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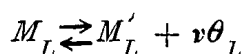
**Chemistry.** — “*Metals and Non-Metals*”. By Prof. A. SMITS. (Communicated by Prof. P. ZBEMAN).

(Communicated in the meeting of May 3, 1919).

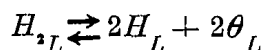
*Introduction*

In a few previous communications I already discussed the unattackable electrodes and their efficiency as gas-electrodes. Only the hydrogen electrode was, however, discussed in detail. It was pointed out that the unattackable electrodes are among the most inert metals, being so inert that even in contact with an electrolyte they do not assume internal equilibrium, so that they are almost always in disturbed condition, and we do not even know the potential of the really unary metal.

When such a metal is immersed in the aqueous solution of an acid, while hydrogen is passed through, the electron concentration of the metal equilibrium in the electrolyte, which we represent by the equation.



becomes equal to the electron concentration of the hydrogen equilibrium.



in agreement with the pressure of the hydrogen that is passed through, which means that the hydrogen phase and the hydrogen-containing metal-phase possess the same potential, the electromotive force of the circuit metal-electrolyte-hydrogen being given by the equation

$$E = -\frac{RT}{F} \ln \frac{(\theta_L)_M}{(\theta_L)_{H_2}} \dots \dots \dots (1)$$

Hence the hydrogen-electrode indicates the potential belonging to the three-phase equilibrium metal phase + hydrogen phase + electrolyte in accordance with the prevailing pressure, temperature, and total ion concentration ( $H$ ) + ( $M'$ ). As, however, as was already stated in the discussion of the  $E, X$ -fig., the said electrolyte contains an entirely negligible concentration of ions of the so-called unattackable electrode, we may substitute the words hydrogen-ion-concentration for “total-ion-concentration”

When we now consider the case that an unattackable electrode is placed in an electrolyte, chlorine being led through, we get the same thing in so far that the electron concentration of the metal equilibrium in the electrolyte is entirely dominated by the electron concentration of the chlorine equilibrium:



in agreement with the pressure of the chlorine that is led through, from which follows that the chlorine-gas phase and the chlorine-containing metal phase will possess the same potential with respect to the electrolyte. Our more recent views about the electromotive equilibria lead to the assumption of an electro-ionisation equilibrium in chlorine gas, though the concentration of ions and electrons in this gas-phase is exceedingly small. That there exists such an electro-ionisation for chlorine, is proved by the exceedingly slight electrical conductivity. Now, however, the above mentioned equilibrium (2) does not suffice, for in electrically neutral chlorine this equilibrium cannot occur *alone*, because here there is only question of particles charged negatively electrically. Besides the chlorine electrode could not assume a positive charge with respect to the electrolyte.

Undoubtedly this difficulty has also been felt in the former view about the electromotive equilibrium. The negative charge which zinc assumes on immersion into an electrolyte was explained as follows: The zinc tends to go into solution as zinc-ion, and it has evidently always been imagined that this happened through a *simultaneous* splitting up of the zinc-atom into zinc-ion + electrons, in which, however, the zinc-ions only went into solution, and the negatively charged electrons remained on the metal.

When we wish to account for the positive charge which the chlorine electrode assumes with respect to an electrolyte in an analogous way, we get into serious difficulties, which have led to the assumption by some physicists that besides the free negatively charged electrons there exist also free positively charged electrons, and that these could render important services for the chlorine electrode and for the other non-metal electrodes. For just as the splitting up



was assumed when the zinc went into solution, the process



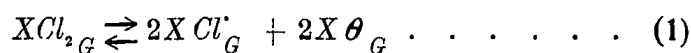
was supposed to take place at the chlorine electrode when chlorine went into solution. The chlorine ions formed go into solution and the positive electrons would be left behind in the chlorine electrode

This solution should, however, be denied all signification, because as yet free positive ions have not been met with, and everything points to the existence of only one kind of electrons, viz. the negative ones.

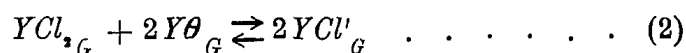
Hence in spite of a desperate attempt, the difficulty remained undiminished of force.

### *The Chlorine-Electrode.*

When considering the just-discussed difficulty, I have come to the conclusion that we must necessarily assume that the chlorine atom possesses the power to split off electrons and to absorb them, and that these two processes take place side by side, which we can represent by the following equations: <sup>1)</sup>



and



in which  $X$  and  $Y$  indicate the fractions of the original number  $Cl_2$  mol. which have undergone a positive resp. negative ionisation.

As the electrons, which are absorbed according to (2) proceed from the electron-ionisation (1) it is clear that

$$Y \leq X.$$

In the limiting case  $Y = X$  the chlorine would contain an equal number of positive and negative ions, and no electrons at all. As we have to do here with a non-metal,  $X$  and  $Y$  will be exceedingly small.

It is now the question how the positive charge of the chlorine electrode is to be explained. It is clear that for this we should have to assume that for the non-metal, chlorine, it is the negative ions that go practically exclusively into solution, and possess, therefore, a much greater solubility than the positive ones.

### *Metals and Non-Metals.*

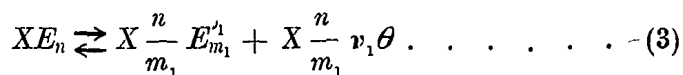
These considerations about the non-metal, chlorine, which necessarily result from the consistent application of the principles of the theory of allotropy to the electromotive equilibria, lead us to the point of view from which we can survey the metals and the non-metals in a very satisfactory way.

<sup>1)</sup> For the sake of simplicity we assume here that the positive ions are also univalent.

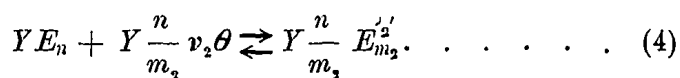
It is, indeed, clear that as the metallic and non-metallic properties in the periodic system of the elements gradually pass into each other, theory will have to make clear that between the metallic and the non-metallic state there exist only quantitative differences, and that there are therefore all kinds of intermediary states possible.

This demand can really be satisfied by an in every way plausible extension.

For this purpose we must assume that the atoms of all the elements, hence both metals and non-metals, can split off and absorb electrons so that the following reactions take place side by side:



and



in which  $E_n$  denotes the molecule of an element and

$E_{m_1}'$  and  $E_{m_2}'$  the ions.

As is known for metals  $m_1$  is mostly = 1, and probably  $m_2$  will as a rule also be = 1. For non-metals  $m$  has often been found = 1, but several times also greater than 1. Of the factor  $m_1$  no doubt the same thing may be expected.

With perfect certainty we may only say this that

$$Y \frac{n}{m_2} v_2 \leq X \frac{n}{m_1} v_1 \dots \dots \dots (5)$$

from which follows that when

$$v_1 = v_2$$

and

$$v_1 = v_2$$

the number of positive ions will be greater than the number of negative ones.

When now the question is put in what respects metals and non-metals will differ, the answer is as follows:

In the first place the factor  $X$  is comparatively great for metals and exceedingly small for non-metals, so that for non-metals also the factor  $Y$  is exceedingly small.

This is among other things in accordance with the great electric conductivity of metals and the exceedingly slight conductivity of non-metals.

In the second place for the metals the positive ions possess the greatest solubility, and for the non-metals the negative ions. This accounts among other things for the difference in electromotive

behaviour between metals and non-metals. In this it is noteworthy that the difference in solubility between the positive and the negative ions for the elements with exclusively metallic resp. exclusively non-metallic properties, is so great as to justify us in taking only positive resp. negative ions into account in the coexisting solution.

For the intermediate amphibious elements as Iodine, Sulphur, Selenium, Tellurium, Arsenic, and Antimony the existence of positive and negative ions also in solution, should certainly be taken into account to obtain a deeper insight, and here lies still an extensive field to be studied more closely, led by the more recent views about the electromotive equilibria.

*Polarisation for non-metals.*

When we indicate the non-metal by  $N$ , we may represent the formation of negative ions by the equation:



Applying the well-known thermodynamic derivation for the potential difference, we get: .

$$\Delta = \frac{RT}{\nu F} \ln \frac{K' N'' N_P^{\nu'}}{(N_L'')^n} \dots \dots \dots (7)$$

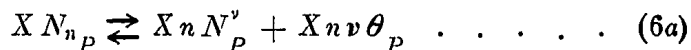
in which  $(N_P'')$  represents the concentration of the negative ions in the phase of which the electrode consists, this may be either a gas, or a liquid, or a solid phase. Starting from the electron formula:

$$\Delta = \frac{RT}{F} \ln \frac{K_\theta(\theta_P)}{(\theta_L)} \dots \dots \dots (8)$$

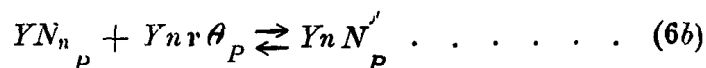
which is general, because the electron is the common constituent part of all matter, we may substitute for  $(\theta_L)$  the value that follows from (6) for the liquid phase, applying the law of the chemical mass action; thus we arrive at the already known equation:

$$\Delta = \frac{RT}{n\nu F} \ln \frac{K' (N_n L)}{(N_L'')^n} \dots \dots \dots (9)$$

In order to study the polarisation phenomenon we cannot make use of equation (9), but we can use the newer equation (7). To get a good insight into this question it is desirable that we indicate the equilibria in the electrode completely; accordingly we must also express the splitting off of electrons, and write therefore:



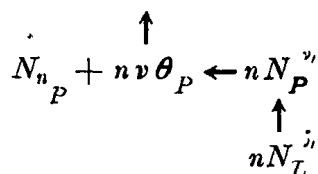
and



When we now make the non-metal electrode  $N$  anode, we withdraw the electrons. If we had to deal with a metal, hence if  $N$  was a metal, the electrode could maintain its potential in consequence of the fact that the withdrawn electrons are supplied in time by the reaction (6a), the positive ions formed going into solution. As  $N$  is however a non-metal, and the positive ions  $N'$  do not practically go into solution, the reaction (6a) will not take place to a degree of any importance.

The only way in which the non-metal  $N$  will be able to maintain its potential in the case supposed here, is this that negative ions  $N''$  from the electrolyte are deposited on the electrode, and there supply the deficit of electrons by the splitting off of electrons.

The processes that take place may be represented as follows:



As the heterogeneous equilibrium in the boundary layer between the negative ions in the electrode and in the electrolyte must set in with very great rapidity, it is clear that it will depend on the velocity of the splitting off of electrons of the negative ions whether the electrode maintains its potential or whether it does not. Above a definite current density, i.e. above a definite velocity of withdrawal of electrons this will no longer be the case, and a consequence of this will be that the electrode will contain too few electrons and too many negative ions.

It follows from equation (7) for this case that the potential difference will become more strongly positive.

This phenomenon of polarisation is called "*supertension*" in the case of gases, but it is not essentially different from the phenomenon of anodic polarisation for metals.

It is clear that when we now proceed to the cathodic polarisation for non-metals this phenomenon should be ascribed to this that the added electrons are not quickly enough absorbed by the uncharged molecules or atoms, so the electron possesses a too high concentration of electrons, and a too small concentration of negative ions. According to our equation (7) this gives rise to a less positive value of the potential difference.

As we do not measure the potential difference, but the experi-

mental electric potential it is obvious that the polarisation phenomena should be discussed in connection with the formula that holds for the "exp. electric potential" in the case that we have to do with a non-metal. This formula is as follows:

$$E = \frac{0.058}{v} \log \frac{Q_N}{(N_L^v)} + 2,8 \dots \dots \dots (10)$$

in which:

$$Q = \frac{(N_L^v)}{(\theta_L)^v}$$

From (7) and (8) follows:

$$\frac{(N_L^v) (\theta_P)^v}{(N_P^v) (\theta_L)^v} = K \dots \dots \dots (11)$$

It has further been shown just now that with anodic polarisation ( $\theta_P$ ) decreases and ( $N_P^v$ ) increases; it follows therefore from this that in this case the *quotient of solubility* must *increase*, and the exp. electrical potential of the non-metal will therefore become more strongly positive.

For cathodic polarisation the quotient of solubility decreases, hence the experimental electrical potential of the non-metal becomes less strongly positive.

#### *Amphibious Elements,*

As has already been said the amphibious elements are characterized by this that they send both positive and negative ions into solution.

If such an element is made anode, positive ions can go into solution, or negative ions can be deposited from the electrolyte on the anode, or the two processes can take place simultaneously.

If the element is made cathode, positive ions can be deposited on the electrode, or negative ions can go into solution, or the two processes can take place side by side.

The closer study of these amphibious elements, which we hope soon to undertake, following the new theory on the electromotive equilibria, will probably give a deeper insight into the character of these so remarkable elements.

*Laboratory for General and Anorganic  
Chemistry of the University.*

*Amsterdam, April 10<sup>th</sup> 1919.*