

PHYSICAL CHEMISTRY

**APPLICABILITY OF NERNST FORMULAE TO THE CASE
OF AMPHOTERIC ADSORBENTS**

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The problem we are to consider is to find out the conditions, under which the dependence of the charge and potential upon hydrogen ion concentration will obey the same law in the case of an amphoteric non-conductive adsorbent as in that of a hydrogen electrode. Our way to do this is in many respects very similar to that of Lindeström-Lang ⁽¹⁾, but differs from the latter by the use of more precisely formulated physical assumptions. Suppose that on a unit surface there are q neutral groups capable to fix hydrogen ions, and q other neutral groups capable to split these ions off. In its initial state the surface is supposed to be free from any hydrogen ion: in this case it carries q negative charges and can obviously fix $2q$ ions of hydrogen. Assume further that the probability for a hydrogen ion to be fixed by any of the $2q$ adsorbing centres would be equal, but for the influence of the electric field created by the surface charges, a factor which can be allowed for if the potential difference between the surface and the bulk of the solution ψ is known. Then the number of hydrogen ions in the unit area of the surface n will be bound with their concentration in the solution $[H^+]$ by the following relation:

$$k_1 [H^+] (2q - n) = k_2 n e^{\frac{\psi}{kT}}.$$

Hence

$$\psi = \frac{kT}{e} \ln \frac{k_1 [H^+] (2q - n)}{k_2 n}$$

where k_1 and k_2 are constants, while the rest of the symbols have their usual meaning. Let us now introduce the symbols $[H^+]_0$ for such a concentration of hydrogen ions when $n = q$ and $\psi = 0$, that is when the surface becomes electroneutral (iso-ionic point). Then $[H^+]_0 = \frac{k_2}{k_1}$ and

$$\psi = \frac{kT}{e} \ln \frac{[H^+]}{[H^+]_0} \frac{2q - n}{n}. \quad (1)$$

Equation (1) does not give by itself, however, a complete solution of the problem; to find this, we must consider which condition of the surface was taken as the initial one. Let us denote with σ the free charge of a unit surface. We shall have then

$$\sigma = (n - q) e \quad (2)$$

and

$$\psi = \frac{4\pi\sigma\lambda}{D} \quad (3)$$

where λ is the thickness of the double layer. With $|\psi| \ll \frac{2kT}{e}$ the value of λ can be put equal to the thickness of Debye's ionic atmosphere. With $|\psi|$ high enough, λ becomes the thickness of the Helmholtz layer, but we shall not dwell upon that here. From (1) and (2) it follows that

$$\psi = \frac{kT}{e} \ln \frac{[H^*]}{[H^*]_0} \frac{1 - \frac{\sigma}{q\varepsilon}}{1 + \frac{\sigma}{q\varepsilon}}. \quad (4)$$

If the ratio of the number of surface free charges $\left|\frac{\sigma}{e}\right|$ to the highest possible $|q|$ is small, that is $\left|\frac{\sigma}{q\varepsilon}\right| \ll 1$, we can, following Lindeström-Lang, put

$$\frac{1 - \frac{\sigma}{q\varepsilon}}{1 + \frac{\sigma}{q\varepsilon}} \sim e^{-\frac{2\sigma}{q\varepsilon}}. \quad (5)$$

Then

$$\frac{\psi\varepsilon}{kT} + \frac{2\sigma}{q\varepsilon} = \ln \frac{[H^*]}{[H^*]_0}$$

and in view of (3)

$$\frac{\sigma}{\varepsilon} = \frac{1}{\frac{2}{q} + \frac{4\pi\lambda\varepsilon^2}{DqT}} \ln \frac{[H^*]}{[H^*]_0}. \quad (6)$$

Equation (6) is identical to that deduced by Lindeström-Lang. Its use is limited by the condition $\left|\frac{\sigma}{q\varepsilon}\right| \ll 1$, that is

$$\left| \frac{1}{1 + \frac{4\pi\lambda\varepsilon^2}{DkT} \cdot \frac{q}{2}} \ln \frac{[H^*]}{[H^*]_0} \right| \ll 1. \quad (7)$$

Condition (7) is fulfilled in two cases: when

$$\frac{[H]}{[H^*]_0} \sim 1$$

or when

$$\frac{4\pi\lambda\varepsilon^2}{DkT} \cdot \frac{q}{2} \gg 1. \quad (8)$$

In the first case no real analogy exists between the behaviour of our adsorbent and of a conducting electrode, since, with $\frac{[H]}{[H^*]_0} \sim 1$, the logarithmic dependence between σ and $\frac{[H^*]}{[H^*]_0}$ can with the same accuracy be replaced by a proportional relation between σ and $\frac{[H^*] - [H^*]_0}{[H^*]_0}$ which is obtained, if no allowance is made for the electrostatic interaction between the adsorbing groups: on the other hand, the coefficient of $\ln \frac{[H^*]}{[H^*]_0}$ in the expression for ψ is not equal to $\frac{kT}{e}$.

In the second case it follows from (6) and (3) that

$$\begin{aligned} \sigma &= \frac{DkT}{4\pi\lambda\varepsilon} \ln \frac{[H^*]}{[H^*]_0} \\ \psi &= \frac{kT}{e} \ln \frac{[H^*]}{[H^*]_0}. \end{aligned} \quad (9)$$

From (9) it follows that if condition (8) is fulfilled and the number of charges remains small compared to the highest possible one, the potential difference between the adsorbent's surface and the solution is in fact expressed in terms of the concentration, just as in the case of a hydrogen electrode. Condition (8) may also be written thus:

$$\frac{4\pi\lambda\varepsilon q}{D} \gg \frac{2kT}{e}. \quad (10)$$

This means that the limiting potential value which corresponds to the ionization of all neutral groups should be great as compared to $\frac{2kT}{e}$.

However, the correctness of these deductions depends also upon how far it is possible to express the action of the electrical field at the surface of the adsorbent through some average potential difference value ψ . To fix this condition precisely is a difficult matter at the present stage of the theory of the double layer⁽²⁾. But it is certain, that this conclusion is the more lawful, the smaller the distance between the points on the surface, at which the charges can appear and disappear, as compared to the thickness of the double layer (at the same time we must suppose that the interval, during which the hydrogen ion is exchanged between the adsorbing centre and the solution, is small compared to the time of relaxation of the ionic atmosphere, so that the free charges are uniformly distributed all over the $2q$ groups). In a Helmholtz layer, with usual values for interatomic distances and ionic radii, the relation is always inverse; for a diffuse layer in a sufficient state of dilution the condition that

$$q^{-1/2} \ll \lambda \quad (11)$$

may be realized. The possible use of equation (9) in the case of amphoteric adsorbents is greatly restricted by these considerations. If the potential distribution over the surface can no longer be taken for uniform, there still remains a nearly logarithmic relation between σ and $\frac{[H^*]}{[H^*]_0}$, provided the electrostatic interaction between the different groups is strong enough, but the coefficient of proportionality before $\ln \frac{[H^*]}{[H^*]_0}$ will now take a different value. At last it should be remarked that, irrespective of the electrostatic interaction, the logarithmic dependence between σ and $\frac{[H^*]}{[H^*]_0}$, as follows from M. Temkin's theory, holds good when the adsorbing groups on the surface have different adsorption energies distributed linearly within a sufficiently wide interval of values. In that case the coefficient before $\ln \frac{[H^*]}{[H^*]_0}$ in eq. (9) will, of course, be also different from $\frac{kT}{e}$.

Conclusions. It has been shown that the potential difference between the surface of an amphoteric non-conducting adsorbent and the solution can be expressed through the same relation, as is valid in the case of a hydrogen electrode. This is possible when the number of adsorbing groups on the surface is great enough, which is expressed quantitatively by the conditions (10) and (11).

Received
4. I. 1941.

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Translated by D. Rakhmanov.