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On the Theory of Glass Electrodes

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A glass electrode is considered schematically to be a difficultly soluble electrolyte which absorbs water and further salts present in an adjacent solution. The potential is the distribution potential at the boundary surface between the glass and the solution. According to the theory presented this potential varies if certain reasonable assumptions are made concerning the value of the constants occurring (dissociation constants in the glass, distribution constants between glass and water) over a wide range of concentration in acid and neutral solutions in the same manner as that at an H_2 electrode. The variation of

the potential differs from the latter in a strongly alkaline solution, in the manner ascertained experimentally and predicted in previous communications. The extremely simplified model describes quantitatively with one empirical constant the potentials hitherto observed. It is shown that the systems are completely explicable on the basis of the usual thermodynamic picture of equilibrium. Attempts on the other hand to describe the phenomena on the basis of diffusion potentials have not led to satisfactory results.

I. INTRODUCTION

IT is known that over a wide range of concentration electrodes of soft glass behave like hydrogen electrodes. This behavior is changed, however, in the case of electrodes of highly resistant glass. Glass of this nature may act in neutral and alkaline solutions of cations like a metallic electrode of the cation concerned.

Some time ago the writers proposed a model reproducing the behavior of both kinds of glass in all the details known at that time.¹ They furthermore predicted as a consequence of their formulae that certain intermediary types should be observable. In this successful representation by model the glass is conceived as a salt MeS which is difficultly soluble in water, and which absorbs the water and other salts of the same cation added to the solution, in solid solution.

More recently it has been found² experimentally that the behavior of soft glass deviates in two respects from the ideal behavior of the hydrogen electrode. In the first place, the potentials in strongly alkaline solution become dependent on the concentration of any neutral salts which may be present. In the second place, the potentials of glass electrodes differ from those of hydrogen electrodes when the solution

is not an ideally dilute solution, the water activity therefore not being equal to one.

Proceeding on the assumption that the potentials at glass electrodes are diffusion potentials, Dole has attempted to give an explanation of both of these phenomena. The formulae derived by him for the first case, namely for the deviations in the alkaline range, do not fit the experiments. He therefore introduced for every series of observations a new constant in his formula and changed in every series the value of the second theoretically determined constant to obtain agreement. His formulae thus contain for each series two arbitrary constants neither of which has a theoretical meaning. Although he attempted to justify this alteration by the adduction of supplementary hypotheses, it is safe to say that his formulae can only be regarded as empirical.³

The deviations in the potentials of glass electrodes in concentrated solutions are not all of the same sign. Dole has explained part of the experimental observations by pointing out that the thermodynamic process at a hydrogen electrode is not necessarily the same as that at a glass electrode. At a hydrogen electrode the discharge of a dehydrated hydrogen ion may

¹ Gross and Halpern, *Zeits. f. physik. Chemie* **115**, 54 (1925); **118**, 255 (1925).

² M. Dole, *J. A. C. S.* **53**, 4261 (1931); **54**, 3095 (1932).

³ Judging by the footnote at the beginning of the second paper, we take it that Dole himself is now of this opinion also.

occur while it is perfectly conceivable that hydrated hydrogen ions pass into the glass electrode.

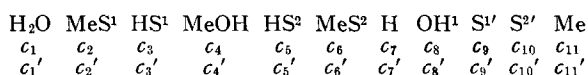
II. DERIVATION OF THE GENERAL FORMULA FOR THE POTENTIAL

We wish to show in the following pages that the scheme previously put forward by the present authors describes quantitatively without the aid of supplementary hypotheses the deviations in alkaline solution, and likewise depicts the second group of deviations, by utilizing the differences in the discharge mechanism mentioned above. To this end, however, it is necessary to carry out the calculations previously made, to a higher approximation, and, since concentrated solutions are in addition to be dealt with, simplifications permissible in the theory of dilute solutions will be avoided. We thus represent the glass by the uni-univalent salt MeS^1 which is capable of absorbing water and electrolytes in a superficial layer in solution. The distribution potential at

the boundary surface concerned is then given by

$$E = (RT/F) \ln (c_k \gamma_k / c_k' \gamma_k') + \text{const.}, \quad (1)$$

in which the c and the γ denote concentrations and activity coefficients, respectively. The index k relates to any one cation for which there is distribution equilibrium, and the dashes relate to the solid phase. The diffusion potential occurring in the glass shall be neglected as small so that Eq. (1) denotes the potential of the glass electrode. We shall limit ourselves, for the sake of simplicity, to the case of *one* cation contained in the glass. The system is characterized by the symbol:



The following equations are then valid for the dissociation equilibria in the liquid phase (2), in the solid phase (3), and the distribution equilibria for the non-dissociated constituents between the two phases (4).⁴

$\frac{c_7 c_8}{c_1} = K_1 \frac{\gamma_1}{\gamma^2}, \quad (2_1)$	$\frac{c_7' c_8'}{c_1'} = L_1, \quad (3_1)$	$c_1 \gamma_1 = M_1 c_1', \quad (4_1)$
$\frac{c_{11} c_9}{c_2} = K_2 \frac{1}{\gamma^2}, \quad (2_2)$	$\frac{c_{11}' c_9'}{c_2'} = L_2, \quad (3_2)$	$c_2 = M_2 c_2', \quad (4_2)$
$\frac{c_7 c_9}{c_3} = K_3 \frac{1}{\gamma^2}, \quad (2_3)$	$\frac{c_7' c_9'}{c_3'} = L_3, \quad (3_3)$	$c_3 = M_3 c_3', \quad (4_3)$
$\frac{c_8 c_{11}}{c_4} = K_4 \frac{1}{\gamma^2}, \quad (2_4)$	$\frac{c_8' c_{11}'}{c_4'} = L_4, \quad (3_4)$	$c_4 = M_4 c_4', \quad (4_4)$
$\frac{c_7 c_{10}}{c_5} = K_5 \frac{1}{\gamma^2}, \quad (2_5)$	$\frac{c_7' c_{10}'}{c_5'} = L_5, \quad (3_5)$	$c_5 = M_5 c_5', \quad (4_5)$
$\frac{c_{10} c_{11}}{c_6} = K_6 \frac{1}{\gamma^2}, \quad (2_6)$	$\frac{c_{10}' c_{11}'}{c_6'} = L_6, \quad (3_6)$	$c_6 = M_6 c_6'. \quad (4_6)$

The activity-coefficients are assumed to be the same for all ions and equal to one for undissociated molecules with the exception of water. The activity-coefficient in the solid phase shall be independent of concentration so that the values of the L are constants. Furthermore, we have the equations of electric neutrality for both

phases, as follows:

$$c_7 + c_{11} = c_8 + c_9 + c_{10}, \quad (5)$$

$$c_7' + c_{11}' = c_8' + c_9' + c_{10}'. \quad (5')$$

⁴ These equations are not all independent of each other, but we have put them all down, for the sake of completeness.

The concentration of the added acid ion is assumed to be known; furthermore according to our assumptions in regard to activity-coefficients

$$c_2' = A. \quad (6)$$

By successive substitution of the equilibria Eqs. (3₁), (3₂), (3₄), (3₆), (4₁), (4₄), (4₆), (2₁), (2₄), (2₆), (6) in the condition of electric neutrality (5') we obtain

$$\frac{c_{11}^2}{c_{11}^2} = \frac{\frac{L_4 K_1 \gamma_1 c_1}{M_4 K_4 c_7^2} + \frac{L_2 A}{c_7 c_{11}} + \frac{L_6 \gamma^2 c_{10}}{M_6 K_6 c_7}}{\frac{c_{11}}{c_7} + \frac{L_1 K_4 M_4}{K_1 M_1 L_4}}. \quad (7)$$

In order to describe the behavior of electrodes of the *soft* glass assume

$$\frac{L_4 K_1 \gamma_1 c_1}{M_4 K_4 c_7} \gg \frac{L_2 A}{c_{11}} \quad \text{and} \quad \frac{L_4 K_1 \gamma_1 c_1}{M_4 K_4 c_7} \gg \frac{L_6 \gamma^2 c_{10}}{M_6 K_6},$$

which is equivalent to the statements: $c_8' \gg c_9'$; $c_8' \gg c_{10}'$. The physical significance of these conditions is roughly as follows: the ionic activity of the boundary layer between glass and water, which determines the behavior, is attributable in the main to the solute water and to the added base.⁵ For the potential of the glass electrode we then obtain from (1) and (7) the expression

$$E_g = \frac{RT}{F} \ln \left[c_7 \gamma \left(1 + \frac{K_1 M_1 L_4 c_{11}}{K_4 M_4 L_1 c_7} \right)^{\frac{1}{2}} \right] - \frac{RT}{2F} \ln \gamma_1 c_1 + \text{const.} \quad (8)$$

and at *constant water activity*

$$E_g = (RT/F) \ln c_7 \gamma + (RT/2F) \times \ln (1 + b(c_{11}/c_7)) + \text{const.} \quad (8')$$

$$(b = K_1 M_1 L_4 / L_1 K_4 M_4).$$

If the glass behaved like a hydrogen electrode,

⁵ This method of dealing with solubility products in accordance with *experimental results* is criticized by Dole as being "highly artificial."

the following would be valid:

$$E_h = (RT/F) \ln c_7 \gamma + \text{const.} \quad (9)$$

The difference between the two potentials is therefore

$$E_g - E_h = \Delta = (RT/2F) \times \ln (1 + b(c_{11}/c_7)) + \text{const.} \quad (10)$$

This quantity is termed by Dole the *error* of the glass electrode.

III. COMPARISON OF THEORY AND EXPERIMENT

In order to bring the equation obtained into a form capable of being checked, we rewrite Eq. (10) as follows:

$$-y = \ln [(e^{2F\Delta/RT} - 1)/c_{11}\gamma] = \ln b + p_H. \quad (11)$$

That is to say, the function y must be linearly independent on the p_H with the slope of 1. We have tested this dependence of the function y on the p_H for all of Dole's experiments in which the solution contains sodium ions in addition to hydrogen ions. In order to depict the experiments made with the remaining salts (lithium, potassium and barium salts), our model would require to be expanded along the same lines since the glass employed by Dole was a sodium-calcium silicate. That is to say of the salts employed only the sodium salts have a cation in common with the glass to which our model applies. The theory was compared with Dole's observations on 0.05 molar sodium phosphate solutions, on unimolar sodium-chloride and acetate solutions and on 3.5 molar sodium acetate solutions. The activities of univalent ions in these solutions are obtained from tables⁶ or by interpolation. We thus arrive at the following values for the activities of the sodium ion:

Na ₂ HPO ₄	$a = 0.078,$	$c = 0.05,$
NaAc	$a = 0.77,$	$c = 1,$
NaCl	$a = 0.685,$	$c = 1,$
NaAc	$a = 3.57,$	$c = 3.5.$

With these values for the various activities the

⁶ Landolt-Börnstein-Roth, 5th Ed., 2nd Suppl., Vol. 2.

function y was calculated and plotted against p_H in Fig. 1. The points are freely grouped about a straight line with the slope of 1. No appreciable alteration in the slope occurs, except possibly in the solution poorest in sodium ions for which only *one* series was measured, but it should be noted that here the "errors" are only small as expected from the theory, and that the possibility of reproducing the potentials is limited.⁷

In order to check the numerical agreement of the theoretical formula, with *one* constant which describes *all* observations with *all* sodium concentrations, we shall calculate the same series as that which Dole tested his formula containing two constants. Note that Dole adapts the two constants of his formula as required to the observations of *one* series (constant sodium ion concentration), that is he employs six constants to represent all the measured points plotted in Fig. 1.

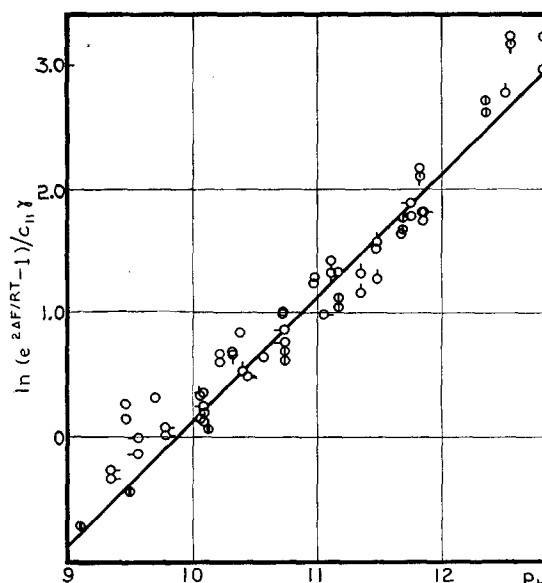


FIG. 1. Text of Eq. (11) $\ln [(e^{2\Delta F/RT} - 1)/c_{11}\gamma] = \ln b + p_H$.
 ○ 0.05 Na_2HPO_4 , ○ 0.9 $\text{NaAc} + 0.05 \text{Na}_2\text{HPO}_4$, ○ 1.0 NaAc , ○ 0.9 $\text{NaCl} + 0.05 \text{Na}_2\text{HPO}_4$, ○ 0.99 $\text{NaCl} + 0.01 \text{NaAc}$, ⊙ 3.5 NaAc .

TABLE I. Test of the Eq. (10). 0.9 c NaAc , 0.05 Na_2HPO_4 .

p_H	$\Delta_{\text{obs. mV}}$	$\Delta_{\text{calc. Dole}}$	δ	$\Delta_{\text{calc. (10)}}$ $b = 1.36 \times 10^{-10}$	δ	$\Delta_{\text{calc. (10)}}$ $b = 1.23 \times 10^{-10}$	δ
9.34	4.3	4.3	0.0	2.6	1.7	2.4	1.9
9.78	7.6	7.4	0.2	6.3	1.3	5.8	1.8
10.44	15.6	15.7	0.1	17.3	1.7	16.4	6.8
11.05	27.6	28.2	0.6	32.7	5.1	31.4	3.8
11.84	50.5	44.3	6.2	55.1	4.6	53.8	3.3
$(\overline{\delta^2})^{\frac{1}{2}} = 2.8$				$(\overline{\delta^2})^{\frac{1}{2}} = 3.27$		$(\overline{\delta^2})^{\frac{1}{2}} = 2.6$	

In the second column of Table I are given the "errors" found, and in the third column the "errors" calculated by Dole. The values for Δ given in the fifth column are calculated according to the Eq. (10), for which we have used the value for the constant $b = 1.36 \times 10^{-10}$ which results from the graphic mean (Fig. 1) of the measurements at *all* sodium concentrations. As

⁷ In certain series differences up to 10 mV occur at different electrodes immersed in the same solution. The potentials depend on the order in which the alkaline concentration is varied. (MacInnes and Belcher, J. A. C. S., 53, 3315 (1931).) According to Dole, the potentials obtained with the addition of potassium salts are also hard to reproduce. We wish to point out that all these observations are thoroughly consistent with our model, since the establishment of equilibrium in the superficial layer is a process which is not always effected momentarily.

will now be seen, the agreement is almost as good as that obtained by Dole. A slight alteration of say 10 percent in our constant ($b = 1.23 \times 10^{-10}$) would lead to agreement better than that obtained by Dole. If it be borne in mind that the constant b is of the nature of a solubility product, the slight uncertainty in the experiments of the different series is plausible. This is all the more so since the absolute potentials similarly differ from each other, presumably on account of uncheckable differences in the composition of the superficial layer. The agreement here obtained justifies the opinion that the proposed scheme is correct in principle, and useful for the description of the behavior of the glass electrode.

We will now turn to the second-mentioned deviations of the hydrogen electrode from a

TABLE II. "Errors" through alteration of the water activity.

% Ethanol	p_H	a_{H_2O}	$\Delta_{obs.}$	$\Delta_{calc. Dole}$	δ	$\Delta_{calc. (12)}$	δ
33	1.30	0.89	-1.3	-3.0	1.7	-1.5	0.2
33	0.41	0.89	-1.3	-3.0	1.7	-1.5	0.2
37	1.86	0.88	-2.0	-3.3	1.3	-1.7	0.3
55	1.36	0.83	-4.2	-4.8	0.6	-2.4	1.8
56	1.99	0.83	-4.6	-4.8	0.2	-2.4	2.2
66	0.71	0.79	-3.9	-6.1	2.2	-3.1	0.8
					$(\bar{\delta}^2)^{\frac{1}{2}} = 1.46$		$(\bar{\delta}^2)^{\frac{1}{2}} = 1.22$

glass electrode, taking into account the difference characterized by Dole. It may be taken to be thoroughly plausible to assume that the hydrogen ion in glass, as in water, is hydrated, while the dehydrated ion is discharged at the platinum-hydrogen electrode. The equilibrium between the two types of hydrogen ions in solution is given by the expression

$$c_1\gamma \times c_1\gamma_1/c_{H_2O} \times \gamma_{H_2O} = \text{const.}$$

There is a corresponding difference in the potentials of the two electrodes, which is dependent on the water activity and an "error," given by (cf. (8))

$$\Delta = (RT/2F) \ln c_1\gamma_1. \quad (12)$$

In comparing theory with experiment, however, we may only proceed to such values for the activity of water as are permissible under the assumption that the water is still present as a solvent in great excess. This is so since all as-

sumptions as to the activity coefficients relate to water as the solvent, and become entirely wrong when applied to other solvents. We therefore limit ourselves to water activities which are not lower than 0.79. In Table II we place the deviations found by Dole alongside those calculated by Dole himself and those calculated by us. As is evident from Table II, the agreement between the observed values and the calculated values by the authors is very fair, and better than the results of Dole's calculations, which are given in the fifth column of the Table II. It should be noted that by proceeding to very slight water activities we have gone beyond the range for which our theory is valid. The fact that the proposed model actually describes only the very slight deviations for water activities in the neighborhood of one, is not a peculiar weakness of the model, but is inherent in our lack of knowledge of the variation of the activity coefficient on change of solvent.