

ELECTRODE POTENTIAL OF NICKEL.
PART III. MECHANISM OF THE RE-ACTIVATION OF
THE PASSIVE STATE OF NICKEL.

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In the former papers⁽¹⁾ only the experimental parts of the measurement of the electrode potential were described, while in the present paper the foregoing results are discussed from a thermodynamical standpoint and further the mechanism underlying the re-activation of the passive state of nickel is explained.

(I) **Catalytic Action of Nickel.** In Parts I and II, it has been shown that, if we exclude all traces of air or oxygen from the cell, the nickel gives a constant and reversible potential of active nickel in an atmosphere of hydrogen, and also of nitrogen; and that, if however the nickel used is one which has been affected by previous exposure to the air, the introduction of hydrogen causes rapid re-activation. The passive state of nickel, therefore, is extremely sensitive to hydrogen, and it is highly probable that the re-activation by hydrogen is a simple reduction of the surface of the superficially oxidized electrode. On the other hand, it has been definitely ascertained that nickel catalyses the combination of hydrogen and oxygen, an action which has a close relation to the above facts. Pease and Taylor⁽²⁾ have suggested that nickel will catalyse this reduction of the oxide even at room temperature. The work of Larson and Smith⁽³⁾ on the measurement of the synthesis of water in the presence of a nickel catalyst has shown that in the case of gas mixtures containing as much as 2% of oxygen the combination of hydrogen and oxygen occurs in contact with metallic nickel—even at low temperatures which are not far from room temperature—and this combination is fairly measurable at 34°C., though at these low temperatures a superficial oxidation of nickel readily takes place. They have also shown that the resulting nickel oxide is completely reduced at 34°C. in the presence of pure hydrogen. The same experimental results were repeated qualitatively by Benton and Emmett.⁽⁴⁾ According to the view of the two latter investigators, the

(1) This journal, 3 (1928), 57 and 253.

(2) *J. Am. Chem. Soc.*, 44 (1922), 1644.

(3) *J. Am. Chem. Soc.*, 47 (1925), 346.

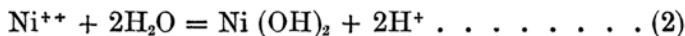
(4) *J. Am. Chem. Soc.*, 48 (1926), 632.

catalytic combination proceeds by a mechanism of successive oxidation and reduction, as found by Pease and Taylor⁽¹⁾ in their experiments on metallic copper. By the measurement of the rate of reduction of nickel oxide they have found that the reduction of this oxide by hydrogen is an interfacial reaction, proceeding at the interface between nickel oxide and nickel, that is, that there is a reaction the rate of which depends on the extent of the area and on the nature of the contact between the two solid phases. Consequently, starting with pure nickel oxide the initial rate is practically zero, but after a certain lapse of time, which is longer at lower temperatures, reduction begins and is accelerated autocatalytically.

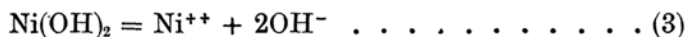
In view of these facts, it is reasonable to consider that the cause of the sudden change in nickel caused by the action of hydrogen from the passive state to the more active upon the introduction of hydrogen into the cell,—as found in cell No. 7' of the present writer's experiment or in the cell of Schoch⁽²⁾, the electrodes of which had been so affected by previous exposure to the air,—is mainly the catalytic reduction of the superficially oxidized surface of the nickel electrode.

The same catalytic action should have prevailed also in cells Nos. 6 and 7. However, for the fuller explanation of the results in the case of these cells, a theoretical calculation of the equilibrium conditions in the nickel half-cells is necessary, and this will be given in the next section.

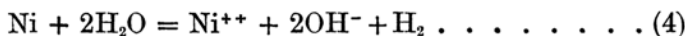
(II) **Nickel-Hydrogen Equilibrium in Aqueous Nickel Salt Solution.** In the nickel half-cell, there should be established an equilibrium between the electrode nickel and the hydrogen ion resulting from the hydrolysis of nickel salt, and the reactions involved will be expressed by the following equations:—



Combining these two with the equation for the dissociation of nickel hydroxide,



we have



Let K_1 , K_2 , K_3 , K_4 be the corresponding equilibrium constant of the reactions, respectively. Then, we have the relation,

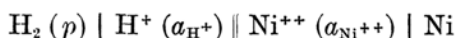
$$K_4 = K_1 \times K_2 \times K_3 = K_1 \times K_w^2 = p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 \dots \dots \dots (5),$$

(1) Loc. cit.

(2) *Am. Chem. J.*, 41 (1909), 208.

where K_w is the dissociation constant of water. Therefore K_4 is obtainable, if K_1 is known.

Reaction (1) takes place in the cell,



The free energy decrease ($-\Delta F$) accompanying the change in state in this cell, and corresponding to the passage of two faradays, may be expressed by the following thermodynamic expression,

$$-\Delta F = 2FE_0 - RT \ln \frac{a_{\text{Ni}^{++}} \cdot p_{\text{H}_2}}{a_{\text{OH}^-}^2}$$

where E_0 is the normal electrode potential of nickel. The value of E_0 is -0.2496 volt at 25°C . according to the present writer's measurement. Therefore,

$$-\Delta F_{298} = 11518 - 1365 \log \frac{a_{\text{Ni}^{++}} \cdot p_{\text{H}_2}}{a_{\text{H}^+}^2}$$

At equilibrium, that is when $-\Delta F = 0$, we obtain

$$K_1 = \frac{a_{\text{Ni}^{++}} \times p_{\text{H}_2}}{a_{\text{H}^+}^2} = 10^{8.4387} \dots \dots \dots (6)$$

Taking $K_w = 1.005 \times 10^{-14}$ at 25°C .⁽¹⁾ from (5), we find that

$$K_4 = K_1 \times K_w^2 = 10^{-19.557}$$

$$p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 10^{-19.557} \dots \dots \dots (7)$$

In this system the value of the product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ at equilibrium varies inversely with the variation of the partial pressure of the hydrogen, p_{H_2} . If the system is subjected to a definite pressure of hydrogen, the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ will be fixed. Then when the partial pressure of the hydrogen is equal, for instance, to one atmosphere, equilibrium is attained at the point where the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]$ equals $10^{-19.557}$. In an actual case, however, equilibrium can be established only when the value of the activity product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ in the solution at the equilibrium is less than or equal to that of the solubility product of $\text{Ni}(\text{OH})_2$. But, if the amount of this product $[a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2]_0$ be greater than that of the solubility product, the true equilibrium, being disturbed by the precipitation of nickel hydroxide, will not result.

Only a small amount of the work connected with the solubility product of $\text{Ni}(\text{OH})_2$ has been published and Britton's data⁽²⁾ are the only ones which

(1) Lewis and Randall, "Thermodynamics."

(2) *J. Chem. Soc.*, 127 (1925), 2118.

were obtained by direct measurement. By an electromotive force method he measured the H^+ concentration in the solution of nickel chloride with a sufficient amount of NaOH solution added to induce the precipitation of $Ni(OH)_2$. It is, however, doubtful whether this method gives the actual value of a_{H^+} , because the precipitate of nickel hydroxide in contact with the platinized-platinum should be continuously reduced by hydrogen, and the nickel thus produced would disturb its action as a reversible hydrogen electrode.

Therefore, the solubility product may be calculated indirectly by combining the hydrolysis constant of nickel sulphate and the solubility of nickel hydroxide in water.

Inserting Denham's value⁽¹⁾ of hydrolysis constant in equation (5), $K_2 = 1.1 \times 10^{-13}$ or $10^{-12.96}$, a value which is somewhat uncertain but the only one existing, we obtain the value of the ionization constant of nickel hydroxide,

$$K_3 = \frac{a_{Ni} \times a_{OH^-}^2}{a_{Ni(OH)_2}} = \frac{K_w^2}{K_2} \\ = \frac{(1.005 \times 10^{-14})^2}{1.1 \times 10^{-13}} = 10^{-15.04} \dots (8)$$

By the combination of this ionization constant with the solubility of nickel hydroxide in water,⁽²⁾ 1.27 mg./L. or 1.37×10^{-4} M/L., the molal concentration of nickel ion in the saturated aqueous solution of nickel hydroxide is found to be 3.16×10^{-7} or $10^{-6.50}$, from which, we have the solubility product,

$$[a_{Ni^{++}} \times a_{OH^-}^2]_{s.p.} = 1.256 \times 10^{-19} \text{ or } 10^{-18.91} \dots (9)$$

Solving equation (7) with this value of the solubility product, we have the corresponding partial pressure ${}_Op_{H_2}$,

$$\log {}_Op_{H_2} = -19.557 - 18.90094 = -0.657 \text{ or } \bar{1}.343 \\ {}_Op_{H_2} = 0.22 \text{ atm.} \dots (10)$$

This is the critical pressure, above which only equilibrium conditions can be attained and if the partial pressure of hydrogen is less than this value, the nickel will tend to go into solution accompanied by the precipitation of $Ni(OH)_2$ until p_{H_2} rises to the critical value. Hence, if p_{H_2} be greater than ${}_Op_{H_2}$, equilibrium will be always set up, but if the p_{H_2} be less than ${}_Op_{H_2}$, true equilibrium can never be attained and the nickel should continue to be attacked.

(1) *J. Chem. Soc.*, 93 (1908), 60.

(2) Almkvist, *Z. anorg. allg. Chem.*, 103 (1918), 240.

(III) **Discussion of the Results.** Now, the experimental results obtained in the former papers will be discussed in the light of the preceding theoretical considerations.

In the first place, the case of cell No. 1 will be considered, where a solution of 0.05 M. NiSO_4 (containing $a_{\text{Ni}^{++}} = 0.05 \times 0.24$) was in contact with the reduced nickel under one atmospheric pressure of hydrogen, and the pressure required for the system to be in equilibrium will be calculated. The hydrogen ion concentration in 0.05 M. NiSO_4 at 25°C . is found to be 3.95×10^{-5} or $10^{-4.40}$ by the graphic interpolation from Denham's values, though they are of less order of accuracy. Then, from equation (6),

$$p_{\text{H}_2} = \frac{K_1 \times a_{\text{H}^+}^2}{a_{\text{Ni}^{++}}} = \frac{10^{8.44} \times 10^{2 \times (-4.40)}}{0.05 \times 0.24} = 35.7 \text{ atms.}$$

The above calculation indicates that the nickel electrode is theoretically less noble than hydrogen under the conditions of the experiment and it should tend to go into solution with the evolution of the hydrogen on the nickel under one atmospheric pressure of hydrogen; the driving force for the corroding reaction is however

$$E_{\text{H}_2} = -\frac{RT}{2F} \ln p_{\text{H}_2} = 0.02958 \log 35.7 = 0.0459 \text{ volt at } 25^\circ\text{C}.$$

It is owing to this relatively small difference in the potential that the evolution of hydrogen is invisible, because the hydrogen overvoltage of nickel is usually high enough to offset the potential difference and prevent the gas evolution in bubbles. According to Thiel and Hammerschmidt,⁽¹⁾ the hydrogen overvoltage of nickel is 0.1375 volt.

On the other hand, in an atmosphere of nitrogen, as in cell No. 6 and No. 7, the nickel should go into the solution and form hydrogen until the solubility product of nickel hydroxide is attained; the oxidized surface of the passive nickel electrode will be reduced by the catalysis of nickel or destroyed, so that the nickel becomes gradually active. But, at the moment when the solubility product of nickelous hydroxide is reached, the value p_{H_2} in the electrode should be equal to $o p_{\text{H}_2}$ and no further solution of nickel can, therefore, take place. These are the reasons why the electromotive force of cells Nos. 6 and 7 rose gradually in the first, and then remained nearly constant at their own maximum values, i. e. above 0.6345 volt and 0.6355 volt, respectively, these values being a little below that of the active nickel in cell No. 1.

(IV) **Results of Previous Workers.** Now, with the above deduction, it seems possible to explain fairly the abnormal passive phenomena observed

(1) *Z. anorg. allg. Chem.*, 132 (1924), 15.

by previous workers in the measurements of the electrode potential of nickel.

In the first place, it is a remarkable fact that the potential of the nickel electrode is changed to an extraordinary degree on being treated with a solution of alkali hydroxide. The reversible potential of the reduced nickel in 1 N. NiSO_4 calculated from the writer's observed value is -0.276 volt, while in the case of the cathodic polarization of the electrode in an alkali solution a much less noble potential, i. e. as much as -0.33 volt, was found by Schweitzer⁽¹⁾; the latter potential, however, gradually changed appreciably. Another interesting experiment giving a very low potential, -0.597 volt was made by Muthmann and Fraunberger.⁽²⁾ The nickel having this low potential was prepared by electrolytic deposition on platinum from a neutral sulphate solution under a certain condition (at room temperature with 8 volts), and by the cathodic polarization of it with hydrogen in distilled water. Their experiment was however examined later by Thompson and Sage⁽³⁾ who found that the high potential observed by the former investigators was that of a green deposit of a basic salt and not one of pure nickel.

In this connection, it may be supposed as the most possible case that a thin muddy coating of some basic salt or a film of colloidal hydroxide precipitate is formed on the electrode by the previous treatment and that this coating or film is catalytically reduced by hydrogen into nickel in a very fine state. Since the lower the electrode potential, the finer the metal powder, it is natural that the extremely fine nickel powder should give such abnormally low potentials as those above mentioned at the moment, but that as this powder would tend to change to a more stable form with time the potential would gradually become normal.

If this is the case, then it is also possible that a similar abnormality may occur when the electrode is polarized even in an acid solution with hydrogen cathodically, so long as it has a chance of producing some basic salt or hydroxide on the very surface of the activated metal. This may possibly be the case when the activated surface, after being washed, has been wetted with water which might or might not contain the trace of acid, and was acted by the air while it was being transferred into the cell, as was done by Schoch.⁽⁴⁾

It will be remembered in this connection that pure iron quenched from an atmosphere of pure nitrogen gave a similar abnormality in its electromo-

(1) *Z. Elektrochem.*, **15** (1909), 607.

(2) *Sitz. Bayer. Akad. Wiss.*, **34** (1904), 201.

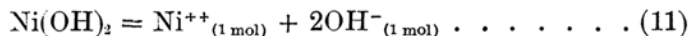
(3) *J. Am. Chem. Soc.*, **30** (1908), 714.

(4) *Loc. cit.*

tive force, as shown by the experiment of Richards and Behr.⁽¹⁾ This matter will be discussed in a paper which will be presented in the near future.

(V) **Free Energy.** The calculation of some important thermodynamic quantities relating to this subject have been made by combining the results obtained above with the existing data.

The Free Energy of the Formation of Nickel Hydroxide. Taking the solubility product of $\text{Ni}(\text{OH})_2$ as $10^{-18.90}$ the free energy change for the equation



may be calculated

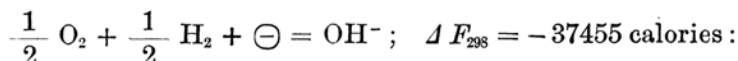
$$\Delta F_{298} = -RT \ln a_{\text{Ni}^{++}} \cdot a_{\text{OH}^{-}}^2 = -1365 \times -18.90 = 25800 \text{ calories.}$$

Then, the free energy of formation of $\text{Ni}(\text{OH})_2$ may be calculated as follows:—

From the first paper



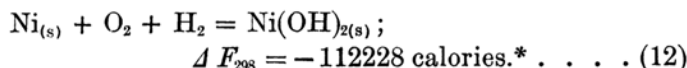
and, according to Lewis and Randall ("Thermodynamics"),



hence

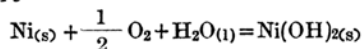


Combining this value with that of (11) determined above, we have for the standard free energy of formation of $\text{Ni}(\text{OH})_{2(s)}$,

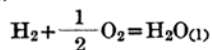


(1) *Z. physik. Chem.*, **58** (1907), 301.

* The value obtained from the solubility product used in the present paper is in good agreement with that obtained from the heat of formation of $\text{Ni}(\text{OH})_2$ using the Nernst heat theorem, the entropy of the elements (Lewis and Randall, "Thermodynamics" p. 464) at 25°C. and the formula proposed by Latimer (*J. Am. Chem. Soc.*, **43** (1921), 818) for the entropy of solid salt. The heat of formation of $\text{Ni}(\text{OH})_2$ in the reaction,



is 60840 cal. according to Thomsen (Landolt-Börnstein, "Physikalisch-Chemische Tabellen"), and that of the reaction



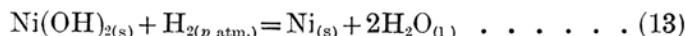
at 25°C. is 68270 cal. according to Lewis (*J. Am. Chem. Soc.*, **28** (1906), 1390), hence for

$$\text{Ni}_{(s)} + \text{O}_2 + \text{H}_2 = \text{Ni}(\text{OH})_{2(s)}; \quad \Delta H = -60840 - 68270 = -129110 \text{ cal.}$$

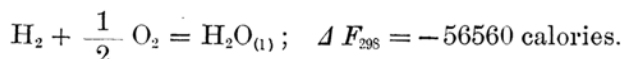
$$\Delta S = S_{\text{Ni}(\text{OH})_2} - S_{\text{Ni}} - S_{\text{O}_2} - S_{\text{H}_2} = -56.5 \text{ entropy unit at } 298^\circ\text{K.}$$

$$\Delta F = \Delta H - T \Delta S = -129110 - (298 \times -56.5) = -112270 \text{ cal.}$$

The Free Energy Change in the Reduction of Nickel Oxide or Nickel Hydroxide. The free energy change in the reaction,



may be obtained from (12) by combination with the free energy of the formation of water. According to Lewis and Randall,⁽¹⁾



hence

$$\Delta F_{298} = 112,228 + 2 \times (-56560) - 1365 \log p_{\text{H}_2}^*$$

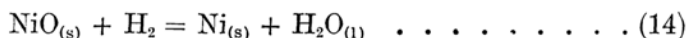
When $p_{\text{H}_2} = 1 \text{ atm.}$, then $\Delta F_{298} = -892 \text{ calories.}$

Therefore, the driving force of this reaction is

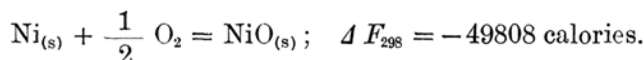
$$E = \frac{892}{2 \times 23074} = 0.0193 \text{ volt.}$$

Even at 25°C. there is a small driving force tending to reduce $\text{Ni}(\text{OH})_2$ to Ni, forming water. This accounts for the fact that the spontaneous reduction of nickelous hydroxide takes place under one atmospheric pressure of hydrogen, especially when it is in contact with a catalyst, such as a platinized platinum or nickel.

The free energy change for the reaction,

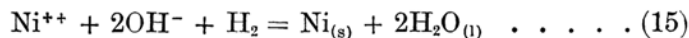


may be obtained using the value of the free energy of formation of NiO. The present writer calculated the free energy of formation of NiO from the experimental data of Pease and Cook,⁽²⁾ and found it to be 49808 calories, while the value reported in Pease and Cook's paper is 56497 calories.



therefore $\Delta F_{298} = 49808 - 56560 = -6752 \text{ calories.}$

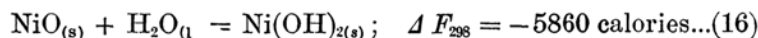
And the free energy for the reaction



may be calculated from (7)

$$\Delta F_{298} = -1365 \times 19.557 = -26695 \text{ calories.}$$

Therefore combining reaction (14) and (15), we obtain

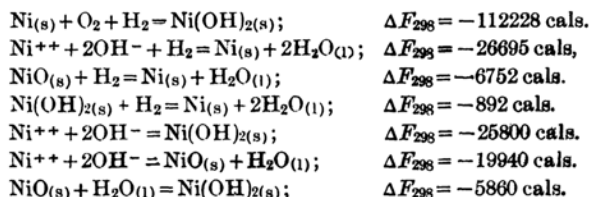


(1) Loc. cit.

(2) *J. Am. Chem. Soc.*, 48 (1926), 1196.

* The value of p_{H_2} which is the critical partial pressure at equilibrium may also be obtained from this equation by putting ΔF equal to zero.

The results above obtained are summarized as follows for the sake of comparison.⁽¹⁾



The writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

Summary.

1. The re-activation by the action of the hydrogen of the nickel electrode, which has once been affected by oxygen, has been explained on the ground that nickel itself behaves as a catalyser, on the combination of oxygen and hydrogen.

2. It has been thermodynamically deduced that the equilibrium conditions in the nickel half-cells are expressed by $p_{\text{H}_2} \times a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 10^{-19.56}$, from which it has been calculated that when the activity-product ($a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2$) attains the solubility product of nickel hydroxide, the corresponding partial pressure of hydrogen is 0.22 atm. This is the critical pressure above which only equilibrium can be established and if the partial pressure of hydrogen is less than this value the nickel will tend to go into solution accompanied

- (1) The writer calculated the solubility product of $\text{Ni}(\text{OH})_2$ also from the experimental data of Britton (*J. Chem. Soc.*, 127 (1925), 2114) by the following method and found it to be 2.0927×10^{-17} , while the value reported in Britton's paper is 8.7×10^{-19} . This was done by taking into consideration the decrease in nickel ion concentration resulting from the addition of 0.8 c.c. of 0.0967 N. NaOH to 100 c.c. of 0.025 M. NiCl_2 to produce incipient precipitation, by obtaining the activity of Ni^{++} in the solution, taking 0.38 as the activity coefficient at that concentration (Lewis and Randall, "Thermodynamics" p. 382), and combining this activity with the observed value of $a_{\text{OH}^-} = 10^{-7.33}$ in the resulting solution.

$$a_{\text{Ni}^{++}} = 0.38 \times \left(2.5 \times 10^{-2} - \frac{0.0967 \times 0.8}{2 \times 100} \right) = 0.00935$$

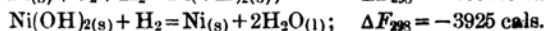
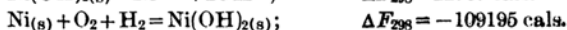
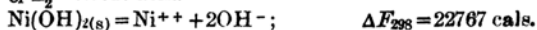
$$a_{\text{OH}^-} = 10^{-7.33}$$

hence,

$$a_{\text{Ni}^{++}} \times a_{\text{OH}^-}^2 = 0.00935 \times 10^{-2 \times 7.33} = 2.0927 \times 10^{-17} \text{ or } 10^{-16.68}$$

This value being adopted the values of ϕ_{H_2} and the free energies of the following reactions become,

$$\phi_{\text{H}_2} = 0.0013 \text{ atm.}$$



by the precipitation of nickel hydroxide until p_{H_2} rises to the critical pressure.

3. On the above deduction, the changes with time in the electromotive force of the cells which were prepared in the atmosphere of hydrogen or of nitrogen have been explained.

4. The abnormal behaviour of the nickel electrode observed by previous investigators has also been discussed on the same basis of proof.

5. The changes in free energy of various reactions have been calculated.

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