glucose does not act as an acid at p_H 6.79. The influence on the acidity may be explained as an influence on the activity of the water of the solutions.

Further we see that the influence on the potential is independent of the temperature. Concerning this phenomenon, it is to be remembered that as the hydration of the hydrions is expressed by the equation

we have

$$\frac{a'_{H^+}}{a^\circ_{H^+}} = \left(\frac{a^\circ_{H_2O}}{a'_{H_2O}} \right)^m = \left(\frac{P^\circ}{P'} \right)^m,$$

where a'_{H^+} , $a^\circ_{H^+}$, a'_{H_2O} and $a^\circ_{H_2O}$ represent the activities of hydrions and water in two solutions, P° and P' the water vapour pressures of these solutions.

According to the van't Hoff-Raoult law P°/P' is independent of the temperature. The curve I in Fig. 2 shows a linear relation between π and g. glucose over a large range of concentrations. This is due to the fact that for the concentrations of glucose examined the values of $\log P^\circ/P'$ calculated by means of the van't Hoff-Raoult law, are proportional to the concentrations:

g. glucose in 100 cc.	10	5	2.5	1.25	0.625	0.3125
$\log P^\circ/P' \times 10^5$	432	217	108	54	26	13

Finally we have compared the electrometric measurements with colorimetric determinations by means of bromothymol blue. We found:

g. glucose in 100 cc.	10	5	2.5	1.25	0
p_H electrometric	6.65	6.72	6.75	6.76	6.79
p_H colorimetric	6.71	6.75	6.78	6.79	6.79

The curve IV (Fig. 2) represents measurements made by Schreiner [1924] with saccharose in 0.005 *M* HCl and shows the influence of saccharose on the acidity of the solution, measured by the potential of a hydroquinhydrone electrode. The curve is drawn so that the abscissae correspond to equimolar concentrations of saccharose and glucose. This curve is almost parallel with our glucose curve.

Fig. 2.

IV. INFLUENCE OF ALCOHOL ON THE p_H OF PHOSPHATE MIXTURE.

Experiments with mixtures of phosphate solution and alcohol were made in the same way as with glucose. Regarding the amounts of alcohol formed by fermentation of glucose, alcohol was applied in concentration varying from about 5 g. in 100 cc. to 1/8 of this amount. The results are recorded in Table IV.

Table IV.

(-) 1/15 <i>M</i> phosphate, p_H 6.79 + alcohol KCl 1/15 <i>M</i> phosphate, p_H 6.79 (+)					
18°					
g. alcohol in 100 cc.	π	Δp_H	π	Δp_H	
5.1	-0.0044	0.076	-0.0045	0.076	
2.55	-0.0020	0.035	-0.0024	0.041	
1.275	-0.0015	0.026	-0.0015	0.025	
0.6375	-0.0006	0.010	-0.0007	0.012	

The values in Table IV are corrected for liquid junction potentials. The highest extrapolation was - 0.0003 volt. First we observe that the influence of alcohol is the opposite of the influence of glucose. The electrode containing alcohol is here the negative one, which means that it is less acid than the same

electrode without alcohol. So we have not to deal with an ordinary influence of a solute on the activity of the water, and the whole matter may be considered rather complicated. On the other hand, we observe here as with glucose an influence practically independent of the temperature. The influence Δp_H on p_H is of the same order as in the case of glucose, but has the inverse sign. In Fig. 2, curve II shows the relation between g. alcohol and π .

V. PHOSPHATE MIXTURES CONTAINING BOTH GLUCOSE AND ALCOHOL.

Finally we have examined mixtures containing both glucose and alcohol. The mixtures are composed according to the transformation of a glucose solution into alcohol by fermentation. The measurements are shown in Table V.

Table V.

1/15 M phosphate, p_H 6.79 + glucose and alcohol KCl 1/15 M phosphate, p_H 6.79				
Glucose g. in 100 cc.	Alcohol g. in 100 cc.	18°	25°	25° calculated
8.0	1.02	+0.0056	+0.0057	+0.0055
5.0	2.55	+0.0020	+0.0019	+0.0020
2.0	4.08	-0.0020	-0.0018	-0.0016

The influence of glucose and alcohol is almost additive. The calculated values of π agree with the observed within 0.2 millivolt. For the calculation are used values obtained by graphic interpolation on curve III in Fig. 2. It represents the sum of the curve for glucose from 0 to 10 g. in 100 cc. and the curve for alcohol from 5.1 to 0 g. in 100 cc. The squares round this calculated curve show the places of the observed values of π from Table V.

VI. LIQUIDS SATURATED WITH CARBON DIOXIDE.

The following experiments deal with solutions of disodium hydrogen phosphate and of sodium bicarbonate saturated with carbon dioxide. The arrangement is shown in Fig. 3. First of all the carbon dioxide passed through a wash-bottle containing a solution of sodium bicarbonate, then a wash-bottle *a* containing some of the examined liquid, whereupon it was led into the electrode

Fig. 3.

vessel *b*, which was constructed as a simple hydrogen-electrode vessel. *a* and *b* were placed in the same thermostat, so that the carbon dioxide was saturated with water vapour at such a pressure that no condensation or evaporation of water was caused by the passage of the gas through the electrode vessel. From *b* the carbon dioxide passes through the vessel *c*, which contains a little water and acts as an air-trap. If higher pressures than the actual barometric pressure were required, the carbon dioxide was led to the bottom of a high glass cylinder filled with water or salt solution.

The electrode vessel contains two electrodes: in the upper part of the liquid a platinum plate, in the lower part a platinum spiral. The latter is placed in the paste of the liquid and solid quinol and quinhydrone. For 25 cc. solution were used 3 g. of a mixture of 10 g. quinol and 1 g. quinhydrone. The liquids were saturated with CO_2 before addition of the quinol-quinhydrone mixture, and then the saturation with CO_2 was continued until the potentials of the platinum plate and the platinum spiral agreed within 0.0001 volt. Then the potential of the electrode was measured against the phosphate standard electrode (p_{H} 6.79). If the stop-cock *d* of the electrode vessel is closed during the measurement, the conductivity will be very feeble. Therefore the carbon dioxide supply is cut off, the clip at *e* is opened for a moment, the stop-cock *d* is opened and the reading is taken. When the electrode vessel was not shaken by these manipulations, the liquid showed a constant and reproducible potential, even if it were saturated with CO_2 at a pressure higher than the actual barometric pressure.

The CO_2 -pressures indicated in the following tables are the pressures of dry CO_2 . The potentials are corrected for liquid junction potentials in the ordinary way.

(a) *Influence of the CO_2 -pressure on p_{H} .*

First we examined the influence of variations in the CO_2 -pressure on the p_{H} -values of secondary phosphate solutions saturated with CO_2 . The experiments were carried out with 0.1 *M* Na_2HPO_4 , and the CO_2 -pressure varied within the limits of the usual variations of the barometric pressure.

Table VI.

18°. 0.1 <i>M</i> Na_2HPO_4		
CO_2 , mm. Hg	π	p_{H}
733	+0.0200	6.444
746	+0.0204	6.437
755	+0.0214	6.419
774	+0.0224	6.402
792	+0.0230	6.392

The examined electrode is positive to the standard electrode.

In Fig. 4, the pressure of carbon dioxide is plotted against p_{H} . The relation is seen to be almost linear. None of the observed values of p_{H} differs more than 0.005 from the values given by the curve. For 0.025 *M* and 0.200 *M* Na_2HPO_4 the change in π was of the same order.

Fig. 4.

Fig. 5.

(b) *Reproducibility of the electrodes.*

The reproducibility of the electrodes saturated with CO_2 is shown in Table VII. Different solutions of Na_2HPO_4 and of NaHCO_3 , containing 5 g. glucose in 100 cc., were measured against the standard electrode with p_{H} 6.79 at 25° .

Table VII.

Na_2HPO_4		mm. CO_2	π
0.2 M	...	733	+0.0112
		728	+0.0111
0.1 M	...	733	+0.0201
		728	+0.0192
NaHCO_3			
0.05 M	...	746	+0.0179
		743	+0.0178
0.025 M	...	743	+0.0335
"		738	+0.0335

The examined electrode is positive to the standard electrode.

It did not seem necessary to compare the different electrodes at exactly the same pressure, as the differences of the pressures will only correspond to one or two tenths of a millivolt. The experiments then show that electrodes saturated with CO_2 are reproduced very exactly.

(c) *Influence of glucose on the p_{H} of phosphate solutions saturated with CO_2 .*

In the same way we have examined a series of solutions of Na_2HPO_4 , in concentrations varying from 0.025 to 0.5 M, without glucose or with 5 g. glucose in 100 cc. The measurements were made at 18° and at 25° . Further, at 25° the p_{H} values of the solutions were determined with bromothymol blue (BTB) and with bromocresol purple (BCP) in order to obtain a comparison between the electrometric and colorimetric determinations of p_{H} in liquids saturated with CO_2 .

The colorimetric measurement was made in the following way. 10 cc. of the solution saturated with CO_2 were placed in a 20 cc. test-tube, to the bottom of which was attached a narrow tube as shown in Fig. 5. Five drops of the indicator solution were added, the test-tube was placed in the thermostat at the requisite temperature, and CO_2 was bubbled through the liquid in the

test-tube (as hydrogen in a hydrogen electrode). First of all the CO_2 was washed with NaHCO_3 solution and then with some of the liquid under examination, as in the electrometric experiments, in order to prevent evaporation of water from the tested solution. When the saturation with CO_2 was complete, the colorimetric determination was made in the ordinary way. For the comparison we used Sørensen's phosphate buffer mixtures; the exact p_{H} values of the mixtures were determined with the simple quinhydrone electrode.

The results are recorded in Tables VIII–X. In all the measurements the examined electrode was positive to the standard electrode.

Table VIII.

18°. Without glucose

Na_2HPO_4	mm. CO_2	π	p_{H}	735 mm. CO_2	
				π	p_{H}
0.025 <i>M</i>	... 737	+0.0431	6.04	+0.0430	6.05
0.050 <i>M</i>	... 737	+0.0306	6.26	+0.0305	6.26
0.100 <i>M</i>	... 749	+0.0204	6.44	+0.0196	6.45
0.200 <i>M</i>	... 749	+0.0122	6.58	+0.0114	6.59

The figures of the third and fourth columns give the directly measured potentials and the corresponding values of p_{H} . In order to compare the values, it is necessary to refer them to the same CO_2 -pressure. This is done by means of the linear relation between the potential, or the p_{H} , and the pressure shown in Table VI and Fig. 4. It may be supposed that the small corrections are almost the same for the different concentrations of phosphate, at least within the accuracy of the measurements. The values of π and p_{H} referred to an average pressure of 735 mm. are recorded in the last two columns of the tables.

Table IX.

25°. Without glucose

Na_2HPO_4	mm. CO_2	π	p_{H}	735 mm. CO_2	
				π	p_{H}
0.025 <i>M</i>	... 728	+0.0399	6.11	+0.0403	6.11
0.050 <i>M</i>	... 728	+0.0272	6.33	+0.0276	6.32
0.100 <i>M</i>	... 722	+0.0175	6.49	+0.0182	6.48
0.200 <i>M</i>	... 722	+0.0097	6.62	+0.0104	6.61
0.500 <i>M</i>	... 735	+0.0025	6.75	+0.0025	6.75

Table X.

25°. With 5 g. glucose in 100 cc.

Na_2HPO_4	mm. CO_2	π	p_{H}	735 mm. CO_2	
				π	p_{H}
0.025 <i>M</i>	... 739	+0.0410	6.10	+0.0408	6.10
0.050 <i>M</i>	... 739	+0.0292	6.30	+0.0290	6.30
0.100 <i>M</i>	... 728	+0.0192	6.47	+0.0196	6.46
0.200 <i>M</i>	... 733	+0.0112	6.60	+0.0113	6.60
0.500 <i>M</i>	... 738	+0.0040	6.72	+0.0038	6.73

The measurements show that in the case of phosphate solutions saturated with CO_2 , glucose has only a very feeble influence on the potential and the p_{H} .

The differences between the potentials of solutions without and with glucose do not seem to depend on the concentration of phosphate. The variations of p_H are nearly parallel in the three series of measurements:

Na_2HPO_4 , M ...	...	0.025	0.050	0.100	0.200	0.500
18°	p_H	6.05	6.26	6.45	6.59	—
25°	"	6.11	6.32	6.48	6.61	6.75
25°, with glucose	"	6.10	6.30	6.46	6.60	6.73

In the solution of secondary phosphate saturated with CO_2 , we have a mixture of secondary and primary phosphate and of bicarbonate, according to the equilibrium

Experiments to be described later show that the phosphate solution saturated with CO_2 does not change its p_H value so much by dilution as a pure bicarbonate solution saturated with CO_2 .

We have carried out a comparison between the electrometric and the colorimetric determination of p_H in solutions saturated with CO_2 . The method has already been described in the introduction to this section of our paper. For the comparison, the electrometric determinations are referred to the CO_2 -pressures at which the colorimetric determinations were made. The values are recorded in Table XI.

Table XI. *Comparison of electrometric and colorimetric determinations at 25°.*

Without glucose					With 5 g. glucose in 100 cc.				
Na ₂ HPO ₄ <i>M</i>	mm. CO ₂	<i>p_H</i>			mm. CO ₂	<i>p_H</i>			
		Electr.	Colorim.			Electr.	Colorim.		
			BTB	BCP			BTB	BCP	
0.025	744	6.09	6.00	6.00	744	6.09	6.00	6.00	
0.050	729	6.33	6.22	6.22	729	6.31	6.22	6.22	
0.100	729	6.48	6.44	6.45	729	6.47	6.44	6.45	
0.200	744	6.60	6.65	6.65	744	6.59	6.65	6.70	
0.500	738	6.75	6.96	—	738	6.72	6.96	—	

The measurements show that the colorimetric method gives lower p_H values than the electrometric one up to 6.4; above this the colorimetric method gives higher values than the electrometric one.

(d) *Influence of glucose on the p_H of bicarbonate solutions saturated with CO_2 .*

The experiments were made exactly as the experiments with phosphate. The bicarbonate solutions were prepared from solutions of sodium hydroxide by saturation with CO_2 . The measurements are recorded in Table XII. In the last two columns of these tables are shown the p_H values referred to a pressure of 740 mm. A comparison between the p_H values of the two series of solutions shows that the influence of glucose on the acidity is very feeble, and that the bicarbonate solutions with glucose seem *less acid* than the solutions without glucose.

Table XII.

25°. Without glucose

NaHCO ₃		mm. CO ₂	π	p_H	p_H at 740 mm.
0.025 <i>M</i>	...	738	+0.0335	6.22	6.22
0.050 <i>M</i>	...	725	+0.0190	6.47	6.46
0.100 <i>M</i>	...	756	+0.0036	6.73	6.74
0.200 <i>M</i>	...	756	-0.0109	6.97	6.98
0.500 <i>M</i>	...	755	-0.0284	7.27	7.28

With 5 g. glucose in 100 cc.

0.025 <i>M</i>	...	738	+0.0335	6.22	6.22
0.050 <i>M</i>	...	746	+0.0179	6.49	6.49
0.100 <i>M</i>	...	754	+0.0032	6.74	6.75
0.200 <i>M</i>	...	756	-0.0109	6.97	6.98
0.500 <i>M</i>	...	755	-0.0276	7.26	7.27

When we make a comparison of colorimetric and electrometric determinations of p_H (Table XIII), the last mentioned being referred to the pressures at which the colorimetric determinations are made, it shows almost the same cross point for the two methods as disodium hydrogen phosphate saturated with CO₂.

Table XIII.

Without glucose					With glucose				
NaHCO ₃ <i>M</i>	mm. CO ₂	Electr.	p_H Colorim.		mm. CO ₂	Electr.	p_H Colorim.		
			BTB	BCP			BTB	BCP	
0.025	738	6.22	6.00	6.06	738	6.22	6.00	6.06	
0.050	725	6.47	6.33	6.35	725	6.50	6.33	6.35	
0.100	756	6.73	6.71	6.79	754	6.74	6.71	6.79	
0.200	756	6.97	7.00	—	756	6.97	7.00	—	
0.500	755	7.27	7.40	7.40 *	755	7.26	7.40	7.40 *	

* Cresol red.

Finally we have tried to verify our determinations with bicarbonate in the following way.

The action of CO₂ on H₂O is

whence

$$a_{\text{HCO}_3^-} \times a_{\text{H}^+} = k \times a_{\text{CO}_2} \times a_{\text{H}_2\text{O}},$$

where a_{CO_2} , $a_{\text{H}_2\text{O}}$, $a_{\text{HCO}_3^-}$ and a_{H^+} represent the activities of CO₂, H₂O, HCO₃⁻ and H⁺. If the pressure P_{CO_2} of CO₂ is constant, and as $a_{\text{H}_2\text{O}}$ may be supposed to vary but very little in comparison with the other activities, we get

$$a_{\text{HCO}_3^-} \times a_{\text{H}^+} = k'.$$

For a_{H^+} we have

$$p_H = -\log a_{\text{H}^+} + 0.04.$$

As for $a_{\text{HCO}_3^-}$, it may be calculated from the concentrations of NaHCO₃ by means of the activity coefficient for HCO₃⁻. According to Warburg [1922] $\log f_a(\text{HCO}_3^-) = -0.46 \sqrt{c}$, where c is the stoichiometric concentration of bicarbonate.

The bicarbonate solutions are measured at different CO_2 -pressures. In Table XII p_{H} values referred to 740 mm. are also to be found. This reference is made by calculation. We have at two pressures P_{CO_2} and P'_{CO_2} (when $a_{\text{HCO}_3^-}$ is constant)

$$\frac{P_{\text{CO}_2}}{P'_{\text{CO}_2}} = \frac{a_{\text{H}^+}}{a'_{\text{H}^+}},$$

or

$$-\log a'_{\text{H}^+} = -\log a_{\text{H}^+} + \Delta,$$

where

$$\Delta = \log \frac{P_{\text{CO}_2}}{P'_{\text{CO}_2}}.$$

In Table XIV are shown the values of $\log (a_{\text{HCO}_3^-} \times a_{\text{H}^+})$, calculated from the experiments in Table XII.

Table XIV.

NaHCO_3	$a_{\text{HCO}_3^-}$	p_{H}	$-\log a_{\text{H}^+}$	$-\log (a_{\text{HCO}_3^-})$	$-\log (a_{\text{HCO}_3^-} \times a_{\text{H}^+})$
0.025 <i>M</i>	0.0179	6.22	6.26	1.747	8.00 ₇
0.050 <i>M</i>	0.0339	6.46	6.50	1.471	7.97 ₁
0.100 <i>M</i>	0.0612	6.74	6.78	1.214	7.99 ₄
0.200 <i>M</i>	0.1076	6.98	7.02	0.968	7.98 ₂
0.500 <i>M</i>	0.2157	7.28	7.32	0.667	7.98 ₇

We see that the constancy of $-\log (a_{\text{HCO}_3^-} \times a_{\text{H}^+})$ is very good. In the calculation we presume that the change of the activity of water may be considered constant. This may not be quite right. But the influence will be very feeble. If we suppose that the influence of the bicarbonate on the activity of the water is nearly the same as of an equimolar solution of potassium chloride, and if we introduce this influence in the calculation we arrive at the following values:

NaHCO_3	...	...	...	0.025	0.050	0.100	0.200	0.500 <i>M</i>
$-\log (a_{\text{HCO}_3^-} \times a_{\text{H}^+})$	...	...	...	8.00 ₇	7.97 ₁	7.99 ₄	7.99 ₁	7.99 ₄

Further in a single case we have found agreement between the calculation of the influence of the CO_2 -pressure on p_{H} and the influence observed experimentally. A 0.1 *M* solution of NaHCO_3 was measured with the hydroquinhydrone electrode in the ordinary way.

CO_2 -pressure	p_{H}	Δp_{H}	
		Found	Calculated
742 mm.	6.669	0.02 ₁	0.02 ₀₆
778 mm.	6.648		

VII. MEASUREMENTS WITH THE SIMPLE QUINHYDRONE ELECTRODE.

In the experiments described above we used the hydroquinhydrone electrode. The following were made with the simple quinhydrone electrode.

First we examined electrodes made with solutions of quinhydrone in 0.01 *N* HCl , 0.09 *N* KCl , with or without glucose. Accordingly we measured cells of the type

and we always found the electrodes with glucose to be more positive than the electrodes in the same electrolyte without glucose.

As, in the case of the simple quinhydrone electrode, there might perhaps be an influence not only on the activity of the hydrion, but also on the activity of the components of the quinhydrone, we examined also the solution with the hydroquinhydrone electrode, which only shows the influence on the activity of the hydrions. The results are recorded in Table XV.

Table XV.

25°. 0.01 *N* HCl, 0.09 *N* KCl

g. glucose in 100 cc.	Quinhydrone π		Hydroquin- hydrone π
10	0.0043	0.0043	0.0041
5	0.0023	0.0022	0.0018
2.5	0.0010	0.0012	0.0012
1.25	0.0004	0.0005	—

We see that the potentials agree well and that also in the simple quinhydrone electrode we have only an influence on the activity of the hydrion.

For 0.1 *N* HCl we found at 25°

10 g. glucose in 100 cc. 0.0042 volt

5 " 0.0021 "

values which agree completely with the figures in Table XV. The curve representing the relation between g. glucose and π is a straight line.

During our measurements we observed that hydroquinhydrone electrodes made with 0.01 *N* HCl, 0.09 *N* KCl are more stable in the presence of glucose than without glucose. While the hydroquinhydrone in this electrolyte was found to change 2 millivolts when kept from one day to the day after, it was quite stable in the presence of 5 % glucose. Two electrodes containing 5 g. glucose in 100 cc. of this electrolyte were kept at 18° and compared with each other and then the next two days with newly prepared electrodes of the same composition. All the examined electrodes agreed within 0.0001 volt.

When we tried to use the simple quinhydrone electrode in a phosphate mixture of p_H 6.79 containing glucose, we observed that the potentials between electrodes with and without glucose were not steady but decreased gradually. In Fig. 6 are shown curves representing our measurements with solutions containing 10 g. glucose (curves I and II), 5 g. (curve III) and 1 g. (curve IV) in 100 cc. The concentration of quinhydrone was 0.0025 *M*.

The shape of the curves shows that we have not to do with a reaction between glucose and quinhydrone, the change in π having a higher velocity in the more dilute glucose solutions than in the more concentrated ones. By and by we convinced ourselves that the phenomenon is a specific influence of glucose on the platinum. In order to test this explanation we made the following two experiments.

1. Two platinum electrodes were kept for 3 hours at 18° in a solution of 10 g. glucose in 100 cc. and used for the measurement of phosphate p_H 6.79 + 10 g. glucose in 100 cc. + quinhydrone against the same mixture without glucose. The measurements are shown in Fig. 7, curve I.

2. Two platinum electrodes were kept for 1 hour at 18° in a phosphate mixture p_H 6.79 containing quinhydrone ($0.0025 M$) and then used for the measurement of the mixture with glucose (10 g.) against the mixture without glucose. Curve II, Fig. 7, represents the measurements.

Fig. 6.

Fig. 7.

In all the electrodes the quinhydrone was $0.0025 M$.

The single potentials of two electrodes, in each individual case corresponding to the curves I and II, agreed well; the maximum discrepancies of the observations from the corresponding curve values were 0.8 millivolt, and most of the observations agreed within 0.2–0.4 millivolt with the curve values. But in shape the two curves are not at all like each other as will be seen from Fig. 7, in which is also drawn a curve III representing the average of the curves I and II in Fig. 6. The agreement of curves III and I in Fig. 7 is very remarkable. Evidently, in these cases, the fall of π must have the same origin. A similar influence of glucose was observed neither in the numerous measurements we have made with the hydroquinhydrone electrode and phosphate or bicarbonate solutions, nor in the solutions of hydrochloric acid. We point out that Warburg [1922, p. 247] observed that hydrogen electrodes in bicarbonate solutions containing saccharose did not establish the potential as rapidly as in the pure salt solutions. We shall not further discuss this rather surprising phenomenon.

SUMMARY.

1. The influence of glucose and of alcohol on the p_H of a phosphate mixture, p_H 6.79, is examined by means of the hydroquinhydrone electrode. Glucose makes the mixture more acid, and alcohol makes it less acid. The influences of glucose and alcohol are additive.

2. Solutions of secondary sodium phosphate and sodium bicarbonate are examined with the hydroquinhydrone electrode after saturation with carbon

dioxide at barometric and higher pressures. The influence of glucose on the p_H values of the liquids saturated with carbon dioxide was examined and found to be very feeble.

3. A hydroquinhydrone electrode in a phosphate mixture, p_H 6.79, was found to be very stable and suitable as a comparison electrode for measurements with hydroquinhydrone electrodes.

4. A hydroquinhydrone electrode in 0.01 *N* HCl, 0.09 *N* KCl is not very stable. It was found that it was stabilised by addition of glucose.

5. It was found that the simple quinhydrone electrode cannot be applied to phosphate solutions containing glucose. A specific action of the glucose on the platinum of the electrode was observed.

REFERENCES.

- Biilmann (1921). *Ann. Chem.* (9), **15**, 109.
— (1923). *Trans. Faraday Soc.* **19**, 676.
Biilmann and Lund (1923). *Ann. Chem.* (9), **16**, 321.
Schreiner (1924). *Z. anorg. Chem.* **135**, 333.
Warburg (1922). *Biochem. J.* **16**, 153.

ERRATUM

Biilmann and Katagiri, p. 451, last line but one

for $-0.46\sqrt{c}$ read $-0.46\sqrt[3]{c}$