

*Citation:*

A.H.W. Aten & A. Smits, The Application of the Theory of Allotropy to Electromotive Equilibria. V, in: KNAW, Proceedings, 19 I, 1917, Amsterdam, 1917, pp. 133-148

**Chemistry.** — “*The Application of the Theory of Allotropy to Electromotive Equilibria*”. V <sup>1)</sup> By Prof. A. SMITS and Dr. A. H. W. ATEN. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated at the meeting of May 27, 1916).

1. *Introduction.*

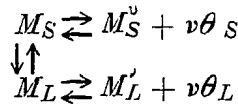
In our preceding communication we introduced a new view of electromotive equilibria, which is based on the assumption that the electrons in a metal phase and in the coexisting electrolyte behave as ions.

Starting from these suppositions we have discussed among other things also the potential difference metal-electrolyte, in which new relations were obtained.

In the derivation of these relations the case was supposed (first case) that the metal was built up exclusively of metal atoms, univalent metal ions and electrons. Now we will in the first place consider the case that the metal consists of atoms, *v*-valent metal ions and electrons, after which we shall proceed to the second case that in the metal there are present by the side of atoms and electrons, metal ions of different valency.

2. *The metal consists of metal atoms, v-valent metal ions, and electrons.*

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



We then get the two following relations for the potential difference:

$$\Delta = - \frac{\mu_{M_S^v} - \mu_{M_L^v}}{F} \dots \dots \dots (1)$$

and

$$\Delta = \frac{v\mu_{\theta_S} - v\mu_{\theta_L}}{vF} = \frac{\mu_{\theta_S} - \mu_{\theta_L}}{F} \dots \dots \dots (2)$$

If we again split up the mol. thermodynamic potential as follows:

$$\mu = \mu' + RT \ln C \dots \dots \dots (3)$$

and if we put:

$$\mu'_{M_S^v} - \mu'_{M_L^v} = RT \ln K_M \dots \dots \dots (4)$$

<sup>1)</sup> In the preceding communication III had been erroneously put for IV.

and

$$\mu'_{\theta_S} - \mu'_{\theta_L} = RT \ln K'_0 \quad \dots \quad (5)$$

we get in perfect agreement with our foregoing communication:

$$\Delta = - \frac{RT}{vF} \ln \frac{K'_M \cdot (M'_S)}{(M'_L)} \quad \dots \quad (6)$$

and

$$\Delta = \frac{RT}{F} \ln \frac{K'_\theta(\theta_S)}{(\theta_L)} \quad \dots \quad (7)$$

The last electron-equation is of course the same as for a univalent metal.

If we now combine these two equations, we get:

$$\Delta = \frac{RT}{2vF} \left[ v \ln \frac{K'_\theta(\theta_S)}{(\theta_L)} - \ln \frac{K'_M \cdot (M'_S)}{(M'_L)} \right] \quad \dots \quad (8)$$

or

$$\Delta = \frac{RT}{2vF} \left\{ \ln \frac{K'_\theta(\theta_S)}{K'_M \cdot (M'_S)} - \ln \frac{(\theta_L)}{(M'_L)} \right\} \quad \dots \quad (9)$$

If we now again write  $K'_\theta(\theta_S) = K_\theta =$  solubility electrons

and  $K'_M(M'_S) = K_M =$  „ metal ions,

we get instead of (8) and (9):

$$\Delta = \frac{RT}{2vF} \left[ v \ln \frac{K_\theta}{(\theta_L)} - \ln \frac{K_M \cdot (M'_S)}{(M'_L)} \right] \quad \dots \quad (10)$$

or

$$\Delta = \frac{RT}{2vF} \left[ \ln \frac{K_\theta}{K_M} - \ln \frac{(\theta_L)}{(M'_L)} \right] \quad \dots \quad (11)$$

The solubility product is in this case:

$$L = (M'_L)(\theta_L) \quad \dots \quad (12)$$

from which therefore follows that when  $(M'_L)$  is doubled, the concentration of the electrons becomes smaller by  $2^{1/v}$ .

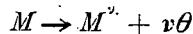
If we take this into account in the discussion of equation (11), we see that this change of concentration causes an increase of the *positive*, or a decrease of the *negative* potential difference.

### 3. Potential difference of the metal with respect to the pure solvent.

From equation (11) the relation for the potential difference for

the case the metal is immersed in a perfectly pure solvent, may be easily derived.

From the equation:



follows that the concentration of the electrons will be  $v$  times as great as that of the metal ions, so that:

$$(\theta_L) = v (M_L^v).$$

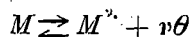
If we now substitute this value for  $(\theta_L)$  in equation (11), we get:

$$\Delta = \frac{RT}{2vF} \left[ \ln \frac{(K_\theta)^v}{K_{M^v}} - v \ln v \right]. \dots \dots \dots (13)$$

This equation expresses that the potential difference between a  $v$ -valent metal and a pure solvent is entirely determined by the valency and by the solubility of the metal ions and electrons.<sup>1)</sup>

4. *Polarisation and passivity of a metal that contains only one kind of metal ions.*

Now the question can be answered whether it is possible that a metal, in which in case of unary behaviour the internal equilibrium



prevails, can be polarized resp. made passive.

To answer this question we start from our equations (6) and (7), from which follows that

$$\frac{(M_L^v)}{K_{M^v} (M_S^v)} = \frac{(K_\theta)^v (\theta_S)^v}{(\theta_L)^v}$$

or

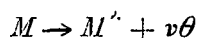
$$\frac{(M_S^v) (\theta_S)^v}{(M_L^v) (\theta_L)^v} = K \dots \dots \dots (14)$$

As was already stated in the foregoing communication equations (6) and (7) hold generally, hence also when the metal is not in internal equilibrium.

When it is asked how in equations (6) and (7) the fact of the internal equilibrium expresses itself, the answer is, in the constancy of the concentrations  $(M_S^v)$  and  $(\theta_S)^v$ . If there is no internal equilibrium, then these are not the equilibrium concentrations; but the equations (6) and (7) hold nevertheless, and also (14) derived from them.

<sup>1)</sup> Of course this potential difference can only be determined after the metal and the solvent have been made perfectly free from gas.

Now we imagine the case that the metal is so rapidly dissolved anodically or in another way, that the reaction



does not proceed rapidly enough to supply the abducted electrons and metal ions, so that the metal gets poorer in these two electrical components. If we now consider that the electrons and the metal ions always neutralize each other electrically, with the exception of only an exceedingly small fraction, then a closer examination of equation (14) gives the following conclusion.

Suppose that the metal ion concentration in the metal ( $M'_S$ ) becomes  $n$ -times smaller by anodic solution etc., then the electron concentration ( $\theta_S$ ) also becomes  $n$ -times smaller, so that the numerator of (14) will become  $n^{v+1}$  times smaller in consequence of this.

If we further assume, what is allowed for a sufficient quantity of solution, that the ion concentration ( $M'_L$ ) is constant in the coexisting electrolyte, ( $\theta_L$ )' will have to become  $n^{v+1}$  times as small, from which it appears that the *electron concentration in the coexisting electrolyte* ( $\theta_L$ ) *will decrease to a greater extent than that in the metal* ( $\theta_S$ ).

From equation

$$\Delta = -\frac{RT}{vF} \ln \frac{K' M^v \cdot (M'_S)}{(M'_L)} \dots \dots \dots (6)$$

follows that when ( $M'_S$ ) becomes smaller, and ( $M'_L$ ) remains constant, the potential difference will become less negative or greater positive.

When ( $M'_S$ ) decreases, the result is — as we have seen just now — that  $\frac{(\theta_S)}{(\theta_L)}$  becomes *greater*, from which appears in connection with the formula :

$$\Delta = \frac{RT}{F} \ln \frac{K'_0(\theta_S)}{(\theta_L)} \dots \dots \dots (7)$$

that the potential difference will become less negative or greater positive.

As was already set forth at length in the preceding communication in the discussion of a univalent metal, this points to the possibility of anodic polarisation and passivity, while perfectly analogous considerations lead to the cathodic polarisation.

These phenomena must then be explained by a too slow establishment of the internal equilibrium between metal atoms, metal ions, and electrons.

5. *The metal contains ions of different valency.*

We shall now suppose that ions of different valency occur in the metal, viz. the ions  $M^1$  and  $M^2$ .

In the metal we then have the equilibria .

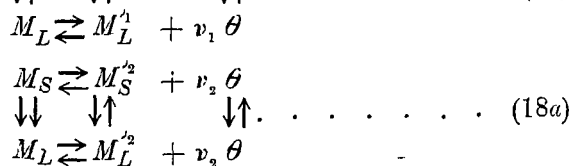
$$M \rightleftharpoons M'^1 + v_1 \theta \quad \dots \quad (15)$$

$$M \rightleftharpoons M'^2 + v_2 \theta \quad \dots \quad (16)$$

and

$$M'^1 \rightleftharpoons M'^2 + (v_2 - v_1) \theta. \quad \dots \quad (17)$$

Between the metal and the electrolyte we can then give the equilibria as follows .



*in which it is noteworthy that these equilibria are probably established in the electrolyte with very great velocity, but that they are not established in the dry metal at the ordinary temperature, or exceedingly slowly.*

In the case that the metal possesses two different kinds of ions, we have to do with two solubility products viz.

$$L_{M_1} = (M'_L{}^1) (\theta_L)^{v_1}. \quad \dots \quad (19)$$

and

$$L_{M_2} = (M'_L{}^2) (\theta_L)^{v_2}. \quad \dots \quad (20)$$

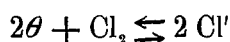
Supposing that  $M'^1$  is a base and  $M'^2$  is a noble ion, then as we have set forth at length in our former communication,  $L_{M_1}$  is comparatively great and  $L_{M_2}$  small. If we immerse a homogeneous mixed crystal phase of two salts with homonymous anion, one of which possesses a great, and the other a small solubility product, in water, we have a state which in many respects corresponds with the case supposed here.

Thus the electrolyte, in which the supposed metal is placed, will possess a comparatively great concentration of  $M'^1$ -ions and electrons,  $\theta$ , but a very small concentration of  $M'^2$ -ions, and that smaller than when the metal contained only  $M'^2$ -ions, because in consequence of the relatively great solubility product  $L_{M_1}$  the electron concentration is much greater.

It is clear that the explanations of different electromotive processes given in our preceding communication through application of the idea "solubility product" of a metal are now just as well applicable to this more complicated case as to the simple one. Now, however,

to account for all the important circumstances, we shall have to occupy ourselves with the *three* equilibria (15) (16) and (17).

If we e.g. suppose that the metal is immersed in pure water, and chlorine is added, the metal will be dissolved in consequence of the removal of electrons on account of the small electron concentration of the equilibrium:



Now equation (17) expresses that a second consequence of this removal of the electrons is an increase of the concentration ratio  $\frac{M_L'^2}{M_L'}$ .

### 6 The equations for the potential difference metal-electrolyte

For the case supposed here we get for the potential difference metal-electrolyte the equations

$$\Delta = -\frac{RT}{v_1 F} \ln \frac{K'_{M^1} (M_S^1)}{(M_L^1)} \dots \dots \dots (21)$$

$$\Delta = -\frac{RT}{v_2 F} \ln \frac{K'_{M^2} (M_S^2)}{(M_L^2)} \dots \dots \dots (22)$$

and the electron-equation

$$\Delta = \frac{RT}{F} \ln \frac{K'_\theta (\theta_S)}{(\theta_L)} \dots \dots \dots (23)$$

From (21) and (22) now follows

$$\left[ \frac{K'_{M^1} (M_S^1)}{(M_L^1)} \right]^{1/2} = \left[ \frac{K'_{M^2} (M_S^2)}{(M_L^2)} \right]^{1/2} \dots \dots (24)$$

or

$$\frac{K'^2_{M^1} (M_S^1)^2}{K'^1_{M^2} (M_S^2)^1} = \frac{(M_L^1)^2}{(M_L^2)^1} \dots \dots \dots (25)$$

We shall now assume that  $K'_{M^1}$  is very great compared with  $K'_{M^2}$  or in other words that the ions  $M^1$  are very much baser than  $M^2$ .

In this case the fraction  $\frac{(M_L^1)^2}{(M_L^2)^1}$  is very great, and much greater than  $\frac{(M_S^1)^2}{(M_S^2)^1} \frac{K'^2_{M^1}}{K'^1_{M^2}}$  being so exceptionally great.

When  $\frac{(M_S^1)^2}{(M_S^2)^1}$  is not very small,  $\frac{(M_L^1)^2}{(M_L^2)^1}$  will always be very great positive. Now  $(M_L^1)$  can however, not be arbitrarily great, though  $(M_L^2)$  can, indeed, be arbitrarily small.

It follows from this that the very great value of the fraction  $\frac{(M_L^1)^2}{(M_L^2)^1}$  is caused by the small value of  $(M_L^2)$  in the case supposed here.

If we now call the total concentration of the ions  $C$ , practically  $M_L^1$  will be  $= C$ .

In this case we can therefore write for (21)

$$\Delta = -\frac{RT}{v_1 F} \ln \frac{K' M^1}{C} - \frac{RT}{v_1 F} \ln (M_S^1) \dots \dots (26)$$

It then follows from this equation that when the total ion concentration  $C$  is constant, the potential difference in the metal will become more strongly negative on increase of the concentration of the base ion  $M^1$ , in the metal and more strongly positive on decrease of this concentration.

7. *The metal assumes internal equilibrium.*<sup>1)</sup>

Now we shall suppose that in the electrolyte the equilibrium sets in between atoms, ions, and electrons, which is accompanied with a setting in of the internal equilibrium in the metal. If the metal is in internal equilibrium, its state is perfectly determined for definite temperature and pressure, i.e. the concentrations of the atoms, ions, and electrons in the metal are then under these circumstances constant quantities.  $(M_S^1)$  and  $(M_S^2)$  are constants; hence in connection with (25)

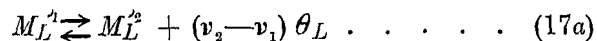
$$\frac{(M_L^1)^2}{(M_L^2)^1} = K' \dots \dots \dots (27)$$

will hold for the coexisting electrolyte.

We can also arrive at this conclusion by another way. When internal equilibrium prevails in the metal, the same equilibria will occur in the coexisting electrolyte as in the metal, viz.:

<sup>1)</sup> The internal equilibrium may be defined as the equilibrium in a phase of a unary system.





If we now apply the law of mass action to this equation, we get:

$$K_1 = \frac{(M_L^{v_1}) (\theta_L)^{v_1}}{(M_L)} \quad \dots \quad (28)$$

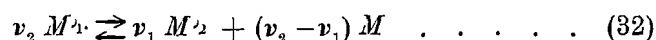
$$K_2 = \frac{(M_L^{v_2}) (\theta_L)^{v_2}}{(M_L)} \quad \dots \quad (29)$$

$$K_3 = \frac{(M_L^{v_2}) (\theta_L)^{v_2 - v_1}}{(M_L^{v_1})} \quad \dots \quad (30)$$

If by combination of two of these three equations we eliminate the electron concentration, we get the relation:

$$K_4 = \frac{(M_L^{v_2})^{v_1} (M_L)^{v_2 - v_1}}{(M_L^{v_1})^{v_2}} \quad \dots \quad (31)$$

from which appears, as also follows directly by elimination of the electron concentration from the equations (15a) and (16a), that as far as the *final result* is concerned, the equilibrium in the electrolyte, and of course also in the metal, can be considered as follows:



If we now bear in mind that  $(M_L)$  is a saturation concentration in the electrolyte, which is in contact with the metal, we get for this case:

$$K_4' = \frac{(M_L^{v_2})^{v_1}}{(M_L^{v_1})^{v_2}} \quad \dots \quad (33)$$

Now that we know that with constant temperature and pressure  $\frac{(M_L^{v_1})^{v_2}}{(M_L^{v_2})^{v_1}}$  must be a constant quantity, it is easy to examine the influence of a change of concentration on the potential difference in case of internal equilibrium.

If e.g. we double the concentration, the ratio (27) would become  $2^{v_2 - v_1}$  times as great, when no internal transformations took place. As, however, this fraction has to remain constant in case of internal equilibrium  $(M_L^{v_1})$  will decrease and  $(M_L^{v_2})$  will increase. When we only want to determine in this increase of concentration the direction of the shifting of the equilibrium, of course equation (32) will be sufficient, because, when it is borne in mind that the concentration

of the metal atoms is a saturation concentration, it immediately follows from this equation on application of the principle of the shifting of equilibrium that the equilibrium shifts to the right,  $v_2$  being  $> v_1$  on increase of concentration.

It is here the place to point out how easy the application of the electron equation is, at least when our purpose is to indicate the direction of the potential changes.

On examination of equation.

$$\Delta = \frac{RT}{F} \ln \frac{K_0'(\theta_S)}{(\theta_L)} \dots \dots \dots (23)$$

and the equilibrium:

$$M_L^1 \rightleftharpoons M_L^2 + (v_2 - v_1) \theta_L \dots \dots \dots (17a)$$

we can immediately answer the questions under consideration.

When e.g. with constant total concentration we increase the concentration of the  $M_L^2$ -ions, the equilibrium (17a) will shift to the left; and the concentration of the electrons ( $\theta$ ) will decrease.

Equation (23) then expresses that the potential difference will increase.

If we raise the total concentration, the equilibrium (17a) will also shift to the left; also in this case the potential difference rises.

If there were an easy way to find out the electron concentration, it appears from this that the electron equation would be preferable.

#### 8. *Polarisation and passivity of metals with ions of different valency.*

We have seen that for the metals which contain only one kind of ions, polarisation and passivity can occur in consequence of a decrease of the number of ions and electrons in the surface of the metal caused by an insufficiently rapid setting in of the internal equilibrium.

Let us now consider a metal built up of two different kinds of ions, then for the reason mentioned polarisation and passivity will take place also here, but when the internal equilibrium does not set in quickly enough, a second circumstance will take place here causing polarisation and passivity, viz. this that as was already shown in earlier communications, the concentration of the noble ion in the metal surface will increase, and that of the base ion will decrease. It is, therefore, clear that such a metal will be the most suitable material to exhibit the phenomena of polarisation and passivity in all their particulars.

We will once more elucidate this phenomenon somewhat further

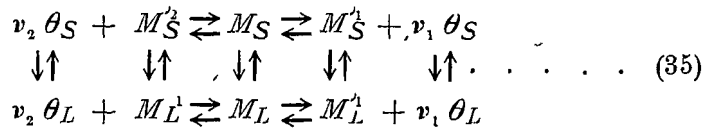
here. The most rational proceeding is to start from the case that heterogeneous equilibrium always prevails between the metal and the adjoining liquid layer, that therefore the electrochemical equilibrium always continues to exist.

We can represent this by the following symbols:



These equilibria, therefore, always exist.

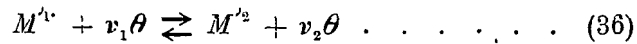
The equilibrium



on the other hand only exists, when the unary metal and the electrolyte are in electromotive equilibrium.

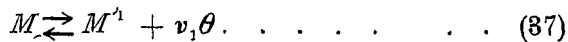
During the anodic polarisation, however, only the equilibria represented by (34) exist, the homogeneous equilibria having been interrupted, but transformations take place which, when the current has been interrupted, will again reduce the metal to the unary state, and cause the original electromotive equilibrium to reappear.

Only metals with different kinds of ions being considered, the slow establishing of the internal equilibrium



has been given as the cause of the polarisation and the passivity in the preceding communications.

This is perfectly correct, but we may add to this, that even if this equilibrium set in with great velocity, polarisation and passivity would occur all the same when the following equilibria:



and



set in slowly.

Reversely it is immediately seen that when the internal equilibrium (36) does not set in by a direct way, but (37) and (38) set in rapidly, the equilibrium (36) would yet set in with great velocity, but now in an indirect way.

Hence it is clear that the real ground for the possibility of the occurrence of polarisation and passivity is the slow establishment of the internal equilibrium of the equations (37) resp. (38).

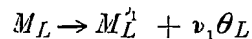
Now all kinds of phenomena point to the fact that hydrogen ions very considerably accelerate the setting-in of the internal equilibrium in the metal surface moistened with an electrolyte, and this makes it clear on one side why the polarisation assumes large amounts when we succeed in removing the hydrogen from the metal surface, and why on the other hand the potential of the unary metal (formerly called potentials of equilibrium) sets in most easily when the metal contains many hydrogen ions.

If after anodic polarisation the current is broken off, the disturbance is comparatively quickly cancelled, when the polarisation has not lasted long, and no or little generation of  $O_2$  has taken place, so that the metal was still comparatively rich in hydrogen. If, however, the polarisation has taken place a long time during generation of oxygen, the metal surface has become very poor in hydrogen, and the disturbance continues to exist a relatively long time also after interruption of the current.

This shows the strongly positive catalytic influence of the hydrogen or the negative influence of the oxygen.

The fact that metal poor in hydrogen or rich in oxygen slowly assumes internal equilibrium after interruption of the polarizing current even when in contact with the electrolyte, is astonishing on superficial consideration, when we consider that a rapid setting in of the equilibrium in the liquid, which is, indeed, to be expected, can bring about an internal equilibrium in the metal, even if the velocity of the internal transformations in the metal is practically zero.

For this it is only necessary that the reaction:

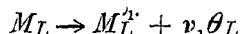


takes place in the electrolyte, and further that uncharged metal atoms go into solution, the metal ions  $M^+$  and electrons from the electrolyte passing into the metal. This astonishment, however, immediately vanishes, when we consider that the saturation concentration of the uncharged metal atoms is so exceedingly small that even if the reaction constant of the reaction (37) were very great, the quantity of metal ions and electrons formed per unity of time, would be exceedingly small. In a separate chapter we shall treat the influence of the small value of the concentration of one of the components of a chemical system on the course of a process. It is, therefore, clear that the transformations in the liquid can practically have *any* part in the establishment of the internal equilibrium in the metal only when a process is concerned that requires a very long time.

Generally, however, the internal equilibrium has been established

in a short time, and then it is, indeed, clear that we must *exclusively* look for the cause of this setting in of the equilibrium in the metal surface.

In this it is supposed that the metal remains in contact with the liquid in which it is polarized, or is transferred to a liquid in which the concentration of the  $M^{\prime}$ -ions and electrons is smaller than in the liquid which is in electromotive equilibrium with the unary metal. In this case the reaction



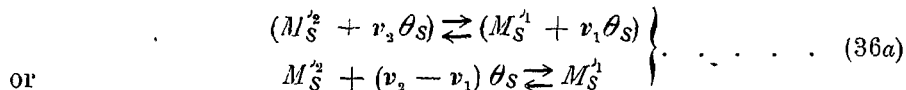
would have to cause a sufficient increase of the concentration of the  $M_L^{\prime}$ -ions and electrons in a short time, so that these by deposition on the metal could reduce the latter to the state of internal equilibrium.

In some cases, however, it will be possible to bring the metal in an electrolyte in which the concentration of the  $M^{\prime}$ -ions and electrons is greater than in the liquid in electromotive equilibrium with the unary metal, and then, of course, the case is different, for then the  $M^{\prime}$ -ions and electrons will deposit on the metal without there being any necessity of the above-mentioned reaction taking place, and in this case the electrolyte will certainly be able to reduce the metal to the state of internal equilibrium in a comparatively short time. If in this way a sufficient quantity of baser ions is deposited, also the occurrence of local currents will greatly accelerate the establishment of the internal equilibrium.

If, however, we do not make use of such a liquid, the electrolyte, as has been said, will have to be left out of account for a rapidly proceeding activation, and the setting in of the internal equilibrium takes place exclusively by transformations in the metal surface, in which the reaction:

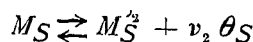
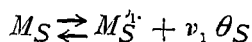


will take place, till the equilibrium corresponding to the unary metal:



has again set in.

After anodic polarisation it is, therefore, the reaction (38a) that governs the setting in of the internal equilibrium, and speaking generally we may say that a metal can be thrown out of its state of internal equilibrium through the comparatively slow progress of the reversible reactions



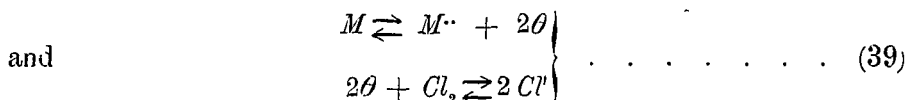
in the metal surface in the absence of catalysis.

This explains not only the anodic polarisation, but also the cathodic and chemical disturbance of the metal.

9. *The influence of the smallness of the concentration of a component on the course of a process.*

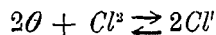
In connection with the remark in the preceding chapter that the quantity of metal, which comes to equilibrium via the coexisting liquid, is exceedingly slight, even when the constant of the reaction is very great, we will point out that the same thing holds for all reactions in which one of the reacting components is present in very slight concentration. This should also be taken into consideration with the explanation of different electromotive processes by the application of the idea "Solubility product of the metal" given in the foregoing paper.

That e.g. the action of chlorine water on a metal can be represented by the equations:



does not imply that a metal brought into chlorine water reacts exclusively or chiefly in this way that the metal dissolves as atom, and splits up into metal ions and electrons, of which the latter are bound to chlorine ions by the chlorine. These equations only mean that the reaction *can* and partly also *will* take place in this way. That the part of the total transformation which takes place according to (39) can be very slight, easily appears in the following way. If the solution is permanently saturated with respect to  $M$ , and if  $M^{\cdot\cdot} = 1$  then  $(\theta) = \sqrt{L_M}$ .

The velocity of the reaction



is given by

$$\frac{d(Cl')}{dt} = k (Cl_2) \cdot L_M.$$

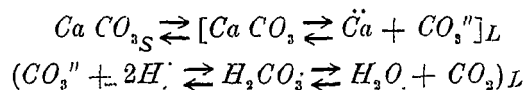
The solubility product of a metal that does not decompose water being smaller than  $10^{-10}$ , the quantity  $Cl'$  formed in this way will be only insignificant, even for a very great value of  $k$ .

As the same thing holds for all other reactions in which a metal

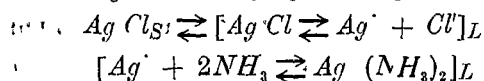
reacts, as has been set forth here for the action of chlorine, we shall have to assume that the transformations to which a metal is subjected, practically take exclusively place at the surface of the solid metal. Thus e.g. the generation of hydrogen, the deposition of a nobler metal by a less noble one etc. Considerations like those that have been applied in § 3 of the preceding papers, have also been frequently applied for other transformations, not however for the purpose of showing how the reaction in reality proceeds for the greater part, but to indicate *in what direction the transformation must take place, and what final state is reached.*

We remind e.g. of the transformation of one modification of a substance into another. The most stable form having the smallest vapour tension and the smallest solubility, it is clear that the metastable form must be transformed into the more stable form in contact with vapour or solution. This, however, does not mean that this transformation always takes place chiefly over the vapour or the solution, on the contrary it may be predicted with certainty in virtue of what was derived above, that these transformations, when they take place quickly, do not take place via the vapour or the solution; this can only take place when the transformation takes place exceedingly slowly.

Also for the dissolving of a deposit by the addition of reagents generally the conception is used that the deposition goes into solution, and is then converted in the aqueous solution by the added substance. The solution of  $CaCO_3$  into  $HCl$  e.g. is represented as follows:



and the solution of  $AgCl$  in  $NH_3$  by the equations:



The equations, however, only serve to show that  $CaCO_3$  dissolves in  $HCl$  and  $AgCl$  in  $NH_3$ , and what conception can be used then in connection with the equilibria that can occur in the said system.

But it does not follow at all from this that  $CaCO_3$  really chiefly goes into solution in this way. In connection with the slight solubility of the substance in water this is certainly by no means the case, and the solution must therefore take place by the action of  $HCl$  or  $H_2$  on the *solid*  $CaCO_3$ , and of  $NH_3$  on the *solid*  $AgCl$ . The same objection that a reaction would proceed quickly with a very small concentration of one of the reacting components has already been discussed with the electrolytic deposition of metal from

solutions of complex cyanides. HABER <sup>1)</sup> showed, namely, that when we wanted to attribute the metal deposition in these cases to direct discharge of the elementary metal ions, the velocity with which these are formed from the complex ions, would have to be exceedingly great, much greater than any known velocity. HABER, therefore, assumes that the deposition of metal takes place, not by the discharge of the elementary metal ions, which are present in a very small quantity, but because the complex ions  $M(CN)_2$  present in large quantities, combine with an electron, and split up into  $M$  and  $2CN$ .

10. *Polarisation during the electrolytic generation of halogens, oxygen etc.*

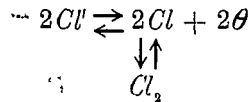
It has therefore appeared from what precedes that the ionisation or the splitting off of electrons is a process that proceeds comparatively slowly in some cases.

Also in the electrolytic generation of the halogens, of oxygen etc., polarisation phenomena have been observed, which points to the fact that here too relative retardations come into play. The electrolytic generation consists in a splitting off of electrons, as the following equation indicates:



And as for metals we are compelled to assume that the splitting off of an electron from a neutral atom proceeds comparatively slowly, it is natural to assume that the splitting off of an electron from a negatively charged atom does not proceed with an infinite velocity either, so that this process too can be relatively retarded for a definite current density.

The concentration of the electrons in the liquid being exceedingly small, the generation of  $Cl$  will take place practically exclusively at the metal surface. We can now imagine that at the surface of the metal which is in equilibrium with chlorine and chlorine ions, the following equilibria exist:



When the splitting of chlorine ions in atoms and electrons at the boundary surface metal-solution is relatively retarded above a certain current density, the concentration of the chlorine ions will be too great in the boundary layer, and that of the electrons too small.

<sup>1)</sup> Z. Elektr. 10 (1904) 433, 773.



Consequently the metal will exhibit a potential that is more positive than the equilibrium potential.

#### OBSERVATION.

Analogous considerations as those on page 135, given there of a metal in a solution of its ions and electrons, hold for every equilibrium between coexisting phases which contain charged particles of different solubility. In this case a potential difference will always occur, given by the equation  $\Delta = -\frac{\mu_1 - \mu_2}{vF}$ , where  $\mu_1$  and  $\mu_2$  indicate the molecular thermodynamic potentials of the charged particles in the two phases. As these in general will not be the same, there must exist a potential difference.

This applies then also e.g. for a salt in equilibrium with its saturate solution, for a solid salt in equilibrium with its melt etc.

*Amsterdam, May 25, 1916. Anorg. Chem. Lab. of the Univ.*

**Physics.** — “*On Diffusion in Solutions.*” I. By Dr. J. D. R. SCHEFFER and Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 27, 1916).

1. *Introduction.* EINSTEIN has derived expressions which indicate how the mean square of the deviation of a Brownian particle and the diffusion constant depend on the nature of the substances and the temperature<sup>1</sup>). The relation between the Brownian movement, indicated by :

$$\overline{\Delta^2} = \frac{RT}{N} \frac{1}{3\pi a \zeta} t, \dots \dots \dots (1)$$

and the diffusion constant is expressed by :

$$D = \frac{\overline{\Delta^2}}{2t}, \dots \dots \dots (2)$$

so that for the latter

$$D = \frac{RT}{N} \frac{1}{6\pi a \zeta}, \dots \dots \dots (3)$$

is found, an expression, which can also be found by a direct way by making use of the osmotic pressure, which as apparent force causes the diffusion, and the law of STOKES, which gives the resist-

<sup>1</sup>) EINSTEIN. Ann. d. Phys (4) 19. 289. 371 (1906). Zeitschr. f. Elektrochem. 14. 235 (1908)