180°, probably because increasing vibrational energy enables more and more of the molecules to open out to an extended structure in which the —COOC₂H₅ groups are independent of one another, the moment at 180° being identical with those of the very long chain dicarboxylic acid esters.

As three of these substances and also ethylene bromide, which has been studied previously, show moments in heptane solution different from those found in benzene solution, it is evident that the moment of a molecule containing two or more dipoles, the axes of which may alter their positions relative to one another, may be affected by both temperature and environment.

PRINCETON, NEW JERSEY

THE THEORY OF THE GLASS ELECTRODE[1]

BY MALCOLM DOLE

Introduction

The practical utility of the glass electrode for measuring the hydrogen-ion activity or P_H of biological fluids has been well demonstrated in the past.[2] More recently it has been used with excellent success for precision acid–base titrations in the presence of oxidizing and reducing potentials,[3] and for the determination of the P_H of such widely unrelated systems as growing tissue cultures,[4] ferric oxide sols[5] and tanning liquor extracts,[6] to mention a few.

The theoretical significance of the glass electrode is equally interesting and important particularly from the standpoint of phase boundary, interfacial, semi-permeable membrane and liquid junction potentials. There is no doubt that a complete understanding of the glass electrode would throw considerable light not only on the vexing and elusive problem of the boundary potentials mentioned above, but also on the nature and origin of

[1] The beginnings of the theoretical treatment of the glass electrode presented in this paper were conceived by the author while employed as an assistant at the Rockefeller Institute for Medical Research, New York. He wishes to express to Dr. W. J. V. Osterhout and Dr. D. A. MacInnes of that Institute his appreciation of their interest in this work.

[2] A complete bibliography is given in "The Determination of Hydrogen Ions," W. M. Clark, Williams and Wilkins Co., Baltimore, 1928.

[3] D. A. MacInnes and Malcolm Dole, *Ind. Eng. Chem., Anal. Ed.*, 1, 57 (1929).

[4] As carried out by the author in coöperation with Dr. Alexis Carrel. See D. A. MacInnes and Malcolm Dole, *J. Gen. Physiol.*, 12, 805 (1929).

[5] Fred Hazel and C. H. Sorum, THIS JOURNAL, 53, 49 (1931).

[6] D. H. Cameron and G. D. McLaughlin, *J. Am. Leather Chem. Assoc.*, 25, 325 (1930); D. H. Cameron, *ibid.*, 26, 7 (1931).

bioelectrical phenomena observed in living cells.[7] This paper represents an initial attempt of the author to place the theory of the glass electrode on a sound basis both from the experimental and thermodynamic standpoints.

Part A.   Experimental Technique

The glass electrodes were made in the manner first described by MacInnes and Dole; glass films colored red and green by interference fringes and 0.001 mm. thick were sealed onto the end of ordinary soft glass tubes about 3 mm. in internal diameter.   It is important that the glass film be of the proper composition, namely, 72% SiO_2, 22% Na_2O and 6% CaO as pointed out by MacInnes and Dole.[8] Inasmuch as glass electrodes made of other types of glass give inconstant potentials in alkaline solutions it is somewhat doubtful if the results of other investigators of the glass electrode can have any significance from a reversible, thermodynamic point of view. The glass electrodes were always made at least one day before use, their electrical resistances were measured, and they were then allowed to stand in 0.1 c HCl while not in use.   The silver–silver chloride electrode was used inside the glass electrode to lead the current to the electrometer. These electrodes were the reduced silver oxide type first made by Jones and Hartmann[9] and proved to be more convenient, more easily prepared and more permanent than the plated type described by MacInnes and Dole.[3]   The hydrogen electrodes were of the usual platinum black variety (the platinum black deposited freshly each day).   Commercial tank hydrogen was purified by passing over an active copper catalyst at 450°.[10] The hydrogen was led into the cell by a glass system free of rubber connections or stopcocks with one exception, the joint between the glass and the quartz combustion tube.   The hydrogen electrodes in general gave no trouble.   For a reference electrode the saturated calomel half cell was used.

The experimental procedure of directly comparing the glass and hydrogen electrodes in the same solution and at the same time with consequent elimination of any liquid junction potential or temperature fluctuation

[7] See W. J. V. Osterhout, *J. Gen. Physiol.*, 11, 83 (1927), for a classic example of an attempt to correlate glass electrode potentials with the potentials observed across the walls of the single cells *valonia* and *nitella*.

[8] D. A. MacInnes and Malcolm Dole, THIS JOURNAL, 52, 29 (1930).   Glass having this composition was kindly furnished by the Corning Glass Works, Corning, N. Y.

[9] Grinnell Jones and M. L. Hartmann, *ibid.*, 37, 752 (1915).

[10] See D. A. MacInnes and I. A. Cowperthwaite, THIS JOURNAL, 53, 558 (1931), for a recent description of this method of purification.   They heated their catalyst to a much higher temperature than 450°.   This was found unnecessary in the present research, perhaps due to the fact that the copper catalyst was alternately oxidized and reduced several times and at frequent intervals in order to obtain and maintain the surface in an active condition.

uncertainty was first invented by W. S. Hughes,[11] and later followed by MacInnes and Dole.[8] Essentially the same procedure was used in this research with a few minor modifications. Two glass electrodes and two hydrogen electrodes were compared at the same time in order to get comparable results. MacInnes and Dole used only one of each. The saturated potassium chloride salt bridge from the calomel electrode did not make contact with the solution under investigation inside the cell, but in the bore of a stopcock outside the cell. This prevented any saturated potassium chloride solution from contaminating the cell solution. The cell was so arranged that either acid or base solution could be run into the cell. The cell and the calomel reference electrode were kept at 25° by immersion in a thermostat filled with "Finol," a paraffin oil. Water was first used but had to be abandoned due to electrical troubles.

A new Leeds and Northrup Type K-2 potentiometer with a Type R reflecting galvanometer measured the potentials of the hydrogen electrode calomel electrode combination to 0.1 mv., while exactly the same system with a Compton quadrant electrometer[12] replacing the galvanometer as an indicating instrument measured the potentials of the glass electrode calomel electrode combination to 0.2 mv. A Bureau of Standards calibrated Weston cell was the source of standard potential.

The buffer solutions were made up of commercial c. p. salts without further purification, as this was considered unnecessary. The solutions were made up volume normal (moles per liter) with an uncertainty of about 1%. Inasmuch as the effect (the divergence of the glass electrode from the hydrogen electrode) was a secondary effect, the purity and concentration of the buffer solutions were of secondary importance. In setting up the cell, the solution inside the glass electrode was removed during manipulation as this made the glass membrane less fragile. The electrodes were inserted through glass tubes in the rubber stopper of the cell, and finally through rubber tubing tips where they were wired into place. The hydrogen electrodes were inserted in such a way that the platinum black surfaces of the two electrodes were at different heights in the cell, which enabled one to ascertain if the solution inside the cell was thoroughly mixed by the hydrogen gas bubbling through it. It was found necessary to heat the solutions used and then saturate them with hydrogen gas before assembling the cell; otherwise, small gas bubbles would rise in the cell and would collect on the surface of the glass membranes, thus hindering the solution from coming in contact with the glass electrode and thereby disturbing the potential of the electrode. The heating and sweeping out with hydrogen gas effectively eliminated all tiny bubbles from the cell. The larger hydrogen bubbles passing through the cell would not collect on the glass

[11] W. S. Hughes, THIS JOURNAL, **44**, 2860 (1922).

[12] Made by Charles R. Stryker, Kingston, N. J.

membranes.   The apparatus was so arranged that excess of solution could be removed from the cell at any time during the course of an experiment without admitting any oxygen.   After the cell had been filled with solution and the rubber stopper carrying the electrodes, acid and base reservoirs, and connections to the calomel electrode and hydrogen line had been inserted and wired firmly into place, the cell was immersed in the thermostat, and the hydrogen allowed to bubble through the solution in the cell and through the acid and base solutions for one or two hours before making any measurements.   A complete experiment required six to eight hours for its successful consummation.

Part B.   The Experimental Results

The behavior of the glass electrode appears to differ in three well-defined P_H regions.   Between a P_H of 1 and 9 it gives potentials which vary with the hydrogen-ion activity in exactly the same way as a hydrogen electrode.   Above P_H 8 or 9 and below P_H 0 or 1 it behaves anomalously.[13] Since all the theories invented to explain the glass electrode coincide in acid solutions, it is necessary to turn to alkaline solutions or strongly acid solutions to differentiate between them.   The potentials of the glass electrode of the proper construction have been shown to be constant[8] and reversible[14] in alkaline solutions and for that reason this study of the glass electrode was carried out in the region of high P_H.   In brief, the experiments consisted of a direct comparison between the glass and the hydrogen electrodes over a wide P_H range and in the presence of various neutral salts.

In the solution of any scientific problem it is important to vary only one variable at a time.   In comparing the glass electrode with the hydrogen electrode and in testing the effect of change of activity of the hydrogen ion, lithium ion, sodium ion, etc., on the observed potentials, it is advisable to maintain either the hydrogen-ion activity constant or the activity of the other positive ion present constant (in this research the lithium, sodium, potassium and barium ions).   Other investigators of the glass electrode have invariably varied both at once and thus made it practically impossible to interpret their data.   Since it is possible to change the hydrogen-ion activity many-fold merely on the addition of a few drops of base, while holding the sodium or lithium-ion activity practically constant, it was decided to use this technique in carrying out the experiments.   As a concrete example of the procedure, the data for one experiment are given in full

[13] The anomalous behavior of the glass electrode in alkaline solutions has been demonstrated by a number of investigators.   The field of very acid solutions, however, has not yet been touched upon except in a recent research of MacInnes and Belcher. (Private communication from Dr. D. A. MacInnes.)

[14] Malcolm Dole, unpublished results.   This fact may also be gleaned from the data in Table I of this paper.

in Table I. The results for this experiment were particularly concordant and were perhaps the best that were obtained.

The original buffer solution was 0.9 c^{15} in sodium acetate and 0.05 c in disodium phosphate and was made slightly acid by the addition of a few drops of concentrated acetic acid. The P_H of this solution was altered by adding 1.0 c sodium hydroxide, thereby maintaining the sodium-ion activity practically constant. In all of the experiments a base having the same positive ion concentration as the solution was used to increase the P_H. The actual measurements were of the following cells

(A) $^+$Hg | HgCl | sat. KCl || buffer soln. | H$_2$, Pt$^-$

(B) $^+$Hg | HgCl | sat. KCl || buffer soln. || glass || 0.1 c HCl | AgCl | Ag$^-$

By subtracting cell B from cell A it is possible to compute the potential of the cell C

(C) $^+$Ag | AgCl | 0.1 c HCl || glass || buffer soln. | H$_2$, Pt$^-$

Cell C should have at all P_H values of the buffer solution the same potential *as long as the glass electrode acts as a perfect hydrogen electrode.* This value depends only on the concentration of the hydrochloric acid inside the glass electrode, the asymmetric potential across the glass film and the pressure of the hydrogen gas. If the acid concentration is exactly 0.1 c, if the glass asymmetric potential is zero and if the hydrogen gas is at one atmosphere pressure and the whole cell at 25,° the net potential should be 0.3524 v. (the silver–silver chloride electrode being the positive electrode). Actually in the particular experiment described below the potential was 0.3380 v. for glass electrode C-73 and 0.3372 for glass electrode C-71. Finally, the potential of a fourth cell may be obtained by subtracting from the actual value of cell C its theoretical value. This gives the potential of the cell D, hydrogen electrode | buffer soln. | corrected glass electrode. Poten-

TABLE I

POTENTIALS OF ELECTRODES IN THE BUFFER SOLUTION 0.9 c NaAc, 0.05 c Na$_2$HPO$_4$ AT 25°

P_H	Cell A H$_2$-1	H$_2$-2	Cell B C-71	C-73	Cell C C-71 against H$_2$-2	C-73	Cell D C-71	C-73
6.485	0.6291	0.6293	0.2924	0.2916	0.3370	0.3378	0.0	0.0
7.493	.6886	.6890	.3516	.3510	.3374	.3380	.0	.0
9.341	.7979	.7983	.4567	.4563	.3416	.3420	.0045	.0040
9.779	.8240	.8242	.4793	.4787	.3449	.3455	.0078	.0075
10.435	.8628	.8630	.5103	.5095	.3527	.3535	.0156	.0155
11.047	.8991	.8992	.5344	.5338	.3648	.3654	.0277	.0274
11.836	.9459	.9459	.5582	.5574	.3877	.3885	.0506	.0505
6.088	.6065	.6065	.2692	.2684	.3371	.3381	.0	.0

[15] In accordance with a recommendation made by Professor Kilpatrick at the Indianapolis meeting of the American Chemical Society moles per liter of solution will be designated by the letter c.

tial of the cell D should be zero as long as the glass electrode functions as a hydrogen electrode, but as the glass electrode deviates from the hydrogen electrode, the potential of D will assume an appreciable magnitude. Potential D is defined and will be called in this paper the *error of the glass electrode*. The potentials of the cells A, B, C and D are given in Table I.

The potentials in the bottom line were obtained by adding acid to the solution at P_H 11.836 until P_H 6.088 was reached. The close agreement of the potentials of cell C with those first observed constitutes an excellent check upon the accuracy and reproducibility of the experiment. In Table I only the potentials of cell D are of any theoretical significance; hence in Tables II to XIV, which include all the results obtained, only these potentials are given.

In order to visualize the errors of the glass electrode (the potentials of cell D) and to see the agreement that was obtained, the data of several of the tables are plotted in Figs. 1 to 4. Errors of the glass electrode read directly off the curves of the figures are given in Table XV. The errors in the sodium and lithium solutions agreed very well among different electrodes, but the potassium and barium results were more discordant, different glass electrodes giving different results, and the same electrode giving different results on different days In these cases the rounded off values can have only an approximate significance.
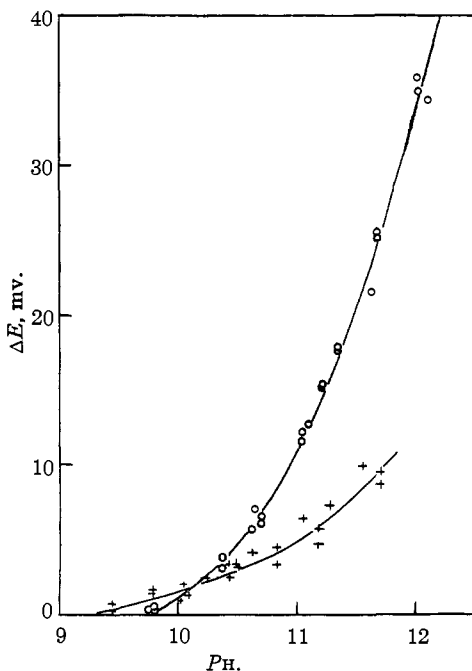

Fig. 1.—Errors of the glass electrode in LiAc solutions: top curve, 1.0 *c*, bottom curve, 0.1 *c*.

TABLE II

ERRORS OF THE GLASS ELECTRODE IN 0.1 *c* LiAc SOLUTION (IN MILLIVOLTS)

P_H	9.43	9.77	9.99	10.05	10.22	10.42	10.43	10.49
C-49	0.3	1.4	0.9	1.4	2.6	2.6	3.5	3.4
C-51	0.7	1.5		2.1		3.2		
P_H		10.62	10.83	11.06	11.18	11.27	11.57	11.72
C-49		4.3	3.5	6.6	4.8	7.3	10.0	8.7
C-51			4.6		5.8			9.5

TABLE III
ERRORS OF THE GLASS ELECTRODE IN 1.0 *c* LiAc (MILLIVOLTS)

P_H	9.77	9.80	10.37	10.62	10.64	10.70	11.05	11.11
C-49....		0.3	3.3			6.1	11.5	
C-50....		0.6	3.8			6.5	12.2	
C-55....	0.4			5.7	7.0			12.7
P_H		11.23		11.35	11.63	11.68	12.02	12.12
C-49		15.3				25.2	35.8	
C-50		15.2				25.2	34.8	
C-55					21.5			34.3

TABLE IV
ERRORS OF THE GLASS ELECTRODE IN 2 *c* LiAc (MILLIVOLTS)

P_H	8.90	9.99	10.73	11.39	11.45	11.84	12.70
C-50	2.3	12.6	26.9	48.2	50.0	66.6	107.1
C-55	1.6	11.6	23.0	40.9	43.3	58.7	96.5
Av.	1.9	12.1	25.0	44.5	46.6	62.7	101.8

TABLE V
ERRORS OF THE GLASS ELECTRODE IN 0.05 *c* Na_2HPO_4 (MILLIVOLTS)

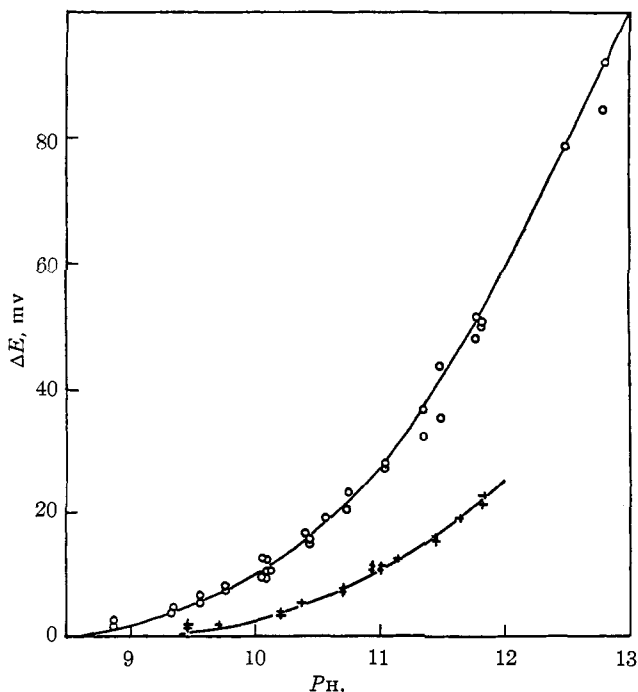| P_H	9.46	9.70	10.22	10.38	10.72	10.97	10.98	11.17	11.47	11.67	11.85
C-75	1.7	1.9	4.0	5.5	7.3	11.4	11.5	12.6	16.4	19.1	23.0
C-78	1.3		3.5		7.4	11.0	11.9		16.1		21.4

Fig. 2.—Errors of the glass electrode in sodium solutions: top curve, 1.0 Na⁺; bottom curve, 0.1 Na⁺.

TABLE VI

ERRORS OF THE GLASS ELECTRODE IN 1.0 c NaAc (MILLIVOLTS)

P_H	10.06	10.09	10.40	10.57	11.35	11.48	12.51	12.81
C-33	12.6	10.2			36.5	43.4		92.2
C-37	9.3	9.1	16.4	18.9	32.1	35.2	78.9	84.6

TABLE VII

ERRORS OF THE GLASS ELECTRODE IN 0.9 c NaCl, 0.05 c Na$_2$HPO$_4$ (MILLIVOLTS)

P_H	8.86	9.56	10.09	10.74	11.75
C-70	1.4	5.1	10.2	20.6	48.1
C-73	2.4	6.6	12.0	23.1	51.3

TABLE VIII

ERRORS OF THE GLASS ELECTRODE IN 0.99 c NaCl, 0.01 c NaAc (MILLIVOLTS)

P_H	10.32	11.11	11.82	12.55
C-70	17.9	35.3	57.6	88.9
C-73	18.8	36.7	59.5	90.8

TABLE IX

ERRORS OF THE GLASS ELECTRODE IN 3.5 c NaAc (MILLIVOLTS)

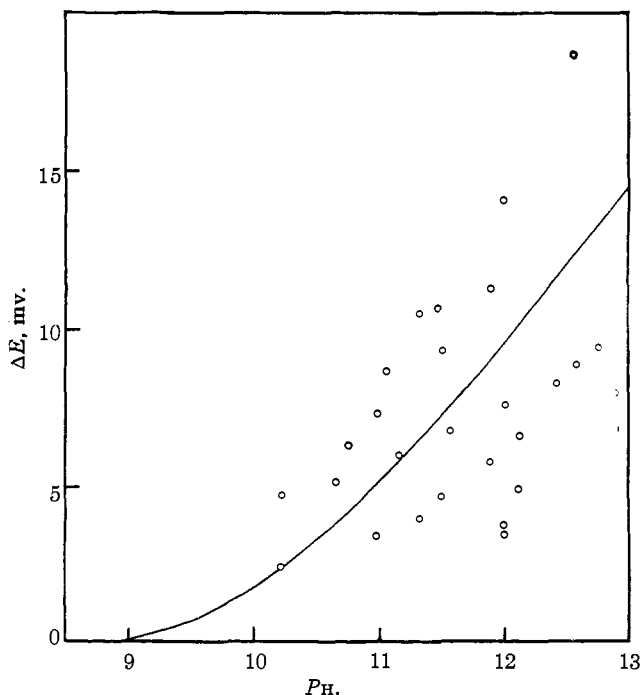| P_H	7.78	9.10	9.50	10.12	10.74	11.17	11.69	12.35
C-39	1.2	6.6	10.7	20.7	36.4	49.6	68.6	96.8
C-41	2.3	6.5	10.5	20.9	35.1	47.2	65.7	93.8
Av.	1.7	6.6	10.6	20.8	35.7	48.4	67.1	95.3

Fig. 3.—Errors of the glass electrode in 1.0 c KAc.

TABLE X
ERRORS OF THE GLASS ELECTRODE IN 0.1 c KAc (MILLIVOLTS)

PH	9.82	10.14	10.29	10.38	10.83	10.89	11.20	11.43	11.76	11.94
C-56	1.4	1.5		1.8		2.8		3.0		3.9
C-58			1.9		3.2		4.1		5.9	
C-59	4.8	9.9		8.4		10.5		13.6		16.5
C-60			3.6		4.8		5.0		6.5	

TABLE XI
ERRORS OF THE GLASS ELECTRODE IN 1.0 c KAc (MILLIVOLTS)

PH	10.23	10.67	10.75	10.98	11.07	11.15	11.33	11.48	11.51	11.56
C-58	2.4		6.3	3.4	8.7		4.0	10.7	4.7	
C-59	4.7		7.3				10.5		9.3	
C-63		5.1				6.0				6.8

PH	11.89	11.99	12.00	12.02	12.12	12.43	12.57	12.60	12.77	12.92
C-58	5.8	14.1					18.7	8.9		
C-59	11.3							15.0		
C-63				7.6		8.3			9.4	
C-86			3.5		4.9					6.8
C-89			3.8		6.6					8.0

TABLE XII
ERRORS OF THE GLASS ELECTRODE IN 5 c KAc (MILLIVOLTS)

PH	10.08	10.09	10.71	10.90	11.37	11.64
C-59		3.3	5.0		9.1	
C-64		3.2	5.7		9.9	
C-89	1.9			2.9		5.4

PH	11.97	12.22	12.48	12.99	13.05	13.50
C-59	13.8		19.0		28.2	
C-64	14.3		19.6		31.2	
C-89			8.1	14.6		20.1

TABLE XIII
ERRORS OF THE GLASS ELECTRODE IN 0.1 c BaAc₂ (MILLIVOLTS)

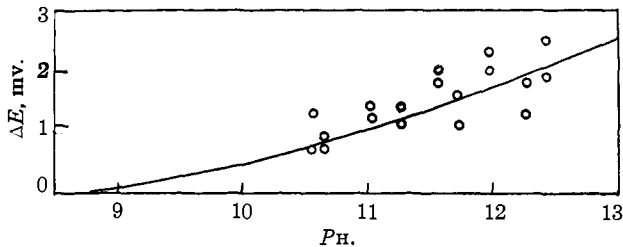| PH	9.90	10.51	10.51	11.02	11.07	11.51	11.54	12.12	12.25	12.56
C-63	3.1	3.8		3.9		3.9			3.8	
C-65	3.1	4.0		4.3		4.6			4.6	
C-82			0.2		0.2		0.5	1.1		1.9
C-84			0.2		0.5		1.1	1.9		3.7

Fig. 4.—Errors of the glass electrode in 0.5 c BaAc₂.

TABLE XIV

ERRORS OF THE GLASS ELECTRODE IN 0.5 c BaAc$_2$ (MILLIVOLTS)

p_H	10.55	10.65	11.03	11.27	11.57	11.72	12.00	12.25	12.43
C-63	0.7		1.2		1.8		2.3		2.5
C-68	1.3		1.4		2.0		2.0		1.9
C-82		0.7		1.1		1.1		1.3	
C-84		0.9		1.4		1.6		1.8	

TABLE XV

ROUNDED OFF VALUES FOR THE ERRORS OF THE GLASS ELECTRODE IN MILLIVOLTS

p_H	0.1 c LiAc	1.0 c LiAc	0.05 c Na$_2$HPO$_4$	1.0 c Na$^+$	0.1 c KAc	1.0 c KAc	5.0 c KAc	0.1 c BaAc$_2$	0.5 c BaAc$_2$
9.5	0.5	0	1.6	5.0	0.8				
10.0	1.5	1.2	3.4	9.8	1.5	1.8	1.8		0.5
10.5	3.0	4.6	6.0	17.2	2.5	3.3	2.6	1.8	0.8
11.0	5.3	10.6	10.8	27.2	3.6	5.2	6.0	2.2	1.1
11.5	8.6	20.2	16.4	42.0	4.9	7.2	8.6	2.6	1.4
12.0		33.3	24.3	59.2	6.2	9.6	11.8	3.1	1.7
12.5						12.0	15.2	3.7	2.1
13.0						14.6	19.0		

Part C.   Review of Previous Theories of the Glass Electrode

From the time that Cremer[16] in 1906 discovered the ability of a thin glass membrane to produce potentials which were a function of the hydrogen-ion concentration, there have been numerous attempts to give a sound theoretical interpretation of the glass electrode. These theories may be divided roughly into three groups: the phase boundary theories of Haber,[17] Gross and Halpern,[18] and Hughes;[19] the ion adsorption or "ion exchange" theories of Horovitz,[20] Schiller,[21] and Lengyel;[22] and finally the membrane or diffusion potential theories of Cremer,[16] Michaelis,[23] and Quittner.[24]

Haber's theory may be briefly outlined as follows. Consider the cell

$$H_2, Pt \mid H_2O \text{ (liquid)} \parallel H_2O \text{ (glass)} \mid H_2, Pt$$
$$A \qquad\qquad B \qquad\qquad C$$
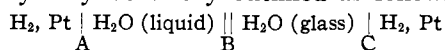
Let the hydrogen gas pressure be everywhere the same and constant; at equilibrium the total e. m. f. (E) of the cell must be zero

$$E_A + E_B + E_C = E = 0 \tag{1}$$

The potential at A is given by the equation

$$E_A = \frac{RT}{F} \ln a_H + \text{const.}_H \tag{2}$$

[16] M. Cremer, *Z. Biologie*, **47**, 562 (1906).

[17] F. Haber and Z. Klemensiewicz, *Z. physik. Chem.*, **67**, 385 (1909).

[18] P. Gross and O. Halpern, *ibid.*, **115**, 54 (1925); **118**, 255 (1925).

[19] W. S. Hughes, *J. Chem. Soc.*, 491 (1928).

[20] K. Horovitz, *Z. Physik*, **15**, 369 (1923); *Sitzb. Akad. Wiss. Wien*, Abt. IIa, **134**, 335 (1925); *Z. physik. Chem.*, **115**, 424 (1925).

[21] H. Schiller, *Ann. Physik*, [4] **74**, 105 (1924).

[22] Béla v. Lengyel, *Z. physik. Chem.*, Abt. A, **153**, 425 (1931).

[23] L. Michaelis, *Die Naturwiss.*, **14**, 33 (1926).

[24] F. Quittner, *Ann. Physik*, [4] **35**, 745 (1928).

To go any further than this in his derivation of an equation for the glass electrode, Haber had to make the necessary assumption that as the hydrogen-ion concentration in the aqueous phase is changed, *the hydrogen-ion concentration in the glass must remain constant.* If this assumption is granted, then

$$E_C = \text{const.}_C$$

and

$$E_A + E_C = -E_B = \frac{RT}{F} \ln a_H + \text{const.} \tag{3}$$

Haber knew nothing about the peculiar potentials of the glass electrode in alkaline solutions, and since his Equation 3 fails to predict these potentials, his theory must be rejected as inadequate.

Hughes has modified Haber's theory to the extent of saying that the hydrogen-ion concentration in the glass will remain constant by virtue of the glass being a buffer solution of silicic acid and sodium silicate. However, when a P_H of 9 is reached, the buffer action of the glass will break down since the dissociation constant of the first hydrogen of silicic acid is approximately 1×10^{-9}. With the failure of the glass to act as a buffer solution, the hydrogen-ion concentration will no longer remain constant and Equation 3 will no longer be valid. This theory fails to explain the marked differences between lithium, sodium, potassium and barium solutions. Furthermore, in some solutions the glass electrode potentials deviate from Equation 3 before a P_H 9 is reached (3.5 c NaAc, for example, see Table IX).

Gross and Halpern have also modified Haber's theory in an attempt to explain the potentials in alkaline solutions. They assume that water is dissolved in the glass and that the glass is dissolved in the water at equilibrium. When an electrolyte is added to the system, it also distributes itself between the two phases until equilibrium is reached. Equation 3 is obtained from the equilibrium relationships that may be set up on the assumption that the ionic concentration in the glass is due to hydrogen and hydroxyl ions exclusively. Any acid or base added to the aqueous solution must remain undissociated in the equilibrium layer between the glass and the water. To explain the alkaline solution potentials, it is necessary to postulate that the ionic concentration in the determinative glass layer is now due to added electrolyte. All these assumptions seem to be highly artificial, and as yet the authors have been unable to obtain any quantitative agreement between their theory and the actual potentials observed. A general objection to any phase boundary potential theory is that it is quite doubtful if in a rapid titration with the glass electrode, equilibrium in the sense of complete distribution between the two phases is ever set up.

Horovitz in his first paper[25] advanced a theory of ion adsorption on the

[25] K. Horovitz, *Z. Physik*, 15, 369 (1923).

glass surface.   In acid solutions, hydrogen ions will be adsorbed, giving
the glass electrode a certain solution tension of hydrogen ions (somewhat
analogous to the solution tension of metal electrodes), enabling the glass
electrode to function as a hydrogen electrode.   In neutral or basic solu-
tions the glass surface will adsorb other positive ions instead of the hydrogen
ion and then the glass electrode will function as either a sodium or potas-
sium or lithium reversible electrode, depending on the base used.   Horo-
vitz has found several glasses which he claims will act as a reversible
sodium electrode, but *he has never directly compared these glass electrodes
with a sodium electrode*, so that it is still open to question whether the glass
electrode will give exactly the same change of potential as a sodium elec-
trode as the sodium ion *activity* is changed.   Horovitz's adsorption theory
was strongly criticized by Hughes and by Gross and Halpern, who pointed
out that the work of Freundlich and Rona showed[26] that the ionic adsorp-
tion on the glass electrode surface (as determined by the electrokinetic
potential) bore no relationship to the thermodynamic potentials of the
glass electrode.   Accordingly, Horovitz modified his theory[27] to the ex-
tent of saying that what he meant by adsorption was really "ion exchange."
However, in a brief note recently published[28] he has found that this idea
also is inadequate and must be modified to consider ionic mobilities.
Furthermore, according to the abstract of his paper presented at the
Indianapolis meeting of the American Chemical Society, this last modifica-
tion must also be modified once again to take into account "the heat of
mixture on the surface."   Just what heat of mixture on the surface has to
do with glass electrode potentials is difficult to see; we must wait, how-
ever, for the detailed publication of these ideas before considering them
at any greater length here.

   Schiller and very recently Lengyel have accepted Horovitz's adsorption
theory.   Lengyel even goes so far as to consider the quartz membranes
(Lengyel worked with quartz instead of glass but obtained potentials en-
tirely analogous to the glass electrode potentials) as condensers whose capa-
cities are enough greater than the capacity of the binant electrometer
used so that the potential of the quartz membrane condenser may be meas-
ured without the condenser being appreciably discharged.   In the case of
glass membranes it has recently been shown[29] that considerable direct
currents may be carried across the glass membranes without changing
the potential.   Hence it is somewhat dubious to consider the potentials of
these membranes as being the potentials of condensers.   The experimental
work of Horovitz and his co-workers and of Lengyel is important, however,

[26] H. Freundlich and P. Rona, *Sitzb. Preuss. Akad. Wiss.*, **20**, 397 (1920).

[27] K. Horovitz, *Z. physik. Chem.*, **115**, 424 (1925).

[28] K. Lark-Horovitz, *Nature*, **127**, 440 (1931).

[29] Malcolm Dole, THIS JOURNAL, **53**, 620 (1931).

in showing that quartz and paraffin membranes will also act as hydrogen electrodes and that the deviations in alkaline solutions are quite similar to the deviations of the glass membrane potentials in alkaline solutions.

We come finally to the consideration of semi-permeable or diffusion potentials. Cremer has considered the glass membranes as being permeable only to the hydrogen ions.[30] On this basis it is possible to derive the equation for the hydrogen electrode from Donnan's semi-permeable membrane equations[31] or from any liquid junction potential equation by setting the negative ion mobility equal to zero. Michaelis[23] has extended this idea by assuming that in alkaline solutions the sodium or other positive ions can also diffuse through the glass, thereby causing the deviations of the glass electrode from the hydrogen electrode at high P_H. Michaelis does not believe in complete equilibrium but that a diffusion potential is set up across the membrane which can be calculated by use of the liquid junction equations. It is possible to test this theory by performing two parallel experiments, one with the same sodium ion concentration in the solutions on both sides of the glass membrane, and the other with no sodium ions on one side of the glass wall. If the glass acts solely as a semi-permeable membrane, one might expect a difference of potential in these two cases. Actually, no difference at all could be detected, the two electrodes agreeing quite as well as could be expected, as the data in Table XVI show.

TABLE XVI

TEST OF SEMI-PERMEABLE MEMBRANE THEORY OF THE GLASS ELECTRODE

Cell	Corrected potential, volt
0.1 c HCl ‖ glass electrode ‖ 0.1 c NaOH	0.6098
.1 c HCl ‖ .1 c NaCl ‖ glass electrode ‖ .1 c NaOH	.6090

Quittner[24] carried out electrolysis experiments on glass electrodes and found that hydrogen ions migrated through the glass in acid solutions and sodium ions in basic solutions. He concluded that the electromotive behavior of the glass depended upon the ion which migrated. He did not develop this idea any further. J. Meyer[32] and MacInnes and Burgess[33] have also carried out electrolysis experiments on glass and have confirmed Quittner's results in so far as the migration of the hydrogen ion is concerned (see also Newman[34]).

[30] See G. Müller, "Inaugural Dissertation," Berlin, 1923; also Cremer's *Beiträge zur Physiologie*, **2**, 229 (1924).

[31] F. G. Donnan, *Chem. Rev.*, **1**, 73 (1924).

[32] J. Meyer, *Beiträge zur Physiologie*, **4**, 129 (1930).

[33] D. A. MacInnes and L. Burgess, presented before the fall meeting of the American Chemical Society, 1930. I have not yet noted the publication of this work.

[34] F. H. Newman, "Electrolytic Conduction," John Wiley and Sons, Inc., New York, 1931, p. 200.

Part D.   A New Theoretical Treatment of the Glass Electrode

Since the conduction of the glass is electrolytic and not electronic, on the passage of a current it is necessary that ions pass from the region of one activity to that of another.   In case this transfer is carried out isothermally and reversibly, the potential of the junction between the glass and the aqueous solution is given by the fundamental differential thermodynamic equation (which has, apparently, never been applied to the glass electrode before)[35]

$$dE = -t_H \frac{RT}{F} \, d \ln a_H - t_{Na} \frac{RT}{F} \, d \ln a_{Na} - \ldots$$
$$+ t_{OH} \frac{RT}{F} \, d \ln a_{OH} + t_{Cl} \frac{RT}{F} \, d \ln a_{Cl} + \ldots \quad (4)$$

In this equation t is the transference number of an ion across the boundary, E, R, T, F have their usual significance, ln represents the natural logarithm and a is the ionic activity.   If the transference numbers of ions other than the hydrogen ion are very small, t_H becomes unity and we have the equation of a perfect hydrogen electrode (the sign is negative but as we measure the glass electrode taking the more concentrated side as negative this difference cancels out).   When this is true, Equation 4 is indistinguishable from the equations of Haber, Horovitz, Michaelis and Cremer.   It is important to note, however, that the electrolysis experiments on glass which were supposed to prove that only hydrogen ions migrate through the glass do not exclude the possibility of hydroxyl ions also migrating through the glass.   By analyzing the products of electrolysis, it is impossible to tell whether hydrogen ions have entered the glass or hydroxyl ions have entered the solution.   In both cases the solutions will become basic to the extent of one equivalent per faraday of electricity.   It is also impossible to distinguish the two cases thermodynamically.   Starting with the equation

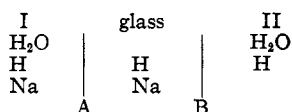$$dE = -t_H \frac{RT}{F} \, d \ln a_H + t_{OH} \frac{RT}{F} \, d \ln a_{OH} \quad (5)$$

it is possible to derive either

$$dE = \frac{RT}{F} \, d \ln a_{OH} \quad \text{or} \quad dE = -\frac{RT}{F} \, d \ln a_H \quad (6)$$

remembering that $t_H + t_{OH} = 1$.   Thus it is impossible to prove either experimentally or thermodynamically that the glass electrode is a hydrogen ion electrode or an hydroxyl ion electrode or a mixture of both.   As regards the migration of additional ions across the glass–water boundary, the integration of Equation 4 in the general case becomes important.   Unfortunately, it is impossible to do this rigorously since the transference numbers are some unknown function of the concentration.   Accordingly, we must make some simplifying assumptions and use less exact methods.   The

[35] This equation neglects transfer of solvent.   In the case of glass against an aqueous solution, the transfer of solvent is somewhat to be doubted.

first assumption to be made is that positive ions only are of importance in determining the potentials in alkaline solutions. This assumption seems amply justified inasmuch as the glass electrode shows markedly different properties on changing the positive ion of the electrolyte in whose solution the glass electrode is immersed while changing the negative ion makes no detectable difference (see Tables VI and VII). The next step will be to use the Henderson and Planck liquid junction equations, realizing that these theoretical equations are based on assumptions of constant mobility through the boundary, of homogeneous solvent, and of the validity of the perfect gas laws, all three of which are certainly not true for the glass–water junction. For definiteness consider the cell

$$
\begin{array}{ccc}
\mathrm{I} & \mathrm{glass} & \mathrm{II} \\
\mathrm{H_2O} & & \mathrm{H_2O} \\
\mathrm{H} & \mathrm{H} & \mathrm{H} \\
\mathrm{Na} & \mathrm{Na} & \\
& \mathrm{A} \quad\quad \mathrm{B} &
\end{array}
$$

According to both the Henderson and Planck equations the potential at A is given by the equation

$$
E_A = \frac{RT}{F} \ln \frac{u_H c'_H + u_{Na} c'_{Na}}{u_H c^G_H + u_{Na} c^G_{Na}} \tag{7}
$$

The potential at B is given by the equation

$$
E_B = \frac{RT}{F} \ln \frac{u_H c^G_H + u_{Na} c^G_{Na}}{u_H c''_H} \tag{8}
$$

and the net potential of the cell is

$$
E_G = \frac{RT}{F} \ln \frac{u_H c'_H + u_{Na} c'_{Na}}{u_H c''_H}
$$

where u may be conceived as the mobility of the particular ion in the boundary layer. Substituting activities for concentrations, and performing a slight transformation, we get

$$
E_G = \frac{RT}{F} \ln \frac{a'_H + \frac{u_{Na}}{u_H} a'_{Na}}{a''_H} \tag{9}
$$

If the glass acted as a perfect hydrogen electrode, the potential would be given by the equation

$$
E_H = \frac{RT}{F} \ln \frac{a'_H}{a''_H} \tag{10}
$$

By subtracting E_H from E_G we obtain an equation for the error of the glass electrode, namely

$$
\Delta E = E_G - E_H = \frac{RT}{F} \ln \frac{a'_H + \frac{u_{Na}}{u_H} a'_{Na}}{a'_H} \tag{11}
$$

This equation explains qualitatively all the facts of the glass electrode as regards its behavior in alkaline solutions. It predicts (1) that the error

will increase with diminishing hydrogen-ion activity and diminish with increasing hydrogen-ion activity, (2) that the error will increase with increasing sodium-ion activity at constant P_H, (3) that the error will vary from sodium to lithium depending upon the relative mobility of these ions to one another, (4) that if the activity of the hydrogen becomes small enough, the error will be directly proportional to the logarithm of the activity of the sodium ion and the glass electrode will act as a sodium electrode in agreement with the claims of Horovitz. All these predictions agree
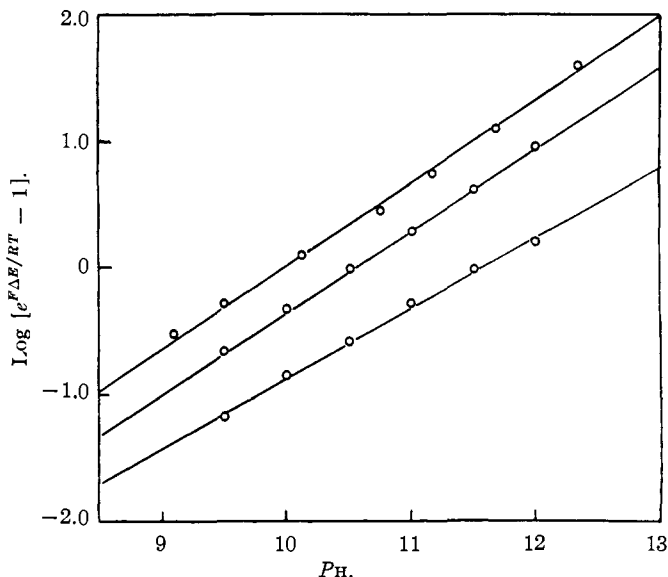
Fig. 5.—Top curve, 3.5 c NaAc; middle curve, 1.0 c NaAc;
bottom curve, 0.1 c NaAc.

qualitatively with the facts; but it is important to test this equation quantitatively. This may be done most readily by putting Equation 11 into the form of an equation of the straight line, to wit

$$e^{F\Delta E/RT} - 1 = \frac{u_{Na}\, a_{Na}}{u_H\, a_H} \quad \text{or} \tag{12}$$

$$\log [e^{F\Delta E/RT} - 1] = \log \frac{u_{Na}}{u_H} a_{Na} - \log a_H = \log B + P_H$$

where B is a constant at constant sodium-ion activity. By plotting log $[e^{F\Delta E/RT} - 1]$ as the y variable and the P_H as the x variable, a straight line should result with unit slope and with the intercept on the abscissa equal to $-\log B$. In Fig. 5 the results for the sodium solutions taken from Tables IX and XV are plotted according to this new function. The agreement is very striking, all the points falling on the straight lines very closely. Furthermore, the intercept on the P_H axis when y equals zero diminishes

with increasing sodium-ion concentration in quite the expected manner. There is one striking difficulty, however, and that is, the slopes of the lines are not all the same and are not equal to unity as Equation 12 predicts. The slope is approximately 0.6 and increases slightly as the sodium-ion concentration is increased. The increase is so slight that the experimental uncertainty makes it impossible to decide whether this increase is significant or not. Before discussing the divergence of the slope from unity and before considering the application of Equation 12 to the data for the lithium, potassium and barium solutions, it is interesting to see what quantitative agreement may be obtained between this function and some actual results. Table I contains the detailed data for the 0.9 c sodium acetate solution. Averaging the results for cell D and calculating the constants of Equation 12 (including the slope) by the method of least squares and by means of the resulting equation

$$\log \left[e^{F\Delta E/RT} - 1\right] = -6.451 + 0.611 \, P_H \qquad (13)$$

recalculating the experimental data, the figures of Table XVII were obtained.

<div align="center">

TABLE XVII

TEST OF EQUATION 13

</div>

P_H	ΔE observed	$\log \left[e^{F\Delta E/RT} - 1\right]$	ΔE calcd.	Difference
9.34	0.0043	−0.745	0.0043	0
9.78	.0076	− .460	.0074	+0.0002
10.44	.0156	− .080	.0157	− .0001
11.05	.0276	+ .284	.0282	− .0006
11.84	.0505	+ .789	.0443	+ .0062

The agreement is excellent up to a P_H of 11.8, where the difference between the observed and calculated potentials is six millivolts. At still higher values of the P_H the difference would become even greater. Calculations on other data show also that the new function fails, in general, to fit the experimental data above P_H 12. However, between the P_H's 9 and 12 Equation 13 provides an accurate mathematical relationship between the error of the glass electrode and the acidity of the solution.[36]

By allowing for a variable slope it is also possible to apply Equation 12 to the data for the lithium solutions and also to the rounded off data for the potassium and barium solutions. The slopes of the lithium curves (Fig. 6) are steeper than the sodium curves and are nearer the theoretical slope of unity.

[36] Equation 13, of course, does not take into consideration the errors of the glass electrode in very acid solutions which MacInnes and Belcher have recently discovered and which they have kindly shown me in advance of publication. Since these errors have the opposite sign to the alkaline solution errors, it is obvious that to explain them on the basis of the fundamental equation (4) it would be necessary to consider the migration of negative ions. However, until the actual publication of these data, further remarks must be withheld.

On the other hand, the slopes of the potassium curves (Fig. 7) are smaller than the slopes of the sodium curves and are, therefore, even farther away from the theoretical. The results for barium (Figs. 4 and 7) are interesting inasmuch as Horovitz[20] found that his glass electrodes showed no tendency to act as barium electrodes. The results of the writer indicate that there is no essential difference between barium and the other positive ions (see Fig. 7). The barium errors are very small, so small that it is impossible to treat them quantitatively; nevertheless, the effect of increasing
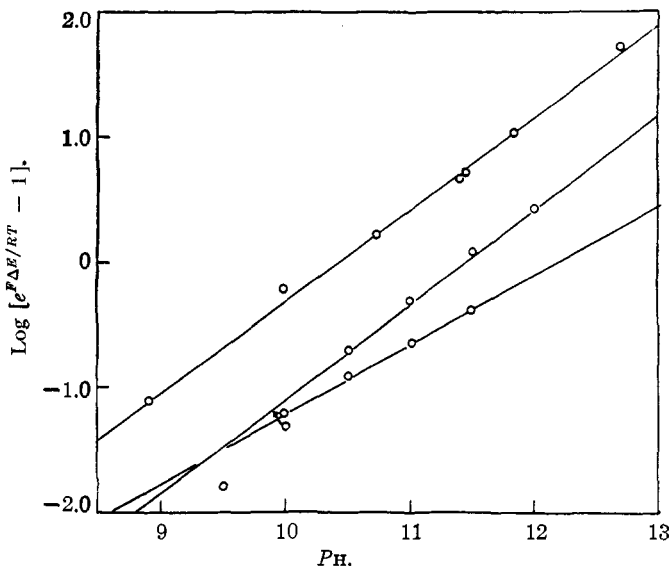

Fig. 6.—Top curve, 2.0 c LiAc; middle curve, 1.0 c LiAc; bottom curve, 0.1 c LiAc.

error with increasing P_H is definitely shown particularly with the results for the 0.5 c solution. Equation 12 may be put into the generalized form, namely

$$\log [e^{F\Delta E/RT} - 1] = A + n P_H \tag{14}$$

The constants of Equation 14 for the various solutions are collected in Table XVIII.

<div align="center">TABLE XVIII</div>
<div align="center">CONSTANTS OF EQUATION 14</div>

Solution	LiAc	LiAc	LiAc	NaAc	NaAc	NaAc	KAc	KAc	KAc
Concn	2.0	1.0	0.1	3.5	1.0	0.1	5.0	1.0	0.1
A	−7.61	−8.64	−6.70	−6.25	−6.45	−6.35	−4.39	−4.11	−4.43
n	0.729	0.755	0.548	0.633	0.611	0.550	0.346	0.315	0.325

We now come to the important question, why is the slope, n, less than unity and variable from ion to ion when the theory demands a unit and in-

variable slope? The possibility of the error being diminished by the migration of negative ions must be excluded since in alkaline solutions the change of negative ions does not affect the potential. It might be due to the migration of the hydroxyl ion, but this is unlikely since the slope of the equation remains constant despite a hundred-fold increase in the concentration of the hydroxyl ion. Another possibility is that the two fundamental assumptions of constant mobility across the boundary and of homogeneity of the solvent may be incorrect. It is highly possible that the large difference in dielectric constant between the two media should be taken into
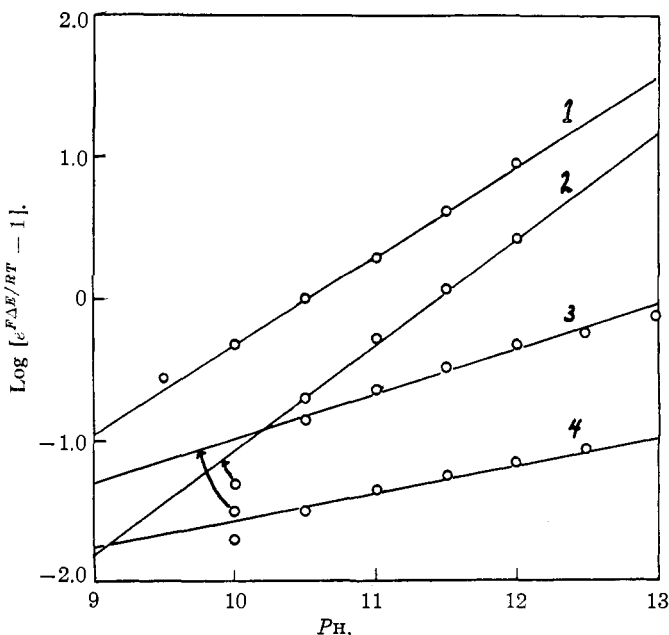

Fig. 7.—Curve 1, 1.0 c NaAc; curve 2, 1.0 c LiAc; curve 3, 1.0 c KAc; curve 4, 0.5 c BaAc₂.

consideration in deriving the theoretical equations.[37] It is interesting to go back from Equation 14 to the original form of the equation for the error of the glass electrode. Instead of Equation 11 we get the equation

$$\Delta E = \frac{RT}{F} \ln \frac{B/a_H^{(n-1)'} + a_H'}{a_H'} \tag{15}$$

This result leads at once to the idea that the relative mobility of the sodium and hydrogen ions may not be constant as the P_H is changed as we originally assumed, but the relative mobility may vary according to the hydrogen ion activity taken to the power $1 - n$. This would indicate that the mobility

[37] As suggested in a private communication from Professor Max Planck.

of the hydrogen ion would increase relatively to that of the sodium ion as the P_H is increased.

Up to this point it has been assumed that the A constant of Equation 14 is the ratio of the mobility of the sodium ion to the mobility of the hydrogen ion multiplied by the activity of the sodium ion.   Since the mobilities are different in different media, the A constant is probably not a direct measure of the mobility ratio.   Taylor[38] has derived an equation for the liquid junction for the special case of mobilities and activity coefficients variable in a certain specified manner from one solution to the other.   His equation would also lead to Equation 14 except that in this case the A constant would be multiplied by another unspecified constant.   Although Taylor's assumptions may not be justified for the glass aqueous solution boundary, nevertheless his calculations suggest that the A constant of Equation 14 will not give the mobility ratio directly.   The subject of ion mobility leads us to the interesting question concerning the selective mobility of the glass–water boundary layer to positive ions.   Since this same selective mobility is also true for collodion, quartz and paraffin water interfaces, the permeability must be connected to the interfacial tension or to the interfacial potential (electrokinetic potential), which is practically the same for these different interfaces.[39]   Further experimental work is planned to test this hypothesis.

In conclusion, the picture of the glass electrode which is presented here may be briefly reviewed as follows.   At the glass–water interface an electric double layer exists which allows in alkaline solutions only positive ions to penetrate the boundary.   The boundary is probably sharp, so that there is a sudden change of concentration and mobility of the ions in going from the glass phase to the aqueous phase.   Complete equilibrium is never set up due to the high viscosity of the glass and ionic exchange will occur only minutely and will be unnecessary for the establishment of the potential. The measured potentials may be considered as somewhat analogous to liquid junction potentials, their comparatively high values being due to the selective mobility of the positive ions across the boundary.   The mathematical analysis of the results indicates that the mobilities are dependent upon the P_H.

Summary

1.   The glass electrode is directly compared with the hydrogen electrode in solutions of lithium, sodium, potassium and barium salts at various concentrations and over the P_H range 6 to 13.

[38] P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

[39] See H. B. Bull and R. A. Gortner, *Proc. Nat. Acad. Sci.*, **17**, 288 (1931).

2. Previous theories of the glass electrode are critically reviewed.

3. A differential thermodynamic equation for the glass electrode in terms of activities and transference numbers is given.

4. A new equation for the glass electrode is discovered and shown to agree with the data up to a P_H of 12. A similar equation may be theoretically derived for uniunivalent salts from the Henderson and Planck liquid junction equations if one allows the relative mobility of the positive ions to be a function of the hydrogen-ion activity.

5. The idea is expressed that the electric double layer at the glass aqueous solution interface determines the selective mobility of the ions across the boundary.

EVANSTON, ILLINOIS

THE MOLECULAR ASSOCIATION, THE APPARENT SYMMETRY OF THE BENZENE RING, AND THE STRUCTURE OF THE NITRO GROUP IN CRYSTALLINE META-DINITROBENZENE. THE VALENCES OF NITROGEN IN SOME ORGANIC COMPOUNDS

BY STERLING B. HENDRICKS AND GUIDO E. HILBERT

Introduction

E. Hertel[1] has recently obtained x-ray diffraction data leading to space group determinations from crystals of ortho, meta and para dinitrobenzene. An unfortunate error in the analysis of the data from m-dinitrobenzene, however, resulted in an incorrect determination of the atomic positions relative to a plane of symmetry. The simple results obtained from a reexamination of this compound have far-reaching significance.

The Structure of the Crystal and the Positions of the Hydrogen Atoms.—m-Dinitrobenzene, in agreement with the analysis of Hertel, has an atomic arrangement derivable from space group Pbnm (V_h^{16}). On the average the carbon and nitrogen atoms of a molecule must be in the same plane perpendicular to the c axis. The oxygen atoms are about 0.96 Å. from this plane as a plane of symmetry.

It is probable that the hydrogen atoms of m-dinitrobenzene occupy fixed positions coplanar with the nitrogen and carbon atoms. Earlier results of crystal structure analyses of some ammonium salts led to the belief that the hydrogen atoms in a crystal need not conform to the symmetry requirements of the crystal.[2] These results, and the apparently high symmetries

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[1] E. Hertel, Z. physik. Chem., **B7**, 188 (1930).

[2] R. W. G. Wyckoff, Am. J. Sci., **5**, 209 (1923).