Chemistry. — *"On the potential-difference, which occurs at the surface of contact of two different non-miscible liquids, in which a dissolved electrolyte has distributed itself."* By Dr. J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

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1. It has already been demonstrated by NERNST [1] in 1892, that a potential-difference must occur at the surface of contact of two liquids, which lie together in layers, such as for instance water and phenol, on account of the unequal distribution of the neutral molecules and the Ions of a dissolved electrolyte. It is true, that his expression for the electromotive force relates to the case, that one of the two phases is a *solid* solution, but it will be perceived at once, that the same formula also applies to our case [2]).

There is, however, at present no prospect of obtaining direct measurements of this potential-difference [3]). But as RIESENFELD [4]) has lately been experimenting on the subject, although in another direction, it may be as well to give the exact theory of the phenomenon, which I worked out about a year ago, when engaged in writing a book on electro-chemistry, which will be published later.

Suppose we have a solution of KCl in the solvents A_1 and A_2.

A_1			A_2
	Cl	K	
KCl_1	Cl	K	KCl_2
	Cl	K	

If now equilibrium has been established between the *non-dissociated*, electrically neutral portions of the dissolved KCl in the two phases, there need not be equilibrium between the *Ions* in the two solvents. Indeed, equating the thermodynamic potentials for equivalent quantities of the non-dissociated portions in the two phases (*equilibrium of partition*), we get:

$$\mu_{KCl_1} = \mu_{KCl_2} \quad \cdots \cdots \cdots (1)$$

But the two dissociation-equilibria give:

$$\mu_{KCl_1} = \mu_{K_1} + \mu_{Cl_1} \; ; \; \mu_{KCl_2} = \mu_{K_2} + \mu_{Cl_2} \quad \cdots \cdots (2)$$

Consequently it will suffice if .

$$\mu_{K_1} + \mu_{Cl_1} = \mu_{K_2} + \mu_{Cl_2} , \quad \cdots \cdots \cdots (3)$$

[1]) Zeitschr. für Physik. Chemie 9, 137 (1892).

[2]) Compare RIESENFELD, Wied. Ann. (4) 8, 617 (1902).

[3]) Ibid., l. c.

[4]) NERNST und RIESENFELD, l. c. p. 600—608; RIESENFELD, 609—615; 616—624; id. Inaug. Diss., Göttingen 1901; HITTORF, Wied. Ann. (4) 9, 243—245 (1902).

and it would be a sheer accident if we also had:

$$\mu_{K_1} = \mu_{K_2} \; ; \; \mu_{Cl_1} = \mu_{Cl_2}.$$

There exists therefore as a rule *no* equilibrium of partition between the *Ions* in the two solvents. For example there may be in the second solvent relatively too few K-Ions, too many Cl-Ions. Since a system out of equilibrium tends to pass into a condition of equilibrium, K-Ions from A_1 will migrate to A_2, and remain there in the boundary-layer, while the corresponding liberated Cl-Ions remain in the boundary-layer of A_1 (inversely Cl-Ions will migrate from A_2 to A_1, whilst the corresponding liberated K-Ions remain in A_2. Both add themselves to the above mentioned similar ions in the boundary-layer). The consequence is the occurrence of an *electrical doublelayer* and therefore of a potential-difference. And it is this potential-difference, which will restore the originally non-existing equilibrium between the Ions.

All this may be put into a very simple mathematical form.

Let V_1 be the electrical potential of A_1, V_2 that of A_2, so that $\Delta = V_2 - V_1$ represents the potential-difference at the boundary (in the case we are dealing with, Δ is therefore *positive*), then the formula for the equilibrium of the K-Ions will be:

$$\frac{\mu_{K_2} - \mu_{K_1}}{\varepsilon} \, de + \Delta \, de = 0,$$

which is at once obvious, when we consider the virtual passage from the left to the right over the boundary of such a quantity of K-Ions, that the quantity of electricity transported is de. As the quantities μ relate to *equivalent*-quantities, and as these do not correspond with one electric unit, but with $\varepsilon (= 96530)$ electric units, $\mu_{K_2} - \mu_{K_1}$ must be divided by ε.

For the equilibrium of the Cl-Ions we find in the same manner:

$$\frac{\mu_{Cl_2} - \mu_{Cl_1}}{\varepsilon} - \Delta \, de = 0.$$

The sign at Δ is now negative, because on account of the negative charge the change in the electrical energy is $-\Delta \, de$.

We therefore obtain from the two relations, after dividing by de:

$$\Delta = -\frac{\mu_{K_2} - \mu_{K_1}}{\varepsilon} = \frac{\mu_{Cl_2} - \mu_{Cl_1}}{\varepsilon}. \quad \ldots \ldots (4)$$

That these two equations for Δ are not conflicting, is at once apparent. For the relation, resulting therefrom

$$\mu_{K_1} - \mu_{K_2} = \mu_{Cl_2} - \mu_{Cl_1},$$

leads at once to (3).

If we introduce:

$$\mu = \mu' + RT \log c,$$

in which c is the *concentration* of the Ions, we may also write:

$$\left. \begin{aligned} \Delta &= -\frac{1}{\varepsilon}\left[(\mu'_{K_2} - \mu'_{K_1}) + RT \log \frac{c_{K_2}}{c_{K_1}} \right] \\ \Delta &= \frac{1}{\varepsilon}\left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + RT \log \frac{c_{Cl_2}}{c_{Cl_1}} \right] \end{aligned} \right\} \quad \dots \quad (5)$$

II. Now everywhere $c_K = c_{Cl}$ (only in the boundary-layer an excess of positive or negative Ions is present, owing to the formation of the doublelayer), therefore also

$$\frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}},$$

and so we find [1]) by addition of the two equations (5):

$$\Delta = \frac{1}{2\varepsilon}\left[(\mu'_{Cl_2} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}) \right] \quad \dots \quad (6)$$

From this last relation it follows at once, that in *dilute* solutions, where the quantities μ' are almost independent of the concentration, *the potential-difference Δ will be also independent of the concentration.* Whether *much* or *little* KCl is distributed through the two solvents, we will always notice about the *same* potential-difference Δ.

If we deduct the two equations from each other instead of adding, then we obtain $\left(\text{observing that } \frac{c_{K_2}}{c_{K_1}} = \frac{c_{Cl_2}}{c_{Cl_1}} \right)$:

$$RT \log \frac{c_{K_2}}{c_{K_1}} = -\frac{1}{2}\left[(\mu'_{Cl_2} - \mu'_{Cl_1}) + (\mu'_{K_2} - \mu'_{K_1}) \right]. \quad \dots \quad (7)$$

If now we put

$$\left. \begin{aligned} \mu'_{K_2} - \mu'_{K_1} &= RT \log K_K \\ \mu'_{Cl_2} - \mu'_{Cl_1} &= RT \log K_{Cl} \end{aligned} \right\}, \quad \dots \quad \dots \quad (a)$$

in which K_K and K_{Cl} are quantities, which depend on the nature of the two solvents (and which in *dilute* solutions will only be functions of *temperature*) — they are the so-called *partition-coefficients* of the positive and negative Ions — then (6) and (7) pass into

$$\Delta = \frac{RT}{2\varepsilon} \log \frac{K_{Cl}}{K_K} \quad \dots \quad \dots \quad \dots \quad (6a)$$

$$\left(\frac{c_{K_1}}{c_{K_2}} \right)^2 = K_K \times K_{Cl} \quad \dots \quad \dots \quad \dots \quad (7a)$$

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[1]) The formula (6) was given already, though with a somewhat different notation, by LUTHER [Z. f. Ph. Ch. **19**, 537 (1896)]. The first thermodynamic theory of the equilibrium of partition was given by me in a paper of 1895 (Z. f. Ph. Ch. **18**, 264—267).

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Nernst's formula for Δ, obtained in a different manner, is identical with our formula (5). (As Nernst's $E = V_1 - V_2$, our $\Delta = -E$). For if we replace $\mu'_{K_2} - \mu'_{K_1}$ by $RT \, log \, K_K$ and $\mu'_{Cl_2} - \mu'_{Cl_1}$ by $RT \, log \, K_{Cl}$, then (5) passes into

$$\Delta = -\frac{RT}{\varepsilon} log \, K_K \frac{c_{K_2}}{c_{K_1}} = \frac{RT}{\varepsilon} log \, K_{Cl} \frac{c_{Cl_2}}{c_{Cl_1}},$$

and this is Nernst's expression. As has already been observed, the quantities K_K and K_{Cl} are the so-called "partition-coefficients" of the positive and negative Ions. For instance for the positive Ions we should have, when equilibrium of partition occurs:

$$\mu_{K_2} - \mu_{K_1} = 0,$$

or

$$\mu'_{K_2} - \mu'_{K_1} + RT \, log \frac{c_{K_2}}{c_{K_1}} = 0,$$

so that we obtain $\dfrac{c_{K_1}}{c_{K_2}} = K_K$. The same for the negative Ions.

The relation, given by Nernst [1])

$$K_K \times K_{Cl} = \frac{C_1}{C_2} \times K_{KCl},$$

in which K_{KCl} is the coefficient of partition of the neutral KCl-molecules, and C_1 and C_2 are the *dissociation*constants in the two phases, follows directly from the thermodynamical meaning of these quantities. For if we write this relation in the form

$$RT \, [log \, K_K + log \, K_{Cl}] = RT \, [log \, C_1 - log \, C_2 + log \, K_{KCl}],$$

it passes, taking into account equation (a) and the relations

$$RT \, log \, K_{KCl} = \mu'_{KCl_2} - \mu'_{KCl_1}; \qquad RT \, log \, C_1 = \mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1};$$

$$RT \, log \, C_2 = \mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2},$$

immediately into the identity

$$(\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) = (\mu'_{KCl_1} - \mu'_{K_1} - \mu'_{Cl_1}) -$$
$$- (\mu'_{KCl_2} - \mu'_{K_2} - \mu'_{Cl_2}) + (\mu'_{KCl_2} - \mu'_{KCl_1}).$$

Not the formula (5), but the formula (6) or (6a), derived by us from (5), deserves however the preference, because the concentrations of the Ions have been eliminated therein, and an expression has been obtained, in which only the coefficients of partition K_K and K_{Cl} occur.

III. If the dissolved electrolyte has now distributed itself so, that

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[1]) Z. f. Ph. Ch. **8**, 138 (1891).

the total concentration is c_1 in A_1 and c_2 in A_2, we shall have:

$$c_{K_1} = a_1 c_1 \quad ; \quad c_{K_2} = a_2 c_2,$$

in which the quantities c_1 and c_2 may be found by chemical analysis, and a_1 and a_2 by determinations of the conductivity. As soon as Δ can be determined by experiment, $\dfrac{K_{Cl}}{K_K}$ may be calculated from the equation (6a), and $K_K \times K_{Cl}$ from (7a), and we can therefore get to know separately the quantities K_K and K_{Cl}, consequently also the quantities

$$\mu'_{K_2} - \mu'_{K_1} \quad \text{and} \quad \mu'_{Cl_2} - \mu'_{Cl_1}.$$

From (6a) it further follows, that Δ will be *positive* (as supposed in the figure), when

$$K_{Cl} > K_K.$$

Only when by accident $K_{Cl} = K_K$, Δ can be 0. *In general a potential difference will always occur between two non-miscible solvents, when an electrolyte is partitioned between them.* This potential-difference is given by (6a).

From the equation (7a) it follows, that the relation of the concentrations of the *Ions* in the two solvents in the case of *dilute* solutions will be practically independent of the total concentrations. This equation may also be deduced directly from (3). For this, being a result of (1) and (2), that is to say of the equilibrium of partition and the two equilibria of dissociation, may be written:

$$(\mu'_{K_2} - \mu'_{K_1}) + (\mu'_{Cl_2} - \mu'_{Cl_1}) = -RT \left[log \frac{c_{K_2}}{c_{K_1}} + log \frac{c_{Cl_2}}{c_{Cl_1}} \right],$$

and this after substitution passes at once into (7a). For

$$log \frac{c_{K_2}}{c_{K_1}} + log \frac{c_{Cl_2}}{c_{Cl_1}} = 2 \, log \frac{c_{K_2}}{c_{K_1}} = - log \left(\frac{c_{K_1}}{c_{K_2}} \right)^2.$$

The equations (6a) and (7a) moreover lead to an important conclusion.

As the quantities K_K and K_{Cl} are, in the case of *dilute* solutions, *specific* quantities, we must therefore find about the *same values* for these quantities in the case of *other* salts, when employing the same solvents A_1 and A_2. For NaCl for instance we will have:

$$\Delta' = \frac{RT}{2\varepsilon} log \frac{K_{Cl}}{K_{Na}}; \qquad \left(\frac{c_{Na_1}}{c_{Na_2}} \right)^2 = K_{Na} \times K_{Cl},$$

from which by experimental determination of Δ' and the quantities c_{Na_1} and c_{Na_2}, the two quantities K_{Na} and K_{Cl} may be determined. The value, found for K_{Cl} from KCl-solutions in A_1 and A_2, must then be practically *identical* with the value for K_{Cl}, determined from solutions of NaCl in these solvents.

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The quantities Δ will show an almost complete additive character, on account of K_K and K_{Cl} being independent of the concentration in the case of dilute solutions. For instance, in the same solvents A_1 and A_2 we must find:

$$\Delta_{KCl} - \Delta_{NaCl} = \Delta_{KNO_3} - \Delta_{NaNO_3} .$$

And the same for other combinations.

The above considerations may be readily extended to the case of *non-binary* electrolytes such as $CaCl_2$, $ZnCl_2$, etc. In the different equations the valencies v of the Ions will then also occur, because the fundamental relation (4) then passes into the more general one:

$$\Delta = - \frac{\overset{+}{\mu_2} - \overset{+}{\mu_1}}{\overset{+}{v\varepsilon}} = \frac{\overset{-}{\mu_2} - \overset{-}{\mu_1}}{\overset{-}{v\varepsilon}} .$$

IV. The question in how far and in what manner the value of Δ, given in (6) or (6a), is still dependent on the concentrations of the Ions, can only be answered, when we calculate the values of μ'_{K_1} etc. with the aid of an equation of condition. If we accept the equation of VAN DER WAALS as also applying to liquid-phases, we obtain for instance for the molecules n_p:

$$\mu_p = - k_p T (log\,T - 1) - RT \left(log \frac{V-b}{n_1} - 1 \right) + [(e_p)_0 - T(\eta_p)_0] +$$

$$+ RT \frac{\Sigma n_1}{V-b} b_p - \frac{2}{V}(n_1 a_{p1} + n_2 a_{p2} + ...) + RT\, log \frac{n_p}{n_1} .$$

n_1 stands here for the molecular number of the solvent. For b and a we write:

$$b = n_1 b_1 + n_2 b_2 + \cdots$$
$$a = n_1{}^2 a_{11} + 2\,n_1 n_2 a_{12} + 2\,n_1 n_3 a_{13} + \cdots$$

Let us now calculate the value of

$$(\mu'_{Cl_2} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{K_1}),$$

or, what amounts to the same, of

$$(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2}).$$

If we indicate the solvent by the index 1, the non-dissociated KCl, dissolved therein, by 2, the two Ions by 3 and 4, we obtain for $\mu'_{K_1} - \mu'_{Cl_1}$ the expression

$$- (k_3 - k_4) T (log\,T - 1) + [((e_3)_0 - (e_4)_0) - T((\eta_3)_0 - (\eta_4)_0)] +$$

$$+ RT \frac{\Sigma n_1}{V-b}(b_3 - b_4) - \frac{2}{V}[n_1(a_{31} - a_{41}) + n_2(a_{32} - a_{42}) + n_3(a_{33} - a_{43}) + n_4(a_{34} - a_{44})].$$

Remembering, that $n_3 = n_4$, $a_{34} = a_{43}$, the last term may be simplified to

$$- \frac{2}{V} [n_1 (a_{31} - a_{41}) + n_2 (a_{32} - a_{42}) + n_3 (a_{33} - a_{44})].$$

For $\mu'_{K_2} - \mu'_{Cl_2}$ we find a similar expression. In this, however, the quantities k_3, k_4 (the heat-capacities of the same Ions, at infinite volume) and $(e_3)_0$, $(e_4)_0$, $(\eta_3)_0$, $(\eta_4)_0$ (the energy and entropy-*constants* of these Ions) will be exactly the same. a_{32}, a_{42}, a_{33} and a_{44} will also remain unaltered, so that for the difference $(\mu'_{K_1} - \mu'_{Cl_1}) - (\mu'_{K_2} - \mu'_{Cl_2})$ we may write:

$$RT \left[\frac{\Sigma n_1}{V-b}(b_3-b_4) - \frac{\Sigma n'_1}{V'-b'}(b'_3-b'_4) \right] - 2 \left[\left(\frac{n_1(a_{31}-a_{41})}{V} - \frac{n'_1(a'_{31}-a'_{41})}{V'} \right) + \right.$$
$$\left. + (a_{32}-a_{42}) \left(\frac{n_2}{V} - \frac{n'_2}{V'} \right) + (a_{33}-a_{44}) \left(\frac{n_3}{V} - \frac{n'_3}{V'} \right) \right].$$

The quantities, relating to the second solvent, are indicated by accents.

We may now go a step further and accept as a first approximation:

$$b_3 = b_4 \; , \; b'_3 = b'_4 \; , \; a_{33} = a_{44}.$$

If we then also write

$$\frac{V}{n_1} = v \; , \; \frac{V'}{n'_1} = v' \; , \; n_2 = n(1-\alpha) \; , \; \frac{n}{n_1} = c, \text{ etc.,}$$

we finally obtain for Δ:

$$\Delta = \frac{1}{\varepsilon} \left[\left(\frac{a'_{31}-a'_{41}}{v'} - \frac{a_{31}-a_{41}}{v} \right) + (a_{32}-a_{42}) \left(\frac{(1-\alpha')c'}{v'} - \frac{(1-\alpha)c}{v} \right) \right]. \quad (6b)$$

As, in consequence of the equilibrium of partition, $\dfrac{(1-\alpha')c'}{(1-\alpha)c}$ is constant, Δ will have the form

$$\Delta = \Delta_0 + \lambda(1-\alpha)c,$$

or since, on account of the equilibrium of dissociation, $\dfrac{(\alpha c)^2}{(1-\alpha)c} = $ constant, also the form

$$\Delta = \Delta_0 + \lambda'(\alpha c)^2.$$

Whether Δ will be positive or negative, depends chiefly on Δ_0. If

$$\frac{a_{31}-a_{41}}{v} < \frac{a'_{31}-a'_{41}}{v'},$$

Δ will be positive. We also see, that $\Delta - \Delta_0$ will increase or decrease with the *second* power of αc, that is to say in the case of strongly dissociated electrolytes, where α is nearly 1, almost with c^2.

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