The Relation between the Glass Electrode Theory of B. Nicolsky and that of my own

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Nicolsky[1] has recently published an interesting and important theory of the glass electrode in which he assumed:

1. that positive ions such as hydrogen ions and sodium ions will enter into the exchange reaction between the glass and aqueous solution

$$(H^+)' + (Na^+) \rightleftarrows (H^+) + (Na^+)', \tag{1}$$

where the primes (') refer to the glass phase;

2. that negative ions do not take part in the electrode reaction;

3. that the Law of Mass Action can be applied to the above equilibrium yielding the equation

$$\frac{a_{H^+} \times a'_{Na^+}}{a'_{H^+} \times a_{Na^+}} = K; \tag{2}$$

4. that the total concentration of the positive ions in the glass phase remains constant,

$$N_0 = N'_{Na^+} + N'_{H^+} = \text{const.}; \tag{3}$$

5. and that the activity coefficients of the ions in the glass phase are constant and so defined as to be equal to unity.

In the statistical theory of the glass electrode developed in 1934[2] exactly the same or equivalent assumptions were made as those listed above; thus we assumed

1. that hydrogen ions on the glass surface and sodium ions in the solution can exchange and *vice versa*;

[1] B. Nicolsky, Acta Physicochimica URSS, 7, 597 (1937).
[2] M. Dole, J. Chem. Phys., 2, 862 (1934).

2. that the fraction of unit glass surface occupied by the hydrogen ions is γ and by the sodium ions $1-\gamma$;

3. that exchange transitions take place until equilibrium is established;

4. and that negative ions play no rôle in the glass electrode mechanism.

However, in our theory we did not introduce the complicating factor of activity coefficients although we might very well have done so.

Since the physical ideas underlying our theory and the theory of Nicolsky are identical, it is interesting to examine the resulting mathematical expressions to see if they also are equivalent. We find indeed that they are, that the equation for the glass electrode presented by Nicolsky can easily be shown to be the same as our own.

Making use of the concept of electrochemical potential and applying the Law of Mass Action and eq. (3) Nicolsky derives the glass electrode equation

$$\psi = \frac{(\mu^0_{H^+}) - (\mu^0_{H^+})'}{F} - \frac{RT}{F} \ln N_0 + \frac{RT}{F} \ln (a_{H^+} + a_{Na^+} \times K), \quad (4)$$

where ψ is the interfacial potential at the glass electrode surface, and $(\mu^0_{H^+})'$ is the standard electrochemical potential of the hydrogen ion in the glass, so defined as to make its activity coefficient equal to unity. Equation (4) may be written

$$\psi = k + \frac{RT}{F} \ln (a_{H^+} + a_{Na^+} \times K), \quad (5)$$

where k is a constant and ψ is the interfacial potential.

In our paper on the statistical theory of the glass electrode we derived the equation

$$C_{H^+} e^{(Q_{H^+} - F\psi)/RT} + C_{Na^+} e^{(Q_{Na^+} - F\psi)/RT} = 1 \quad (6)$$

which can be solved for the e. m. f. giving

$$\psi = \frac{Q_{H^+}}{F} + \frac{RT}{F} \ln \{C_{H^+} + C_{Na^+} e^{(Q_{Na^+} - Q_{H^+})/RT}\}. \quad (7)$$

Equation (7) is thus seen to be identical with Nicolsky's eq. (5)

provided we identify his constant k with our constant Q_{H^+}/F and his Law of Mass Action constant K with our expression

$$e^{(Q_{Na^+}-Q_{H^+})/RT}. \tag{8}$$

But from the van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \tag{9}$$

we know that the equilibrium constant K can be represented by an exponential function of the temperature such as expression (8); therefore there seems to be no essential difference between Nicolsky's eq. (5) and our eq. (7).

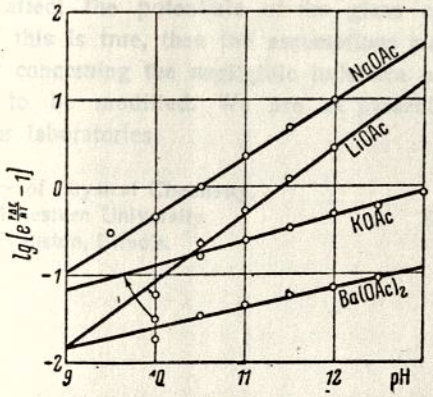

Fig. 1.
Test of equation (12).

Nicolsky's theory can be further developed in the manner of our original paper. If the glass electrode acts as a perfect hydrogen electrode, the e. m. f., ψ_0, will be given by the equation

$$\psi_0 = k + \frac{RT}{F} \ln (a_{H^+}). \tag{10}$$

Subtracting (10) from (5) we have an equation for the error of the glass electrode, ΔE, namely

$$\Delta E = \psi - \psi_0 = \frac{RT}{F} \ln \left\{ \frac{a_{H^+} + a_{Na^+} \times K}{a_{H^+}} \right\}; \tag{11}$$

or rearranging eq. (11) and taking logarithms

$$\lg \{e^{F\Delta E/RT} - 1\} = \lg \{a_{Na^+} \times K\} + \mathrm{pH}, \qquad (12)$$

where lg is the logarithm to the base ten (Briggsian logarithms); eq. (12) can be tested by plotting $\lg [e^{F\Delta E/RT} - 1]$ as a function of the pH; such a plot based on the data of Dole[3] is shown in Fig. 1. Although at first sight the resulting straight lines seem to verify the essential correctness of eq. (12), nevertheless the slopes of the lines are less than the value of unity required by the theory. Dole[2] and Dole and Wiener[4] have discussed possible explanations for this deviation of the slopes of the lines from unity.

There have recently been obtained some indications that negative ions may affect the potentials of the glass electrode in alkaline solution. If this is true, then the assumptions made by Nicolsky and myself concerning the negligible influence of the negative ions will have to be modified. We are at present investigating this point in our laboratories.

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Received
December 25, 1938.

[3] M. Dole, J. Am. Chem. Soc., 53, 4260 (1931).
[4] M. Dole a. B. Z. Wiener, Trans. Electrochem. Soc., 72, 107 (1937).