Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Chemistry. — *"On the Electro-Chemical Behaviour of Nickel."* By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of June 30, 1917).

1. Nickel is a metal that assumes internal equilibrium exceedingly slowly, and can therefore very easily be disturbed. When nickel, immersed in a solution of $NiSO_4$ or $Ni(NO_3)_2$ is made anode, resp. cathode, a very strong polarisation is found already at very small current densities. Also when attacked by chemical reagents as HNO_3, H_2SO_4 etc. nickel is very easily disturbed in noble direction.

In a solution of $NiSO_4$, which is in contact with the atmosphere, nickel does not assume the equilibrium potential, simply because the attack to which Nickel is subjected under these circumstances by the air oxygen dissolved in the electrolyte, is sufficient to give rise to a pretty great disturbance of the internal equilibrium in the metal surface. That these small quantities of oxygen exert so great an influence is owing to this that the oxygen is at the same time a negative catalyst for the setting in of the internal equilibrium. What is remarkable is this that not only oxygen but also hydrogen has appeared to be a negative catalyst for this process, so that nickel does not assume the equilibrium potential in a solution under a hydrogen atmosphere either.

2. These circumstances being unknown, the nickel potential has always been measured in a hydrogen atmosphere or in air and it was thought that in this way the equilibrium potential of this metal was measured. Only SCHOCH has measured the nickel potential also in vacuum, and found that it differs from that which is found in a hydrogen-atmosphere.

Led by the new considerations about the internal state and the chemical and electromotive behaviour of metals, we have made some experiments with the result that the behaviour of nickel, which is still much more remarkable than we thought, can be explained in an exceedingly simple way.

To show this it is necessary to discuss the condition for the hydrogen generation from a solvent containing hydrogen ions by means of a metal (here nickel).

As was already stated before, in this case we have to do with the two following equilibria (in the liquid)

$$Ni \rightleftarrows Ni^{\cdots} + 2\theta$$

and

$$H_2 \rightleftarrows 2H^{\cdot} + 2\theta.$$
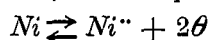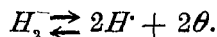
When the electron concentration of the nickel equilibrium is greater than that of the hydrogen equilibrium corresponding to a hydrogen pressure of an atmosphere, hydrogen generation will have to be found.

We have:

$$L_{Ni} = (Ni^{\cdots})(\theta)^2 \quad \text{and} \quad L_{H_2} = (H^{\cdot})^2 (\theta)^2$$

from which follows ·

$$(\theta)^2_{L_{Ni}} = \frac{L_{Ni}}{(Ni^{\cdots})} \quad \text{and} \quad (\theta)^2_{L_{H_2}} = \frac{L_{H_2}}{(H^{\cdot})^2}$$

so that the condition for the H_2-generation is ·

$$\frac{L_{Ni}}{(Ni^{\cdots})} > \frac{L_{H_2}}{(H^{\cdot})^2}$$

or

$$L_{Ni} > L_{H_2} \frac{(Ni^{\cdots})}{(H^{\cdot})^2}$$

Put $(Ni^{\cdots}) = 1$, then :

$$L_{Ni} > \frac{L_{H_2}}{(H^{\cdot})^2}$$

or

$$(H^{\cdot})^2 > \frac{L_{H_2}}{L_{Ni}}$$

Now

$$L_{H_2} = 10^{2 \times -48} \quad \text{and} \quad L_{Ni} = 10^{2 \times -45}$$

hence $(H^{\cdot})$ must be $> 10^{-3}$.

When therefore the hydrogen-ion concentration is more than 10^4 times the concentration in pure water, the metal nickel must give hydrogen generation, which, however, is not the case.

How to account for this will appear from what follows.

For this purpose we consider here the equilibrium that we have to do with in the system Ni — electrolyte, viz. :

$$Ni_S \rightleftarrows Ni_S^{\cdots} + 2\theta_S$$
$$\updownarrow \qquad \updownarrow \qquad \updownarrow$$
$$Ni_L \rightleftarrows Ni_L^{\cdots} + 2\theta_L.$$
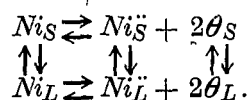
Now we know that hydrogen generation occurs when the electrons combine with the hydrogen-ions to hydrogen molecules. These

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electrons would, therefore, have to be withdrawn from the metal equilibrium, here therefore from the nickel equilibrium, which would cause this equilibrium to be disturbed. If nickel behaved normally, this disturbance would be immediately negatived, and it is easy to see in what way this disturbance would be annulled.

This cannot take place through the reaction:

$$Ni_L \rightarrow Ni_L + 2\theta_L$$
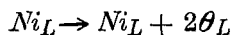
for, the concentration (Ni_L) being very small, this is a reaction that can produce but exceedingly few Ni-ions and electrons per second. What would have to happen is this: the electrons and nickel ions would have to go into solution from the metal and in the metal the reaction

$$Ni_S \rightarrow Ni_S + 2\theta_S$$
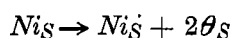
would have to take place.

In this case the potential difference during the hydrogen generation would be exclusively determined by the Ni-ion concentration prevailing at the moment.

The metal nickel however, behaves quite differently.

As was already observed, nickel is exceedingly inert, i e. its internal equilibrium is very slowly established, and to this comes that the hydrogen, which dissolves in the nickel to a small degree, greatly retards the setting in of internal equilibrium.

Now we may imagine the phenomenon to be like this : when electrons have been withdrawn from the solution by the reaction:

$$2H^{\cdot} + 2\theta \rightarrow H_2$$
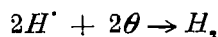
and in consequence of this ions and electrons have gone into solution from the metal, the disturbance of the internal equilibrium is not abolished any longer, and the potential difference Ni-electrolyte has consequently become less negative.

For nickel, which is so exceedingly inert under the influence of the dissolved negative catalyst, hydrogen, the supposition suggests itself that this process can continue till the electron concentration of the nickel equilibrium in the electrolyte has become equal to that of the hydrogen equilibrium.

It is self-evident that it is supposed here that the electrolyte is perfectly free from oxygen and that the result in question is to be expected when we work e.g. in vacuum or in a hydrogen atmoshere. We shall now examine what the potential difference nickel-electrolyte has become in this case.

For this purpose we return to the derivation of the equation of electrons for the potential difference. The condition of equilibrium

for the equilibrium between the electrons in the metal and in the coexisting electrolyte is:

$$(\mu_{\theta S})_{\Delta=0} - FV_S = (\mu_{\theta S})_{\Delta=0} - FV_L \quad \cdot \quad \cdots \quad (1)$$

in which $(\mu_{\theta S})_{\Delta=0}$ and $(\mu_{\theta L})_{\Delta=0}$ indicate the molecular thermodynamic potentials of the electrons in the metal and in the coexisting electrolyte for the case that the potential difference $= 0$, V_S and V_L being the electric potentials of the metal and of the electrolyte, so that $F V_S$ and $F V_L$ denote the molecular electrical potentials of the electrons in these two phases.

It now follows from this equation that when we omit the index $\Delta = 0$:

$$V_S - V_L = \Delta = \frac{\mu_{\theta S} - \mu_{\theta L}}{F} \quad \cdots \quad (2)$$

As it was our purpose to derive an equation for the potential difference in which not only the concentration of the electrons in the electrolyte occurs, but also that in the metal, the splitting up of the molecular thermodynamic potential into a concentration-free term and into a concentration member, viz.:

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

has been applied both to the electron in the electrolyte and to the electron in the metal. We then get:

$$\Delta = \frac{\mu'_{\theta S} - \mu'_{\theta L} + RT \ln (\theta_S) - RT \ln (\theta_L)}{F} \quad \cdots \quad (4)$$

If we now put:

$$\mu'_{\theta S} - \mu'_{\theta L} = RT \ln K'_{\theta} \quad \cdots \quad \cdots \quad (5)$$

we get:

$$\Delta = \frac{RT}{F} \ln \frac{K'_{\theta} (\theta_S)}{(\theta_L)} \quad \cdots \quad \cdots \quad (6)$$

the electron equation, derived by SMITS and ATEN, for the potential difference.

When we now again return to equation (5), and add $RT \ln \theta_S$ to the two members, we get:

$$\mu'_{\theta S} + RT \ln (\theta_S) = RT \ln K'_{\theta} (\theta_S) + \mu'_{\theta L} \quad \cdots \quad (7)$$

or

$$RT \ln K'_{\theta_S} (\theta_S) = \mu_{\theta S} - \mu'_{\theta L} \quad \cdots \quad \cdots \quad (8)$$

We get for the potential difference of 2 different metals:

$$\Delta_1 = \frac{RT}{F} \, ln \, \frac{K'_{\theta_{S_1}} \, (\theta_{S_1})}{(\theta_{L_1})} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

and

$$\Delta_2 = \frac{RT}{F} \, ln \, \frac{K'_{\theta_{S_2}} \, (\theta_{S_2})}{(\theta_{L_2})} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

From which follows that the electromotive force of a circuit consisting of these two metals, immersed in the corresponding salt solutions is:

$$\Delta_1 - \Delta_2 = \frac{RT}{F} \, ln \, \frac{K'_{\theta_{S_1}} \, (\theta_{S_1})}{K'_{\theta_{S_2}} (\theta_{S_2})} - \frac{RT}{F} \, ln \, \frac{(\theta_{L_1})}{(\theta_{L_2})}. \quad \cdot \quad \cdot \quad (11)$$

Let us now apply the just found relation (8), then we get:

$$\Delta_1 - \Delta_2 = \frac{\mu^{\circ}_{\theta_{S_1}} - \mu'_{\theta_{L_1}}}{F} - \frac{\mu_{\theta_{S_2}} - \mu'_{\theta_{L_2}}}{F} - \frac{RT}{F} \, ln \, \frac{(\theta_{L_1})}{(\theta_{L_2})} \quad \cdot \quad \cdot \quad \cdot \quad (12)$$

Now μ'_{θ_L} is the same for different solutions with the same solvent, so that we get:

$$\Delta_1 - \Delta_2 = \frac{\mu_{\theta_{S_1}} - \mu_{\theta_{S_2}}}{F} - \frac{RT}{F} \, ln \, \frac{(\theta_{L_1})}{(\theta_{L_2})} \quad \cdot \quad \quad \cdot \quad \cdot \quad (13)$$

The term:

$$\frac{\mu_{\theta_{S_1}} - \mu_{\theta_{S_2}}}{F}$$

represents the volta-effect, viz. · the potential difference that appears when the two metals are brought in contact in dry condition. Now we know that this potential difference is very small, so that this equation (13) tells us that when the electron concentrations (θ_{L_1}) and (θ_{L_2}) have become equal, $\Delta_1 - \Delta_2$ will be very small or zero, so that then

$$\Delta_1 = \Delta_2.$$

will hold in first approximation.

This result tells us, therefore, that finally the potential difference nickel-electrolyte will have become equal to the potential difference hydrogen-electrolyte. The experiment was, in fact, entirely in accordance with this.

3. An $NiSO_4$-solution, in which a slight cloudiness had been brought about by the addition of a little NaOH, to make the solution as little acid as possible, was brought in a vessel with 5 tubes. These were closed by means of rubber stoppers, through which were led two nickel electrodes [very pure KAHLBAUM Ni-wire 3 mm. thick,

_fastened in a glass tube by means of sealing-wax], a platinized Platinum electrode, which could be immersed in the liquid just before the measurement, a bevel, which was in connection with the calomel electrode, and a supply and exit tube for the hydrogen. In the middle tube there was placed a stirrer with mercury closure to make stirring possible if necessary. Very pure hydrogen which was obtained by leading the hydrogen from a cylinder or from an electrolytic hydrogen apparatus (with nickel electrodes) through a glass tube with Pt-asbestos, which was heated up to ± 500° in a furnace, and then through two blown washing bottles with a suspension of $Fe(OH)_2$, was first led through and later over the $NiSO_4$ solution, while from time to time the potential differences of the different electrodes were measured.

The result was:

$Ni - 0.640\ V$ } electrolyte $2,5\ n\ NiSO_4$; potential
$Pt - 0\ 640\ V$ } with respect to $1\ n$ calomel-electrode.

As follows from WILSMORE's [1] *calculation and* SCHOCH's *determinations* [2], *as also from determinations made by us, the equilibrium potential of Ni lies at* ± — 0,48 V. *with respect to* 1 n *calomel electrode. Hence the above found nickel potential is not the equilibrium potential, but the potential of a state disturbed superficially in the base direction. We see here that the nickel has assumed the same potential as the* H_2-*electrode, which is in agreement with the above given theoretical derivation.*

When we consider the solutions of $ÑiSO_4$ with increasing H-ion concentration by continually adding more H_2SO_4, we see that the equality continues to exist also for other values of the H-ion concentration:

| Ni	Pt
— 0.640 V	— 0.640 V
— 0.517 ,,	— 0.517 ,,
— 0.350 ,,	— 0.348 ,,

On measurement in hydrogen atmosphere the found Ni-potential is accordingly quite dependent on the H-ion concentration, and always equal to the H_2 *potential.*

Before going on we will anticipate and mention already here that according to the here given theoretical considerations the potential of the unary nickel, or the nickel in internal equilibrium, can only be measured in a solution in which the electron concen-

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[1]) Z. phys. Chem **35** [1900] 291.
[2]) Amer. Chem. J. **41** [1909] 208.

tration of the hydrogen equilibrium is smaller than that of the nickel equilibrium. We shall, therefore, have to make the H-ion concentration as small as possible by the addition of a base. In this case a few nickel ions and electrons will go into solution, and, no hydrogen separating on the metal, the internal equilibrium can set in. In the determination of the equilibrium potential, however, we may have no hydrogen atmosphere, for hydrogen of a pressure of 1 atmosphere would render the electron concentration of the hydrogen equilibrium too large. Nor may we have an oxygen atmosphere, because when there is oxygen present in the solution, the equilibrium

$$O_2 + 2 H_2O + 4 \theta \rightleftarrows 4 OH'$$
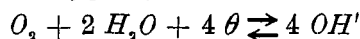
exists, in which case the electron concentration is much smaller than would correspond with the unary nickel equilibrium. The consequence is then that electrons are withdrawn from the nickel equilibrium, and the nickel sends ions and electrons into solution. The nickel is therefore attacked, and it results from the inertia of the nickel, together with the negative catalytical action of the dissolved oxygen that this disturbance is not negatived, and the nickel is superficially in such an ennobled condition that the corresponding electron concentration is in agreement with the electron concentration of the oxygen equilibrium. Accordingly the potential of Ni with respect to a nickel salt solution measured in contact with the air, lies at a much less negative value than would correspond with the equilibrium potential.

It is therefore clear that to find the unary equilibrium potential of nickel, we shall have to work in a solution, in which for $(Ni\cdot\cdot) = 1$ *the H-ion concentration is* $< 10^{-3}$, *and in an atmosphere free from* H_2 *and* O_2 *or in vacuum.*

Thus we really easily find the unary equilibrium potential.

Schoch[1]) and in imitation of him later on Schildbach[2]) are the only investigators who as far as we know, have also worked in vacuum. They have, however, not succeeded in finding the true explanation of the disturbing influence of H_2 and O_2.

In a determination of the equilibrium potential in a 1 N . NiSO$_4$-solution boiled out in vacuum, the following values were found:

Potential	$- 0.453\,V$	$- 0.477\,V$	$- 0.480\,V$	$- 0.480\,V$
of the nickel:	after 4 hours	after 47 h.	after 52 h.	after 70 h.

Then hydrogen was led through the same solution, and the H$_2$-potential was measured. After 48 hours we found :

¹) loc. cit.

²) Z. f. Electr. Chem. **22** [1910] 977.

$$Ni \quad\quad - 0.630 \ V$$

$$Pt\,(H_2) - 0.640 \ V$$

and the nickel electrode had therefore again assumed the H_2-potential.

That in this measurement the H-ion concentration must be smaller than 10^{-3} follows from an analogous determination with an $NiSO_4$-solution boiled out in vacuum and acidified with H_2SO_4 as electrolyte.

The Ni-potential was now constant at $- 0,317 \ V$ immediately after the boiling.

On conduction of H_2 through the same solution $- 0,315 \ V$ was found later for the H_2-potential.

4. When we consider the different determinations of the equilibrium potential of Ni, the following facts are worth noticing:

NEUMANN [1]) finds $- 0,538 \ V$ for electrolytic Ni, hence Ni charged with H_2 and disturbed towards the base side. He does not speak about the atmosphere in which the determination has been made.

PFANHAUSER [2]) and SIEMENS [3]), who worked in the same way as NEUMANN, found values deviating comparatively little from the real value.

MUTHMAN and FRAUEMBERGER [4]) find $- 0,880 \ V$ as most negative value for nickel charged with H_2, which value they took for the equilibrium potential. The values found by PFANHAUSER and SIEMENS can probably be explained by this, that two counteracting influences, the H_2 charge and the air atmosphere, compensated each other. PFANHAUSER could only obtain the most negative value $- 0,466 \ V$ found by him when the electrode was measured in the vessel in which it was formed by electrolysis. Transmission through the air always yielded less negative values.

KÜSTER [5]) found $- 0,800 \ V$ as minimum value for the tension of separation of nickel.

SCHWEITZER [6]) carries out the measurement in the H_2-atmosphere, because he wanted to exclude the influence of O_2. He finds $- 0,616 \ V$, a value, which as was set forth above, is not the equilibrium potential, but a value which is determined by the H-ion concentration in the electrolyte used.

[1]) Z. phys. Chem. 14 [1894] 215.

[2]) Z. f. El. Chem. 7 [1901] 698.

[3]) Z f. Anorg. Chem 41 [1904] 249.

[4]) Sitz.ber. Bayr. Akad. Wiss. 34 [1904] 201.

[5]) Z. f. El. Chem. 7 [1900] 257.

[6]) Z. f. El. Chem. 15 [1909] 602.

SCHOCH [1]) found — 0,48 V by the method described above, and also when measuring in an N_2-atmosphere.

SCHILDBACH [2]), working according to the method SCHOCH, likewise finds a value which is in very good agreement with that of SCHOCH.

It was of importance to examine whether in a solution of $NiCl_2$ the same influences of H_2 and O_2 would be found. The Cl-ions exerting so strong a catalytic influence on the setting in of the internal equilibrium of iron, it was possible that here too the influence was noticeable, and would prove to be stronger than the disturbing influence of O_2 and H_2. This has not appeared to be the case.

In 2.5 n. $NiCl_2$ in H_2-atmosphere we found :

$$Ni\,I \; -0.604 \; V, \quad Ni\,II \; -0.600 \; V, \quad H_2 \; -0.607 \; V$$

after addition of HCl :

$$Ni\,I \; -0.379 \; V, \quad Ni\,II \; -0.372 \; V, \quad H_2 \; -0.376 \; V.$$

The behaviour of nickel in $NiCl_2$ is therefore quite analogous to that in $NiSO_4$.

SUMMARY.

The researches on the electromotive behaviour of some metals, made in the Amsterdam laboratory of late years show that one of the most characteristic properties of a metal is the velocity with which it assumes equilibrium at a definite temperature and pressure. At the ordinary temperature and pressure this velocity is on the whole exceedingly small for a metal in dry condition. In contact with an electrolyte this is, however, quite different, but at the same time we meet then with complications through the appearance of catalytic actions, both positive and negative ones, which render a comparison of the behaviour of different metals difficult. It occurs namely that in the same metal the equilibrium sets in quickly in one electrolyte and slowly in another ; thus iron assumes internal equilibrium e.g. with great velocity, when it is immersed in a solution of $FeCl_2$, and this takes place much more slowly in a solution of $FeSO_4$.

There are, however, metals that also in contact with an electrolyte assume internal equilibrium slowly, and nickel, which has been discussed in this communication, is one of these metals.

Now it has appeared of late, that not only oxygen, but also hydrogen can be negative catalyst for the establishment of the internal

[1]) l.c.
[2]) Z.f. Electr. Chem. 22 [1910] 977.

equilibrium, and the remarkable feature in the behaviour of nickel is this that the influence of these negative catalysts is exceedingly great.

This is accompanied with something very remarkable, viz. this that when hydrogen of e. g. 1 atm. is conducted through an $NiSO_4$-solution, in which Ni-electrodes stand, the metal through the deposition of electrons + nickel-ions resp. through the going into solution of these compenents, is disturbed so far in base resp. noble direction till the electron-concentration of the metal equilibrium in the liquid has become equal to that of the hydrogen equilibrium in the electrolyte.

It can be demonstrated that in this case the potential difference of the nickel with respect to the electrolyte, with exception of the Volta-effect, must become equal to the potential difference of the hydrogen electrode.

Experimentally it was found that under the circumstances given here, practically equality of the two potential differences is found.

The theoretical considerations led us further to expect that the unary equilibrium potential for nickel was only to be expected in the experiment in an atmosphere free from O_2- and H_2, or in vacuum, and when an Ni-salt solution was used in which the H-ion concentration is smaller than 10^{-3} for an Ni-ion concentration of 1.

Experiments made in this direction gave as result —0,480 V. with respect to the 1n. calomel-electrode, a value that agrees entirely with the value calculated by WILSMORE and also with that found by SCHOCH in an experiment in vacuum.

In the many potential measurements of the metal nickel which were carried out in the air or in a hydrogen atmosphere, the equilibrium potential of the unary nickel has not been measured, but the potential of a state of this metal that was disturbed in base or in noble direction.

Amsterdam, June 29 1917.

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