ELECTRODE POTENTIAL OF NICKEL. PART II. EFFECT OF OCCLUDED HYDROGEN ON THE ELECTRODE POTENTIAL OF NICKEL.

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In the first paper(1) it was reported that the nickel electrodes which had been freshly prepared from finely powdered nickel oxide by being reduced in hydrogen, and which probably occluded hydrogen, gave an accurately reversible and reproducible electrode potential. But Schoch,(2) and Richards and Behr(3) reported that in their experiment the occluded hydrogen in nickel or iron gave an indefinite and abnormally lower potential. Their results are in conflict with those obtained by the present writer for a nickel electrode. The experiments described in this paper were therefore undertaken with the purpose of deciding whether such occluded hydrogen has actually any considerable effect on the potential or not.

According to Thiel and Hammerschmidt(4) while ordinary nickel does not occlude much hydrogen when it is simply heated in the gas, (0.15 times its volume of hydrogen at 200°C, and 0.68 times at 800°C.), it can take up 11–18 volumes of hydrogen at room temperature under the stimulus of a prolonged cathodic polarization. These values perhaps are not to be taken as absolute but only show the relative absorbing power under varying conditions. Considerable differences have been reported by other observers; these being mainly due to the varying modes and temperatures of preparation and to the conditions of absorption to which it is subjected. Thus, according to Taylor and Burns(5) who made a most thorough study of this subject, some powdered nickel which had been reduced from the oxide at various temperatures absorbed an amount varying from 0.2 to 5 of its volume of hydrogen, decreasing rapidly as the temperature rise. Sieverts(6) has shown that nickel dissolves from 0.18 to 1 volume of hydrogen at the temperatures between 200° and 1000°C., the solubility increasing almost proportionally with increasing temperature, and also that the amount of hydrogen retained by nickel is proportional to the square root of the gaseous pressure.

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(1) This journal, **3** (1928), 57.
(2) *Am. Chem. J.*, **41** (1909), 208.
(3) *Z. physik. Chem.*, **58** (1907), 301.
(4) *Z. anorg. allg. Chem.*, **132** (1924), 15.
(5) *J. Am. Chem. Soc.*, **43** (1921), 1277.
(6) *Z. physik. Chem.*, **77** (1911), 591.

Hence the gas absorbed will be given off when the partial pressure is smaller.

On the other hand, Raoult⁽¹⁾ reported that a very porous nickel when polarized cathodically can be made to absorb about 165 times its volume of hydrogen. The amount actually occluded depends on the strength of the current and on the physical nature of the nickel. This extraordinary occlusion of hydrogen is only temporary and the main part of the excess is gradually evolved as the current ceases but the rest of the hydrogen is very tenaciousl yretained by the nickel, forming a kind of solid solution, and can be removed from it only on heating under a reduced pressure. It is well known that electrolytically deposited nickel when heated under reduced pressure gives off hydrogen showing that it, too, occludes hydrogen.

Consequently the first experiment was undertaken in order to find the effect of the hydrogen, produced in nickel by cathodic polarization, on the potential of the nickel electrode.

The second series of experiments was carried out, in an atmosphere of nitrogen in order to determine the effect of the hydrogen occluded by the nickel during its reduction. However, there seemed to be no doubt that the nitrogen used by the present writer was not pure but contained a trace of oxygen owing to the great difficulty in its complete removal, and there is some ambiguity, therefore, in the results of these experiments.

For this reason, the third experiment was carried out in an atmosphere of nitrogen mixed with a little excess of hydrogen over the quantity required to remove the oxygen, with the purpose of deciding the point by comparing the effects of the various concentrations of hydrogen.

Apparatus and Method of Experiment. The electrode vessel and the apparatus for preparing the nickel half-cell were the same as those which served for the former experiments (see " Electrode potential of nickel. Part I," Fig. 1, this journal, **3** (1928), 59). When it was desired to polarize the nickel electrodes with hydrogen, the cell was filled with dilute sulphuric acid which had been stored in one of the reservoirs, H′, and freed from air by passing hydrogen through it, as done in the case of the electrolyte in reservoir H. After the cell had been filled with the acid, as an anode against the nickel electrode a long platinum wire was inserted into the branch tube, f, by releasing the pinch-cock, Q, and through that tube a slow current of the acid solution was allowed to flow freely before and during the course of polarization, in order to prevent any possible diffusion of oxygen into the electrode chamber. After closing the cocks Q and k, the cell having been carefully washed was filled with nickel sulphate solution.

On the other hand, when it was required to work with nitrogen or nitro-

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(1) *Compt. rend.*, **69** (1869), 826.

gen with hydrogen added, the cell, after the reduction was completed, was freed from hydrogen through i by an oil pump, the cocks Q and k being closed. The cell was allowed to stand under the reduced pressure for about half an hour and then filled with the gas. The pumping out and filling was repeated several times at 300° C. to remove any hydrogen which might have been occluded by the nickel electrode. In other respects, the procedure was nearly the same as was described in the former paper.

Results of Measurements of Electromotive Force. The combination of the cell was as follows:

$$\mathrm{Ni}\,|\,\mathrm{NiSO_4}\ (0.05\ \mathrm{M.})\,|\,\mathrm{Saturated\ KCl}\,|\,\mathrm{KCl}\ (0.1\ \mathrm{N.}),\ \mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}.$$

In these experiments 0.05 mol $NiSO_4$ was always used and the measurements were made at 25°C. The current always flowed in the cell from left to right.

For the sake of comparison the results obtained in the three series of the experiments are summarised in Table 1. In Fig. 1 are plotted the changes with time of the electromotive forces of these cells.

TABLE 1.

E.M.F. of cell: $\mathrm{Ni}\,|\,\mathrm{NiSO_4}\ (0.05\ \mathrm{M})\,|\,\mathrm{Sat.\ KCl}\,|\,\mathrm{KCl}\ (0.1\ \mathrm{N}),\ \mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg}$, at 25°C.

Elapsed time in hours	E.M.F. in volt.				
	Cell No. 5	Cell No. 6	Cell No. 7	Cell No. 7′	Cell No. 8
1	−0.6348	−0.63105	−0.63240	−0.63660	−0.6388
2	−0.6350	−0.63125	−0.63275	−0.63660	−0.6388
4	−0.6353	−0.63130	−0.63345	−0.63655	−0.6387
7	—	—	−0.6338	−0.63655	—
12	—	—	—	—	—
17	−0.6355	−0.6326	−0.6345	—	−0.6385
24 (1 day)	−0.63565	−0.6332	−0.6346	−0.6368	−0.6384
36	−0.63575	−0.6335	−0.6351	−0.6369	−0.6382
48 (2 days)	−0.6359	−0.6337	−0.6354	−0.6370	−0.6380
					H_2 on
60	−0.63600	−0.6339	−0.6355	−0.6372	−0.6379
72 (3 days)	−0.6361	−0.63405	−0.6355	−0.6373	−0.63785
84	—	−0.63415	−0.63545	−0.63725	−0.63780
					O_2 on
85	—	—	—	—	−0.5692
96 (4 days)	−0.6361	−0.6343	−0.6354	—	−0.5868
108	—	−0.6344	−0.6354	—	—
120 (5 days)	−0.6360	−0.6344	−0.6353	−0.63705	—
				O_2 on	
121	—	—	—	−0.5984	—
132	—	−0.6345	−0.6353	−0.6233	—
144 (6 days)	—	−0.6346	−0.6353	—	—
168 (7 days)	—	−0.63455	—	—	—
288 (12 days)	—	−0.6340	—	—	—
		O_2 on			
289	—	−0.5612	—	—	—

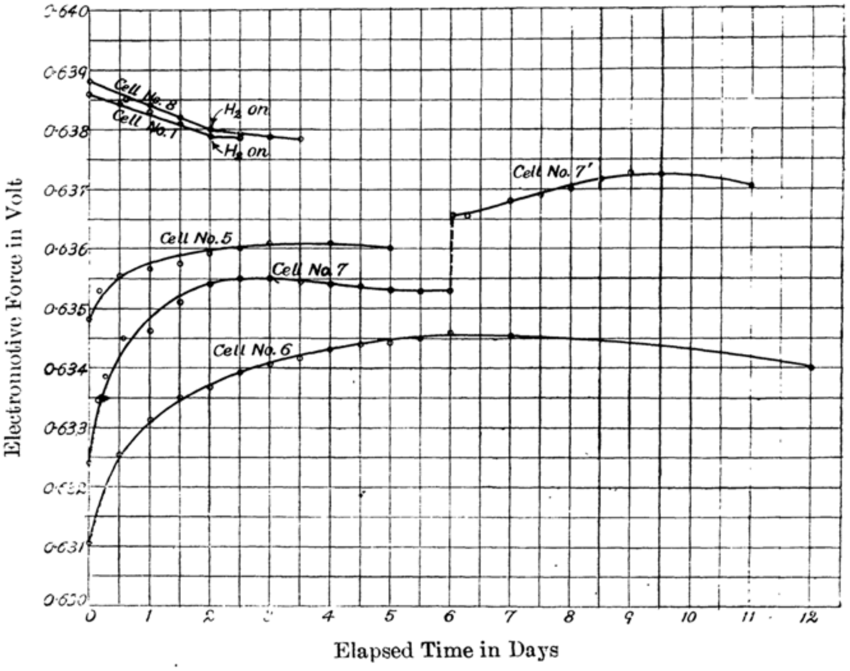

Fig. 1

(*I*) *Effect of the hydrogen produced in nickel by cathodic polarization.* The electrode material in cell No. 5 was prepared exactly in the same way as that in cell No. 1, and it was subjected to cathodic polarization in a decinormal solution of sulphuric acid for five hours with 30 milliampéres at 110 volts. Though the polarization was carefully carried out, the electromotive forces observed with four electrodes in the case of this cell were often found not to agree with each other to a closer precision than ±0.0005 volt at the beginning of the measurement.

From the results in the case of cell No. 5, as compared with those of cell No. 1, it will be seen that a prolonged cathodic polarization in dilute acid does not cause any increase but rather a slight decrease of the electromotive force, this showing that the results are in conflict with those obtained by previous investigators ; i.e. those in the case of the experiments of Schweitzer(1) with the polarized nickel electrode in caustic alkali solution, of Schoch(2) and of others with the nickel polarized in dilute acid or in water, and with the similar experiments of Richards and Behr(3) with iron, and of Schildbach(4) with cobalt, all of which showed that the cathodic polarization

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(1) *Z. Electrochem.*, **15** (1909), 607.
(2) Loc. cit.
(3) Loc. cit.
(4) *Z. Electrochem.*, **16** (1910), 967.

caused the increase in the electromotive forces. But, all these previous inverstigators worked under conditions in which there was the possibility that their electrodes might have come in contact with the air during the course of their preparation.

The initial value of the electromotive force in cell No. 5, contrary to expectation, showed a value about 4 millivolts smaller than that in cell No. 1; but this value increased with time to the extent of as much as a few millivolts. At present it is impossible to explain this diminution in the initial value of the electromotive force clearly, but it is supposed that it may be the effect of a trace of the free acid, which might have remained in the cell, owing to the difficulty of the replacing it,—it is impossible to avoid this trouble completely,—especially as the nickel was placed on the platinum wire in the cell as the electrode material, since nickel, which was reduced by the writer's method, evolves hydrogen instantaneously when it comes in contact with sulphuric acid, even when the acid is very dilute. According to the record of the subject, Schoch(1) in his experiments on the influence of free acid on the nickel-calomel cell found that even a trace of it caused a marked decrease in the electromotive force. A similar phenomenon was observed by the author in the investigation of an iron electrode (unpublished).

(*II*) *Measurements in an atmosphere of nitrogen.* The electrode materials in cell Nos. 6 and 7 were prepared in the same way as those in cell No. 1, and then the hydrogen was replaced by nitrogen. In the case of cell No. 6, nitrogen was passed through the electrode vessel for an hour with a speed of two or three bubbles per second (about 50 c.c. per minute) and no repetition was made, while in that of cell No. 7 the method was carried out in the same way as has already been stated. The electrolyte used in both cells was prepared from the same stock solution, and was given as nearly as possible the same treatment.

As the result, for the two cells curves of nearly the same type were obtained as shown in Fig. 1. The initial values of the electromotive forces in both cases were considerably less as compared with that of cell No. 1 and, increasing at first, rapidly arrived at their own maximum values and remained almost constant. There is, however, a considerable difference (1.4 mv.) between the initial values of the two cells, an amount which is too large to be neglected as an experimental error, because the agreement of the individual electrodes of each cell was excellent, and the mean deviation was within only 0.05 mv.

In the case of cell No. 7, after six hours of measurement, the entire solution was removed, the electrodes thoroughly washed, and the cell was refilled with a fresh solution which had been saturated with hydrogen. The result-

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(1) Loc. cit.

ing value of the electromotive force measurements increased almost immediately to 0.6366 volt then gradually approached the value of cell No. 1, and finally in three days reached the maximum value of 0.6373 volt where it remained nearly constant. The results given in Fig. 1 are those of cell No. 7′.

The low initial electromotive force of cells Nos. 6 and 7 as compared with that of cell No. 1 may at first sight be attributed to the removal of the hydrogen which had been absorbed by the nickel in the course of reduction. But, such an explanation is inconsistent with the fact that cell No. 7, in which a more complete removal of hydrogen must have been accomplished by the repeated evacuation, did not show a greater lowering of the electromotive force than cell No. 6. This discrepancy led the writer to find the cause in an entirely different direction which is explained as follows.

The nitrogen used in these experiments was obtained by the fractional distillation of liquid air and contains 2–3% of oxygen. It was purified by being passed through three washers of alkaline solution of potassium permanganate, and then through a solid caustic alkali tube, was freed from oxygen by being passed through a combustion tube filled with copper, and was then dried by being passed through a solid caustic soda tube. But, it has been noticed by several workers(1) that by such an ordinary method as was used by the present writer a small amount of the oxygen in nitrogen cannot be completely removed from the nitrogen.

On the other hand, it has already been stated at the beginning of the first paper that even a trace of oxygen greatly affects the potential of nickel. It was actually observed by the writer himself that electromotive forces were almost immediately lowered more than 30 millivolts further by the introduction of a small amount of air after the above measurements had been made. Putting these facts together, it seems very proper to attribute the low electromotive forces in cells Nos. 6 and 7, as compared with cell No. 1, to the effect of the oxidation of nickel occurring during the passage of nitrogen. Then, the higher electromotive force of cell No. 6, as compared with that of cell No. 7, is very well accounted for by the fact that a much larger volume of nitrogen was used in the former and accordingly, a comparatively heavier oxidation took place in it than in the latter.

In the end, this experiment in an atmosphere of nitrogen did not conclusively clear up the effect of the hydrogen contained in nickel on the electrode potential of the metal.

As for the gradual rise of the electromotive force in both cells, a full discussion will be given in the next paper in connection with the mechanism of the reactivation of passive metal.

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(1) For example, Kautsky and Thiele, *Z. anorg. allg. Chem.*, **152** (1926), 342.

In the second place, the sudden rise of the electromotive force in cell No. 7′ will be discussed. A sudden rise of the electromotive force caused by the solution saturated with hydrogen in cell No. 7′ seems to have a close connection with the lowering of the electromotive force above explained. Schoch⁽¹⁾ has also observed that in a cell of the same type but with 1N•$NiSO_4$ there is remarkable sudden rise in the electromotive force upon passing hydrogen through the cell, in which all the electrodes used were those which had been kept in air or those that have had a chance of coming in contact with the air. In his experiments the electromotive force was increased by 150 mv. by the passage of hydrogen, reached the abnormally high value of 0.337 volt, and then decreased gradually to the normal value—the electromotive force of the cell with 1N•$NiSO_4$ calculated from the electromotive force for a 0.1N•$NiSO_4$ solution measured by the present writer is 0.276 volt.

From these facts, as compared with the results in the case of cell No. 1 where no appreciable change occured upon the passing of hydrogen, it seems that the introduction of hydrogen causes a marked change in the potential only when the electrode has been previously brought into superficial oxidation by exposure to the air or oxygen, and that the change depends on the degree to which it has been affected.

There is no doubt that the sudden rise in the electomotive force of cell No. 7′ is due to the change on the very surface of the nickel which instantly takes place on its contact with the hydrogen dissolved in the solution. However it is not easy to understand how, under the conditions, such a sudden and remarked change can occur merely as the result of the physical adsorption of hydrogen by the nickel electrode.

Such a change must be considered to be very probably the result of the reduction of the oxide, once formed by the action of oxygen contained in the nitrogen. But the behaviour of hydrogen acting as an electrode must also be taken to into account. The question as to which is the true cause of the sudden change above mentioned was answered by the next experiment which was made in an atmosphere of a mixture of nitrogen and hydrogen with the purpose of clearing up the nature of the effect of the hydrogen contained in nickel on the electrode potential of the metal.

(*III*) *Measurements in an atmosphere of nitrogen with the addition of hydrogen.* The experiment on cell No. 8 was carried out under the same conditions as in that of cell No. 7 with the exception of the atmosphere. The gas used in this experiment was prepared by mixing 9 volumes of N_2 and 1 volume of H_2, which is a little over the quantity required to remove the oxygen contained in the nitrogen, and by passing the mixture through

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(1) Loc. cit.

a heated palladised asbestos tube.⁽¹⁾ The electrodes were allowed to stand for about an hour at 300°C., a condition which is considered to be sufficient for the establishment of the equilibrium between the partial pressure of hydrogen in the gas phase and the hydrogen dissolved in the nickel.

At the beginning cell No. 8 gave an electromotive force of just the same high value and also the same type of change as that in cell No. 1 which was prepared in an atmosphere of hydrogen only. By this experiment, it was conclusively shown that the hydrogen dissolved in nickel has no effect on the electrode potential of nickel, because if there were any such effect, cell No. 8 should have given a value intermediate between those of cells Nos. 1 and 6.⁽²⁾

Secondly, if, as shown by Smits and Lobry du Bruyn⁽³⁾ the nickel electrode behaves as a hydrogen electrode in an atmosphere of hydrogen, as is the case with one of platinum, it is expected to produce a change of potential of nearly 0.08 volt, but as a matter of fact this result is not produced. Accordingly, it was confirmed that the sudden rise of the electromotive force of cell No. 7′ by the introduction of hydrogen is due to the activation of the passive surface of the nickel. Further discussion of the mechanism of this activating action will be given in the next paper.

In short, as the result of the foregoing series of experiments the conclusion is reached that the hydrogen occluded by nickel has no effect upon the true electrode potential. For the measurement of the electrode potential of nickel, the complete exclusion of oxygen is the essential requirement and the use of the hydrogen atmosphere facilitates only the fulfillment of this requirement.

In conclusion, the writer wishes to express his great indebtedness to Professor G. Fuseya for his kind direction.

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(1) The gaseous mixture was collected on water at 20°C. in a gas holder. Therefore, according to the writer's rough calculation the amount of hydrogen required to remove all the oxygen in the nitrogen and also that dissolved in water in the gas holder was found to be about 8% of the nitrogen. The quantity of oxygen dissolved in water was calculated from the solubility of air in water at 20°C. and the whole volume in the gas holder. No attempt was made to find the concentration of hydrogen remaining in the gas, but from the quantity of the oxygen in the nitrogen it was calculated that the concentration of hydrogen was not more than 5% at most.

(2) If the quantity of hydrogen absorbed by nickel is proportional to the square root of the hydrogen pressure, as reported by Sieverts (loc. cit.), the hydrogen content of the nickel in cell No. 8 must have been less than twenty two hundredths of that in cell No. 1, since the hydrogen content of the gas was less than 5%.

(3) Smits, "Die Theorie der Allotropie" (1921), p. 412 ; *Proc. Acad. Sci. Amsterdam*, **20** (1918) 394.

Summary.

1. A prolonged cathodic polarization of the nickel electrode in dilute acid and in an atmosphere of hydrogen did not cause any increse, but rather a slight decrease in the initial value of the electromotive force of the cell, Ni | $SiSO_4$ (0.05 M.) | KCl (0.1 N.), Hg_2Cl_2 | Hg. The effect of hydrogen produced in the metals of the iron group by cathodic polarization, i.e. of making the metals less noble as found by previous investigators, was not be repeated in the case of reduced nickel powder. The slight diminution in the initial value of the electromotive force is supposed that it may be the effect of a trace of the free acid which might have remained in the cell, owing to the difficulty of the replacing it.

2. The potentials of the nickel electrode in an atmosphere of nitrogen, and of nitrogen mixed with a little hydrogen were measured. As a result of these series of experiments the conclusion is reached that the occluded hydrogen in nickel has no effect upon the true electrode potential. But, it was observed that in the case of an electrode which has been once affected by oxygen, the effect of hydrogen is very remarkable, and the electrode returns to its active state even at a low temperature.

3. For the measurement of the potential of nickel electrode, the complete exclusion of oxygen is the essential requirement.

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