

Citation:

J.J. van Laar, On the asymmetry of the electro-capillary curve, in:
KNAW, Proceedings, 4, 1901-1902, Amsterdam, 1902, pp. 560-577

for which T_{cr} is a minimum. But it may be advisable to wait with the discussion of this and similar cases till an experimental investigation has brought them to light.

If by increase of temperature the surface of coexistence has so far contracted that it no longer covers the whole triangle oxy , a tangent cylindre may be drawn normal to the xy -surface. All the points, in which the tangent cylindre and the surface of coexistence touch, represent mixtures which are in critical tangent-point circumstance. A plaitpoint can never lie on this apparent circumference of the surface of coexistence, except in some special cases. For as the generatrices of this tangent cylindre are parallel to the volume-axis and p must have the same value for the pair of phases coinciding in a plaitpoint, we have

$$\frac{\partial^2 \psi}{\partial v^2} = 0$$

for such a special case. In order not to have $\frac{\partial^2 \zeta}{\partial x_1^2}$ or $\frac{\partial^2 \zeta}{\partial y_1^2}$ negative,

$\frac{\partial^2 \psi}{\partial x \partial v}$ and $\frac{\partial^2 \psi}{\partial y \partial v}$ must be equal to 0. Such a mixture behaves as a

simple substance even under critical circumstances. See for a similar circumstance with a binary system Cont. II page 116. So the plaitpoints lie either on the liquid sheet, or on the vapour sheet of the surface of coexistence. In the first case all mixtures, indicated by points of the xy -surface, lying between the section of the tangent cylindre and the projection of the curve on which the plaitpoints are situated, have retrograde condensation of the first kind. If the plaitpoints lie on the vapour sheet, then such mixtures have r. c. II.

(To be continued).

Physics. — “On the asymmetry of the electro-capillary-curve.” By Dr. J. J. VAN LAAR (communicated by Prof. VAN DER WAALS).

I. We may suppose, that it is well known, that the new theory of the so called *Capillary-Electrometer* of LIPPMANN may be described as follows.

Two mercury surfaces, one large (A), the other small (B) — this latter in the so called capillary — are separated by a conductive liquid C , diluted H_2SO_4 , a solution of KCl , or any other solution. In all

these cases some mercury is solved and a saturated though very diluted solution of Hg_2SO_4 or Hg_2Cl_2 ¹⁾ is formed.

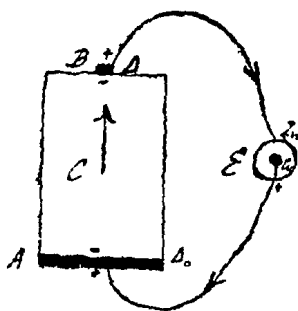


Fig. 1.

The mercury and the solution assume therefore a different potential. The difference between those potentials I call „natural difference of potential”. The concentration of the solved Hg_2^{++} -ions being greater than that, at which the Hg-electrode and these ions are in equilibrium, some Hg_2^{++} -ions are deposited on the mercury, where they are discharged immediately. So at the separating surface between the mercury and the solution is established a so called electric double-layer: on the side of the mercury $+$ electrons, on the side of the solution $-$ ions $\overline{\text{SO}}_4$ or $\overline{\text{Cl}}$. The thus established difference of potential be $V_2 - V_1 = \Delta_0$. (I always indicate the solution by means of the index 2). In the normal case this quantity is negative.

We know however, that the absolute value of this difference of potential will decrease, when the concentration of the Hg_2^{++} -ions in the solution decreases. When we extend the dilution beyond a certain point, the difference reverses its sign, the potential of the mercury becoming $-$, that of the solution $+$, so the electric behaviour of mercury becomes comparable to that of zinc.

How can this dilution at one of the electrodes be brought about?

To that purpose we apply an electromotive force E in a manner as is indicated by the figure. In consequence of the transport of ions, the concentration of the Hg_2^{++} -ions in the solution near the large mercury surface will become greater, that near the small surface will decrease. At this latter surface namely, Hg_2^{++} (and H^+ or K^+) will be continually deposited in consequence of the transport of $\overline{\text{SO}}_4$ or $\overline{\text{Cl}}$ towards the large surface; but when the current of the inserted cell has only passed for a very short time, the concentration of the Hg_2^{++} -ions near the large surface will practically not have varied, near the small surface however it will have varied considerably in consequence of the much greater density of the current.

¹⁾ Not HgCl . The mercurio-ion being proved to be Hg_2^{++} and not Hg^+ . [See e. g. *Oss, Zeitschr. f. Ph. Ch.* 27, 298 (1898)].

The more so, as the solubility of $\text{Hg}_2 \text{SO}_4$ (or $\text{Hg}_2 \text{Cl}_2$) is so small, that the number of $\overset{++}{\text{Hg}_2}$ -ions present in the solution was already very small from the beginning.

Because of this considerable change in concentration near the small surface, the difference of potential soon varies at that place, and it is easy to see, that this „kathodical” polarisation causes the current to cease quite, or nearly quite ¹⁾. Be E namely the electromotive force of the inserted cell, then the intensity of the current has become zero, as soon as the original difference of potential Δ_0 at the small surface has varied so much, that the new value Δ satisfies the equation

$$E = \Delta - \Delta_0,$$

from which follows :

$$\underline{\Delta = \Delta_0 + E} \quad (1)$$

When this value is reached, the concentration ceases to vary and a stationary state is established.

Δ_0 being negative, Δ will, when E increases, first reach a value zero and afterwards when E increases still more, Δ will become positive. For every electromotive force E , which we may apply, we get a definite value of Δ , and so — measuring every time the surface-tension γ of the mercury in the capillary — we get a series of values, which form together a curve

$$\gamma = f(\Delta) \quad \text{or} \quad = F(E),$$

which is called the electro-capillary-curve. This is the curve whose properties we will discuss in this paper.

On purpose I have given the above explanation rather elaborately, because for the theoretical considerations which follow, a clear insight is required in what takes place in the capillary-electrometer according to the new electrochemical theories of NERNST, PLANCK and others. These theories are confirmed brilliantly by the experi-

¹⁾ We shall leave out of account the so called „residual current”, which will be caused by the slow depolarisation by diffusion, the intensity of that current being extremely small.

ments of PALMAER ¹⁾, SMITH ²⁾ and many others, and so the old theory of VON HELMHOLTZ, that of the so called "charging current" has been overthrown. The electromotive forces, calculated according to the old theory, do not agree at all with the experimental data, whereas those, calculated according to the new theory, agree quite well.

II. We will now deduce two relations. First one, giving Δ as a function of the concentration of the Hg_2^{++} ions in the solution; in the second place one, giving γ as a function of Δ .

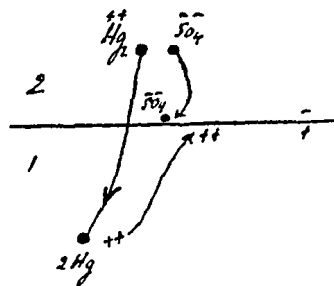


Fig. 2.

In order to find the conditions of equilibrium between a metal (mercury) and a solution (in which the ions of the metal must occur), we imagine a Hg_2^{++} ion to pass the separating surface in the direction from the solution towards the mercury. The mercury is thought +, the solution —. The

molecular *thermodynamic* potential of Hg_2^{++} in the solution be μ_2 , and that of 2Hg in the mercury be μ_1 , then the change of the thermodynamic potential per gram-ion will be :

$$\mu_1 - \mu_2.$$

As in every gram-ion $2\epsilon_0$ electric units are stored, the change of the thermodynamic potential for the passage of a quantity Hg_2^{++} , corresponding with de electric units, will be:

$$\frac{\mu_1 - \mu_2}{2\epsilon_0} de \dots \dots \dots (a)$$

The *electric* potential of the liquid being represented by V_2 , and that of the mercury by V_1 , the passage of de electric units through the bordering layer will work a change of the electric energy equal to

$$(V_1 - V_2) de \dots \dots \dots (b)$$

¹⁾ Z. f. Ph. Ch. 25, 265 (1898); 28, 257 (1899); 36, 664 (1901).

²⁾ Id. 32, 433 (1900).

Finally an accessory process takes place — and to this no sufficient attention has been paid as yet. As soon as a $\overset{++}{\text{Hg}_2}$ -ion has passed from the solution into the mercury, a superfluous $\overline{\text{SO}_4}$ -ion (or $\overline{\text{Cl}}$ -ions) will go to the bordering layer, and in the mercury the + electron, which is liberated, will also move to the bordering layer. In the bordering layer therefore *changes* take place. Let φ_s be the so called *capillary energy* (s representing the surface). This quantity changes, when the $\overline{\text{SO}_4}$ - (or $\overline{\text{Cl}}$ -)ions go from the interior to the bordering layer. For the transport of a quantity $\overline{\text{SO}_4}$, corresponding with de electric units, this change will be:

$$\frac{\partial(\varphi_s)}{\partial e} de (c)$$

In combining (a), (b) and (c), we get the following condition of equilibrium :

$$\frac{\mu_1 - \mu_2}{2 \varepsilon_0} + (V_1 - V_2) + \frac{\partial(\varphi_s)}{\partial e} = 0,$$

or when we call $\mu_2 - \mu_1 = \mu_{12}$, and $V_2 - V_1 = \Delta$, as we have already done :

$$\underline{\frac{\mu_{12}}{2 \varepsilon_0} + \Delta - \frac{\partial p}{\partial \omega} = 0, (2)}$$

where $\omega = \frac{e}{s}$ represents the *surface density* of the charge of the bordering layer.

If we had made the supposition, that the mercury is negative, the solution positive (as is the case when the concentration of the $\overset{++}{\text{Hg}_2}$ -ions is exceedingly small), the electrons in the mercury at the bordering layer would have been negative, and in the solution positive $\overset{++}{\text{Hg}_2}$ -ions would have occurred instead of the $\overline{\text{SO}_4}$ - or $\overline{\text{Cl}}$ -ions. In that case we should have deduced the conditions of equilibrium, by imagining $2 \text{Hg} +$ positive electrons to pass from the mercury into the solution, where they would have formed $\overset{++}{\text{Hg}_2}$. The superfluous negative electrons in the mercury would then go to the bordering layer, while in the solution the $\overset{++}{\text{Hg}_2}$ -ions go thence. In this case we should have got:

$$\frac{\mu_2 - \mu_1}{2\varepsilon_0} + (V_2 - V_1) + \frac{\partial\varphi}{\partial\omega} = 0,$$

where $\frac{\partial\varphi}{\partial\omega}$ is related to the change of the number of Hg_2^{++} -ions in the bordering layer of the solution. So equation (2) would have been :

$$\frac{\mu_{12}}{2\varepsilon_0} + \Delta + \frac{\partial\varphi}{\partial\omega} = 0 \quad (2bis)$$

Let us pay attention to the fact, that in (2) and also in (2bis) the surface-density of the charge ω is always taken positive; Δ can be + or -, but ω is always +.

Formula (2) has already been found by PLANCK ¹⁾, though in another form and deduced in a somewhat different manner. We shall see how great the importance of the supplementary term $\frac{\partial\varphi}{\partial\omega}$ is for the explanation of the asymmetry of the capillary-curve.

Before we proceed to express γ as a function of Δ , we will show how the usual expression of NERNST may be deduced from equation (2). To that purpose the term $\frac{\partial\varphi}{\partial\omega}$, whose value is small, compared with the two other terms, is neglected. So we find :

$$\Delta = - \frac{\mu_{12}}{2\varepsilon_0}.$$

But for μ_{12} we may write :

$$\mu_{12} = \mu_2 - \mu_1 = (\mu_2' + RT \log c) - \mu_1,$$

where, when the solutions are diluted, μ_2' will be independent of the concentration of the Hg_2^{++} -ions. [As we mentioned above, the solubility of Hg_2SO_4 (or Hg_2Cl_2) is so small, that the solutions will always be extremely diluted]. If we write :

$$\mu_1 - \mu_2' = RT \log C,$$

then

$$\mu_{12} = RT \log \frac{c}{C},$$

¹⁾ WIEDEMANN's Annalen 44, 385 (1891).

and therefore:

$$\Delta = \frac{RT}{2 \epsilon_0} \log \frac{C}{c}, \quad \dots \dots \dots (2a)$$

which is the well known formula of NERNST. This formula represents Δ as dependent on the concentration c of the Hg_2^{++} -ions in the solution. C is a constant.

If we express Δ in Volts, and introduce Briggian logarithms, we get as a factor 0,0002, and the equation becomes:

$$\Delta = 0,0001 T \log^{10} \frac{C}{c} \dots \dots \dots (2b)$$

For mercury at 18° the quantity C is $10^{-33,7}$, when we namely put $c=1$ for *normal* concentration of the Hg_2^{++} -ions. For *normal* solutions we get therefore as the value of the difference of potential ($T = 291^\circ,2$):

$$\Delta = 0,0291 \times -33,7 = -0,980 \text{ Volts,}$$

as also NEUMANN and others have found [with the exceedingly small concentration of $\text{Hg}_2 \text{Cl}_2$ in $\frac{1}{10}$ normal KCl-solutions, $\Delta = -0,616$ Volts (OSTWALD)].

From formula (2a) it is clear, that Δ will reverse its sign, when $c = C$, i.e. 10^{-34} -normal.

III. Let us now calculate the surface-tension γ as a function of Δ or ω .

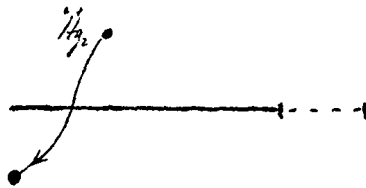


Fig 3.

To that purpose we increase the surface s virtually with an element ds . In that element a new state of the surface must be established. We have called φ the *total* increase of the thermodynamic energy per unit of surface, accompanying this change; therefore an increase of the surface with ds will involve an increase in energy with

$$\varphi ds \dots \dots \dots (a)$$

But this quantity φds , including the formation of a new double-layer, this formation must have been rendered possible by transition of the required number of $\overset{++}{\text{Hg}_2}$ -ions from the solution into the mercury. [We will namely first discuss the case that the mercury is +, the solution -]. Then in the solution $\overset{-}{\text{SO}_4}$ -or $\overset{-}{\text{Cl}}$ -ions are left free, and in the mercury + electrons, which may move to the new separating surface. The total number $\overset{++}{\text{Hg}_2}$ -ions required, is obviously that, corresponding with ωds electric units. But we saw in II, that the change of energy, accompanying the passing of $d\epsilon$ electric units, is (only (a) and (b) have to be added):

$$\frac{\mu_1 - \mu_2}{2 \epsilon_0} d\epsilon + (V_1 - V_2) d\epsilon .$$

When in consequence ωds units pass, this quantity will amount to

$$- \omega \left(\frac{\mu_{12}}{2 \epsilon_0} + \Delta \right) ds .$$

According to (2), we may write this:

$$- \omega \frac{\partial \varphi}{\partial \omega} ds. \dots \dots \dots (b)$$

Moreover for the formation of a new electric double-layer (mercury +, solution -) a (negative) electric energy $\omega ds (V_2 - V_1)$ is required, viz.

$$\omega ds \cdot \Delta \cdot \dots \dots \dots (c)$$

Adding (a), (b) and (c), and representing the mechanical energy, which must counterbalance these changes, by γds ,

we get finally:

$$\gamma = \varphi - \omega \frac{\partial \varphi}{\partial \omega} + \omega \Delta .$$

ω being always +, we have in the case we are treating of (mercury +, solution -):

$$\Delta = - k \omega ,$$

and finally we get the equation

$$\underline{\gamma = \varphi - \omega \frac{\partial \varphi}{\partial \omega} - k \omega^2} \dots \dots \dots (3)$$

and not simply $\gamma = \varphi - k\omega^2$, as was assumed in the old theory, in which the changes of the bordering layer were neglected.

Had we started from the supposition, that the mercury was —, the solution +, a transition of 2 Hg + positive elections from the mercury into the solution — where they would have formed $\overset{++}{\text{Hg}}_2$, — would have been required, in order to render the formation of a new double layer possible; and that would have caused the above deduction to be modified as follows.

The part (b) would have been derived from

$$\omega \left(\frac{\mu_{12}}{2 \epsilon_0} + \Delta \right) ds.$$

But, according to (2bis), this would still have yielded $= - \omega \frac{\partial \varphi}{\partial \omega} ds$, so this part is not modified. The change of the (negative) electric energy on the other hand becomes now $\omega ds (V_1 - V_2)$, i. e.

$$- \omega ds \cdot \Delta,$$

where now Δ is positive $= k\omega$; so finally equation (3) is yielded quite unmodified.

This equation therefore is of general application, as well in the case, that in the solution at the bordering layer negative $\overline{\text{SO}}_4$ - or $\overline{\text{Cl}}$ -ions occur, as in the case that there occur positive $\overset{++}{\text{Hg}}_2$ -ions.

But — and this is a circumstance of great importance — the term $\omega \frac{\partial \varphi}{\partial \omega}$ will in the two cases *not* have the same value for equal values of ω . For it would be a curious coincidence, that the change of energy in the bordering layer, occasioned by adding an infinitely small quantity of $\overset{++}{\text{Hg}}_2$, would be the same as that, occasioned by adding an equal quantity of $\overline{\text{SO}}_4$ or $\overline{\text{Cl}}$. In fact this does not happen. The experiments show clearly, that the curve represented by (3) is *not* symmetrical on the two sides of the point, where ω is zero; and that the curve does *not* consist of one continuous parabola, *but of two parts of quite different parabolae*, which meet in the point where $\omega = 0$. *Only one* of them, namely the *ascending branch* (mercury +, solution —), presents a *maximum near* the point where $\omega = 0$ (so not exactly *at* that point.)

In order to enter into more details, we must first examine what is the form of φ as a function of the quantity ω .

IV. Let us to this purpose state the fact, that φ represents the excess of the thermodynamic potential in the bordering layer above that in the mercury and the solution. Therefore we may write in any case:

$$\varphi = (\varphi_0 + \alpha \omega + \beta \omega^2 + \dots) + A \omega \log c,$$

where c represents the concentration of the $\overline{\text{SO}}_4^-$ or $\overline{\text{Cl}}^-$ ions in the bordering layer, or — when the sign of Δ is reversed — that of the Hg_2^{++} ions. The constant A may have the positive, as well as the negative sign. When the charge spreads in such a way, that it penetrates rather deeply into the bordering layer — as the experiments seem to prove for the case that the Hg_2^{++} ions form the $+$ charge (the mercury being negative) — then A will be positive. So this is the case for the descending branch of the electro-capillary-curve. But when the charge remains more at the surface of the bordering layer, as is the case, when $\overline{\text{SO}}_4^-$ or $\overline{\text{Cl}}^-$ ions form the negative charge in the solution (the mercury being positive), then A is negative. We find this realised in the ascending branch of the curve.

Writing $a\omega$ for c , we get:

$$\omega \frac{\partial \varphi}{\partial \omega} = (\alpha \omega + 2 \beta \omega^2 + \dots) + A \omega \log a\omega + A \omega,$$

and equation (3) takes the following form:

$$\gamma = \varphi_0 - A\omega - (k + \beta) \omega^2 \text{)} (4)$$

This is the accurate equation of the electro-capillary-curve, and in what follows we will determine the value of φ_0 , A and $k + \beta$ for the two parts of the curve — on the left and on the right of the point, where $\omega = 0$.

The maximum is obviously to be found in one of the branches, when

¹⁾ φ_0 is in this equation still a function of the concentration of the electrolyte, as appears from the experiments of SMITH. See i.a. OSTWALD, Lehrbuch I, 531 ff.; EULEB, Z. f. Ph. Ch. 28, 625 (1899); 39, 564 (1901).

$$\omega_m = - \frac{A}{2(k + \beta)}$$

As $k + \beta$ is always positive, and ω must be positive, the maximum can only be found in a branch where A is negative, i.e. in the ascending branch. The value of the maximum is given by the equation

$$\gamma_m = \varphi_0 + \frac{A}{4(k + \beta)}$$

Before we pass to the calculation of a series of experiments of SMITH, we will give to equation (4) another form, where not ω , but the electromotive force E of the inserted cell is used as argument. According to equation (1), we have

$$\Delta = \Delta_0 + E.$$

For the *descending* branch Δ is positive, namely

$$\Delta = k\omega.$$

So we may write for (4):

$$\gamma = \varphi_0 - A \frac{\Delta}{k} - (k + \beta) \frac{\Delta^2}{k^2},$$

or

$$\gamma = \varphi_0 - \frac{A}{k} (\Delta_0 + E) - \frac{k + \beta}{k^2} (\Delta_0 + E)^2 \dots (a)$$

For the *ascending* branch Δ is negative, namely

$$\Delta = -k\omega.$$

So we get:

$$= \varphi_0 + \frac{A}{k} (\Delta_0 + E) - \frac{k + \beta}{k^2} (\Delta_0 + E)^2 \dots (b)$$

When developing, we find:

$$\gamma = \left[\varphi_0 \mp \frac{A}{k} \Delta_0 - \frac{k + \beta}{k^2} \Delta_0^2 \right] + \left[-2 \frac{k + \beta}{k^2} \Delta_0 \mp \frac{A}{k} \right] E - \frac{k + \beta}{k^2} E^2, (5)$$

where the higher sign relates to the descending branch, the lower sign to the ascending branch. This equation may be represented by

$$\gamma = a + bE - cE^2, \dots \dots \dots (6)$$

of which we will determine the coefficients a , b and c .

I have chosen to this purpose a series of experiments of SMITH¹⁾ with $\frac{1}{10}$ -normal KCl as electrolyte. The concentration of the solved Hg_2Cl_2 is here exceedingly small, and the difference of potential between the solution and the mercury is for this "normal-electrode" accurately known (OSTWALD²⁾), namely:

$$\Delta_0 = -0,616 \text{ Volts.}$$

The place, where ω (or Δ) becomes zero, may be determined without difficulty. For from $\Delta = \Delta_0 + E$ follows, that if $\Delta = 0$:

$$E = -\Delta_0 = 0,616 \text{ Volts.}$$

Now in the experiments of SMITH E is expressed in such units that $E = 500$ corresponds to 0,102 Volts. The value

$$0,616 \text{ Volts} = 6,04 \times 0,102 \text{ Volts}$$

corresponds therefore in the units of SMITH with

$$E = 6,04 \times 500 = 3020.$$

V. For the calculation of the *descending* branch we have therefore to take into account only such values of E as are greater than 3020. From this I calculated:

$$a = 29,766, \quad b = \frac{0,8318}{0,102}, \quad c = \frac{0,090}{(0,102)^2}.$$

The following table shows, that these values represent the descending branch in fact with great accuracy.

¹⁾ Zeitschr. f. Ph. Ch. **32**, 460 and 467 (1900).

²⁾ Zeitschr. f. Ph. Ch. **35**, 335 (1900).

	γ calculated.	Found.	Δ
$E = 3000 = 6 \times 0.102 \text{ V.}$	$\gamma = 29.77 + 4.99 - 3.24 = 31.52$	31.41	+ 0.11
3500 = 7 »	$5.82 - 4.41 = 31.18$	31.20	- 0.02
4000 = 8 »	$6.65 - 5.76 = 30.66$	30.70	- 0.04
4500 = 9 »	$7.48 - 7.29 = 29.97$	29.99	- 0.02
5000 = 10 »	$8.32 - 9.00 = 29.09$	29.10	- 0.01
5500 = 11 »	$9.15 - 10.89 = 28.03$	28.00	+ 0.03
6000 = 12 »	$9.98 - 12.96 = 26.79$	26.72	+ 0.07
6500 = 13 »	$10.81 - 15.21 = 25.37$	25.33	+ 0.04
7000 = 14 »	$11.65 - 17.64 = 23.78$	23.79	- 0.01
7500 = 15 »	$12.48 - 20.25 = 22.00$	22.00	± 0.00
8000 = 16 »	$13.31 - 23.04 = 20.04$	20.01	+ 0.03
8500 = 17 »	$14.14 - 26.01 = 17.90$	17.90	± 0.00
9000 = 18 »	$14.97 - 29.16 = 15.58$	15.60	- 0.02

As we see, formula (6) with these values for a , b and c represents the descending branch with extraordinary accuracy. If we leave out of account the value for $E = 3000$, which no longer belongs to the descending branch, as I have shown above, the difference between the calculated and the observed value surpasses nowhere $\frac{1}{6}\%$; only once (at $E = 6000$) the difference is $\frac{1}{4}\%$.

If in (6) we substitute for E the value 6.04×0.102 , we get γ for $\omega = 0$, i. e. φ_0 . So we find

$$\varphi_0 = 31,508.$$

In order to calculate $\frac{A}{k}$ and $\frac{k + \beta}{k^2}$, we combine (5) and (6):

$$\frac{k + \beta}{k^2} = c = \frac{0,090}{(0,102)^2} = 8,651.$$

$$- 2 \frac{k + \beta}{k^2} \Delta_0 - \frac{A}{k} = b = \frac{0,8318}{0,102}.$$

Taking into account, that $\Delta_0 = -0,616$, the latter equation yields

$$\frac{A}{k} = 2 \times \frac{0,090}{(0,102)^2} \times 0,616 - \frac{0,8318}{0,102} = 10,658 - 8,155 = 2,503.$$

It is superfluous to mention, that the manner in which φ_0 is calculated, involves that equating the first term of (5) with $a = 29,766$, an identical value $\frac{A}{k}$ is found.

For the *descending* branch we may therefore write either (according to (6))

$$\gamma = 29,766 + \frac{0,8318}{0,102} E - \frac{0,090}{(0,102)^2} E^2 \left. \vphantom{\gamma} \right\} \dots \dots (7)$$

or, according to (4) $\gamma = 31,508 - 2,503 \Delta - 8,651 \Delta^2$,

putting again Δ for $k\omega$ (Δ positive).

For the calculation of the *ascending* branch we have to make use of the values of E between 0 and 3000. From these I calculated as the most probable values:

$$a = 25,456, \quad b = \frac{2,153}{0,102}, \quad c = \frac{0,1906}{(0,102)^2}$$

At once we see, that we have to deal here with a branch of another parabola than in the descending branch of the electrocapillary-curve; b being nearly three times, c more than twice as great. The slope of the ascending branch is therefore, as all experiments show, steeper than that of the descending one.

The following table may serve to verify the values, found for a , b and c , by means of the experiments. We notice, that the experimental data for the ascending branch are few in number, and moreover are considered as *unreliable* by the experimentators. ¹⁾

Notwithstanding the agreement may be considered to be satisfactory.

¹⁾ See i. e. SMITH, l. c. pag 455.

	γ calculated.	Found.	Δ
$E = 0 = 0 \times 0.102 \text{ V.}$	$\gamma = 25.46 + 1.00 - 0.00 = 25.46$	24.78 ?	+ 0.68?
500 = 1 »	2.15 - 0.19 = 27.42	27.40	+ 0.02
1000 = 2 »	4.31 - 0.76 = 29.00	29.00	± 0.00
1500 = 3 »	6.46 - 1.72 = 30.20	30.20	± 0.00
2000 = 4 »	8.61 - 3.05 = 31.02	30.65 ?	+ 0.37?
2500 = 5 »	10.77 - 4.77 = 31.46	31.33	+ 0.13
3000 = 6 »	12.92 - 6.86 = 31.51	31.41	+ 0.10

The values for $E = 0$ and $E = 2000$, namely $\gamma = 24,78$ and $\gamma = 30,65$, have been marked with a note of interrogation by the experimentator himself; so these values may be left out of consideration (l. c. page 460 and 467). The greatest difference is then about $\frac{1}{2}\%$. We have still to mention that for

$$E = 3020 = 6,04 \times 0,102 \text{ Volts}$$

the values, calculated for a , b and c , yield $\gamma = \varphi_0 = 31,51$, as they ought to do. The two parabolae meet there.

For $\frac{k + \beta}{k^2}$ and $\frac{A}{k}$ we find in the same way as above:

$$\frac{k + \beta}{k^2} = c = \frac{0,1906}{(0,102)^2} = 18,320.$$

$$- 2 \frac{k + \beta}{k} \Delta_0 + \frac{A}{k} = b = \frac{2,153}{0,102},$$

so putting $\Delta_0 = - 0,616$:

$$\frac{A}{k} = - 2 \times \frac{0,1906}{(0,102)^2} \times 0,616 + \frac{2,153}{0,102} = - 22,570 + 21,108 = - 1,462.$$

$\frac{A}{k}$ appears to be negative, i. e. the negative charge ($\overline{\text{Cl}}$ -ions) is situated in the solution at the surface of the bordering layer, and not — as the positive charge of the Hg_2^{++} -ions — deeper in that layer.

For the *ascending* branch we may write for this case either

$$\text{or } \left. \begin{aligned} \gamma &= 25,456 + \frac{2,153}{0,102} E - \frac{0,1906}{(0,102)^2} E^2 \\ \gamma &= 31,508 - 1,462 \Delta - 18,320 \Delta^2, \end{aligned} \right\} \dots (8)$$

putting $-\Delta$ for $k\omega$ (Δ being negative).

The maximum, which is to be found in the ascending branch, may be calculated from the first of these equations ($E_m = \frac{b}{2c}$):

$$E_m = \frac{2,153}{2 \times 0,1906} \times 0,102 = 5,65 \times 0,102 \text{ Volts,}$$

i. e.

$$E_m = 5,65 \times 500 = 2820.$$

Further we find for

$$\gamma_m = a + \frac{b^2}{4c}:$$

$$\gamma_m = 25,456 + \frac{(2,153)^2}{4 \times 0,1906} = 25,456 + 6,080 = 31,54.$$

In the descending branch no maximum is to be found, because a maximum requires there a negative value of Δ , and Δ is here positive.

We see, that the maximum ($E = 2820$) does *not* coincide with the point, where $\omega = 0$ ($E = 3020$, as we found above). The difference is not great, but still $(6,04 - 5,65) \times 0,102 \text{ Volts} = 40 \text{ millivolts}$. And in other instances it may be greater of course. It depends wholly on the value of A .

The figure represents the accurate course of the two parts of parabolae. The dotted curves indicate, how the course should have been, if the branches had been continued on the other side of $\Delta = 0$.

The abscissae are the electromotive forces E of the inserted cell, and increase with $500 = 0,102 \text{ Volts}$; so they are respectively 1×500 , 2×500 , 3×500 etc. The ascending branch is AP , and would have been continued in PA' , if the coefficients remained the same after $\Delta = 0$. The maximum is to be found at M , somewhat to the left of P , the point which separates the two different parabolae. The descending branch is PB , and would be continued along PB' . Its maximum is to be found at M' . So the curve, *really* passed through, is APB . The experimental values agree perfectly with the calculated values, now that the figure is made on this scale; only those found for $E = 0$ and $E = 4 \times 1,02$ (those with \times) do not agree (as is indicated in the figure by the sign \times).

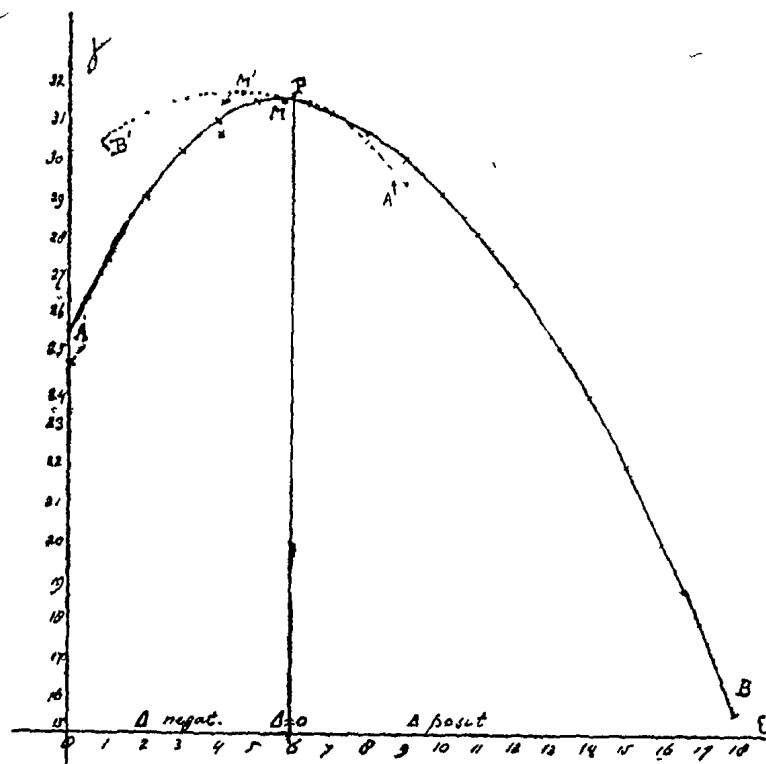


Fig. 4.

We may therefore summarise the above conclusions as follows.

1st. An accurate theoretical investigation of the capillary-electrometer shows, that the surface-tension as a function of the charge of the double-layer is not to be expressed by the simple equation $\gamma = \varphi_0 - k\omega^2$, but by the relation

$$\gamma = \varphi_0 - A\omega - (k + \beta)\omega^2.$$

2nd. The coefficients A and β differ as to whether the charge of the solution is negative (Δ negative) or positive. For a $1/10$ -normal solution of KCl $k + \beta$ is in the first case twice as great as in the second, and A is in the former case negative, in the latter positive.

3rd. The electro-capillary-curve consists of two parts of different parabolae, which meet each other at $\Delta = 0$, and of which the course of the ascending branch is much deeper than that of the descending branch.

4th. The ascending branch presents a maximum, and this maximum need *not* coincide with the point, where $\Delta = 0$. In our example this difference amounts to 40 millivolts.

5th. The hitherto unexplained peculiarities of the electro-capillary-curve are in this way fully explained.

6th. The capillary-electrometer of LIPPMANN is according to 4th not at all reliable for an accurate measuring of the differences of potential between metal and electrolyte.

March 1902.

Mathematics. „Right lines on surfaces with multiple right lines”
by Prof. JAN DE VRIES.

§ 1. If a surface S^n of order n possesses a line l of multiplicity $n-2$, it is cut in a conic by any plane passing through l . In order to find the locus of the centre of these conics we consider the section C_∞^n of S^n by the plane at infinity. The point L_∞ on l at infinity is a point of multiplicity $n-2$ on this curve; so C_∞^n is of class $(4n-6)$ and admits of $2(n-1)$ tangents passing through L_∞ and touching it elsewhere. Each of these tangents determines a plane through l cutting S^n in a parabola; so the locus of the center is a curve of order $2(n-1)$, of deficiency zero, cutting l $2n-3$ -times. This curve meets S^n a number of $(2n-3)(n-2)$ -times on l and $2(n-1)$ -times at infinity; the remaining points of intersection are double points of degenerated conics. From this ensues the known property that the line l of multiplicity $(n-2)$ is met by $(3n-4)$ pairs of single lines.¹⁾

§ 2. If l is chosen for the axis OZ of a right-angular system of coordinates the surface S^n can be represented by an equation of the form

$$A_n(x, y) + A_{n-1}(x, y)z + B_{n-1}(x, y) + \\ + A_{n-2}(x, y)z^2 + B_{n-2}(x, y)z + C_{n-2}(x, y) = 0,$$

the indices $n, (n-1), (n-2)$ denoting the order of the corresponding functions A, B, C .

From this is evident that an S^n with given $(n-2)$ -fold line l can be made to pass through $(6n-3)$ more points chosen at random. As we have $6n-3 = 5(n+1) + (n-8)$ it seems that for $n > 7$ we

¹⁾ See e. g. R. STURM, Math. Annalen, vol. IV, p. 249.