ABSORPTION OF HYDROGEN BY ELECTROLYTIC NICKEL

THESIS FOR THE DEGREE OF M. S.

Alfred Clark

1932

Nickel

Adsorption of Hydrogen by Electrolytic Nickel

A Thesis Submitted to the Faculty
of
Michigan State College

In Partial Fulfillment of the Requirements
for
the degree of Master of Science

Department of Chemistry

by

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May, 1932.

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Introduction

The physical and chemical properties of metals are effected by the crystalline structure. X-ray studies in recent years show that the structure of metals deposited electrolytically varies with the amount of hydrogen co-deposited. Whether or not such results can be attributed to the gas which is held by the crystals or to a different structure caused by the presence of a g s film on the metal surface during the formation of the crystals is a proposition open to question.

This investigation is limited to the study of the quantity of hydrogen held by electrolytic nickel together with observations on the factors which effect the amount of gas adsorbed and the magnitude of the forces of adsorption.

It has been the usual practice until quite recently to deposit nickel from acid solutions of 5.2 - 6.0 pH. It was believed that a more acid solution would permit the evolution of hydrogen and thus cause the nickel to be more brittle. In this connection Phillips (Trans. Am. Elect. Chem. Soc., LIX, 393, 1931) has shown that nickel deposited from solutions of greater acidity may be rather soft ... at least not more brittle than nickel from solutions ranging from a pH of 5.2 - 6.0. It seems from the work of Phillips that the temperature is a more important factor than acidity in the determination of the hardness of a deposit.

Theories

Benton and White (J.A.S.S. 52, 2325, 1930) have given evidence for assuming two distinct types of adsorption of hydrogen upon nickel; physical adsorption prevalent at very low temperatures and decreasing rapidly from -210 to -183 deg. C., until at higher temperatures this type of adsorption is entirely superceded by chemical or activated adsorption. The physical or "secondary" type of adsorption as it is sometimes called involves only the hydrogen molecules whereas in "primary" or chemical adsorption, the molecules suffer an activation or even complete dissociation.

Another type of retention of hydrogen by nickel is the diffussion of hydrogen through the nickel. This is not a surface phenomena, and is comparable to a process of solution. The amount of hydrogen dissolved in nickel is of much lower order than that physically adsorbed. Sieverts (Z. Physik. Chem. 60, 129, 1907; 68, 115, 1910; Ber. 42, 338, 1909; 43, 893, 1910; 45, 221 and 2576, 1912) has determined the solubility of several gases in the more common metals. His values for the solubility of hydrogen in nickel are as follows; At 764 mm. of mercury and at a temperature of 923° C., 2.63 cc. of hydrogen were dissolved in 26.97 gms of nickel, whereas at the same temperature and a pressure of 129 mm. the solubility had decreased to 0.98 cc. At 822° C. and 764 mm. pressure 2.20 cc. of hydrogen were dissolved and this value decreases to 0.50 cc. at the same temperature and a pressure of 52 mm. From all of his data on the solution of hydrogen in nickel, Sieverts deduced that the amount dissolved varied as the square root of the pressure. He concluded also that the amount of nickel surface exposed did not effect the amount of hydrogen dissolved, the amount depending on the weight of the sample. It is evident on this score then that the hydrogen was not being adsorbed at these temperatures.

Sieverts gives the following summary in regards to the solubility of various gases in certain metals;

Nitrogen; Not dissolved by metals, forms nitrides with aluminum and iron.

Carbon dioxide; insoluble in copper.

Oxygen: soluble in molten silver.

Sulphur dioxide; soluble in molten copper.

Hydrogen; soluble in copper, iron, nickel, palladium; insoluble in cadmium zinc, lead, bismuth, tin, antimony, silver and gold.

Mayer and Altmayer (Ber. 41, 3063-74, Sept.) take issue with Sieverts on the results which he obtained on nickel, stating that Sieverts did not allow time enough for complete adsorption. According to Sieverts, the volume of hydrogen taken by by 1 volume of nickel at 360° C. and 1 atmosphere is 2 volumes. Mayer and Altmayer report 5.5 to 50 volumes of hydrogen per 1 volume of nickel under the same conditions of temperature and pressure. In both cases the nickel was obtained by the reduction from the oxide, Mayer and Altmayer state that the adsorption of hydrogen on nickel is directly proportional to the pressure, thus obeying Henry's Law.

Kahlenberg and French (Trans. Am. Elect. Chem. Soc. LIV, 163, 1928) have shown that there is a correlation between the lowering of the potential of a metal electrode when gas is bubbled through the electrolyte and the adsorptive power of the metal for the gas in question. The greater the adsorptive power of the metal the greater the lowering of potential. Nickel shows a drop superceded only by that of palladium and platinum.

Clausthal (Ber. Phys. Ges., 1003-22, 1911) carried out some work on the adsorption of hydrogen by various metals at very low temperatures. From his experimental results he concluded that the amount of adsorbed gas is conditioned by solution and a surface condensation.

Much contradiction exists in data published on the affinity of metals for gases, particularly in the case of adsorption rather than in the case of solubility, where the state of division of the metal, that is, the amount of surface exposed plays so important a role. There is also great confusion as to which of the three types of retention; physical, chemical or solution are taking place under certain conditions.

The adsorption of gases on metals appears to be a special case of adsorption of gases on solids, and most of the common formulas for such adsorption do not hold even approximately in their case. The amounts of gases adsorbed on metals are all of very low order. Perhaps no general law of adsorption of gases on solids is possible, for as Langmuir states, the aspects of adsorption may differ greatly from case to case in accordance with the variation in atomic structure and in the kind and distribution of forces in the solid surfaces.

The amount of adsorption of gases on the surfaces of metals undergoing a process of electrodeposition, it must be admitted, is a special case of the adsorption of gases upon metals. And even though the same laws, whatever they may be, apply; the conditions such as surface area, surrounding media, and surface forces, are so peculiarly characteristic that entirely different results may be expected. In the process of electrodeposition of a metal, the integral surface area must be exceedingly large, dependent on the size of the individual nuclei deposited.

Apparatus and Materials

The apparatus used is shown in Drawing 1 and also in the photograph. It is entirely of glass and consists of a tube (A) wherein the metal is placed, a drying bulb (B) to take up the water vapor adsorbed by the nickel, a manometer (C) for measuring changes in pressure due to the gas evolved from the metal. The rest of the apparatus is used in purifying the nitrogen which is used as in inert atmosphere, and consists of a Tube (D) containing a copper gauze heated by a nichrome wire coil for the purpose of taking the oxygen out of the nitrogen, and a tube (E) to which a drying bulb is attached. The nitrogen can be introduced into the main system at will through the two-way stop-cock (F). A Hy-vac Cenco pump was used to produce a vaccuum. (G) is an electric heating unit for driving the gas from the metal, and (H) a thermo-couple for measuring the temperature of the unit. Mercury levels were read with a cathetometer to .05 mm. The nickel deposit sealed in a small tube was introduced into the vaccuum by breaking the tube with an iron weight lifted by an electromagnet (I).

Composition of the nickel electroyte;

The same solution was used throughout the entire experiment and the pH successively lowered by the addition of sulphuric acid. The composition was as follows;

140 gms. of nickel sulphate per liter.

15 gms. of Boric Acid per liter.

15 gms. of Ammonium Sulphate per liter.

Current densities were measured with a milliameter in the electrical circuit.

pH measurements were made with the new type Hellige Comparator, using brom-cresol purple and thymol blue standard color discs and indicator solutions.

Nitrogen:

The commercial gas supplied in tanks was used and purified as described.

Drying Agent:

Phosphorus pentoxide was found to be a much more rapid drying agent than magnesium perchlorate, commonly known as Anhydrone. The latter was used throughout the work.

Procedure

The nickel was deposited upon steel plates one square decimeter in area, and the deposit peeled from them easily and dried at room temperature. The nickel deposit is placed in a small tube, sealed and placed with a soft iron weight in a larger tube. This larger tube is sealed to the apparatus at (A). The system is then evacuated at J and sealed off from the pump. Stop-cock (F) is opened to admit nitrogen into the main system enough being admitted to give a pressure of about 100 mm., and the stop-cock closed. The tube containing the metal is broken by the iron weight lifted by the electromagnet. The manometer levels are read, and the metal then heated to about 500° C. for thirty minutes. The system is allowed to cool, mercury levels again noted, and enough mercury withdrawn from the manometer through the stop-cock (K) to bring about the same difference in levels as prior to the heating.

One arm of the manometer is accurately calibrated in cubic centimeters, and the difference in the mercury levels of this arm before and after heating and adjustment give the volume of the gas expelled from the metal. The barometric pressure is taken and the gas volume converted to standard conditions. The metal is weighed after the run.

The nitrogen is purified in the following manner: With stop-cock (F) open, the system is evacuated at (L) and sealed off from the pump. Stop-cock (F) is closed and nitrogen admitted until the pressure is approximately atmospheric as shown by the gauge (M). The gas is retained here in the presence of the heated copper gauze for fifteen minutes. Stop-cock (F) is then opened, part of the nitrogen rushing into (E). (F) is closed and the gas allowed to remain in (E) for fifteen minutes after which time it is ready to be introduced into the main system.

The copper gauze is reduced at intervals by exposure while hot, to methyl alcohol vapors.

The calibration of the manometer arm was carried out by weighing water drawn out at 2 cc. intervals, and then checking against a standardized burrette.

Nitrogen was introduced into the apparatus in order to bring the mercury levels to such a position that mercury can be withdrawn without exceeding the limits of the manometer. Oxygen was not used because of the caralyric action of nickel upon hydrogen and oxygen to form water vapor.

Data on Hydrogen Adsorbed at pH 5.6

Manometer levels before heating		Manometer levels after heating and adjusting		amps/dm^2	Temperature	Barometer Press	Weight of Nickel	c.c.H_2/ gm. nickel
78.545	14.012	78.543	14.012	1	22.4	73.52	.8917	0.00
77.209	13.876	77.209	13.876	1	22.7	73.81	.6843	0.00
78.430	13.906	78.430	10.890	1	22.7	73.62	.5136	0.00
78.975	14.145	75.745	9.861	3	22.7	73.52	.6694	.98
77.650	13.321	74.190	7.749	3	22.5	73.65	.8102	.94
78.364	14.129	71.984	8.562	5	22.8	74.01	.7963	1.85
78.125	13.962	72.725	7.495	5	22.7	73.81	.6972	1.76
77.321	13.765	71.051		7	22.4	73.52	.8105	1.82

Data on Hydrogen Adsorbed at pH 1.7

Manometer levels before heating		Manometer levels after heating and adjusting		amps/dm^2	Temperature deg. C.	Barometer Pressure	Weight of Nickel	c.c. H_2/ gm. nickel
77.670	16.155	74.505	12.990	3	22.6	74.31	.6888	1.49
78.425	17.651	73.563	12.791	3	22.9	73.58	.8342	1.76
77.428	16.362	72.228	11.162	3	22.7	73.82	.9126	1.83
77.625	16.106	76.605	15.090	5	22.7	74.41	.2557	1.33
78.695	14.630	75.315	11.240	5	22.6	74.90	.5302	1.81
78.321	14.451	73.311	9.441	5	22.8	74.35	.7125	1.74
77.630	15.362	74.260	11.992	5	22.5	74.28	.4862	1.96
78.710	14.832	74.330	10.452	7	22.7	73.97	.5179	1.85
77.362	15.717	73.542	11.897	7	22.6	74.51	.7632	1.52
78.125	17.362	76.475	15.712	7	22.8	73.56	.2917	1.72
77.862	15.365	74.622	12.125	9	22.7	73.81	.4325	1.99
77.912	15.876	74.262	12.226	9	22.7	74.20	.6271	1.67

Data on Hydrogen Adsorbed at pH 2.8

&

Manometer levels before heating		Manometer levels after heating and adjusting		amps/dm^2	Temperature deg. C.	Barometer Pressure	Weight of Nickel	C.C. H_2/ gm. nickel
84.515	21.055	80.455	16.995	5	22.7	73.59	.6922	1.50
81.845	18.940	76.010	13.105	5	22.7	73.86	1.0778	1.503
83.215	20.862	77.015	14.662	5	22.4	73.97	.9143	1.86
82.305	18.425	73.660	9.790	5	23.0	73.70	1.0760	2.00
81.406	18.213	76.416	13.223	5	22.7	73.82	.8765	1.43
81.925	18.600	71.930	8.605	5	22.7	74.51	1.3470	2.10
80.203	18.921	73.373	12.091	5	22.7	74.23	1.2132	1.72
80.721	19.320	80.721	19.320	1	22.5	74.51	1.1057	0.00
83.652	20.473	83.652	20.473	1	22.5	73.72	.9068	0.00
82.324	19.632	82.324	19.632	1	22.7	73.72	.9567	0.00
81.831	19.621	76.361	14.151	7	22.7	74.35	.8912	1.76
82.435	18.234	76.565	12.364	7	22.9	74.06	.8756	1.56
81.620	18.830	78.395	15.600	7	22.7	74.55	.7586	1.28

Calculations:

The calculations are very simple. The following formula express the cubic centimeters of hydrogen per gram of nickel at N:T:P:

$$x = \frac{273 x p' x X'}{760 x T w}$$

Where X is the amount of hydrogen adsorbed, p' is the pressure in mm. during the run, and w is the weight of the nickel sample.

A sample calculation follows:

Difference in levels before heating	62.805 cm.
Difference in levels after heating	62.905 cm.
Lowering in height of the mercury levels	5.835 cm.
Average Length of Manometer Arm per CC volume	1.03 cm.

Volume of gas at 738.6 = Bar. Press. - 629.05 = 109.55 cm. is

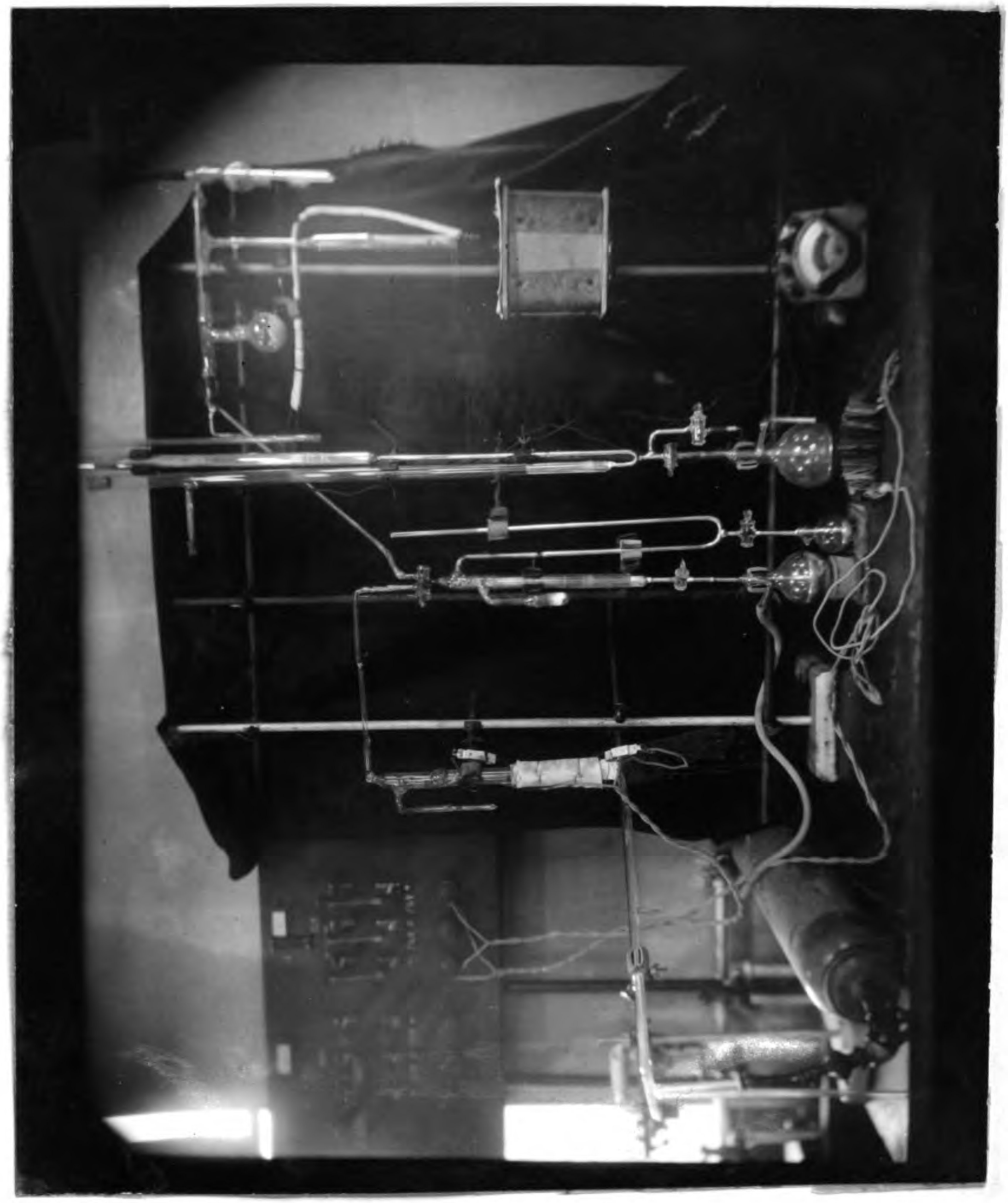
$$\frac{2 x 5.835}{1.03}$$

Temperature = 22.7° C.

Weight of sample = 1.0778 gm.

CC of hydrogen per gram of nickel corrected to N:T:P: =

$$\frac{273 x 2 x 5.835 x 109.55}{760 x 1.03 x 295.7 x 1.0778} = 1.503 \text{ cc/gm. of nickel}$$



Discussion

It will be observed on looking at the table of data that the amount of hydrogen adsorbed by the nickel is roughly constant at most current densities and Ph's. The results could not as a rule be exactly duplicated, due no doubt to the changing conditions of the electrolyte upon continued electrolysis. However, the values lie well within a range of 1/2 cc. The amount of gas adsorbed is logically dependent to some extent on the amount evolved at the cathode, and indirectly dependent upon the current density and the Ph in so much as these two properties effect the ratio of the amount of gas adsorbed to the nickel deposited. Beyond a certain point, however, an increase in the amount of hydrogen evolved per unit amount of nickel deposited seems to have no effect upon the amount of hydrogen adsorbed. This may be explained as follows;

In the formula, $a = kp^{1/n}$, expressing the variation in the amount of adsorption, a, with pressure p, k and n being constants characteristic of the adsorbent, when the pressure has reached a certain value, adsorption does not increase, the parabolic curve flattening out into a line practically parallel to the abscissa. It is assumed that at low pressures the number of gas particles are not sufficiently great in number to entirely cover the surface of the adsorbent, thus maximum adsorption does not take place. As the pressure increases, the number of particles of gas present per unit volume increases, and at some definite pressure the adsorbent may become entirely covered with the gas particles thus bringing about maximum adsorption. Further increase in pressure will cause no increase in adsorption. This is comparable to the case of adsorption during electrodeposition. When the amount of gassing is low enough so that the surface

of the nickel is not completely covered then maximum adsorption will not take place. By lowering the pH or increasing the amount of current, that is, increasing the amount of gassing, a point will be reached where the gas will completely cover the surface of the metal and further increasing of current density or lowering of the pH will not increase the amount of adsorption. In this type of adsorption then at any constant pH, the current density plays the same role as the pressure in the above formula. Thus it is seen from the data that at 1 ampere per square decimeter, and a pH of 2.8, no appreciable quantity of hydrogen is adsorbed, whereas at 3 amperes per square decimeter 1.5 cc. per gram are adsorbed, which is the average maximum amount adsorbed. Thus somewhere between 1 and 3 amperes is the value of the current density which will just cause maximum adsorption. Now by determining the current efficiencies in this range, the value for the rate of evolution of hydrogen which will just cause maximum adsorption may be obtained, i.e. the amount of gas which will just completely cover the surface of the nickel.

The time of deposition has no appreciable effect on the amount of gas adsorbed, so that the rate of diffusion may be considered negligible.

The hydrogen is held upon the nickel quite tenaciously; in fact a sample of nickel may be exposed to a vaccuum of 1 or 2 mm. for several hours at ordinary temperatures without releasing its gas. When heated to approximately 175° C. it commences to lose its gas.

Electrodeposited nickel adsorbs some water vapor, but the predominating adsorbed substance is hydrogen, probably because of the smaller size of the hydrogen molecules, which allow them a greater penetration than the water molecules.

Whether the presence of hydrogen has any deleterious effects upon the nature of the nickel deposit was not ascertained. However, it has been shown that whatever may be the ill effects of adsorbed hydrogen they are not increased in the low pH baths where gassing is greater. Of course greater gassing may have a tendency to produce a more honeycombed structure even though the gas may not be adsorbed.

A very interesting argument was instigated by an article by Harding and Smith (J.A.C.S., 40, 1508-31, 1918). In this article it was stated that while hydrogen was being deposited upon a metal, the resistance first rose to a maximum and then lowered. The rising to a maximum was explained by assuming that during this period an alley was being formed, and the lowering was explained by assuming that a transient type of hydrogen which was conducting was then being formed.

Newbery (J.A.C.S., 41, 1887-92, 1919) criticises the formation of a transient hydrogen. He believes that hydrides are formed under the great pressures produced by high current densities, and are decomposed on cessation of the current. He bases his argument on the fact that the single potential of platinum electrode saturated with hydrogen is sometimes .72 v. higher than that of the hydrogen electrode and, therefore, a hydride must be assumed.

Harding and Smith (J.A.C.S., 41, 1892-4, 1919) return with more proof of their theory, believing that on the basis of the hydride theory it would be necessary to attribute to such a compound a volume condensation greater than that of the metal and of a higher order than any hitherto observed for compounds or solid solutions. On the other hand the accumulation of transient hydrogen may raise the electrical solution pressure of hydrogen and in general involves no sweeping assumptions as the co-existence of solid solutions and metallic compounds.

Summary

This work can not be classed more than a preliminary survey of the adsorpiton of hydrogen by electrodeposited nickel. The results are considered accurate to within 0.10 cc. at standard conditions. The amount of hydrogen adsorbed on nickel has been determined at the pH's 5.6, 2.8, 1.7, and at the current densities 1, 3, 5, 7, 9, amperes per square decimeter.