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Chemistry. — “*On the Significance of the Volta-Effect in Measurements of Electromotive Equilibria*”. By Prof. A. SMITS and J. M. BIJVOET. (Communicated by Prof. P. ZWEMAN).

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Introduction.

Many physicists are of opinion that the Volta effect amounts to only a few milli volts, and that the electromotive force of an electrical cell resides practically exclusively in the potential differences metal-electrolyte, so that these alone need be taken into consideration; there are even those who think that the Volta-effect is theoretically zero. It is chiefly the German school that assumes that the Volta-effect may be neglected with respect to the potential difference metal-electrolyte. On the other hand a great number of investigators think they have found that the Volta-effect can constitute $\frac{1}{2}$, $\frac{3}{4}$ and even a still larger fraction of the electromotive force of a cell, and can accordingly amount to as much as 1 Volt.

The opinions concerning the value of the Volta-effect are therefore greatly divided, which is owing to the great difficulties which attend the determination of the Volta-effect.

In the application of the recent views about the electromotive equilibria¹⁾ to the Volta-effect it appears, that even though this effect should be small for metals in the state of internal equilibrium, it must become great for phenomena of polarisation, so that we may certainly not neglect the Volta-effect for these cases.

2. *The variation of the Volta-effect on polarization and passivation.*

The following equation holds for the potential difference of a metal in active state with respect to an electrolyte:

$$\Delta_{M \text{ active}-L} = - \frac{0,058}{\nu} \log \frac{K' M^{\nu'} (M_S^{\nu'})_{\text{active}}}{M_L^{\nu'}}$$

and thus we get for the passive state:

$$\Delta_{M \text{ passive}-L} = - \frac{0,058}{\nu} \log \frac{K' M^{\nu'} (M_S^{\nu'})_{\text{passive}}}{(M_L^{\nu'})}$$

from which follows.

¹⁾ Zeitschr. f. physik. Chemie **88**, 743 (1914).

“ ” ” ” **90**, 723 (1915).

$$\Delta_{M_{active}-L} - \Delta_{M_{passive}-L} = -\frac{0,058}{\nu} \log \frac{(M_{S'}^{\nu})_{active}}{(M_{S'}^{\nu})_{passive}}$$

For the Volta-effect holds the relation:

$$\Delta_{M_1-M_2} = \frac{\theta_{M_1} - \theta_{M_2}}{F}$$

from which follows in the same way as we have derived this for the potential difference metal-liquid, that the following equation holds for the Volta-effect:

$$\Delta_{M_1-M_2} = 0,058 \log \frac{K'_{\theta}(\theta_{M_1})}{(\theta_{M_2})}$$

so that:

$$\Delta_{M_1_{active}-M_2} - \Delta_{M_1_{passive}-M_2} = 0,058 \log \frac{(\theta_{M_1})_{active}}{(\theta_{M_1})_{passive}}$$

When we call:

$$\frac{(M_{1s'})_{active}}{(M_{1s'})_{passive}} = n$$

then also

$$\frac{(\theta_{M_1})_{active}}{(\theta_{M_1})_{passive}} = n$$

It follows from this that when on polarisation or passivation the change of the potential difference metal-electrolyte is:

$$\frac{0,058}{\nu} \log n$$

that of the Volta-effect amounts to:

$$0,058 \log n$$

hence ν times the value.

What we measure is the sum of these two changes:

$$\frac{\nu + 1}{\nu} 0,058 \log n.$$

Hence the part $\frac{\nu}{\nu + 1}$ of this total change is due to the Volta-effect. This is, therefore, $\frac{1}{2}$ for a uni-valent metal, and $\frac{2}{3}$ for a bi-valent one etc.

When it is now borne in mind that on passivation through anodic solution the potential difference metal-electrolyte, as it is found by measurement, can change by an amount of 1 or 2 Volt. (e. g. 1.7 Volt, is found for iron), it follows from this that according to these considerations also the Volta-effect is subjected to a great change¹⁾.

¹⁾ It must still be pointed out that the case iron is certainly more intricate than the case considered above, because iron contains ions of different valency.

This throws, indeed, a peculiar light on the Volta-effect, for it now appears clearly that when really the Volta-effect for metals in the state of internal equilibrium should be zero or very small, which comes to the same thing as equality or nearly equality of the molecular thermodynamic potential of the electrons in those metals, this would be a special characteristic property according to the theory of electrons for metals in the state of internal equilibrium.

But apart from the value of the Volta-effect, in the logical development of the given theory of the electromotive equilibrium, the Volta-effect cannot be neglected.¹⁾

¹⁾ In this we will also point out that when the new views about the rôle of the electrons and the electromotive equilibrium are consistently applied to an arbitrary electrical circuit, we arrive at the result that everywhere where a potential difference occurs, a reaction takes place on passage of the current, in which the change in free energy of the reaction proceeding at that place, determines the value of the potential difference. It is known that according to the given theory at the places of contact metal-electrolyte this reaction consists: 1. of the splitting up of metal ions into ions and electrons; resp. of the formation of metal atoms from the electrically charged dissociation products mentioned here and 2. of the transition of ions and electrons from the metal phase into the electrolyte or vice versa. In this transition from one phase into the other the ions take a preponderant part.

When we consider the contact metal-metal, the just-mentioned transition consists to by far the greater part of the displacement of electrons from the metal M_1 to the metal M_2 .

This view differs accordingly from that which is particularly met with in German handbooks, in which the opinion is embraced that the reactions during passage of the current exclusively take place at the places of contact metal-electrolyte.

It is clear that on application of the relation:

$$E = A - T \frac{dA}{dT}$$

to the transition of electricity from one metal into the other we may only conclude to:

$$A = T \frac{dA}{dT}$$

when in the process mentioned here no change of the thermo-dynamic energy takes place ($E = 0$).

LEBLANG does so in his handbook p. 227 (1914), and thus comes to the conclusion that the Volta-effect must be small, because $\frac{dA}{dT}$ is small.

According to the theory of electrons the difference in solubility heat of the electrons in the two metals will, however, have to be taken into account. In the isotherm transition of electricity between the two metals *the free energy* of the electrons will change, and be converted into electrical energy in case of a reversible process, the occurring change of the bound energy becoming manifest through the latent heat, which heat is the heat of PELTIER.

It is this quantity, the heat of PELTIER which, is represented by $T \frac{dA}{dT}$, and not the Volta-effect.

3. *The experimental electrical potential.*

When we measure the potential difference metal-electrolyte, we do so by the aid of an auxiliary electrode, e.g. a calomel or hydrogen electrode, in other words, we then make an electrical circuit, which is closed during the measurement. The electro-motive force of this circuit, in which we suppose the diffusion potential between L_1 and L_2 annulled, then becomes:

$$E = \Delta_{M_1-L_1} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2}$$

in which $\Delta_{M_1-M_2}$ is a Volta-effect.

When in this we put $\Delta_{M_2-L_2} = \text{zero}$ (N. hydrogen-electrode), we get:

$$E = \Delta_{M_1-L_1} - \Delta_{M_1-M_2},$$

in which we shall call E the *experimental electrical potential*.

This expression, therefore, always contains the Volta-effect, and until this quantity is known, and until we introduce further suppositions about its value, we can of course not determine the difference $\Delta_{M_1-L_1}$ alone in this way, and consequently not the saturation concentration of the metal-ions either (which quantity is equivalent with NERNST's "Lösungstension"), which was calculated from:

$$E = -\frac{RT}{v_1 F} \ln \frac{K_{M^+}}{(M_L^{v_1})} \dots \dots \dots (1)$$

in which $\Delta_{M_1-M_2}$ has been neglected.

Nor can we draw conclusions about the order of the saturation concentrations of the metal-ions from the so-called tension series, until the Volta-effect shall be known. From the fact that the metal M_1 immersed in a normal solution of one of its salts appears on measurement to be more negative than the metal M_2 , immersed in a 1 norm.-solution of a corresponding salt, we conclude namely that:

$$\Delta_{M_1-L_1} \text{ is more negative than } \Delta_{M_2-L_2},$$

but strictly speaking this conclusion is not permissible, because the measurement only says that $\Delta_{M_1-L_1} - \Delta_{M_1-M_2}$ is more strongly negative than $\Delta_{M_2-L_2}$.

We demonstrated that the equations for the exp. elec. potential in the form in which they contain the saturation-concentration of the ions or the "Lösungstension", have the drawback that the unknown Volta-effect occurs in them. It is entirely different with the new already before given equation, in which the *solubility product* of the metal or the *solubility quotient* of the metalloid occurs, and the same thing may be said of the electron equation.¹⁾

¹⁾ Zeitschr. f. physik. Chemie 92, 1 (1916).

Thus the following equation was namely derived:

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = \frac{RT}{v_1 F} \ln \frac{(M_1' L)}{L_{M_1}} - \frac{RT}{v_2 F} \ln \frac{(M_2' L)}{L_{M_2}} + \frac{\mu_{M_1} - \mu_{M_2}}{F} \quad (2)$$

we measure, however,

$$E = \Delta_{M_1-L_2} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2} \quad (3)$$

and the Volta-effect being:

$$\Delta_{M_1-M_2} = \frac{\mu_{M_1} - \mu_{M_2}}{F}$$

it follows from this that:

$$E = \frac{RT}{v_1 F} \ln \frac{(M_1^v)}{L_{M_1}} - \frac{RT}{v_2 F} \ln \frac{(M_2^v)}{L_{M_2}} \quad (4)$$

in which the Volta-effect has been eliminated.

This equation enables us, therefore, to find the ratio of the solubility-products from the electromotive forces.

In the practical application the hydrogen electrode may be taken for the metal M_2 , and for L_{H_2} the value may be substituted which had already been given before, viz. $10^{2 \times -48.1}$;

in this case we get:

$$E = \frac{0,058}{v} \log \frac{(M_L^v)}{L_M} - 2,8 \quad (5)$$

When equation (4) is compared with the expression for E , which contains the saturation-concentrations of the metal-ions found by substituting the values of $\Delta_{M_1-L_1}$ and $\Delta_{M_2-L_2}$ given by equation (1) in equation (3), which gives:

$$E = -\frac{RT}{v_1 F} \ln \frac{K_{M_1}}{(M_1^v)} + \frac{RT}{v_2 F} \ln \frac{K_{M_2}}{(M_2^v)} - \Delta_{M_1-M_2} \quad (6)$$

the great advantage which equation (4) resp. (5) have over equation (6) is very apparent, for the latter equation contains a still unknown Volta-effect. While the construction of a series of the potential differences metal-electrolyte is not yet possible, on account of our ignorance of the Volta-effect, equation (5) enables us to draw up a series for the solubility-products of the metals, and from such a relation there may be found a series for the solubility-quotients of the metalloids, as has been done already²⁾.

The determination and order of this series is of course the same as that of the so-called tension-series, which gives the order in which

¹⁾ Zeitschr. f. physik. Chemie **92**, 1 (1916).

²⁾ SMITS and LOBRY DE BRUYN. Verslag Kon. Ak. **26**, 270.

the metals oust each other from equally concentrated solution. We demonstrated, however, that in a theory which assumes the existence of Volta-effects, the quantities derived from the electromotive equilibria should not be considered as the saturation-concentrations of the metal-ions or as the "Lösungstensionen".

The electron equation gives a relation that agrees with equation (2), viz.:

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = -\frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} + \frac{\mu_{M_1} - \mu_{M_2}}{F},$$

so that

$$E = -\frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})}, \quad \dots \quad (7)$$

Of course the Volta-effect does not occur in this relation either, so that when a definite value is assumed for the electron conc. (θ_{L_2}) in the electrolyte in which the hydrogen electrode is found, the electron-concentration (θ_{L_1}) , which belongs to the other electromotive equilibrium, can be found.

Equations (4) and (7) are, therefore, not approximate, but perfectly rigorous, which also appears from the consideration that equation (7),

from which (4) is found by substitution of $\frac{L_M}{(M_L)^v}$ for $(\theta_L)^v$, follows immediately from the condition for electron equilibrium between the liquids E_1 and L_2 . The derivation of this electromotive force as sum of the potential differences occurring in the circuit was accordingly only followed here in order to keep in agreement with the derivation given before.

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4. As appears from a previous communication¹⁾, the experimental elec. potential of a Ni-electrode, immersed in an electrolyte through which hydrogen was led, was found equal to the hydrogen potential. In order to account for this fact that the electromotive force E of the closed circuit nickel-electrode-electrolyte-hydrogen-electrode is zero according to our considerations we must show, as follows directly from equation (7), in what way the electron concentration of the nickel equilibrium has become equal to that of the hydrogen equilibrium.

This phenomenon is already explained in a very simple way²⁾ by the assumption that the nickel-electrode is, at least superficially,

¹⁾ SMITS and LOBRY DE BRUYN loc. cit.

²⁾ SMITS and LOBRY DE BRUYN loc. cit.

disturbed, which disturbance for a very inert metal will go so far till the electron concentration of the nickel equilibrium in the electrolyte has conformed to the electron concentration of the hydrogen equilibrium, and has become almost equal to it.

For the limiting case of an ideal inert metal this equality will become perfect, as is also required by E becoming zero in this case.

In a former discussion of these phenomena the neglect of the Volta-effect led on the other hand to the conclusion that the electromotive force of the circuit, in case of equal electron-concentrations in the electrolyte of the two metal equilibria, would be zero *only in approximation*.

It will have become clear through what precedes that while up to now the Volta-effect has been neglected in the Δ, X -figure, it is better to draw the experimental potential E (e.g. with respect to hydrogen) as ordinate instead of the potential difference metal-liquid; then the thus obtained E, X -figures are perfectly rigorous. They then indicate that for the three-phase equilibrium the two electrodes possess the same experimental potential; the difference between their potential differences with the electrolyte then being equal to the Volta-effect between the two metals.

In this point the following equation then holds:

$$\Delta = \frac{0.058}{v_1} \log \frac{(M_1^v)_L}{L_{M_1}} = \frac{0.058}{v_2} \log \frac{(M_2^v)_L}{L_{M_2}}$$

or

$$\frac{L_{M_2^v}}{L_{M_1^v}} = \frac{(M_2^v)_L^{v_1}}{(M_1^v)_L^{v_2}}$$

so that from the ratio of the solubility-products the situation of the coexisting electrolyte immediately follows. Though this has been shown already before, this circumstance is once more pointed out here, to make clear that equation (6) is of no use to us here, for this equation gives for the three-phase equilibrium:

$$-\frac{0.058}{v_1} \log \frac{K_{M_1^v}}{(M_1^v)_L} = -\frac{0.058}{v_2} \log \frac{K_{M_2^v}}{(M_2^v)_L} + \Delta_{M_1-M_2}$$

In this form the equation contains, however, the unknown Volta-effect and the unknown saturation-concentrations, so that a calculation as above is not possible.

Summary.

By application of the more recent views on the electromotive

equilibria to the Volta-effect the result was obtained that on polarisation and passivation the *change* in the Volta-effect must be great according to this theory, and that in these phenomena the Volta-effect would even constitute the greatest part of the total change in the electromotive force. It was further pointed out that if the Volta-effects between metals in which the state of internal equilibrium prevails, should be really very small, on which the opinions are still divided, but which has, indeed, become probable by the experiments made of late, this would have to be considered according to the theory as a very characteristic property for metals in the state of internal equilibrium.

As in principle the Volta-effect at any rate in the given theory of the electromotive equilibria may not be neglected, it was here taken into account. The quantities that are found on measurement of potential differences metal-electrolyte, and which are here called *experimental electrical potentials*, always contain an unknown Volta-effect; which is the cause that from the said potentials the saturation concentrations of the metal ions (resp. the "Lösungstensionen") cannot be calculated.

The newly derived relations, in which the *solubility product* of the metal, the *solubility quotient* of the non-metal resp. the electron concentration in the electrolyte occurs, do not contain the Volta-effect, however, and enable us to draw up a *solubility-product-series* of metals, and a *solubility-quotient-series* of metalloids, as has indeed already been done, from which conclusions can be drawn about the chemical and electrochemical behaviour of the elements.

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