ELECTRODE POTENTIAL OF NICKEL.
PART I. MEASUREMENTS IN AN ATMOSPHERE OF HYDROGEN WITH REDUCED NICKEL POWDER.

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Although much has been written concerning the phenomena which are observed when nickel is involved in the electrolytic process, only a small amount of work has been published dealing with the direct determination of the electrode potential of nickel, and as the measured values of the electrode potential, as shown in Table 1, can by no means be said to be in agreement with one another, it is desirable to find some means of making a reliable nickel electrode which will give a reproducible, constant, and reversible potential.

TABLE 1.

The equilibrium potential of nickel in N/1 $NiSO_4$ solution.

B. Neumann, *Z. physik. Chem.*, 14 (1894), 215.	−0.255 volt
A. Siemens, *Z. anorg. Chem.*, 41 (1904), 249.	−0.221 „
H. Euler, *Z. anorg. Chem.*, 41 (1904), 93.	−0.183 „
W. Muthmann & F. Fraunberger, *Sitz. Bayer. Akad. Wiss.*, 34 (1904), 201.	−0.597 „
E. P. Schoch, *Amer. Chem. Journ.*, 41 (1909), 208.	−0.197 „
A. Schweitzer, *Z. Elektrochem.*, 15 (1909), 607.	−0.33 „
R. Schildbach, *Z. Elektrochem.*, 16 (1910), 967.	−0.25 „
A. Smits and Lobry de Bruyn, *Proc. Acad. Sci. Amsterdam*, 20 (1918), 394.	−0.197 „
The writer (calculated* from the normal electrode potential)	−0.276 „

* The other necessary data for this calculation were obtained from the writer's paper on the conductance of nickel sulphate sulution (this journal, 3 (1928), 47). The value of relative viscosity was obtained by assuming that its deviation from unit is approximately proportional to the concentration.

A close study of previous works on the nickel electrode potential, above cited, especially those by Schoch, Schildbach and Schweitzer and the works of Richards and Behr⁽¹⁾, Foerster⁽²⁾ and Schildbach on the electrode potentials of the metals of the same group, i.e. iron and cobalt, show why the observed values of the electrode potential of nickel differ one from another.

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

(2) Foerster, *Abhandl. Deut. Bunsen Gesellsch.*, No. 2 (1909).

The potential of nickel electrode changes very considerably with the mode of preparation, previous treatment, and the state of the electrode, which causes can be divided into two factors, i.e. physical and chemical. Schoch and Schweitzer obtained higher and more constant values of the electrode potential with powdered nickel than with solid. It is well known that this physical factor has a similar effect on the electrode potential in the cases of other metals also and that the finely divided state of the metal is more favourable for the reproducibility and the constancy of the electrode. It has been suggested by G. N. Lewis⁽¹⁾ that the lack of reproducibility in the case of solid metal is due to the highly strained condition or unstable physical state of the metal whether it be produced by rolling or by electrolysis. Then it is natural that there is no agreement even in the measurements of these two investigators both working with powder but from different sources. Turning to the chemical factor, it is an important fact, observed definitely by Schoch, that the potential is diminished by the presence of air and increased by the introduction of hydrogen into the cell. As this effect of oxygen is rather specific to metals of the iron group and to chromium, it must have a close relation with the phenomena of passivity. It is therefore necessary to avoid any contact with oxygen by both the electrode and the solution, for the purpose of obtaining the true potential of active nickel. In this respect the above three investigators were careful in preparing the electrolyte and they boiled the solution before introducing it into the cell. On the other hand, in their mode of preparation of the electrode there still remains a little which leads us to suspect that they did not measure the true potential of active nickel. All the nickel used were those which had been kept in air and even the reduced nickel powder used by Schoch must have had the probable chance of coming into contact with the air while moving from the furnace into the cell. Schweitzer in all of his experiments polarised the electrodes cathodically in the cell with a solution of caustic potash to reduce any trace of oxide on the surface and, after washing, filled the cell with the electrolyte entirely in the absence of air. Schoch also once used the polarised electrode. As for the results with such electrodes, full discussion will be made later together with the results of the writer's experiments with polarised electrodes.

The writer obtained a reproducible and fairly constant electrode which gave a reversible electrode potential of active nickel by using powder electrode reduced in the cell, and using an apparatus which allows the cell to be filled in an atmosphere of hydrogen. But, as Schoch, and Richards and Behr reported that the occluded hydrogen raises the potential of nickel

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(1) Lewis and Randall, "Thermodynamics," (1923), p. 388.

or iron, similar experiments were made in an atmosphere of nitrogen and in an atmosphere of a mixture of nitrogen and hydrogen, the results of which experiments might lead to the conclusion that the occluded hydrogen has no effect in the case of nickel. The report on those latter experiments will be made in the second part of this paper which will be published in the very near future.

Materials. *Water.*—Throughout the experiment conductivity water which had a specific conductance of less than 1.2×10^{-6} was used.

Nickel Oxide.—The nickel oxide was prepared by precipitation from a hot (90°C.) dilute (1%) solution of Kahlbaum's cobalt-free nickel nitrate with redistilled ammonia, washed thoroughly by decantation and filtration and dried. The dried material was crushed in an agate mortar into powder and then heated, to remove any nitrate that remained, in a furnace by passing an air current for about six hours at 600° to 700°C. and for one additional hour at 700° to 800°C.

Electrolyte.—In the experiments, nickel sulphate was employed as the electrolyte, because uni-bivalent salt is liable to form intermediate ions, and also for the convenience of comparing the result of these measurements with those of the previous investigators. Kahlbaum's cobalt-free sulphate was recrystallized twice from conductivity water and used. The concentrations were determined by electrolysis for nickel(1).

Apparatus and General Procedure. As was stated above the half cell for the nickel electrode was so designed as to allow the reducing of powdered

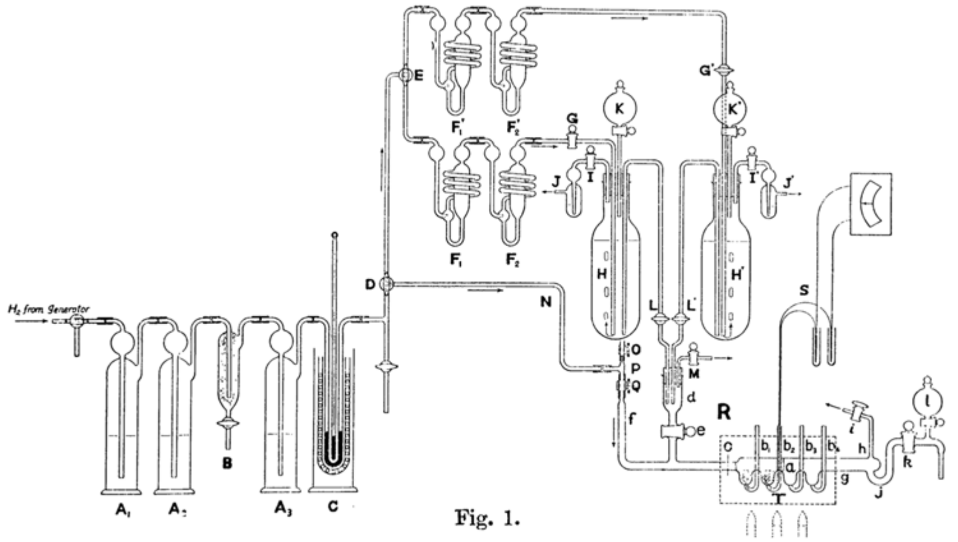

Fig. 1.

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(1) Treadwell-Hall, "Analytical Chemistry" II, (1915), p. 136.

nickel oxide with hydrogen directly in the cell, and if desired, of permitting prolonged evacuation at high temperature to remove hydrogen occluded in the nickel electrode. And the apparatus was so arranged that the electrolyte could be transferred into the cell without contact with air.

Fig. 1 shows the whole arrangement of the apparatus and the half cell. R is the electrode vessel which is made of glass, having four separate electrode compartments b_1, b_2, b_3, b_4. At the bottom of each compartment a platinum wire was sealed and was covered with finely powdered nickel oxide. The cell is provided with two sealed-on inlet tubes, one tube, f, which serves for hydroegn and the other, d, for the solution.

To introduce the nickel oxide into the vessel, the inlet side was cut off from the compartment part, a, at a point, marked c in the figure, as close as possible to the compartments, so that any nickel oxide which may adhere to the inner wall of the tube, c, may be reduced at the same temperature zone of the oven as is the oxide in the electrode compartments. After the introduction of nickel oxide the two parts were joined together and then the electrode vessel was connected with the other parts of the apparatus as shown in the figure.

The oven, T, was made of copper plate covered with thick asbestos plates and packed with asbestos fiber.

The hard glass flask H, of the capacity of 250 c.c. was the reservoir of a nickel sulphate solution and was fitted with a rubber stopper covered with bees-wax. Through this stopper was fitted a separating funnel K which served for conducting the solution into the flask and three tubes; one is an inlet of hydrogen, one which is connected to the trap J containing the same solution is an outlet of hydrogen, and the other one serves for introducing the solution into the electrode vessel. The other end of the tube L was thrust through the rubber stopper into one of the inlet tubes of the electrode vessel, d. Another flask, H′, of the same construction, served for the solution of the other concentration.

The hydrogen used was generated from Kipp's apparatus by the action of hydrochloric acid on Kahlbaum's C.P. zinc or pure electrolytic zinc and was purified by successively passing it through three alkaline solutions of potassium permanganate A_1, A_2, A_3, a layer of glass wool, B, and then over heated, fresh, palladized asbestos in the tube, C, to remove any trace of oxygen that might be present. Then the gas could be saturated with water vapour, before entering into the flask H, or H′ by passing humidifiers F_1 and F_2, or F_1' and F_2' with the same solution as is contained in the flask, Before the operation was started, all the parts of the apparatus were tested for its air-tightness.

In the reduction of nickel oxide, the hydrogen was introduced into the cell through the tube N, until all the air in the electrode vessel was washed out, with cocks i, k and then e, M being open.

The oven was put in its place and was gradually heated with three Bunsen burners. It was noticed that the reduction usually began at about 200°C., as was evidenced by the appearance of condensed water in the outlet tube of the gas. But the most part of the reduction was performed at 300°C. which is a temperature below the recognized transition point of nickel and the furnace was kept at this temperature for one hour more after the ceasing of water evolution, for the purpose of the assurance of complete reduction. During this operation the flow of hydrogen was kept at a rate of two or three bubbles per second. The condensed water was allowed to fall in the bent tube j, and to flow out from time to time through k by the pressure of hydrogen. Then the cell was left to cool to the room temperature, and was ready for being filled with the electrolyte, having been removed the furnace.

On the other hand, the electrolyte was freed from air in the following manner. Approximately the required amount of nickel sulphate solution was placed in the flask and purified hydrogen from the humidifiers was introduced into the flask. The gas bubbling up in small bubbles, saturating and stirring the whole liquid, left the flask through a trap. At the same time a part of the hydrogen was introduced into this reservoir also through the path N, e, L to replace the air in the tube L with hydrogen. After most of the air in the flask had been replaced by hydrogen, the stopcock G was closed and the flask was evacuated by an oil pump attached to the trap J. A mercury trap was also connected between the flask and the pump to prevent any back flow of air. G was then opened and the gas was readmitted slowly. This operation was repeated several times and the solution was made as free as possible from air and then the solution was preserved in the flask under an atmosphere of hydrogen to prevent the diffusion of oxygen from the atmosphere.

The electrolyte was allowed to flow down into the cell by the pressure of the gas. With the form of construction shown, it is an easy matter to fill the cell without leaving any bubbles of gas. The reservoir, l, of the cell was also filled with the same solution which served to rinse out the tube. The half-cell was then disconnected and placed in the thermostat where it was allowed to stand for half an hour before the electromotive force measurements were made. The filling up of the cell usually took about half an hour and therefore the first measurement was made one hour after the instant of the contact of the electrolyte with the nickel electrode. All the electromotive force measurements were made in a water thermostat, which was kept constant within 0.02°C.

For the measurements a Leeds and Northrup's K-type potentiometer and an H-type mirror galvanometer were used. As a standard of potential difference a Weston standard cell, which had been standardized by the Electrotechnical Laboratory of the Department of Communications, was used. A U-tube was used as the vessel for the junction solution. The decinormal calomel electrodes used were made from calomel prepared electrolytically and Kahlbaum's C.P. potassium chloride, and their potentials agreed very well with one another.

Results of Measurements of E.M.F. The combination of the cell was as follows:

Ni | $NiSO_4$ (0.05 or 0.005 M) | saturated KCl | KCl (0.1 N), Hg_2Cl_2 | Hg.

Table 2 contains the results of a series of measurements made on the cells of the solutions of the two different concentrations i.e. 0.05 M and 0.005 M. The time elapsed gives the hours after the contact of the electrolyte with the electrode.

TABLE 2.

E.M.F. of cell: Ni | $NiSO_4$ | sat. KCl | KCl(0.1N), Hg_2Cl_2 | Hg, at 25°C.

Elapsed time in hours	E.M.F. in volt.			
	0.05 M $NiSO_4$/L.		0.005 M $NiSO_4$/L.	
	Cell No. 1.	Cell No. 2.	Cell No. 3.	Cell No. 4.
1	−0.63860*	−0.63840	−0.66095*	−0.66032
2	−0.63860*	—	−0.66093*	−0.66030
3	—	—	—	−0.66255
4	−0.63858*	—	−0.66085*	—
12	−0.63846*	—	—	—
15	—	—	—	−0.6600
20	—	—	—	−0.6598
22	−0.63832**	—	−0.6604**	—
24	−0.63830**	—	—	—
36	−0.63810**	—	—	—
48	−0.63790**	—	−0.6600**	—
	H_2 on			
50	−0.63790	—	—	—
60	−0.63785	—	—	—

* After these measurements with cells Nos. 1 and 3 the temperature of the thermostat was lowered to 18°C. and measurements were made at this temperature, the results of which are given in Table 3.

** After the measurements at 18°C., the temperature was again raised to 25°C. and these measurements were made.

Each two of the platinum electrode wires of each cell were coated electrolytically with nickel from ammoniacal nickel sulphate solution, and covered with nickel powder in the manner already stated. The electrode thus prepared, having been annealed at about 300°C. gave the potential which agrees with that of the naked platinum, covered with nickel powder within about 0.05 millivolt.

The agreement of the potential of each two cells with the solution of the same concentration and constancy is very good as compared with the results of the previous investigators. The change in potential of the same cell was not greater than 0.5 millivolt for 24 hours. Furthermore, the electromotive force was reversible with respect to temperature as will be shown in the next paragraph. Besides, it was observed that the electromotive force changed by not more than 0.05 millivolt by the passage of hydrogen through the solution in the cell for about half an hour which was done at the end of the measurements with cell No. 1 and also that by shaking the powdered electrode, the values of the electromotive forces fluctuated around a certain corresponding value temporarily, but did not show any tendency to change continuously in one direction.

The measurements of the electromotive force were made also at 18°C. with cells Nos. 1 and 3, after twelve hours measurement at 25°C. in the case of the former cell and after four hours measurement in the case of the latter. The results at 18°C. are given in Table 3.

After the measurements at 18°C., the temperature was again raised to 25°C. and further measurements were made, the results of which are given in Table 2. It will be observed that there is no hysteresis but only a continuous and slow lowering of the electromotive force.

TABLE 3.

E.M.F. of cell: Ni | $NiSO_4$ | sat. KCl | KCl(0.1 N), Hg_2Cl_2 | Hg, at 18°C.

	Mols $NiSO_4$ per litre	E.M.F. in volt.
Cell No. 1	0.05	−0.63820
Cell No. 3	0.005	−0.66105

By the combinations of data for cells No. 1 and No. 3, given in Table 2 and Table 3, it will be found that the difference in electromotive force between 18°C. and 25°C. are 0.00066 and 0.00020 volt for the cells of 0.05 and 0.005 mol, respectively. Taking the difference in the potential of the standard decinormal calomel electrode between these two temperatures as

-0.00040 volt⑴, the temperature coefficients of these cells are calculated to be:

$$\frac{\Delta E}{\Delta t} = -0.00009 \text{ volt per degree for the 0.05 mol NiSO}_4.$$

$$\text{"} \quad = -0.00003 \quad \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad \text{"} \quad 0.005 \quad \text{"} \quad \text{"} \quad .$$

Calculation of Normal Electrode Potential. The normal electrode potential was computed on the ground of two different concepts of the strong electrolytes, one being that the ion concentration is involved in the expression of the electromotive force of the concentration cell and the other being that the activity of the ion is involved.

(1) *Ion concentration being used.* The normal electrode potential E_0 can be calculated by using the following well-known eqution

$$E = E_0 + \frac{RT}{2F} \ln C\alpha \qquad (1)$$

where E is the potential in the solution used, referred to the molal hydrogen electrode, C is the concentration of the solution in mols per litre and α is its degree of ionization which is defined by $\frac{\lambda}{\lambda_0}$ for a dilute solution or by $\frac{\lambda\eta}{\lambda_0\eta_0}$ for a concentrated solution. As the values of λ, and ionic conductance of nickel ion, from which λ_0 must be calculated, given in Kohlrausch-Holborn's table of conductances are inaccurate and the viscosity data are lacking, the writer's own values were used⑵.

The data in Table 2 give, as a mean value for the cell,

$\text{Ni} \mid \text{NiSO}_4(0.05\text{ M}) \parallel \text{KCl}(0.1\text{ N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$; $e = -0.6385$ volt at 25°C.

Taking the potential of the decinormal calomel electrode, Ec, to be -0.3376 volt, $\text{H}_2 \mid \text{H}^+(1\text{ M}) \parallel \text{KCl}(0.1\text{ N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$; $Ec = -0.3376$ volt,
then $\text{Ni} \mid \text{NiSO}_4(0.05\text{ M}) \parallel \text{H}^+(1\text{ M}) \mid \text{H}_2$; $E = -0.3009$ volt.

For 0.05 M nickel sulphate solution, the values of λ, λ_0 and $\frac{\eta}{\eta_0}$ at 25°C. are 50.75, 133.0 and 1.0175, respectively and

$$\alpha = \frac{\lambda\eta}{\lambda_0\eta_0} = \frac{50.75 \times 1.0175}{133.0} = 0.3883$$

Then, we obtain $-0.3009 = E_0 + 0.02958 \log 0.05 \times 0.3883$
from which $E_0 = -0.2503$ volt at 25°C.

Similarly, as the mean value for the cell,

$\text{Ni} \mid \text{NiSO}_4(0.005\text{ M}) \parallel \text{KCl}(0.1\text{ N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$; $e = -0.6607$ volt at 25°C.
and $\text{H}_2 \mid \text{H}^+(1\text{ M}) \parallel \text{KCl}(0.1\text{ N}), \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$; $Ec = -0.3376$ volt at 25°C.

Combining these two, we obtain

$\text{Ni} \mid \text{NiSO}_4(0.005\text{ M}) \parallel \text{H}^+(1\text{ M}) \mid \text{H}_2$; $E = -0.3231$ volt at 25°C.

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(1) Clark, "Determination of hydrogen ions," (1920), p. 203.

(2) This journal, **3** (1928), 47.

Taking $\frac{\lambda}{\lambda_0}=82.69/133=0.62173$ as the degree of ionization of 0.005 M $NiSO_4$. By equation (1), we obtain

$$-0.3231=E_0+0.02958 \log 0.005\times 0.62173$$

from which $E_0=-0.2489$ volt at 25°C.

Consequently, as a mean value of the potential for the electrode $Ni \mid Ni^{++}(1M)$, we find $E_0=-0.2496\pm0.0007$ volt at 25°C.

In a similar manner, E_0 at 18°C. was calculated. The electromotive force of the cell,

$$Ni \mid NiSO_4(0.05\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg; \quad e=-0.6382 \text{ volt at } 18°C.$$

Taking the potential of the decinormal calomel electrode to be -0.3380 volt, then, $Ni \mid NiSO_4(0.05\ M) \parallel H^+(1\ M) \mid H_2;\quad E=-0.3002$ volt.

For 0.05 M $NiSO_4$, the values of λ, λ_0 and $\frac{\eta}{\eta_0}$ at 18°C. are 43.833, 113.6 and 1.0209, respectively and

$$a=\frac{\lambda\eta}{\lambda_0\eta_0}=\frac{43.833\times 1.0209}{113.6}=0.3939.$$

Inserting these values in equation (1), we obtain

$$-0.3002=E_0+0.02888 \log 0.05\times 0.3939$$

$$E_0=-0.2509 \text{ volt at } 18°C.$$

The electromotive force for the cell,

$$Ni \mid NiSO_4(0.005\ M) \parallel KCl(0.1\ N),\ Hg_2Cl_2 \mid Hg; \quad e=-0.66105 \text{ volt at } 18°C.$$

Subtracting the potential of the decinormal calomel electrode from this value, we obtain $Ni \mid NiSO_4(0.005\ M) \parallel H^+(1\ M) \mid H_2;\quad E=-0.32305$ volt.

And, $$a=\frac{\lambda}{\lambda_0}=\frac{70.89}{113.6}=0.62403.$$

Then, $E_0=-0.2507$ volt at 18°C.

We find, as a mean value,

$$E_0=-0.2508\pm0.0001 \text{ volt at } 18°C.$$

(2) *Activity of the ion being used.* If the activity of the ion, but not the ion concentration, is considered to be involved in the free energy change in the cell, the normal electrode potential E_0 at the unit activity of the ion must be calculated by the equation

$$E=E_0+\frac{RT}{2F}\ln m\,\gamma_{Ni^{++}} \qquad (2)$$

where $\gamma_{Ni^{++}}$ is the activity coefficient of the nickel ion at the molarity m of nickel sulphate.

Unfortunately, there are no data from which the activity coefficients of the nickel ion can be calculated. But, Lewis and Randall⁽¹⁾ have compiled a

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(1) Lewis and Randall, "Thermodynamics," (1923), p. 382.

table of the activity coefficients of individual ions at various ionic strengths by using certain assumptions. This table shows that the activity coefficients of ions of the same valency are nearly the same when the ionic strengths are not large. Therefore, without any other means for the time being until the actual measurements of the activity of the nickel ion can be made, an attempt was made to calculate the normal potential of nickel on the assumption that the activity coefficients of the nickel ion are the same as those of bivalent ions given in the table above cited. The necessary values at the ionic strengths used in this investigation were obtained by an interpolation or an extrapolation.

The electromotive force of the cell,

$Ni \mid NiSO_4(0.05\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $e = -0.6385$ volt at 25°C.

Taking Lewis and Randall's value of the potential of the decinormal calomel electrode(1).

$H_2 \mid H^+(1\ M\ of\ a_{H^+}) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $Ec = -0.3351$ volt at 25°C.

By the combination of these two,

$Ni \mid NiSO_4(0.05\ M) \parallel H^+(1\ M\ of\ a_{H^+}) \mid H_2$; $E = -0.3034$ volt at 25°C.

By a slight extrapolation from the table of activity coefficients of individual ions, we find the activity coefficient of bivalent metallic ion to be 0.24 at this concentration. Taking the activity coefficient of nickel ion for 0.05 M $NiSO_4$ as 0.24, we obtain for the above cell

$$-0.3034 = E_0 + 0.02958 \log 0.05 \times 0.24,$$

from which $E_0 = -0.2466$ volt at 25°C.

The electrolotive force of the cell

$Ni \mid NiSO_4(0.005\ M) \parallel KCl(0.1\ N), Hg_2Cl_2 \mid Hg$; $e = -0.6607$ volt at 25°C.

from which

$Ni \mid NiSO_4(0.005\ M) \parallel H^+(1\ M\ of\ a_{H^+}) \mid H_2$; $E = -0.3256$ volt at 25°C.

The value of $\gamma_{Ni^{++}}$ at 0.005 M is 0.53. Substituting these values in equation (2),

$$-0.3256 = E_0 + 0.02958 \log 0.005 \times 0.53,$$

we obtain $E_0 = -0.2494$ volt at 25°C.

As a mean value, $E_0 = -0.2480 \pm 0.0014$ volt at 25°C.

Similarly, we may calculate E_0 at 18°C. For this purpose, however, it is necessary to evaluate the potential at 18°C. of decinormal calomel electrode referred to the standard hydrogen electrode.

The electromotive force measurements of the cell, $H_2 \mid HCl(0.1\ M), Hg_2Cl_2 \mid Hg$, by J. H. Ellis(2) give -0.3978 volt at 18°C. Using this observed value, and taking 0.814 as the activity coefficient of 0.1 molal acid,

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(1) Lewis and Randall, "Thermodynamics," (1923), p. 406.

(2) Ellis, *J. Am. Chem. Soc.*, 38 (1916), 754.

the electromotive force of the cell where both a_{H^+} and a_{Cl^-} are equal to unity can be calculated by the following equation.

$$-0.3978 = E_0 + \frac{RT}{F} \ln a_{H^+} a_{Cl^-} = E_0 + \frac{2RT}{F} \ln m\, a_{\pm}$$

$$E_0 = -0.3978 - 0.1853 \log 0.1 \times 0.814 = -0.2720 \text{ volt at } 18^\circ\text{C.}$$

From this value, the potential of the decinormal calomel electrode at 18°C. can be calculated by the equation

$$H_2 \,|\, H^+(1 \text{ M of } a_{H^+}) \,||\, KCl(0.1 \text{ N}),\ Hg_2Cl_2 \,|\, Hg\,; \quad E = E_0 - \frac{RT}{F} \ln \frac{1}{a_{Cl^-}}$$

Taking 0.794 as the activity coefficient of 0.1 molal KCl⁽¹⁾ and accordingly as that of chloride ion in the same solution, we obtain $E = -0.3355$ volt at 18°C. Combining this value with the results given in Table 3, E_0 of the nickel electrode at 18°C. can be calculated.

Let us first consider the cell

$$Ni \,|\, NiSO_4(0.05 \text{ M}) \,||\, KCl(0.1 \text{ N}),\ Hg_2Cl_2 \,|\, Hg\,; \quad e = -0.6382 \text{ volt at } 18^\circ\text{C.,}$$

then, $Ni \,|\, NiSO_4(0.05 \text{ M}) \,||\, H^+(1 \text{ M of } a_{H^+}) \,|\, H_2\,;$ $E = -0.3027$ volt at 18°C.

By equation (2), $-0.3027 = E_0 + 0.02888 \log 0.05 \times 0.24$

$$E_0 = -0.2472 \text{ volt at } 18^\circ\text{C.}$$

Similarly, for the cell

$$Ni \,|\, NiSO_4(0.005 \text{ M}) \,||\, KCl(0.1 \text{ N}),\ Hg_2Cl_2 \,|\, Hg\,; \quad e = -0.66105 \text{ volt at } 18^\circ\text{C.}$$

$$Ni \,|\, NiSO_4(0.005 \text{ M}) \,||\, H^+(1 \text{ M of } a_{H^+}) \,|\, H_2\,; \quad E = -0.32555 \text{ volt at } 18^\circ\text{C.}$$

$$-0.32555 = E_0 + 0.02888 \log 0.005 \times 0.53$$

$$E_0 = -0.2511 \text{ volt at } 18^\circ\text{C.}$$

Consequently, as a mean value

$$E_0 = -0.2492 \pm 0.002 \text{ volt at } 18^\circ\text{C.}$$

For comparison, the values of normal electrode potentials calculated in the above are summarised in Table 4.

TABLE 4.

Values of normal electrode potential in volt.

	(1) Calculated from ion concentration.		(2) Calculated from ion activity.	
	25°C.	18°C.	25°C.	18°C.
From 0.05 M $NiSO_4$	−0.2503	−0.2509	−0.2466	−0.2472
From 0.005 M $NiSO_4$	−0.2489	−0.2507	−0.2494	−0.2511
Mean	−0.2496±0.0007	−0.2508±0.0001	−0.2480±0.0014	−0.2492±0.002

It is important to have found out that, although the nickel electrodes are those which were prepared by reducing finely divided nickel oxide in an

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(1) Lewis and Randall, "Thermodynamics," (1923), p. 362.

atmosphere of hydrogen, and probably some hydrogen was occluded in them, these values of E_0 calculated from the measurements with different concentrations are in perfect agreement with each other at the same temperature.

On the other hand, those values which were calculated from the activities of the ion of the two different concentrations are not so excellent agreement at both 18°C. and 25°C. as in the case of the values from the ion concentrations, though the difference amounts to only a few millivolts. This lack of agreement is probably due to the assumption involved in the calculation of activity of nickel ion. It is expected that more concordant results will be obtained if the activity of the nickel ion is measured accurately.

Change in Free Energy of Nickel Electrode Reaction. The change in free energy of the formation of nickel from its ion per equivalent, that is, $\frac{1}{2}Ni^{++}+\ominus=\frac{1}{2}Ni$, is expressed by the thermodynamic equation,

$$-\Delta F = E_0 F.$$

Taking as the values of E_0 at 25°C. -0.2496 volt which is the average of the normal electrode potential of nickel at one mol of ion concentration, we obtain, $\Delta F=0.2496\times 96500/4.182=5759$ calories at 25°C.
In a similar way, taking -0.2508 volt as the mean value of E_0 at 18°C., we obtain, $\Delta F=5787$ calories at 18°C.

On the other hand, if we take the value of E_0 as -0.248 volt at 25°C. which is the average of the potentials at unit activity, then

$$\Delta F=5723 \text{ calories at } 25°\text{C}.$$

Similarly, from the value of -0.2492 volt at 18°C.

$$\Delta F=5750 \text{ calories at } 18°\text{C}.$$

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Summary.

1. A reproducible electrode, which gives a constant and reversible potential of active nickel was obtained by using powdered nickel reduced with hydrogen directly in the cell and also using an apparatus which allows the cell to be filled with the electrolyte entirely in the absence of air.

2. The potentials of the reduced nickel powder in 0.05 M and 0.005 M nickel sulphate solutions both at 25°C. and 18°C. were measured in an atmosphere of hydrogen.

3. The normal electrode potentials of nickel were calculated from these observed potentials on the ground of two different concepts of the strong electrolytes, one being that the ion concentrations calculated from the conductance viscosity ratios are involved in the expression of the electromotive force of a concentration cell and the other being that the ion activities are involved. The average values of these normal electrode potentials are -0.2496 volt (25°C.) and -0.2508 volt (18°C.) at one molal ion concentration, and -0.2480 volt (25°C.) and -0.2492 volt (18°C.) at one molal ion activity.

4. The change in free energy of nickel electrode reaction per equivalent, that is, $\frac{1}{2} Ni^{++} + \ominus = \frac{1}{2} Ni$ was calculated from the above electrode potentials.

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