Chemistry. — *"The Application of the Theory of Allotropy to Electromotive Equilibria"* IV. By Prof. A. Smits and Dr. A. H. W. Aten. (Communicated by Prof. J. D. van der Waals).

(Communicated in the meeting of Feb. 26, 1916).
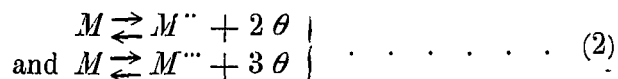
1. *Introduction.*

In some foregoing papers [1]) it has already been demonstrated that the phenomenon of passivity can be explained in a simple way by the application of the theory of allotropy to the electromotive equilibrium metal-electrolyte.

According to this theory the metal is complex, and with this complexity many different cases can present themselves. It is possible that the complexity only consists in this that in the metal we have to do with an *ionisation-equilibrium* of the metal, expressed e.g. by the equation:

$$M \rightleftharpoons M^{\cdot} + \theta \qquad \ldots \ldots \ldots \quad (1)$$
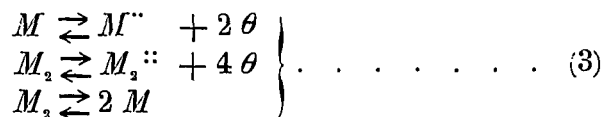
It is, however, also possible, and this will occur in the metals of which ions are known with different valency, that there exist side by side more such ionisation equilibria, and that just as many as there are differently charged metal ions.

If of the metal M there exist the ions $M^{\cdot\cdot}$ and $M^{\cdot\cdot\cdot}$, the two following ionisation equilibria will occur in the metal:

$$\begin{aligned} M &\rightleftharpoons M^{\cdot\cdot} + 2\,\theta \\ \text{and } M &\rightleftharpoons M^{\cdot\cdot\cdot} + 3\,\theta \end{aligned} \qquad \ldots \ldots \quad (2)$$

It has further been pointed out that it is possible that the metal contains different kinds of ions, which have the same charge per atom, but which differ in size, as e.g. the ions $M^{\cdot\cdot}$ and $M_2^{\cdot\cdot}$.

In this case the metal is still more complicated, because then we must assume the following ionisation and dissociation equilibria:

$$\begin{aligned} M &\rightleftharpoons M^{\cdot\cdot} + 2\,\theta \\ M_2 &\rightleftharpoons M_2^{\cdot\cdot} + 4\,\theta \\ M_2 &\rightleftharpoons 2\,M \end{aligned} \qquad \ldots \ldots \ldots \quad (3)$$

Before we examine more closely the phenomena of polarisation and passivity it is desirable to show to what new points of view the assumption of an ionisation equilibrium in a metal leads.

We shall begin with showing this for the simplest case, indicated by equation (1), and not until the conclusions to which this case

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[1]) These Proc. XVI, p. 191; XVI, p. 699; XVII, p. 37.

gives rise, both with regard to the reactions which can take place between a metal and an electrolyte, and to the potential difference metal-electrolyte, have been derived, will the phenomena of polarisation and passivity for this simplest case be discussed.

Thus the whole will constitute an introduction to the more thorough treatment of the other cases, indicated by equations (2) and (3).

2. *Solubility product of a metal.*

The new views which will be developed here, are based on the assumption that the electrons in a metal phase and in the coexisting electrolyte behave as ions, so that the laws which hold for molecules and have been successfully applied to ions, can also be transferred to the electrons.

Let us now consider the simplest case, namely this that exclusively the ionisation equilibrium

$$M \rightleftarrows M^{\cdot\cdot} + 2\,\theta$$
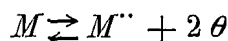
exists in the metal M.

If we now immerge this metal in pure water, uncharged atoms, metalions and electrons will pass into the water with the result that an ionisation equilibrium is also established in this liquid.

If we apply the law of chemical mass action to the above ionisation equilibrium, which exists *in the liquid*, we get:

$$K = \frac{(M^{\cdot\cdot})\,(\theta)^2}{(M)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now the liquid is in contact with the solid metal, so that the liquid will be saturate with respect to the non-electric component, the uncharged metal atoms. The concentration (M) is, therefore, a constant, hence we may write:

$$K' = (M^{\cdot\cdot})\,(\theta)^2 = L_M \quad . \quad . \quad . \quad . \quad . \quad (5)$$
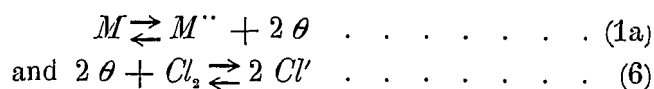
This product, which is, therefore, a constant quantity for constant temperature and pressure, we shall call the *solubility product of the metal*.

The supposition that the complexity of a metal exists in the occurrence of metal atoms, metal ions, and electrons, which in case of unary behaviour of the metal, give rise to the existence of the ionisation equilibrium represented in equation 1, leads therefore to an important idea, namely that of the solubility product of a metal, by means of which a number of electromotive processes can be surveyed from one and the same point of view and can be accounted for in a plausible way.

3. *Explanation of different electromotive processes by the application of the idea*:

"*Solubility product of a metal*".

a. *Dissolving of metals by halogen.* Suppose a metal to be immerged in a vessel of pure water, and then a halogen e.g. chlorine, to be added, it will quite depend on the situation of the two following equilibria

$$M \rightleftarrows M^{..} + 2\,\theta \quad \ldots \ldots \ldots \text{(1a)}$$

$$\text{and } 2\,\theta + Cl_2 \rightleftarrows 2\,Cl' \quad \ldots \ldots \ldots \text{(6)}$$

what will happen.

If the concentration of the electrons in the ionisation equilibrium (1a) of the metal is greater than that in the equilibrium (6), the chlorine will take away the electrons, which causes the homogeneous equilibrium (1a) to shift to the righthand side, and the heterogeneous equilibrium between metal and electrolyte is broken. The metal will then send metal atoms, metal ions, and electrons into solution, and so the metal can entirely go into solution on sufficient addition of chlorine.
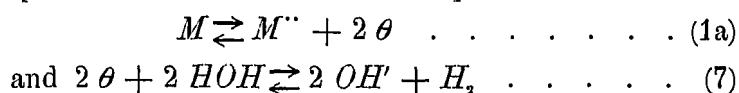
It now follows from what precedes that it will depend on the concentration of the electrons emitted by the metal whether with the prevailing chlorine concentration a shifting of (1a) from left to right is possible.

The electron-concentration mentioned here will depend on the value of the solubility product of the metal, and it may, therefore, be predicted that metals with a relatively large solubility product will dissolve in chlorine water, whereas metals with a small solubility product will not be attacked. It is, however, the question whether there is a metal so noble that the concentration of the electrons which ensues through the ionisation of the metal is smaller than corresponds with equilibrium (6).

It follows already from this that the base metals possess a relatively great, and the noble metals a relatively small solubility product.

b. *Dissolving of metals in pure water.* Now we might also answer the question why one metal dissolves in water and why another does not.

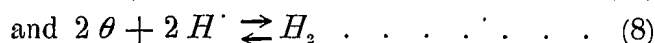For this purpose we have to consider the equilibria:

$$M \rightleftarrows M^{..} + 2\,\theta \quad \ldots \ldots \ldots \text{(1a)}$$

$$\text{and } 2\,\theta + 2\,HOH \rightleftarrows 2\,OH' + H_2 \quad \ldots \ldots \text{(7)}$$

If we now have a metal with a great solubility product, then (θ) is comparatively great in (1a), and the reaction (7) can proceed

from left to right. As the hydrogen then continually escapes, it will continue till the metal has entirely disappeared.

In this way we come to the conclusion that the metals which act most strongly on water, are the metals with relatively great solubility product.

c. *Dissolving of metals in acids.* If we now consider the phenomenon that some metals give hydrogen generation with solutions of acids as HCl, H_2SO_4, and others do not, we see in the light of these considerations that this phenomenon is entirely controlled by the equilibria:

$$M \rightleftarrows M^{\cdot\cdot} + 2\,\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

$$\text{and } 2\,\theta + 2\,H^{\cdot} \rightleftarrows H_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

from which we see that the metals with a relatively large solubility product will generate hydrogen, whereas the other metals do not do so. Metals as copper and silver etc. or in other words the noble metals, do not dissolve, because they have a too small solubility product.

d. *Dissolving of metals in the solution of a mixture of a ferro- and a ferrisalt.*

We can now easily give an explanation of the different conduct of the metals with respect to a solution of a mixture of a ferro- and a ferrisalt. In this case we have to consider besides the metal ionisation equilibrium:

$$M \rightleftarrows M^{\cdot\cdot} + 2\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$
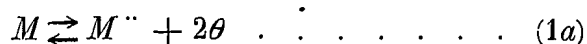
also the equilibrium:

$$Fe^{\cdot\cdot} \rightleftarrows Fe^{\cdot\cdot\cdot} + \theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$
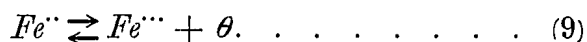
If the electron-concentration of the equilibrium (9) in the solution under consideration is greater than that which corresponds with the solubility product of the metal, the electrons from the solution pass into the metal, and at the same time the ionisation equilibrium (1a) shifts from right to left both in the metal and in the solution, and metal deposits from the solution. The metals that behave thus are, of course, again metals with a small solubility product, hence they behave with respect to the said solution of a mixture of ferro- and ferrisalts as an unassailable electrode.

If on the other hand the metal possesses a relatively large solubility product, electrons will be withdrawn to the equilibrium (1a) both in the solution and in the metal, and the metal goes into solution, the conversion represented by equation (9) proceeding from right to left, in which the ferri-salt is therefore reduced to ferro-salt.

This takes place inter alia when M is the metal Zn.

e. Solution of the metal by withdrawal of metal ions.

We have shown here that a metal will dissolve when electrons are withdrawn from the homogeneous equilibrium:

$$M \rightleftarrows M^{\cdot\cdot} + 2\theta$$
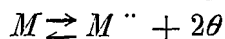
Of course the same thing happens when we succeed in diminishing the concentration of the metal ions $M^{\cdot\cdot}$. For, this purpose we should have to try to add a substance which yields a complex with the ion $M^{\cdot\cdot}$, the dissociation constant of which is exceedingly small. It will be discussed later whether this is possible.

4. *New relations for the potential difference metal-electrolyte.*

If in the derivation of the potential difference metal-electrolyte we take into account the ionisation equilibrium in the metal and in the coexisting electrolyte, we get what follows.

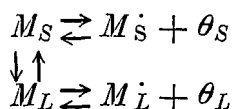For the simplest case for unary behaviour the equilibrium

$$M_S \rightleftarrows M_S^{\cdot} + \theta_S \quad \ldots \ldots \quad (10)$$

will prevail in the metal; the following corresponding equilibrium:

$$M_L \rightleftarrows M_L^{\cdot} + \theta_L \quad \ldots \ldots \quad (11)$$

in the coexisting liquid.

The equilibrium between metal and electrolyte can now be represented by:

$$M_S \rightleftarrows M_S^{\cdot} + \theta_S$$
$$\downarrow\uparrow$$
$$M_L \rightleftarrows M_L^{\cdot} + \theta_L$$

but this equilibrium is as a rule accompanied with a potential difference.

For this potential difference we now get, in contrast with the earlier view, the *two* following equations:

$$\Delta = -\frac{\mu_{M_S^{\cdot}} - \mu_{M_L^{\cdot}}}{F} \quad \ldots \ldots \ldots \quad (12)$$

and

$$\Delta = \frac{\mu_{0S} - \mu_{0L}}{F} \quad \ldots \ldots \ldots \quad (13)$$

In the first place we have therefore a relation (12), in which occurs the difference between the molecular potentials of the metal ion in the metal and in the solution, and in the second place a similar relation (13), in which instead of the molecular potentials of the metal ion, those of the electrons occur.

We shall now follow the method applied by van Laar [1]) in the derivation of Nernst's formula.

Let us now execute the usual splitting up of the molecular thermodynamic potential:

$$\mu = \mu' + RT \ln C \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

in which μ' for diluted states is only a function of the temperature; we then get starting from (12):

$$\Delta = - \frac{\mu'_{M_S} - \mu'_{M_L} + RT \ln (M_S) - RT \ln (M_L)}{F} \quad . \quad . \quad . \quad (15)$$

if we put in this:

$$\mu'_{M_S} - \mu'_{M_L} = RT \ln K'_M \quad . \quad . \quad . \quad . \quad . \quad (16)$$

we get

$$\Delta = - \frac{RT}{F} \left[\ln K'_M + \ln \frac{(M_S)}{(M_L)} \right] \quad . \quad . \quad . \quad . \quad (17)$$

or

$$\Delta = - \frac{RT}{F} \left[\ln \frac{K'_M \cdot (M_S)}{(M_L)} \right] \quad . \quad . \quad . \quad . \quad (17a)$$

If we now start from the equation (13), we arrive in quite the same way at the equation

$$\Delta = \frac{RT}{F} \left[\ln K'_\theta + \ln \frac{(\theta_S)}{(\theta_L)} \right] \quad . \quad . \quad . \quad . \quad (18)$$

or

$$\Delta = \frac{RT}{F} \left[\ln \frac{K'_\theta \cdot (\theta_S)}{(\theta_L)} \right] \quad . \quad . \quad . \quad . \quad (18a)$$

When by a thermodynamic way the formula for the potential difference had been derived by van Laar, it was demonstrated by Smits [2]) what the physical meaning is of the quantity K, which occurs in van Laar's final formula instead of the Lösungstension P. Now we can find in the same way the physical meaning of the products $K'_M (M_S)$ and $K'_\theta (\theta_S)$ in equations (17a) and (18a).

It follows from equation (17a) that

$$\Delta = 0$$

when

$$(M_L) = K'_M \cdot (M_S) \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

In this case also

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[1]) Chem. Weekbl. 41, 1905.
Lehrbuch der theoretischen Elektrochemie (1907).
[2]) These Proc. IX, p. 2.

$$\mu_{M_S} = \mu_{M_L} \quad \cdots \quad \cdots \quad (24)$$

according to equation (12), from which follows that in this case the metal ions in the metal are in equilibrium with those in the solution, *no potential difference* existing between metal and solution. This equilibrium is therefore an equilibrium of saturation and the concentration of the metal ions in the solutions will therefore be a concentration of saturation. Therefore the product K'_M (M_S) represents the saturation concentration of the metal ions at definite temperature and pressure.

That under the said circumstances this product is really a constant follows from this that not only K'_M, but also (M_S) is a constant quantity in case of unary behaviour of a metal at the same temperature and pressure.

If we now represent this concentration of saturation of the metal ions or in other words the metal ion solubility by K_{M}, then

$$K'_M \ (M_S) = K_M \quad \cdots \quad \cdots \quad (25)$$

and then equation (17a) becomes:

$$\Delta = - \frac{RT}{F} \ ln \frac{K_{M}}{(M_L)} \cdot \quad \cdots \quad \cdots \quad (26)$$

This is NERNST's equation, in which instead of the Lösungstension P, the metal ion solubility K_M occurs.

On purpose we have followed this course in order to show that the well known relation for the potential difference is found when we only take the metal ions into account, whereas the rôle of the electrons is at least equally important.

Accordingly we get a much deeper insight when we also take the electrons into account.

For this we must also make use of equation (18a). In this equation first a simplification can, however, be applied. Just as we have been able to demonstrate just now that the product K'_M (M_S) represents the concentration of saturation of the metal ions, we can show in entirely the same way that the product $K'_0 (\theta_s)$ indicates the concentration of saturation of the electrons.

If for this quantity we again introduce a simple symbol e.g.

$$K'_0 \ (\theta_s) = K_0 \quad \cdots \quad \cdots \quad \cdots \quad (27)$$

equation (18a) is simplified to:

$$\Delta = \frac{RT}{F} \ ln \frac{K_0}{(\theta_L)} \cdot \quad \cdots \quad \cdots \quad (28)$$

We see from this that for a base metal (θ_L) is *greater* than K_0. It is here the place to draw attention to an exceedingly remark-

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able phenomenon, viz. this that though e.g. for a base metal the solubility of the metal ions is very great and those of the electrons very small, the solubility product of a base metal possesses a comparatively large value.

The case we meet with here, is quite independent of all others, because in the solubility product of a metal, metal ions and electrons occur, which influence each other and carry each other along, so that they neutralize each other electrically except for a very small fraction.

It is now clear that where the solubility of the metal ions is very great, and that of the electrons very small, the metal ions will not go into solution so much as when the electrons did not check the action, and that reversely the electrons will go *more* into solution than when they were not attracted by the metal ions. Thus the *exceedingly remarkable* case presents itself that the liquid coexisting with a base metal, is unsaturate as far as metal ions are concerned, but supersaturate with respect to the metal as far as electrons are concerned. This is accordingly the reason why the metal is negative with respect to the liquid. For a noble metal exactly the reverse is found. Thus we see that according to these considerations a much clearer idea of the electromotive equilibrium can be obtained than was the case with the old view.

The equation (28), which was as onesided as equation (26), which was used up to now, can be of great service to us in many cases.

We have already seen that a noble metal, so a metal with a very small solubility product, immerged in a solution of a mixture of a ferro- and ferri salt, is not attacked. With regard to the said solution the metal is an unassailable electrode, and electrons of the equilibrium

$$Fe^{\cdot\cdot} \leftrightarrows Fe^{\cdot\cdot\cdot} + \theta \ . \ . \ . \ . \ . \ . \ . \ . \ (9)$$

pass from the solution to the metal, while the ionisation equilibrium of the metal shifts.

Here where the two homogeneous equilibria in the solution have only one component, viz. the electrons, in common, the application of our electron equation (28) immediately gives the potential difference, when we consider that from equation (9) follows:

$$K = \frac{(Fe^{\cdot\cdot\cdot})\,(\theta_L)}{(Fe^{\cdot\cdot})} \ . \ . \ . \ . \ . \ . \ . \ (29)$$

hence :

$$(\theta_L) = K \frac{(Fe^{\cdot\cdot})}{(Fe^{\cdot\cdot\cdot})}$$

so that according to equation (28)

$$\Delta = \frac{RT}{F}\left[ln\ K_\theta + ln\ \frac{1}{K}\frac{(Fe^{...})}{(Fe^{..})}\right]. \quad \ldots \ldots \quad (30)$$

from which it therefore appears that our formula differs from the older one:

$$\Delta = \frac{RT}{F}\ ln\ \frac{1}{K}\frac{(Fe^{...})}{(Fe^{..})}$$

in this that here the term $ln\ K^\theta$ is wanting.

This term, however, is very important because it appears from it that different unassailable electrodes yet cannot give entirely the same potential difference, the electron solubility for the metals being different.

By combining equations (26) and (28) we now get a relation for the potential difference, in which both the metal ions and the electrons are taken into account.

When we add these equations we get:

$$\Delta = \frac{RT}{2F}\left[ln\ \frac{K_\theta}{K_M} - ln\ \frac{(\theta_L)}{(M_L)}\right] \quad \ldots \ldots \quad (31)$$

That this new equation gives us a much better insight into the electromotive equilibrium than the old one follows already from this that it enables us immediately to derive the equation for the potential difference for the case that a metal is immerged into a *perfectly pure* solvent.

In this case too metal atoms, metal ions, and electrons of course go into solution, and as in the metal and in the liquid the metal ions and electrons practically neutralize each other everywhere except in the border layer

$$(\theta_L) = (M_L) \quad \ldots \ldots \ldots \quad (32)$$

for this case where the metal ions and electrons originate exclusively from the metal, so that the equation for the potential difference becomes in this case:

$$\Delta = \frac{RT}{2F}\ ln\ \frac{K_\theta}{K_M}. \quad \ldots \ldots \ldots \quad (33)$$

It follows therefore from this that the potential difference between a metal and e.g. pure water can be sharply defined and possesses a finite value which is entirely determined by the solubility of the electrons and by that of the metal ions.

If the solubility of the metal ions is greater than that of the electrons, the metal will be charged negatively with respect to the water, and positively in the opposite case.

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5. *Introduction of the solubility product of the metal in the equation of the potential difference.*

It has been shown in chapter 3 that the solubility product of a noble metal must be smaller than that of a base one, from which it follows that the potential difference metal solution must be a function of the solubility product, and that such a one that for a greater value of the solubility product the metal gets a more negative potential.

In the following way the solubility product is easy to introduce into the equation for the potential difference. For:

$$\Delta = \frac{\mu_{\theta S} - \mu_{\theta L}}{F}$$

we may write: [1]

$$\Delta = \frac{\mu_{\theta S} - \mu_{\theta L} - \mu_{M' L} + \mu_{M L}}{F}$$

If we write $\mu = \mu' + RT \ln c$ we get:

$$\Delta = \frac{\mu_{\theta S}}{F} + \frac{\mu'_{M' L} - \mu'_{M L} - \mu'_{\theta L} + RT \ln (M_L) - RT \ln (M_L)(\theta_L)}{F}$$

$$\Delta = \frac{\mu_{\theta S}}{F} - \frac{\mu'_{\theta L}}{F} + \frac{RT}{F} \ln (M_L) - \frac{RT}{F} \ln (M_L)(\theta_L).$$

The last term of this equation contains the above mentioned solubility product of the metal, which is indicated by L_M, hence:

$$\Delta = \frac{\mu_{\theta S}}{F} - \frac{\mu'_{\theta L}}{F} - \frac{RT}{F} \ln (L_M) + \frac{RT}{F} \ln (M_L) \quad . \quad . \quad . \quad (34)$$

Besides the solubility product of the metal and the metal ion concentration, also the thermodynamic potential of the electrons in the metal and the term $- \dfrac{\mu'_{\theta L}}{F}$ occur in this equation.

The last is independent of the concentration of the electrons, and only dependent on the temperature and the nature of the solvent. Hence this term has the same value for all metals.

The term $\dfrac{\mu_{\theta S}}{F}$ has values for different metals which differ little inter se.

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[1] Here for shortness' sake we suppose the metal univalent, so $\nu = 1$.

The difference $\dfrac{\mu_{0_{S_1}} - \mu_{0_{S_2}}}{F}$ is, namely, the potential difference, which occurs when two metals come in contact, and which is always small in comparison with the potential difference metal-solution

Though equation (34) is little suitable to indicate the potential difference between a metal and a solution, it gives a very simple relation for the potential difference between two metals, e.g. Cu and Zn, which are each immerged in a solution of their ions.

In this case we get, namely,

$$\Delta_1 - \Delta_2 = \frac{RT}{\nu F} \, ln \left(\frac{L_{M_2}}{L_{M_1}} \right) + \frac{RT}{\nu F} ln \left(\frac{M_{L_1}}{M_{L_2}} \right) \quad . \quad . \quad . \quad (35)$$

because $\dfrac{\mu'_{0_L}}{F}$ and $\dfrac{\mu_{0_S}}{F}$ are practically equal for the two metals. In this it has been assumed that the valency ν is the same for the two metals.

When now the concentration of both metal ions in solution is 1, we get:

$$\Delta_1 - \Delta_2 = \frac{RT}{\nu F} \, ln \left(\frac{L_{M_2}}{L_{M_1}} \right) = \frac{0.058}{\nu} \, {}^{10}log \left(\frac{L_{M_2}}{L_{M_1}} \right) \quad . \quad . \quad . \quad (36)$$

It follows from this that the difference between the normal potentials of two metals is equal to $0.058.{}^{10}log$ of the ratio of the solubility products.

If the valency of the metal ions is different, then

$$\Delta_1 - \Delta_2 = \frac{RT}{\nu_2 F} \, ln \, (L_{M_2}) - \frac{RT}{\nu_1 F} \, ln \, (L_{M_1}) \quad . \quad . \quad . \quad (37)$$

in general for $(M_L) = 1$.

If we take the hydrogen electrode as zero point, through which Δ_2 becomes $= 0$, then:

$$\Delta_1 = 0{,}058 \, 10_{log} \, (L_{H_2}) - \frac{0{,}058}{\nu_1} \, 10_{log} \, (L_{M_1}) \quad . \quad . \quad . \quad (38)$$

The normal potential of a metal with respect to $H_2 = 0$ is therefore, exclusively determined by the solubility product of the metal and that of the hydrogen. By this latter we then understand the value which the product $(H^{\cdot})(\theta)$ has in a solution which is saturate with respect to hydrogen of one atmosphere.

When the solubility product of a metal was known, then by the aid of the known normal potentials we should be able to calculate the solubility products of all other metals. This, is, however, not the case. We *may*, however, say that the most negative metal, Li,

must have the greatest solubility product. Now the concentration of the metal ions and electrons can certainly not be greater in a solution than in the pure metal, when this is totally ionized. The atomic weight of $Li = 7$, and the sp.gr. about 0.6. Hence 1 litre of metallic Li weighs about 500 gr. and contains not quite 100 gramatoms Li. Hence the concentration of the Li-ions cannot be greater than 100. The solubility product of Li can, therefore, as $(Li) = (\theta)$, not be greater than 10^4.

This value, which is certainly much too large, only indicates a maximum value. The solubility product will therefore also be smaller than this value, because the concentrations of the ions and electrons are smaller in the coexisting solution than in the metal.

By the aid of it we can indicate an upper value for all other metals. For hydrogen we find e.g., $\Delta_{Li} - \Delta_{H_2}$ being $= -3.0$:

$$L_{H_2} < 10^{-48}$$

for silver, for which $\Delta_{Li} - \Delta_{Ag} = -3.8$ becomes $L_{Ag} < 10^{-61}$.

It appears therefore from this that the solubility products of most metals have very small values. Even for a metal so strongly negative as Na L_{Na} must be $< 10^{-4}$.

Now it appears also from these values that a direct determination of the solubility products is impossible.

As a metal that decomposes water, with formation of hydrogen is more negative than hydrogen and $L_{H_2} < 10^{-48}$, only those metals are not attacked by water for which $L_M < 10^{-48}$, a value which is still much smaller than that of the least soluble salts.

6. Polarisation and Passivity.

We shall now examine if it is possible that a metal in which in case of unary behaviour the ionisation equilibrium

$$M \rightleftarrows M + \theta$$
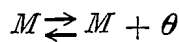
exists, will allow of polarisation, resp. passivation. For this purpose we consider the equations (17a) and (18a)

$$\Delta = -\frac{RT}{F} \ln \frac{K'_M(M_S)}{(M_L)} \quad \ldots \ldots \quad (17a)$$

and

$$\Delta = \frac{RT}{F} \ln \frac{K'_\theta(\theta_S)}{(\theta_L)} \quad \ldots \ldots \quad (18a)$$

From these relations follows:

$$\frac{RT}{F} \ln \frac{K'_\theta(\theta_S)}{(\theta_L)} = \frac{RT}{F} \ln \frac{(M_L)}{K'_M(M_S)}$$

or
$$\frac{(\theta_S)(M_S)}{(\theta_L)(M_L)} = K \quad \ldots \ldots \ldots \quad (9)$$

Now it should be stated here that the equations (17a) and (18a) always hold whether or no the coexisting metal and liquid phases are in internal equilibrium.

Equation (39) says therefore that whether the coexisting phases are in internal equilibrium or not, the quotient of the products of the concentrations of electrons and metal ions in the metal and in the coexisting liquid is a constant quantity at constant temperature and pressure.

This equation (39) is of use to us in answering the question what will happen when the metal is anodically dissolved and the reaction

$$M \rightarrow M^{\cdot} + \theta$$
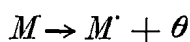
does not proceed quickly enough. so that through the electrons being led off and the metal ions going into solution, the metal becomes poorer in both electric components. In this we must keep in view that these processes take place in such a way that the metal ions and the electrons in the metal always electrically neutralize each other with the exception of an exceedingly small fraction.

We may, therefore, say that when the electron concentration (θ_S) becomes n-times smaller, the same thing will happen with the metal-ion-concentration (M_S). It is further clear that the circumstances may easily be chosen so that the metal-ion-concentration in the liquid (M_L) remains practically constant, from which then follows in connection with equation (39) that the electron-concentration in the liquid (θ_L) must become n^2-times as small.

Thus we arrive at the conclusion that *a decrease of the electron concentration in the metal is attended with a still greater decrease of the electron concentration in the coexisting liquid.*

Now that this has once been established, we can, with application of the equations (17a) and (18a) immediately give an answer to the question in what way the potential difference will change when the concentration of the metal ions and electrons diminishes in consequence of the ionisation proceeding too slowly as has been supposed here. It follows from (17a) that when the concentration of the metal ions in the metal (M_S) becomes smaller, the potential difference will become *less negative* or *positive*.

The influence of a change of the electron concentration follows from equation (18a). If the electron concentration in the metal diminishes, then as we saw before, the electron concentration in the

coexisting liquid will diminish to a still greater degree, so that $ln \left(\dfrac{\theta_S}{\theta_L}\right)$ will become smaller negative or greater positive. It is evident that the two equations, if they are correct, must give the same result, as is really the case here.

Hence we have come to the conclusion in this way that a metal with the most simple constitution can exhibit the phenomenon of anodic polarisation, resp. passivity as well and in virtue of the same circumstance as a more complicated metal. The said phenomena will present themselves for every metal when the removal of metal ions and electrons from the metal takes place more rapidly than their formation in the metal [1]). It is clear that a passivity brought about by chemical action, might be explained in exactly the same way when we consider that ions and electrons react chemically more quickly than uncharged atoms. We have not mentioned cathodic polarisation here, but it is clear that this phenomenon is to be expected here too, and can then be explained according to the same principle. In a following communication the cases will be treated represented by the equations (2) and (3).

The views given here are new, as far as we have been·able to ascertain. In our subsequent study of the literature we have only in one place come across statements which suggest that the writer had views tending in the same direction in which the problem is treated here, but the thoughts were not elaborated. We allude here to a paper by HABER and ZAWADSKY [2]); this paper ends with an "Anhang", and in this the statements above referred to are found.

(To be continued).

Anorganic Chemical Laboratory of
Amsterdam, February 24, 1916.   the University.

Chemistry. — *"On the allotropy of the ammonium halides".* II [3]).
     By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of Feb. 26, 1916).

10. *The transformation heat of ammonium chloride at the transition point.*

I have determined the difference of energy of the two modifica-

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[1]) From this must ensue that the superficial electric conductivity of a metal must be smaller in the passive state than in the active state.

[2]) Zeitschr. f. physik. Chem. **78**, 228 (1911).

[3]) First communication. These Proc. XVIII p. 446.