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On the Theory of Electrocapillarity : I.

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Symbols used throughout this communication :—

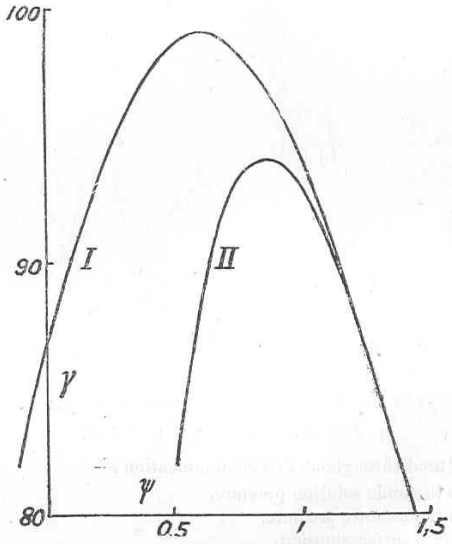
P is the ionic solution pressure.
p is the osmotic pressure.
γ is the surface-tension.
ϵ is the electric charge on unit surface.
ψ is the potential difference between a decinormal calomel electrode and the mercury in the solution.

THE classical theory of electrocapillarity of Lippman-Helmholtz, which considered the process of polarization as the charge of a condenser, led to the following equation of the electrocapillary curve

$$\frac{\partial \gamma}{\partial \psi} = \epsilon. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

According to this theory, the maximum surface-tension corresponds to the zero of the potential difference between the mercury and the solution. The experimental investigations of Rothmund*, Smith †, and Gouy ‡ have shown that this relation cannot hold generally: solutions of electrolytes which give complex salts with mercury show anomalies; the maximum of the electrocapillary curve is depressed and displaced from its normal position so as to correspond to greater values of ψ (see fig. 1, where the electrocapillary curves of $n/1$ KNO_3 and $n/1$ KI are drawn).

Fig. 1.



I.—$n/1$ KNO_3. II.—$n/1$ KI.

Nernst § showed that equation (1) may also be deduced from his "osmotic" theory of potential differences. To explain the observed anomalies, Nernst conjectured that the ions which form the double layer may have an influence on

* *Zeit. phys. Chem.* xv. p. 1 (1894).
† Phil. Trans. A. cxciii. p. 83 (1900).
‡ *Ann. chim. phys.* (7) xxix. p. 145 (1903).
§ Wied. *Ann.* lviii. (1896), *Beilage*; *Zeit. Electrochemie*, vii. p. 253 (1900).

the surface-tension independent of their electric charges and not involved in equation (1).

Freundlich * and Gouy † directed their attention to the importance of adsorption phenomena in the study of electrocapillarity. According to Gouy, ϵ is zero at the maximum of the electrocapillary curve, but there may be a potential difference between the solution and the mercury, caused by adsorbed layers of ions. I shall try to show that this point of view is the correct one and that it is incompatible with Nernst's theory of ionic solution pressure. First, we must consider the problem of the dropping electrode.

With the object of explaining the mechanism of working of a dropping electrode, the Lippman-Helmholtz theory assumes a constant quantity of electricity to be on an insulated mass of mercury; therefore the charge on unit surface and the potential difference between the solution and mercury both decrease with increase of surface. But Palmaer's ‡ experimental investigations, in agreement with Nernst's theory, have shown that the primary effect of a dropping electrode is to change the concentration of ions of mercury in the solution. If $P > p$, the potential difference between mercury and solution and the charge of the mercury surface are both negative; when the mercury surface is increased ions enter into the solution and the potential of mercury therefore increases. If $P < p$, the potential difference and the charge of the mercury are positive, by surface increase ions of mercury are removed from the solution and the potential of mercury decreases. Finally, if $P = p$—"null" solution—the potential difference and the charge of the mercury are zero, surface increase does not influence the concentration of ions of mercury, and the potential of a dropping electrode has the same value as the potential of a still one. The potential of every dropping electrode is bound to approach, independently of p, the same value, when the rate of surface increase becomes infinite; practically we obtain the limit value, as Paschen § has shown, if the end of the continuous part of the jet is in the surface of the solution.

Thus, if Nernst's "osmotic" theory were exact, Paschen's dropping electrodes and Palmaer's null solutions would give us a method of measuring absolute potentials not influenced

* *Kapillarchemie*, p. 184.
† *C. R.* cxlvi. p. 622 (1908): cxxxi. p. 939 (1900).
‡ *Zeit. phys. Chem.* xxv. p. 265 (1898); xxviii. p. 257 (1899); xxxvi. p. 664 (1901); lix. p. 129 (1907).
§ Wied. *Ann.* xli. p. 42 (1890); xliii. p. 585 (1891).

by the anomalies of the electrocapillary curves. But the investigations of Paschen, and especially those of Smith and Moss*, have shown that the potential of the dropping electrode corresponds to the maximum of the electrocapillary curve even in the case of anomalous curves of electrolytes forming complex salts. The only attempt to explain quantitatively this coincidence, which we shall call with Smith and Moss Paschen's relation, was made by Krueger†. Krueger assumes that on the mercury surface there occurs adsorption of mercury salt and arrives at the following equation :

$$\frac{\partial\gamma}{\partial\psi}=\epsilon+\mathrm{F}(k-1)c\delta,$$

where F is 96541 coulombs, k the distribution coefficient of mercury salt between the surface-layer and the bulk of the solution, c the concentration of mercury salt in the solution, and δ the thickness of the surface-layer. Let us compare two solutions like KI and KCl at equal values of ψ : the concentration of mercury in the KI solution will be much higher on account of the complex salt which HgI_2 gives with KI ; the term $\mathrm{F}(k-1)c\delta$ will have a considerable value and cause the observed anomaly of the electrocapillary curve.

The maximum corresponds to a value of ψ which makes ϵ equal to $-\mathrm{F}(k-1)c\delta$; the quantity of mercury salt adsorbed on unit surface therefore exactly corresponds to the quantity of mercury which entered the solution in the form of ions when the surface was increased by unity. It is obvious that under these conditions surface increase does not produce any change of concentration and the solution is a "null" one. Further, the negative value of ϵ increases with increasing stability of the corresponding complex salts, and accordingly the maximum corresponds to greater values of ψ, *i. e.* it is displaced to the right.

Krueger's reasoning is quite correct, but, as we shall show later, his supplementary term is probably much too small to account for the anomalies observed ; at any rate, Krueger's theory is not applicable to the anomalous curves of organic substances which Gouy‡ has discovered. A suitable example of these curves may give the electrocapillary curve

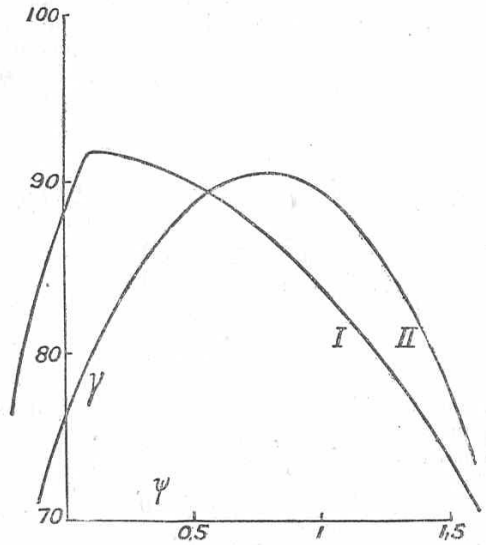
* Phil. Mag. (6) xv. p. 478 (1908).

† *Nachr. d. Ges. d. Wiss. Göttingen Math.-phys. Klasse*, 1904, p. 33 ; *Zeit. Electr.* xix. p. 681 (1913).

‡ *Ann. chim. phys.* (8) viii. p. 291, and ix. p. 75 (1906).

of $n/1$ Na_2SO_4 saturated with paraldehyde (fig. 2, I.). The middle part of the curve is here cut away and the maximum is displaced to the left. Other organic substances, like pyrogallic acid, give curves with a maximum displaced to the right (fig. 2, II.). The potential difference solution / mercury

Fig. 2.



I.—Na_2SO_4+paraldehyde. II.—Na_2SO_4+pyrogallic acid.

does not change when paraldehyde or pyrogallic acid is added to the solution, no complex salts are therefore formed and Krueger's supplementary term must vanish. Besides, this term can cause only a displacement of the maximum to the right and never one to the left, as we usually observe in solutions of organic substances.

We shall show that Paschen's relation still holds with these solutions and that this relation can be deduced from purely thermodynamical considerations without any special assumptions as to the nature of the observed anomalies. With this purpose let us consider the classical demonstration of equation (1).

Let us suppose that a drop of mercury and an electrode, reversible for an anion, are immersed in a solution. We shall assume the concentration of the corresponding anion to be great as compared with the concentration of ions of mercury.

In consequence we may assume that the potential of the electrode remains constant when the potential of the mercury or its surface area is varied. Between the mercury and the electrode an electromotive force is inserted.

Let c be the concentration of mercury in the solution in gram-equivalents per c.cm., s the surface area of the mercury, ψ the potential difference between the electrode and the mercury, and E the quantity of electricity which has passed through the solution from the electrode to the mercury since a certain moment. Independently of the original composition of the solution the state of the system is wholly determined by the quantities s and ψ. If we increase s by ds and E by dE, the work performed will be

$$dA=\gamma ds+\psi dE=\left(\gamma+\psi\frac{\partial E}{\partial s}\right)ds+\psi\frac{\partial E}{\partial \psi}d\psi,$$

whence

$$\frac{\partial\left(\gamma+\psi\frac{\partial E}{\partial s}\right)}{\partial\psi}=\frac{\partial\left(\psi\frac{\partial E}{\partial\psi}\right)}{\partial s}$$

and

$$\frac{\partial\gamma}{\partial\psi}+\frac{\partial E}{\partial s}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let us now consider the change in potential of an insulated mercury mass by surface increase.

Since now dE is zero,

$$\frac{\partial E}{\partial s}ds+\frac{\partial E}{\partial\psi}d\psi=0$$

and

$$\frac{\partial\gamma}{\partial s}=-\frac{\frac{\partial E}{\partial s}}{\frac{\partial E}{\partial\psi}}=\frac{\frac{\partial\gamma}{\partial\psi}}{\frac{\partial E}{\partial\psi}};$$

$\frac{\partial E}{\partial\psi}$ is the quantity of electricity which must pass through the solution to increase ψ by unity. This quantity is partly spent in changing the concentration of the solution, partly in charging the double layer

$$\frac{\partial E}{\partial\psi}=\left(\frac{\partial E}{\partial\psi}\right)_{s=0}+\int_0^s\frac{\partial^2 E}{\partial s\partial\psi}ds=-v\mathrm{F}\frac{\partial c}{\partial\psi}-\int_0^s\frac{\partial^2\gamma}{\partial\psi^2}ds,$$

whence

$$\frac{\partial\psi}{\partial s}=\frac{-\frac{\partial\gamma}{\partial\psi}}{v\mathrm{F}\frac{\partial c}{\partial\psi}+\int_0^s\frac{\partial^2\gamma}{\partial\psi^2}ds}, \quad . \quad . \quad . \quad . \quad (3)$$

v being the volume of the solution.

If $\frac{\partial\gamma}{\partial\psi}$ is zero, $\frac{\partial\psi}{\partial s}$ must also be zero, consequently, if the concentration of ions of mercury in the solution corresponds to the maximum value of the surface-tension, the potential of an insulated mercury mass does not change when its surface is increased, *i. e.* such a solution is a "null" one.

The denominator of the right-hand side of equation (3) is always negative; in fact, $\frac{\partial c}{\partial\psi}<0$, and as Gouy's * numerous determinations have shown $\frac{\partial^2\gamma}{\partial\psi^2}<0$; $\frac{\partial\psi}{\partial s}$ and $\frac{\partial\gamma}{\partial\psi}$ are therefore quantities of the same sign and the potential of mercury approaches, when its surface is increased, the value which corresponds to the maximum surface-tension.

Up to the present, we have considered a solution of uniform composition, depending on the value of s; if matters were adequate to our supposition, we could, by increasing the surface, approach the maximum of the electrocapillary curve as closely as we wished and thus convert the solution into a "null" one.

In reality a dropping electrode changes the composition of the solution only in its immediate neighbourhood and a steady state soon results, determined by the rate of increase of the surface and by the rate of diffusion. If the concentration of mercury in the solution is low and the end of the continuous part of the jet is just in the surface of the solution, the influence of diffusion nearly vanishes and the potential of the dropping electrode must correspond to the maximum of the electrocapillary curve.

To verify this inference I measured both quantities in different solutions of organic substances with anomalous electrocapillary curves. The results are given in Table I. Column I. contains the maximum E.M.F., determined with a sensitive capillary electrometer of the form used by Gouy, the large mercury electrode being immersed in a $n/10$ solution of KCl; column II. the E.M.F. of the cell: Paschen dropping electrode solution/decinormal calomel electrode, both in volts.

TABLE I.

	I.	II.
$n/1$ NaCl+paraldehyde (saturated)	0·225	0·216
$n/1$ NaCl+ethyl acetate „	0·257	0·259
$n/1$ NaCl+isoamyl alcohol „	0·307	0·315
$n/4$ HCl +metachloraniline „	0·612	0·582
$n/1$ NaCl+pyrogallic acid (M)	0·809	0·770
$n/2$ KCN+ „ „ „	0·900	0·889

* *Ann. chim. phys.* (7) xxix. p. 230 (1903).

We see that, in spite of the great difference in the positions of the maxima, Paschen's relation always holds within the limits of experimental error.

Let us now examine two circumstances which can cause an apparent contradiction with Paschen's law.

(1) Let us suppose that there is in the solution a very active substance, which even at low concentrations displaces the maximum of the electrocapillary curve. Every mercury drop adsorbs and removes from the solution a certain quantity of the active substance. Its concentration in the immediate neighbourhood of the dropping electrode must be less than the concentration of the original solution, and therefore the potential of the dropping electrode has a less displaced value than that one which corresponds to the maximum of the electrocapillary curve, as determined by the capillary electrometer.

This discrepancy may be of importance only if the concentration of the active substance is very low, at any rate, when the concentrations of all components of the solution (ions of mercury of course excepted) are high enough, it vanishes as we see from Table I.

(2) With the capillary electrometer we measure the static values of the surface-tension which correspond to an equilibrium of the distribution of all components between the surface-layer and the bulk of the solution. If this equilibrium has not time to establish itself while the drop is being formed, there must be a discrepancy between the data as given by the dropping electrode and the capillary electrometer. We may expect this discrepancy to be especially great in the case of solutions which contain a small quantity of an active substance in presence of a great excess of an inactive one. Such solutions, according to Gouy *, show "electrocapillary viscosity," *i. e.* the meniscus of the capillary electrometer follows the variations of pressure and potential with some delay, and there is a perceptible difference between the surface-tension of a fresh meniscus and the final value of surface-tension. In fact, Palmaer's "null" solution $0{\cdot}1\,n$ KCl + $0{\cdot}01\,n$ KCN, which shows electrocapillary viscosity, shows also a contradiction with Paschen's relation: the dropping electrode potential is here 0·574 volt, in good agreement with the position of the maximum of the electrocapillary curve of pure $0{\cdot}1\,n$ KCl (0:57), whereas a curve plotted from the final surface-tension values of $0{\cdot}1\,n$ KCl + $0{\cdot}01\,n$ KCN has a maximum corresponding to 0·64 volt. A fresh meniscus gives data which are included

* *Ann. chim. phys.* (7) xxix. p. 239 (1903).

between these two limits. Obviously in such a case equation (2) cannot be verified by means of a dropping electrode, and it would be advisable to use a slowly increasing surface.

Let us now consider the transition from equation (2) to the classical equation (1). We shall admit that the change of the potential difference solution / mercury caused by surface increase, depends only on the change of the concentration of mercury. This is not quite correct, as the value of the potential difference may also be influenced by other components of the solution, but as $d\psi$ is proportional to $\frac{dc}{c}$ and the concentration of mercury in the solution is very small as compared with the concentrations of other components, we may neglect their influence.

Let us suppose that there are M gram-equivalents of mercury in the solution when s and E are zero; if a quantity of electricity equal to E passes through the solution $\frac{E}{F}$ gram-equivalents of mercury are removed from the solution; likewise $\frac{\epsilon}{F}+\Gamma_{Hg}$ gram-equivalents are removed if the surface is increased by unity, where Γ_{Hg} is the excess of mercury in gr.eq. per cm.^{2} of the dividing * surface; where

$$c=\frac{M-\frac{E}{F}-\int_0^s\left(\frac{\epsilon}{F}+\Gamma_{Hg}\right)ds}{v}$$

and

$$\left(\frac{\partial E}{\partial s}\right)_\psi=-\epsilon-\Gamma_{Hg}F.$$

On substituting this value of $\frac{\partial E}{\partial s}$ in (2) we obtain

$$\frac{\partial\gamma}{\partial\psi}=\epsilon+\Gamma_{Hg}F, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

an equation which can be regarded as a generalized equation of Krueger.

It is easy to show that the second term of the right-hand side of equation (4) may sometimes be of importance. Let us consider a drop of zinc amalgam immersed in a solution of zinc sulphate. In the solution and in the surface-layer

* The position of the dividing surface is chosen as to make Γ_{H_2O} zero.

there are ions of two kinds: $Zn^{\cdot\cdot}$ and SO_4'', so that we can put

$$\epsilon=(-\Gamma_{Zn^{\cdot\cdot}}+\Gamma_{SO_4''})F;$$

further

$$\Gamma_{Zn}=\Gamma_{Zn^{\cdot\cdot}}+\Gamma_{ZnSO_4},$$

and if we neglect the influence of undissociated molecules

$$\Gamma_{Zn}=\Gamma_{Zn^{\cdot\cdot}},$$

whence

$$\frac{\partial\gamma}{\partial\psi}=\Gamma_{SO_4''}F\ ^{*}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

With the help of this equation we can calculate the maximum possible value which $\frac{\partial\gamma}{\partial\psi}$ can have when zinc amalgam is immersed in $n/1000$ $ZnSO_4$. The amalgam is negatively charged, in the surface-layer there is therefore a *deficiency* of SO_4'' ions. We may assume the thickness of the double layer to be approximately equal to 10^{-7} cm. The absolute value of $\Gamma_{SO_4''}$ is at any rate less than 10^{-7} cm. $\times 10^{-6}$ gr. eq./c.cm. $=10^{-13}$ gr. eq./cm.^{2}; this corresponds to a value of $\frac{\partial\gamma}{\partial\psi}$ equal to 10^{-8} coulomb/cm.$^2=10^{-1}$ dyne/volt cm., which can be neglected. The surface-tension of a zinc amalgam immersed in a dilute solution of a zinc salt does not depend therefore on its potential, nor, in consequence, on the concentration of the solution. In this particular case $\frac{\partial\gamma}{\partial\psi}$ is zero because the quantities ϵ and $\Gamma_{Hg}F$ have equal absolute values and opposite signs.

Let us suppose now that in the solution there is a great excess of a salt with another cation, for instance, Na_2SO_4, then

$$\epsilon=-(\Gamma_{Na^{\cdot}}-\Gamma_{Zn^{\cdot\cdot}}+\Gamma_{SO_4''})F,$$

or, if the concentration of $ZnSO_4$ is low as compared with that of Na_2SO_4,

$$\epsilon=(-\Gamma_{Na^{\cdot}}+\Gamma_{SO_4''})F.$$

As there is now an *excess* of $Na^{\cdot}$ in the surface-layer, the value of ϵ is no longer limited and the surface-tension will vary with ψ and in consequence with the concentration of $ZnSO_4$. To verify this inference I measured with the capillary electrometer the surface-tension of a zinc amalgam in solutions of $ZnSO_4$ and Na_2SO_4. The results are given in Table II. (the maximum surface-tension between mercury and water is assumed to be 100).

* The reasoning above is not quite correct, the concentration of $Zn^{\cdot\cdot}$ being, contrary to the assumption we have made previously, of the same order of magnitude as the concentration of SO_4''. Nevertheless, as it is easy to show, equation (5) holds if we denote by ψ the potential difference between an imaginary SO_4'' electrode and the zinc electrode. Besides that does not affect the following considerations.

TABLE II.

n. $ZnSO_4$	91·4
$1/1000\,n$. $ZnSO_4$	91·2
n. $ZnSO_4+n$. Na_2SO_4	91·0
$1/1000n$. $ZnSO_4+n$. Na_2SO_4	89·8

The experimental values are in agreement with the theory; unfortunately, the lack of mobility of the meniscus does not allow of rendering these measurements more accurate or of extending them to still more dilute solutions. Let us now consider the mechanism of working of a dropping electrode in these solutions. To simplify the problem we may neglect the presence of SO_4'' ions. If a drop of amalgam is immersed in a solution of zinc sulphate, zinc ions enter the solution, but, as no other ions are present, they must remain in the double layer to counterbalance the negative charge of the amalgam. The formation of a new surface is therefore not accompanied by any change of concentration, and the potential of a dropping electrode is equal to the potential of a still one. The conditions are quite different when there is in the solution a great excess of sodium ions; these take the place of the zinc ions in the double layer, and the zinc ions enter the bulk of the solution. Thus, in presence of an excess of sodium ions the formation of a new surface lowers the concentration of sodium ions and increases the concentration of zinc ions. The result is an alteration of the potential.

Table III. contains the potential difference between dropping and still amalgam in different solutions of $ZnSO_4$ and Na_2SO_4, the amalgam jet being surrounded by a hydrogen atmosphere.

TABLE III.

$0{\cdot}001n$. $ZnSO_4$	0·003 volt
$0{\cdot}001n$. $ZnSO_4+n$. Na_2SO_4	0·037 ,,
$0{\cdot}0001n$. $ZnSO_4$	0·011 ,,
$0{\cdot}0001n$. $ZnSO_4+n$. Na_2SO_4	0·055 ,,

We see that according to the theory, the addition of Na_2SO_4 greatly increases the potential difference; the small potential difference observed without Na_2SO_4 is due probably to the presence of SO_4'' ions, which we neglected in our

reasoning. Thus the term ΓF is of importance if the double layer is built up by the same ions whose concentration determines the value of the potential difference, but so far as we are dealing with pure mercury its influence is probably very small. In fact, along nearly the whole of the electrocapillary curve the mercury concentration in the solution is very low as compared with the concentration of other ions. If we suppose with Krueger that the anomalies of the electrocapillary curves of anorganic electrolytes are due to the adsorption of mercury, we must assume that salts of mercury are much more adsorbed at the mercury surface than any other known substances. Thus, the addition of $n/100$ KI to $n/1$ Na_2SO_4 lowers the surface-tension which corresponds to $\psi=0{\cdot}6$ volt by 5 per cent. To produce such a lowering effect, a very active substance like amyl alcohol ought to be present at a concentration as high as M/10, whereas the corresponding concentration of mercury in the solution, as we may easily calculate with the help of Nernst's formula from the experimental data of Abegg and Sherill*, is 10^{-16}. Therefore it seems to me reasonable to admit that the lowering effect is not caused by the mercury salts, but by the KI (viz. by I'), whose concentration is high enough.

Krueger quotes in favour of his theory that the anomaly of the electrocapillary curves increases with increasing stability of the corresponding complex salts, *i. e.* with the concentration of mercury in the solution at constant potential; but it is easy to show that this relation does not hold. In fact, the stability of complex salts increases in the following order: nitrates, sulphates, iodides, cyanides, whereas the maximum surface-tension of normal solutions are: KNO_3, 98·95; K_2SO_4, 100·17; KI, 94·0; KCN, 96·6.

In the following we will make the probable assumption that the adsorbability of mercury salts is a quantity of the same order of magnitude as that of other substances and neglect the term $\Gamma_{Hg}F$. Equation (4) becomes then identical with the classical equatiom (1)

$$\frac{\partial\gamma}{\partial\psi}=\epsilon, \quad \ldots\ldots\ldots \quad (1)$$

where

$$\epsilon=(\Gamma_{\text{Anions}}-\Gamma_{\text{Cations}})F.$$

In equation (1) ϵ is a function of ψ, whose form is determined by the composition of the solution.

In particular, the value of ψ which makes ϵ zero may vary between very wide limits (0·2 v.–1 v.).

* Abegg's *Handbuch der anorganischen Chemie*, Bd. ii. Abt. 2, p. 648.

When mercury comes in contact with the solution, ions of mercury will enter the solution if $\epsilon<0$, although their osmotic pressure may be greater than the ionic solution pressure of mercury; if $\epsilon>0$, they will be removed from the solution, their osmotic pressure may thereby be less than the ionic solution pressure. Thus we see that, whilst the value of the potential difference between the solution and the mercury is determined only by the osmotic pressure of ions of mercury, contrary to Nernst's theory the direction of the reaction

$$2Hg \rightleftarrows Hg_2^{\cdot\cdot}+2\theta,$$

which takes place when a new surface is formed, depends on the sign of ϵ, and therefore on all active components of the solution.

Also, contrary to Nernst's theory, the existence of a potential difference between solution and mercury is not at all connected with the exchange of ions of mercury. In fact, if the concentration of the ions of mercury corresponds to the zero value of ϵ, no ions at all are exchanged when a new surface is formed; the potential difference which we must assume between solution and mercury to account for the displacement of the maximum can be caused only by adsorbed layers of anions and cations: we are justified in calling it adsorption potential difference.

In conclusion, I gladly take this opportunity of expressing my gratitude to Professor A. Sakhanow for the interest he has taken in the progress of this work.

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