Chemistry. — *"On the Electrochemical Behaviour of Metals"*. By Prof. A. SMITS. (Communicated by Prof. ZEEMAN).

(Communicated in the meeting of March 23, 1918).

1. *Introduction.*

By application of the considerations on which the theory of allotropy is based to the internal state of the metals and to their chemical as well as to their electromotive behaviour, we are enabled to consider all the metals, also those which serve as so-called unattackable electrodes, from the same point of view.

These considerations rest on the more than probable assumption that every metal contains metal atoms, one or more kinds of metal ions, and electrons, which can be in equilibrium under definite circumstances. When a metal is immersed in an electrolyte, then in agreement with NERNST's views of the phenomenon of solution, the heterogeneous equilibrium between the metal and the boundary layer will be established with so great velocity, that it may be said that this equilibrium always exists. .

When we, therefore, restrict ourselves to the simple case that the metal consists of metal atoms, v-valent ions, and electrons, we may say, that when this metal is immersed in an electrolyte the following heterogeneous equilibria will at once set in.

$$
\begin{array}{ccc}
M_s & M_s{}^{v\cdot} & v\theta_s \\
\updownarrow & \updownarrow & \updownarrow \\
M_L & M_L{}^v & v\theta_L
\end{array}
$$
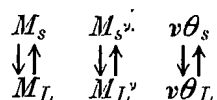
Whether the homogeneous equilibrium will also exist in the two coexisting phases between the metal atoms, metal ions, and the electrons, depends on different circumstances. Whereas it seems that a metal in perfectly dry condition can assume internal equilibrium as a rule only at comparatively high temperature, this often takes place very quickly when in contact with an electrolyte, but it may also occur that the metal gets in equilibrium very slowly, or not at all, under these circumstances at the ordinary temperature.

The velocity with which a metal assumes internal equilibrium under definite circumstances is undoubtedly one of the most characteristic properties of the metal.

2. *The Potential Difference Metal-Electrolyte when the Metal is Attacked.*

When a metal in contact with an electrolyte superficially assumes internal equilibrium with very great velocity, the internal state in the metal surface remains unchanged, in whatever way the metal may be attacked.

Let us suppose that we immerse zinc in an aqueous solution of hydrochloric acid; then hydrogen generation takes place, because the electron concentration of the metal equilibrium

$$Zn_L \rightleftarrows \overset{..}{Zn}_L + 2\theta_L \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

in the solution is greater than the electron-concentration of the hydrogen equilibrium:

$$H_{2L} \rightleftarrows 2\overset{.}{H}_L + 2\theta_L . \ . \ . \ . \ . \ . \ . \quad (2)$$

Hence the electrons of the equilibrium (1) are removed, and through this the equilibrium is disturbed. It is now the question how the equilibrium can be restored.

The concentration of the zinc-atoms in the liquid is so small that even if the reaction constant of the conversion

$$Zn_L \rightarrow \overset{..}{Zn}_L + 2\theta_L$$
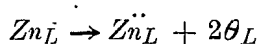
was very large, yet only exceedingly few zinc ions and electrons would be split off per second in this way.

The only way in which the state of equilibrium can be restored is this that the metal sends electrons into solution, which is of course accompanied by zinc ions going into solution, because zinc-ions and electrons, with a difference of only a very small amount, are always present in the same concentration.

Through this process the internal equilibrium in the metal surface is disturbed, which can be restored again by the reaction:

$$Zn_s \rightarrow \overset{..}{Zn}_s + 2\theta_s \ .$$
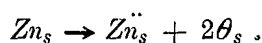
As the heterogeneous equilibrium in the boundary layer sets in with very great velocity, the question whether the metal zinc during solution in an acid will be disturbed, comes to this, whether the internal equilibrium in the surface of the metal sets in with so great velocity that the concentration remains practically unchanged.

This is actually the case for zinc under certain circumstances. Mr. HÜFFER S. J., who examined some metals at my request, found among others, that when the potential difference between zinc and a solution of zinc-chloride is measured during vigorous stirring, and then that between zinc and a zinc-chloride solution of the same

concentration acidified with hydrochloric acid, *the potential difference retains the same value, notwithstanding a strong hydrogen-generation takes place in the latter case.*

The metal zinc is, therefore, not disturbed through solution in hydrochloric acid, and this result is in perfect agreement with what is found when zinc is anodically brought to solution in a zinc-chloride solution. In this process, which likewise rests on the withdrawal of electrons from the metal, the potential difference, zinc-electrolyte, does not change appreciably, even for comparatively great densities of current, so that our investigations about the potential difference *during* the solution of zinc in a hydrochloric acid solution, as well as the measurements of the potential difference of the same metal on anodic solution in a solution of zinc-chloride lead to the result that the equilibrium in the metal zinc in contact with the above-mentioned electrolyte sets in with a velocity which is very great compared with the velocity with which electrons and ions are withdrawn from the metal.

3. *General consideration.*

When we now consider the phenomenon in general, we can distinguish the following cases.

On immersion of a metal in an acid we have in the simplest case among others the two following equilibria in the electrolyte:

$$H_{2_L} \rightleftarrows 2H'_L + 2\theta_L.$$

and

$$M_L \rightleftarrows \dot{M}_L + \theta_L$$
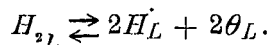
The electron-concentrations of these two equilibria are in general different, and a consequence of this is that either the electrons of the metal equilibrium, in the liquid, combine with the hydrogen ions of the hydrogen equilibrium, which causes electrons + ions from the metal to go into solution, or the electrons of the hydrogen equilibrium with the metal ions of the metal equilibrium pass from the electrolyte into the metal.

Let us first imagine the limiting case, viz. this that the internal equilibrium of the metal surface is established with great velocity, so that this velocity is very great with respect to the velocity with which electrons + ions are withdrawn from the metal or are added to the metal, then the metal surface will not change independent of whether one process takes place or the other, and the potential

difference metal-electrolyte will remain equal to the potential difference of the unary metal.

In the second place the case may present itself that the internal equilibrium of the metal surface does not set in so rapidly as was supposed above, and then it will be possible to disturb the metal surface either in one direction or in the other, i.e. it may become either nobler or baser, hence the potential difference can differ from that of the unary metal in noble or base direction.

A third case, which like the first, represents a limiting case, is this that the metal is so inert that the velocity with which it assumes internal equilibrium is very small compared with the velocity with which the electrons and ions are withdrawn from the metal or added to it.

In the first limiting case the potential difference is entirely governed by the state of internal equilibrium of the metal, and in the last case the potential difference is dominated by the electron concentration of the hydrogen equilibrium in the electrolyte.

4. Nickel as Example of an Inert Metal, the Inertia of which Increases under the Influence of the Dissolved Hydrogen.

An example of the latter case with this particularity, however, that the just mentioned great inertia is only slowly reached, because the metal is converted to this state after some time through the negative catalytic influence of the dissolving hydrogen, is furnished by nickel. As was shown in a previous communication, the case presents itself that when this metal is immersed in such an acid solution that hydrogen generation would have to take place, this phenomenon does not take place to an appreciable degree, and the metal appears to be disturbed after some time so far in a noble direction that its potential difference has become equal to that of the hydrogen electrode.

On that occasion we already gave an explanation of this phenomenon, and pointed out that, nickel being so inert, the electron concentration of the nickel equilibrium in the electrolyte

$$Ni_L \rightleftarrows Ni_L^{..} + 2\theta_L$$
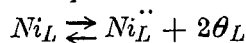
becomes equal to the electron concentration of the hydrogen equilibrium:

$$H_2 \rightleftarrows 2H^{.} + 2\theta$$
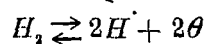
so that finally

$$(\theta_{Ni})_L = (\theta_{H_2})_L .$$

This was demonstrated in the following way. We pointed out

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namely, that on application of the electron equation for the potential difference, metal-electrolyte, for the derivation of the relation for the electromotive force of a circuit consisting of two metals immersed in the corresponding salt-solutions, we arrive at the following equation ·

$$\Delta_1 - \Delta_2 = \frac{\mu_{\theta_{s_1}} - \mu_{\theta_{s_2}}}{F} - \frac{RT'}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})}.$$

so that, taking into consideration, that the first term of the second member denotes the Volta-effect of the two metals, which is a very small quantity, the electromotive force $\Delta_1 - \Delta_2$ will be zero in first approximation, when $(\theta_{L_1}) = (\theta_{L_2})$.

In the case discussed here the metals 1 and 2 are nickel and hydrogen, and experiment has taught that $\Delta_{Ni} - \Delta_{H_2}$ was really practically zero, from which therefore followed $(\theta_{Ni})_L = (\theta_{H_2})_L$.

Through the inertia of the metal nickel, which inertia was still increased by the hydrogen dissolved in the metal, which is here a negative catalyst, as was already stated before, the metal could. therefore, be disturbed so far, that the electron concentration of the nickel equilibrium in the electrolyte had become equal to the electron-concentration of the hydrogen.

We may, therefore, also express ourselves in a different way, and say, that the nickel had been passivated by the acid. Finally the nickel phase and the hydrogen phase present the same potential difference, accordingly these phases, which are in contact with the same electrolyte, can coexist. As in the case discussed here the nickel will of course be covered by a layer of hydrogen, the found potential difference refers to the three-phase equilibrium $Ni + H_2 + $ + electrolyte.

5. *Unattackable Electrodes.*

As follows from the communication cited here, this disturbance is comparatively slowly reached for nickel. There are, however, metals for which this goes much quicker, and these are the metals of which the so-called unattackable electrodes consist, as the platinum metals.

These metals belong to the group of the most inert metals that we know. Even in contact with an electrolyte these metals do not get in internal equilibrium, but they are almost always in passive state, so that the potential difference of the unary metal is not even known to us.

When such a metal is immersed in a solution of HCl or H_2SO_4,

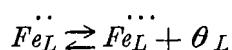and hydrogen is passed through, the electron concentration of the platinum equilibrium in the electrolyte
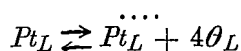
$$Pt_L \rightleftarrows \overset{....}{Pt_L} + 4\theta_L$$

has almost immediately become equal to the electron concentration of the hydrogen equilibrium,

$$H_{2L} \rightleftarrows 2\overset{.}{H_L} + 2\theta_L$$
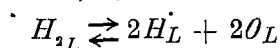
corresponding to the pressure of the hydrogen that passes through, so that e. g. the platinum electrode has almost immediately become electromotively equal to the hydrogen electrode.

For these metals, which behave *ideally inert*, the potential difference is, therefore, governed by the existing electron concentration in the electrolyte. This is also the reason why these exceedingly inert metals may serve not only as gas-electrodes, but also for the determination of the so-called oxidation, resp. reduction potentials.

When e. g. platinum is immersed in a solution in which the equilibrium:

$$\overset{..}{Fe_L} \rightleftarrows \overset{...}{Fe_L} + \theta_L$$

prevails, the electron concentration of the platinum equilibrium in the solution has almost immediately become equal to the electron concentration of the above ferro-ferri equilibrium, so that in the electron equation for the potential difference of the platinum

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

the electron concentration of the ferro-ferri equilibrium may be written instead of (θ_L), in consequence of which we get:

$$\Delta = \frac{RT}{F} ln \frac{K_\theta}{K.} \frac{(\overset{..}{Fe})}{(\overset{.}{Fe})},$$

as was already stated before.

The peculiar feature of these platinum metals is therefore their extraordinary inertia, which causes them to behave ideally passive in most electrolytes.

6. Considerations in the Light of the Theory of Phases.

It is clear that for the explanation of the phenomena discussed here, considerations as have been introduced by us of late, are indispensable.

Phase-theoretical considerations are inadequate here, but all the same it may be of use to represent the obtained results graphically by means of Δ,x-diagrams.

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Let us first consider the case that the metal zinc is immersed in a hydrochloric acid solution of $ZnCl_2$; then it is the Δ-x-figure of the system Zn-H_2 that may serve for the graphical elucidation of the found result.
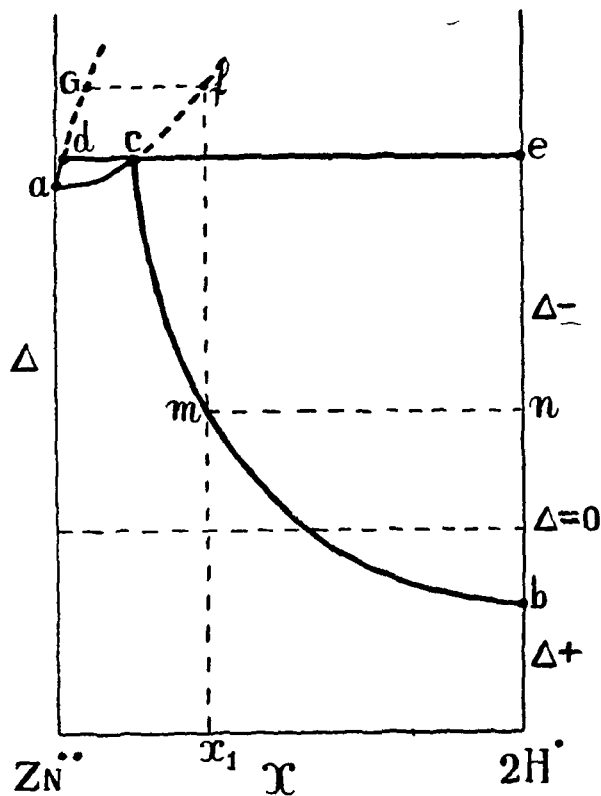

Fig. 1.

Zinc.

A Δ-x-figure holds for constant T, P, and a constant total ion-concentration; for T we choose here the ordinary temperature, and for P the pressure of 1 atm., the total ion-concentration being put here at 2 norm.

The situation of the point C, which represents the electrolyte which coexists with the zinc phase and the hydrogen phase of the pressure of 1 atm., is found from the equation:

$$\frac{RT}{2F} \ln \frac{K_{Zn}}{(Zn_L)} = \frac{RT}{F} \ln \frac{K_{H}}{(H_L)}$$

from which follows:

$$\frac{K_{Zn}}{K_{H}} = \frac{(Zn_L)}{(H_L)^2}$$

or also from the equations for the product of solubility of zinc and hydrogen:

$$L_{Zn} = (\overset{..}{Zn})\,(\theta)^2$$

and

$$L_{H_2} = (\overset{.}{H})^2\,(\theta)^2$$

by putting $(\theta)_{Zn} = (\theta_{H_2})$, in consequence of which:

$$\frac{L_{Zn}}{L_{H_2}} = \frac{(\overset{..}{Zn}_L)}{(\overset{.}{H}_L)^2}$$

or

$$\frac{(\overset{..}{Zn}_L)}{(\overset{.}{H}_L)^2} = \frac{10^{2x-35}}{10^{2x-48}} = 10^{26}.$$

When we put for a moment $(\overset{..}{Zn}_L) = 1$, then:

$$(\overset{.}{H}_L) = 10^{-13}$$

We see therefore, that the point C lies so much on one side that practically it coincides with the zinc-axis. Hence the line d, c, e or the line for the three-phase equilibrium zinc-hydrogen-electrolyte lies practically on the same level as the point a, so that the measured potential difference of the zinc, which contains a little dissolved hydrogen, and is besides covered with a layer of hydrogen, is certainly practically equal to the potential difference of the pure hydrogen-free zinc, the measurement of which is impossible here.

Let us now suppose that we immerse zinc in an electrolyte, the composition of which, as regards the zinc- and hydrogen ions, is x_1; we then see, that zinc *cannot* be in stable electromotive equilibrium with this liquid, but that hydrogen can.

If, however, the hydrogen did not appear as a new phase, but only dissolved in the zinc, a metastable electromotive equilibrium would, indeed, be possible, viz. g f, but the potential difference would be more strongly negative than that of the three-phase equilibrium represented by the line d, c, e.

This metastable electromotive equilibrium does not appear, however; on the contrary, we observe a generation of hydrogen, and we will point out here in a few words, how the experimental fact is to be explained that under these circumstances the potential difference zinc-electrolyte is equal to that which corresponds with d, c, e, or what is practically the same thing, with a.

The explanation is this: when zinc is immersed in the electrolyte of the concentration x_1, the establishment of the three-phase equilibrium between the zinc phase, the electrolytes, and the hydrogen phase takes immediately place in the boundary layer.

Accordingly the concentration c prevails in the boundary layer, whereas the total concentration of the electrolyte is x_1.

The hydrogen ions now diffuse in the boundary layer, where for the maintenance of the concentration c the reaction:

$$2\dot{H} + 2\theta \rightarrow H_2$$
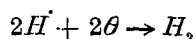
takes place, in consequence of which, as we have already seen, electrons and zinc ions from the metal phase go into solution. The zinc phase assumes internal equilibrium with great velocity, and consequently it remains unaltered during the hydrogen generation, and the measured potential difference is that of the three-phase equilibrium d, c, e, which practically agrees with that of pure zinc, a.

When a platinum electrode is placed in the same electrolyte, it indicates the hydrogen-potential which corresponds with the line $m\,n$. The zinc electrode and the hydrogen electrode present therefore entirely different potential differences in the same electrolyte.

This is the graphical elucidation for our conclusion that the potential difference of zinc with respect to a solution of $ZnCl_2$ acidified with hydrochloric acid is determined by the state of internal equilibrium of the zinc.

Nickel.

Let us now proceed to the case that instead of zinc the metal nickel is taken; then it is worthy of note in the first place that under the same circumstances we then find for the composition of the electrolyte c

$$\frac{K_{Ni}\cdots}{K_{\dot{H}}} = \frac{L_{Ni}}{L_{H_2}} = \frac{(Ni_L^{\cdots})}{(\dot{H})^2} = \frac{10^{2\times-45}}{10^{2\times-48}} = 10^6$$

When we now put $(Ni_L^{\cdots}) = 1$, we get $(\dot{H})^2 = 10^{-6}$ or $(\dot{H}) = 10^{-3}$.

Here, too, the electrolyte c has still a one-sided position. Let us assume that the adjoined figure 2 again holds for 18°, and a pressure of 1 atm. for a total-ion concentration of 2-norm.; then an entirely different phenomenon is observed on immersion of a nickel-electrode in the electrolyte of the concentration x_1 than in the case with zinc discussed just now, because the internal equilibrium in the metal surface cannot maintain itself when electrons and nickel ions go into solution.

The metal is more and more disturbed in noble direction, and the result is, as we demonstrated already, that the electron-concentration of the nickel equilibrium in the solution has become equal to the electron-concentration of the hydrogen-equilibrium in the electrolyte,

in which the potential difference of the nickel electrode has become equal to that of the hydrogen electrode. This may be graphically represented in the way as has been done in fig. 2.
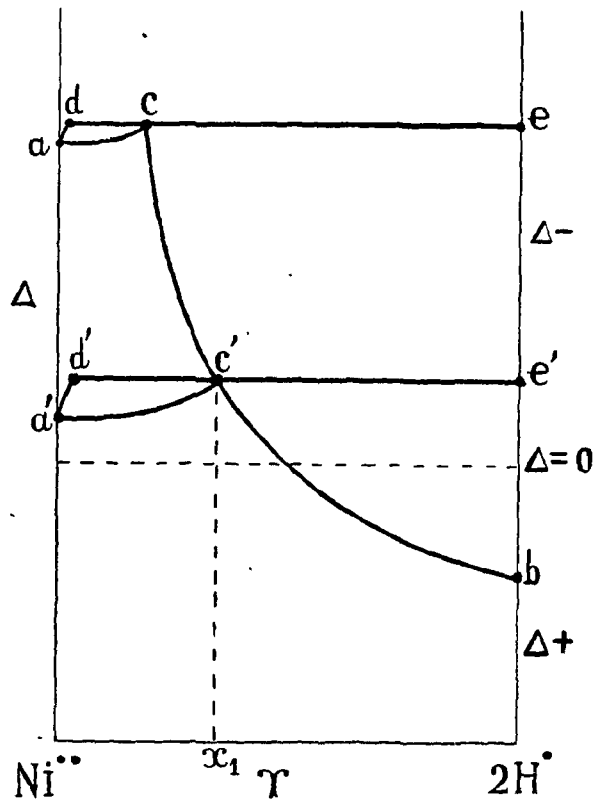

Fig. 2.

In consequence of the disturbance point d has got in point d', and represents, therefore, the ennobled nickel phase which coexists with c' and the hydrogen phase e'.

It could be derived from our considerations how we have to proceed when we want to know the potential of the unary nickel, or in other words the equilibrium-potential. Then the nickel is to be brought into a solution with a hydrogen-ion-concentration, smaller than that in the electrolyte c. Then our Δ, X-diagram 3 shows that under these circumstances e.g. the electromotive equilibrium between the nickel phase d'' and the electrolyte c'' will be established, the potential difference of which practically coincides with that of the unary metal, which is perfectly free from hydrogen and indicated by a.

It is necessary to point out that when a metal is in electromotive equilibrium with a coexisting electrolyte, the electron-concentration

of the metal equilibrium must always be equal to the electron-
concentration which exists in the liquid in consequence of the other
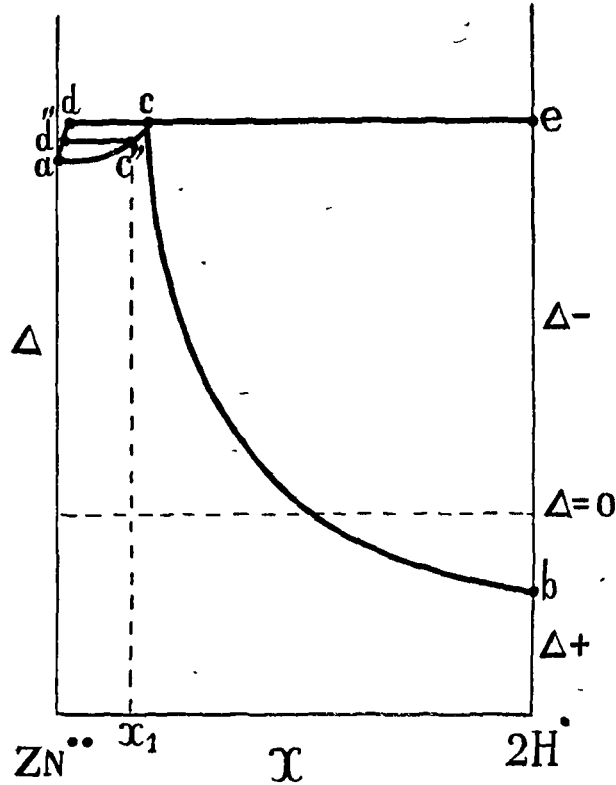prevailing equilibria.

Fig. 3.

In this case we may say, that the metal is really in equilibrium
with the electrolyte. When the metal dissolves in an acid, or when
a metal is deposited, the just mentioned equality of electron-concen-
tration prevails only in the boundary layer between metal and
electrolyte, and diffusion takes continually place in the boundary layer.

The just mentioned equality of the indicated electron-concentrations
must, therefore, also exist when in the case mentioned just now the
metal nickel has got in equilibrium with the electrolyte. Of course
there are always some transformations required for this, but these
are soon over, and can, therefore, not give rise to a permanent
disturbance, at least if the solution has been freed as much as
possible from air and hydrogen by boiling in vacuum.

We have acted upon this principle, and, as was communicated in
the preceding paper by Mr. LOBRY DE BRUIN and myself, by this
procedure the equilibrium-potential was found of nickel that contained

only a trace of hydrogen, so that the found potential difference will
· practically very certainly agree with that of the purely unary metal.

It is supposed here that the potential difference between nickel
and the nickelsalt solution with the exceedingly small hydrogen-ion-
concentration, is measured after the electrolyte has been heated with
the nickel electrode in vacuum, after the whole apparatus has been
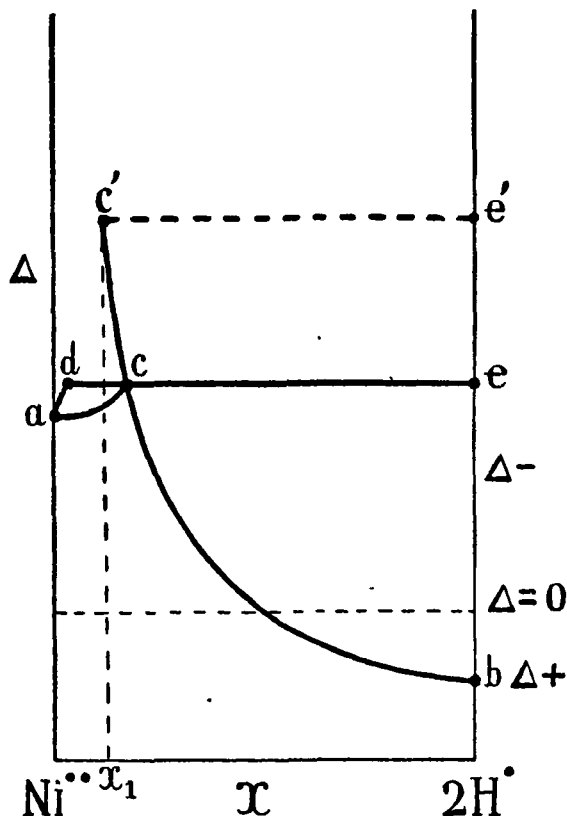

Fig. 4.

· filled with the electrolyte and connected with the 1 N. Calomel
electrode by means of a siphon and a liquid circuit, so that the
pressure under which the electrolyte is, amounts to 1 atm. also in
this case.

An entirely different result is obtained when the foregoing measure-
ment does not take place in vacuum, but in a hydrogen current.

In this case the nickel electrode is disturbed, but the disturbance
does not take place now in a noble direction, but in a base direction,
and as we showed before the potential difference of the nickel has
again become equal to that of the hydrogen-electrode. This result
can again be brought to expression in an exceedingly simple way
by means of a Δ,X-fig. 4.

When we lead hydrogen through the electrolyte, of which the concentration x_1 lies on the lefthand of the point c, the potential of he hydrogen-electrode is indicated by the line $c'\,e'$. In this mode of procedure the nickel electrode gets in contact with gaseous hydrogen, and in the boundary layer which is simultaneously in contact with nickel and hydrogen, the electrolyte c will be formed in consequence of the reaction:

$$H_2L \rightarrow 2H_L^{\cdot} + 2\theta_L,$$
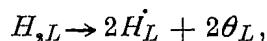
while electrons and nickel ions (and a few hydrogen ions) are deposited on the metal. This renders the metal baser superficially and both the three-phase equilibrium $d\,c\,e$ and the point a rise.
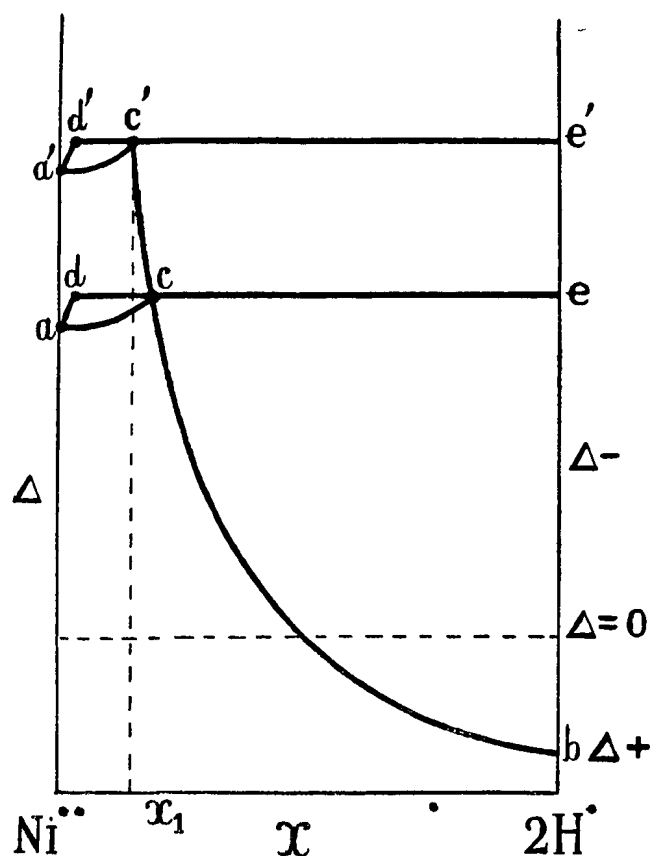

Fig. 5·

This disturbance in base direction continues till the concentration of the electrolyte has become equal to that in the boundary layer.

This is the case when a three-phase equilibrium has formed of which the electrolyte possesses the concentration x_1, hence at the place where the curve bc intersects the vertical which corresponds with this concentration. As fig. 5 shows, this takes place in point c'

and the three-phase equilibrium, which therefore finally is established, is here indicated by the points $d'c'e'$. Accordingly also in this case the potential difference of the nickel electrode is equal to that of the hydrogen electrode.

When we now consider the metals of which the unattackable electrodes consist, we need only remark that because as was just now demonstrated, these metals are ideally inert, the potential difference metal-electrolyte is in almost all cases exclusively determined by the electron-concentration in the electrolyte. Hence, when e.g. a platinum electrode is immersed in an electrolyte through which hydrogen is led, the platinum shows the hydrogen potential almost immediately, which was the case for nickel only after some time had passed. When we want to express this graphically in a Δ, X-fig., we get, of course exactly the same representation as for the case nickel-hydrogen.

That in aqueous solutions we cannot determine the equilibrium potential of platinum, whereas this is still possible for nickel is owing to this that the electrolyte c has such an one-sided situation for platinum-hydrogen, that an aqueous solution of a platinum salt always possesses a concentration on the righthand side of the point c as regards the platinum and the hydrogen ions, so that a disturbance must always take place.

In a subsequent communication I hope to enter into a fuller discussion of the phenomenon of the "super-tension", which has already been repeatedly referred to in our considerations without having been named.

Amsterdam, March 1918. , *General Anorg. Chemical Laboratory*
of the University.