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**Comments on
Some Critical Remarks on the Paper »Fixed Charge Double Layer
Potential Equations — a Derivation« by J. Th. G. Overbeek***

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Professor Overbeek in his paper »Some Critical Remarks on the Paper »Fixed Charge Double Layer Potential Equations — a Derivation« by M. Mirnik published in *Croat. Chem. Acta* 42 (1970) 505, claimed that the criticized paper contains arbitrary assumptions and internal inconsistencies. By careful reading of the criticized paper objective unbiased readers would probably come to the conclusion that Professor Overbeek's claims do not hold. However, in order to demonstrate and prove that Professor Overbeek's criticism is unjustified the following comments are given to it.

a. Lack of Clarity

The unit for a_M is necessarily (gram eq./liter system) and that for $a_{M, \text{layer}}$ (gram eq./gram mole solid) \times (gram mole solid/liter system) = (gram eq./liter system). The latter unit, although formally equal, has a different physical meaning from the former. It would have the same physical meaning if it read (gram eq./liter double layer volume). The double layer volume is, at present, not measurable by a direct method and therefore only the suggested unit can be used. If the quantity of the solid per liter of the system is constant the units (gram eq./gram mole solid) or [(gram eq./gram mole solid)/liter system] can also be used. None of the proposed units does depend on the total amount of the system and therefore μ_M° and $\mu_{M, \text{layer}}^\circ$ are standard chemical potentials, namely $\mu_M(a_M/z = 1) = \mu_M^\circ$ and $\mu_{M, \text{layer}}(a_{M, \text{layer}}/z = 1) = \mu_{M, \text{layer}}^\circ$. Of course, for different units of a_M and $a_{M, \text{layer}}$, μ_M° and $\mu_{M, \text{layer}}^\circ$ have different values.

Different sol particles are either positive or negative. In positive sols the cation is fixed and φ_{outer} , $\Delta\varphi$, $\Delta^1\varphi$, and $\Delta\varphi_M$ are positive, while z , the valency of the counter ion M is negative. In negative sols the anion is fixed and φ_{outer} , $\Delta\varphi$, $\Delta^1\varphi$, and $\Delta\varphi_M$ are negative while z is positive. Then $z \Delta\varphi_M$ is the same product, *i. e.* it has the same significance for positive or negative sols, namely for sols with fixed anions or cations.

When the term absolute values is used for z or $\Delta\varphi_M$ it means that regardless of the sign of the two parameters their positive values are used in the equations and their product is always positive:

$$\begin{aligned} |z| \Delta\varphi_M = z |\Delta\varphi_M| = |z \Delta\varphi_M| > 0 \\ (z < 0, \Delta\varphi_M > 0; z > 0, \Delta\varphi_M < 0) \end{aligned} \quad (22)$$

* J. Th. G. Overbeek, *Croat. Chem. Acta* 42 (1970) 505.

The use of the term »absolute« for this purpose is common in mathematics. For the sake of simplicity the signs || designating absolute values were omitted throughout the paper.

b. Arbitrary Assumptions

There are three possibilities for the assessment of the plots $z \Delta\varphi_M$ against $\log_e (a_M/a_{M, \text{layer}})$ of eq. (8). These are:

1. For any value of $a_M/a_{M, \text{layer}}$, the product $z \Delta\varphi_M$ does not depend on z . Consequently a single plot for all values of z would represent eq. (8).

2. For different z values the plots are parallel lines but not equidistant.

3. For different z values the plots are parallel lines and they are equidistant.

Of these three only case 3. is valid. According to Coulomb's formula $E = ze\varphi$, the energy E of an ion in an electrostatic field φ is the higher the higher is the charge z of the ion. This eliminates case 1. In eq. (8) there is one independent variable only, i. e. $\log_e (a_M/a_{M, \text{layer}})$. Consequently, the plots for different z values are parallel lines and therefore cases 2. or 3. only can be valid. If ions of increasing valencies are brought to a given potential, the energy of the ion will be, because of the Coulomb's formula, proportional to z . It follows that the plots can be equidistant only, which eliminates case 2.

Consequently, the generally accepted definitions (eqs. (4) and (5)) of the electrochemical potential are insufficient and the distance between the plots $\Delta^1\varphi$ can be introduced in eq. (8) in two ways. The first possibility of improving eqs. (4), (5), and (8) is in changing the symbols μ_M° , $\mu_{M, \text{layer}}^\circ$, and $\Delta\mu_M^\circ$ into $\tilde{\mu}_M^\circ$, $\tilde{\mu}_{M, \text{layer}}^\circ$, and $\tilde{\Delta}\mu_M^\circ$. The symbol for standard chemical potential, μ° , stands for terms whose physical significance is that of standard electrochemical potential, $\tilde{\mu}^\circ$. Consequently $\Delta\mu_M^\circ$ (which is in fact $\tilde{\Delta}\mu_M^\circ$) should be divided into the standard chemical part and the standard electrostatic part. This was done by the aid of eqs. (9) and (10).

The second possibility is in dividing the variable product $z \Delta\varphi_M$ into the variable potential and the constant standard electrostatic potential. This was done by the aid of eqs. (4a) and (5a).

In the first case instead of eq. (8) one can write

$$z \Delta\varphi_M = \Delta\mu_{M^\circ}^\circ / F + z \Delta^1\varphi + (RT/F) \log_e (a_M/a_{M, \text{layer}}) \quad (8a)$$

and in the second case

$$(z \Delta\varphi_M)_{z=0} = z (\Delta\varphi_M - \Delta^1\varphi) = \Delta\mu_{M^\circ}^\circ / F + (RT/F) \log_e (a_M/a_{M, \text{layer}}) \quad (8b)$$

It is obvious that in eqs. (4a), (5a), and (8b) μ_M° , $\mu_{M, \text{layer}}^\circ$, and $\Delta\mu_M^\circ$ equal $\mu_{M^\circ}^\circ$, $\mu_{M^\circ, \text{layer}}^\circ$, and $\Delta\mu_{M^\circ}^\circ$, respectively. The ions M are assumed to be equal in all properties (also in standard chemical potentials) except in charge. Equations (8a) and (8b) are identical.

The way in which different plots are arranged in Fig. 1 with respect to each other and the introduction of the constant term $\Delta^1\varphi$ are not arbitrary—they are the only possible correct way to derive the equilibrium conditions from eq. (3).

This also explains how Professor Overbeek (second but last paragraph) obtained, in eq. (11a), the product $2z\Delta^1\varphi$ instead of $z\Delta^1\varphi$. Namely, by inserting in eq. (8b) the term $\Delta\mu_M^0/F = \Delta^0\varphi + z\Delta^1\varphi$ (10) instead of $\Delta\mu_M^0/F = \Delta^0\varphi$ (9) Professor Overbeek calculated twice the same factor $z\Delta^1\varphi$. It is important, however, to note that Professor Overbeek derives also a summand in eq. (11a), which is proportional to z .

In a sol of constant dispersity the surface area and the number of charges are assumed to be constant. Then the volume at disposal to each single ion is proportional to the thickness of the solvent layer surrounding the particles. The thickness of the solvent layer can be assumed infinite. Any variation of the thickness beyond that corresponding to a very small limiting value (probably of the order of several tens of effective radii of solvent molecules), or the variation of a_M , do certainly not affect the activity of the fixed ion or the counter ion, *i. e.* the number of their collisions with solvent molecules. This is equivalent to the assumption that the effective thickness of the double layer, consequently also the double layer volume, are constant. Professor Overbeek should provide a proof to support his claim that the double layer volume cannot be assumed constant during the variation of a_M .

There is no doubt that the basic condition of equilibrium between two ions M and M' of valencies z and z' is given by

$$z'(\tilde{\mu}_M - \tilde{\mu}_{M, \text{layer}}) = z(\tilde{\mu}_{M'} - \tilde{\mu}_{M', \text{layer}}) \quad (23a)$$

or

$$z' \Delta \tilde{\mu}_M = z \Delta \tilde{\mu}_{M'} \quad (23b)$$

which corresponds to the zero free energy ($= \Delta G$) condition in electrochemical systems postulated by thermodynamics, *i. e.* to

$$\Delta G = \sum z_j \Delta \tilde{\mu}_{M_j} = 0 \quad (23c)$$

The equilibrium activities in ion exchange can be defined by the following three parameters: the thermodynamic equilibrium constant using activities K_a , the same constant using equivalent ionic fractions K_α , and the separation factor S . They are defined as follows

$$K_a = (a_M/a_{M, \text{layer}})^{z'} (a_{M', \text{layer}}/a_{M'})^z \quad (24)$$

$$K_\alpha = (\alpha/x)^{z'} [(1-x)/(1-\alpha)]^z \quad (25)$$

and

$$S = (a_M/a_{M, \text{layer}}) (a_{M', \text{layer}}/a_{M'}) = \alpha(1-x)/x(1-\alpha) \quad (26)$$

The total activity is defined by $a_M + a_{M'} = a_{Y^-}$, the equivalent ionic fraction of M in the bulk liquid is defined by $\alpha = a_M/a_{Y^-}$ and of M' by $1-\alpha = a_{M'}/a_{Y^-}$. In the layer the equivalent ionic fractions are $x = a_{M, \text{layer}}/\gamma$ and $1-x = a_{M', \text{layer}}/\gamma$. The ion exchange capacity is $\gamma = a_{M, \text{layer}} + a_{M', \text{layer}}$.

The thermodynamic definitions of the above three parameters can be given in the following way

$$K_a = \exp [z'z(\Delta\varphi_M - \Delta\varphi_{M'}) - (z' - z)\Delta^0\varphi] F/RT \quad (24a)$$

$$K_\alpha = \exp [z'z(\Delta\varphi_M - \Delta\varphi_{M'}) - (z' - z)\Delta^0\varphi] F/RT - (z' - z) \log_e (a_{Y^-}/\gamma) \quad (25a)$$

and

$$S = \exp [(z' - z) \Delta^1\varphi + z \Delta\varphi_M - z' \Delta\varphi_{M'}] F/RT \quad (26a)$$

Professor Overbeek proposes the equality

$$\Delta\varphi_M = \Delta\varphi_{M'} \quad (27)$$

When inserted in the above definitions it gives

$$K_a = \exp [(z - z') \Delta^0\varphi F/RT] \quad (24b)$$

$$K_a = \exp (z - z') [\Delta^0\varphi F/RT + \log_e (a_{Y^-}/\gamma)] \quad (25b)$$

and

$$\begin{aligned} S &= \exp [(z' - z) (\Delta^1\varphi - \Delta\varphi_M) F/RT] = \\ &= \exp [(z' - z) (\Delta^1\varphi - \Delta\varphi_{M'})] F/RT \end{aligned} \quad (26b)$$

The equality we propose reads

$$z \Delta\varphi_M = z' \Delta\varphi_{M'} = \Delta\varphi = \text{var.} \quad (28)$$

When inserted in eqs. (24a), (25a), (26a) it gives

$$K_a = \exp [(z' - z) (\Delta\varphi - \Delta^0\varphi) F/RT] \quad (24c)$$

$$K_a = \exp (z' - z) [(\Delta\varphi - \Delta^0\varphi) F/RT - \log_e (a_{Y^-}/\gamma)] \quad (25c)$$

and

$$S = \exp (z' - z) \Delta^1\varphi F/RT \quad (26c)$$

According to the fixed charge model of exchangers one would expect that at least one of the K parameters is determined, besides of the standard chemical term also by an electrostatic energy term and that it is constant when $z' - z = \text{const.}$ Professor Overbeek proposes eq. (24b) where K_a is not determined by an electrostatic energy term but is constant because the standard chemical potential $\Delta^0\varphi$ is constant. This means that the electrostatic energy forces do not play any role in the equilibrium, or that the ions in the exchanger are not dissociated. K_a (eq. 25b) is not defined by an electrostatic energy term either. Neither K_a nor S (eq. 26b) are constant because a_{Y^-} and $\Delta\varphi_M$ are not constant.

Professor Overbeek's claim expressed by eq. (27) corresponds to the claim that in a mixture of ideal gas molecules of different mass, the velocity of the molecules is constant but not their energy ($= kT$, k Boltzmann constant, T abs. temperature).

The only constant electrostatic term, besides $\Delta^0\varphi$, in an ideal exchanger for which eqs. (4), (5), (8), (11) are valid, is $\Delta^1\varphi$. The latter is explained to be constant because of the constant $\gamma = a_{M, \text{layer}} + a_{M', \text{layer}}$ (eqs. (19), (20), (21)). Therefore, for $z' - z = \text{const.}$ S and K_a are constant in an ideal exchanger (because $\Delta\varphi$, $\Delta\varphi_M$ or $\Delta\varphi_{M'}$ is proportional to $\log_e (a_{Y^-}/\gamma)$ at $\alpha/x = \text{const.}$ eq. (8)), whereas K_a is not constant.

Ion exchange experiments on AgI seem to confirm its ideal properties in the above sense, probably because of its low charge density γ/A .

Synthetical high capacity ion exchangers of the resin type are not ideal since $\Delta\varphi$, $\Delta\varphi_M$ are not proportional to $\log_e a_M$ (eqs. (4), (5)). The mean distance of M from the ionogenic group, and therefore also $\Delta\varphi_M$, are not reversibly variable. In an extreme case $\Delta\varphi$ would be constant and therefore K_a would

be a constant parameter too (eq. (24c)). Consequently $\Delta^1\phi$, S , and K_a (for $z' - z = \text{const.}$) would not be constant. In weak exchangers only one could assume that the ions M are not dissociated and that chemical forces only are responsible for equilibrium, in which case eq. (24b) would define the equilibrium. In this case the fixed charge model is not applicable any more and eq. (24b) can be derived by simple chemical thermodynamics avoiding any electrostatic terms.

c. Inconsistencies

The electrostatic potential ϕ_{outer} in the vicinity of the fixed ion varies according to Coulomb's formula

$$\phi_{\text{outer}} = z^{\pm} e/Dr \quad (32)$$

The elementary electron charge is e , the distance from the ion r , the dielectric constant of the medium D , the valency of the ion z^{\pm} . The potential of the central ion of the Debye-Hückel theory varies in the same way according to Coulomb's formula. The fact that the ions are fixed, even if their arrangement is constant, does certainly not indicate that Coulomb's formula is not valid in this case and that the electrostatic potential is not variable with r . The potential of the (counter) ionic atmosphere equals the potential $z \Delta\phi_M$, but is of opposite sign. By the present theory and by the concept of fixed charges it is suggested how to derive the variation of $\Delta\phi_M = \Delta\phi/z$ with the counter ion activity a_M in the bulk liquid. Professor Overbeek's claim that $\Delta\phi_M = \phi_{\text{outer}} - \phi_{\text{liquid}}$ should be assumed constant is therefore in contradiction with the basic assumption of the Debye-Hückel theory, namely that the potential of the ionic atmosphere defined by

$$\psi = -z^{\pm} e \kappa/D \quad (32)$$

and the radius of the ionic atmosphere $1/\kappa$, depend on the electrolyte concentration. Also, Professor Overbeek's conclusion that a_M should be constant is absurd, simply because his supposition that $\Delta\phi_M$ should be constant, is absurd.

In my opinion Professor Overbeek did not succeed in proving that the derivation of the fixed charge double layer potential equations (1) and (2) contains inconsistencies and arbitrary assumptions or that these equations are incorrect.