[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Equilibrium Reaction $NiCl_2 + H_2 = Ni + 2HCl$. Ferromagnetism and the Third Law of Thermodynamics[1]

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The equilibrium $NiCl_2 + H_2 = Ni + 2HCl$ has been measured over the temperature range 630 to 738°K. Final equilibrium was slow due to the effect of microscopic phases of nickel. It is probable that true equilibrium could not have been reached except for the fact that the appreciable vapor pressure of $NiCl_2$ served to transport nickel from microscopic to macroscopic particles. The heat of reaction at the absolute zero was calculated from each observation with the assistance of the available free energy function. There was no trend in the values with temperature which indicates that the free energy values used were the true thermodynamic quantities. Since these were calculated on the assumption that there was no residual entropy change at 0°K., this is confirmed to within the order of 0.1 cal. deg.$^{-1}$ mole^{-1}. On this basis it seems reasonable to conclude that ferromagnetic nickel approaches zero entropy at the absolute zero. This was expected but the present work represents the only case in which a ferromagnetic substance has been tested by means of the third law of thermodynamics. The following heats of reaction can be given: $NiCl_2 + H_2 = Ni + 2HCl$: $\Delta H^0_0 = 29075$ cal. mole^{-1}, $\Delta H^0_{298.16°K.} = 28888$, $\Delta F^0_{298.16°K.} = 16400$. $^1/_2H_2 + {^1/_2}Cl_2 = HCl(g)$: $\Delta H° = -22000$ cal. mole^{-1}, $\Delta H^0_{298.16°K.} = -22043$, $\Delta F^0_{298.16°K.} = -22757$. $Ni + Cl_2 = NiCl_2$: $\Delta H^0_0 = -73075$ cal. mole^{-1}, $\Delta H^0_{298.16°K.} = -72974$, $\Delta F^0_{298.16°K.} = -61915$. The diffusion rate of hydrogen through Pyrex glass has been determined and represented by the equation $\log_{10} k$ [cm.^{2} sec.$^{-1}$ (cm. Hg)$^{-1}$] $= -6.063 - 3198/T$.

It is the purpose of this work to provide evidence from the application of the third law of thermodynamics that a ferromagnetic substance approaches zero entropy at 0°K. There is no reason to suspect that an elementary ferromagnetic substance, such as nickel, would retain disorder at low temperatures. Rather it would seem that such a system has unusual opportunities to attain a perfectly ordered arrangement. Nevertheless, no ferromagnetic substance has been given a thermodynamic test of this sort and it seems desirable not to proceed indefinitely without one test merely because an idea seems plausible.

It is not easy to obtain the entropy of any of the ferromagnetic metals with high accuracy either from the gas or by means of a chemical reaction. The latter method seemed like the best approach and the reaction

$$NiCl_2 + H_2 = Ni + 2HCl \qquad (1)$$

was selected for several reasons. The thermodynamic properties of hydrogen and hydrogen chloride are very accurately known from spectroscopic data and it was known from the measurements of Berger and Crut,[2] Jellinek and Uloth,[3] and Sano,[4] that the reaction had favorable equilibrium constants in the range 350 to 450°. The low temperature heat capacities of very pure nickel[5] and nickel chloride[6] were measured to provide necessary values of the free energy function. The preparation of the anhydrous nickelous chloride has been described previously.[6]

Apparatus.—The one-liter Pyrex glass reaction vessel is shown at 3, Fig. 1. Its temperature was controlled by surrounding the reaction vessel with the condensing vapor of boiling mercury or boiling sulfur. The pressure of the boiling liquid was held constant to within 0.2 mm. by means of a barostat. The arrangement shown at the far left of Fig. 1, consisted of a mercury manometer with an electrical contact which activated a magnetic valve through a Thyratron relay. The magnetic valve was attached to a vacuum line. Nitrogen gas leaked into the barostat continuously and caused the magnetic valve to operate several times a minute. The barostat was stabilized by means of two 20-liter bottles. The reflux tube, shown at 1 Fig. 1, was attached at one side of the outer jacket so that condensate did not drain onto the reaction vessel. The 250 watt heater was controlled by means of a Variac transformer. The temperature was calculated from the vapor pressure of sulfur by means of the equation given by Stimson.[7] The temperatures corresponding to the vapor pressure of mercury were obtained from the table of Busey and Giauque.[8] The anhydrous nickel chloride was placed in the bottom of the reaction vessel through the 1.5-cm. tube leading to the 2 mm. i.d. capillary buret lead shown at 2 Fig. 1. After the nickel chloride was in the reaction vessel it was treated with dry hydrogen at the boiling point of mercury or sulfur and then evacuated to

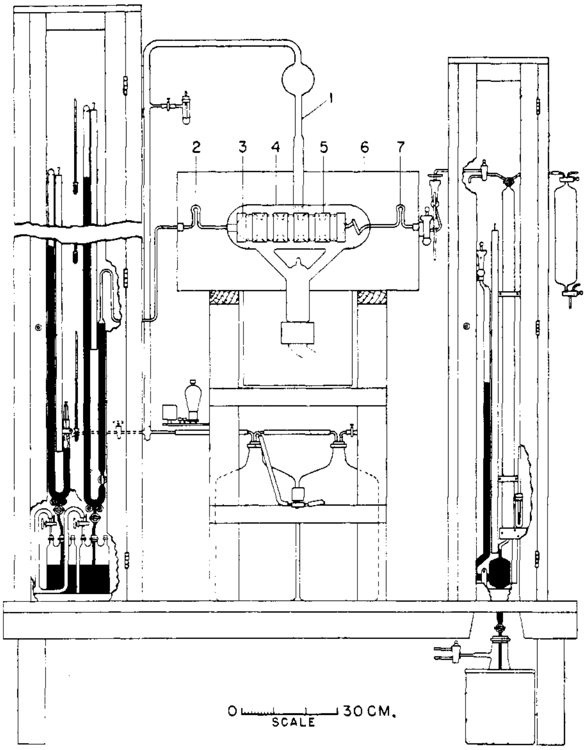

Fig. 1.—Apparatus for measurement of equilibrium $NiCl_2 + H_2 = Ni + 2HCl$.

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[1] This work was supported in part by The Office of Naval Research U. S. Navy.

[2] E. Berger and G. Crut, *Compt. rend.*, **173**, 977 (1921); *Bull. soc. chim.*, **35**, 550, 729 (1924).

[3] K. Jellinek and W. Uloth, *Z. physik. Chem.*, **119**, 161 (1926).

[4] K. Sano, *J. Chem. Soc. Japan*, **58**, 376 (1937).

[5] R. H. Busey and W. F. Giauque, THIS JOURNAL, **74**, 3157 (1952).

[6] R. H. Busey and W. F. Giauque, *ibid.*, **74**, 4443, (1952).

[7] H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

[8] R. H. Busey and W. F. Giauque, THIS JOURNAL, **75**, 806 (1953).

ensure that no basic chloride remained in case any had been produced during the setting up of the apparatus.

An outer case, 6 Fig. 1, was filled with Santocel insulation about 18 cm. thick. The reflux tube, leading to the barostat, was bent to prevent direct entry of radiation and the Y arrangement above the boiling liquid, as shown in Fig. 1, was also designed to prevent radiation from reaching the reaction vessel from the heaters. These precautions were not adequate and the preliminary measurements indicated that the temperature of the nickel chloride was below that of the bath due to radiation. This was partly due to the fact that ordinary Santocel is somewhat transparent to radiation. Another grade of Santocel containing sufficient reduced silicon to render it rather opaque to radiation was substituted. The outer jacket was wrapped in aluminum foil and an iron radiation shield, 5 Fig. 1, was placed between the reaction vessel and its outer jacket shown at 4 Fig. 1. The shield consisted of an inner cylindrical tube with four $^3/_4$ in. slots 3 in. in length at the top and four at the bottom. These were centered under four outer cylindrical covers of larger diameter. The shields were supported and closed by Transite ends.

A 2-mm. capillary tube, 2 Fig. 1, led from the reaction vessel to a mercury manometer with a diameter of 1.7 cm. i.d. and a minimum volume above the meniscus. Another capillary line, 7 Fig. 1, 2 mm., i.d. led to a one-liter gas buret with a mercury manometer attached. The buret and manometers were enclosed in cases which were maintained at uniform temperatures over long periods by means of small currents of air from a compressed air system.

Method of Measurement.—A suitable amount of hydrogen gas was admitted to the reaction vessel, which contained about 30 g. of $NiCl_2$, and allowed to stand until equilibrium was reached. The mercury in the manometer was lowered and raised to its original position occasionally during the equilibrium period to ensure uniform composition throughout the system. The manometer arm represented only about 1–2% of the volume. In preliminary measurements the stopcock was opened to the evacuated buret for less than 2 seconds and about $^2/_3$ of the gas was withdrawn for analysis. The hydrogen chloride was absorbed in sodium hydroxide and the chloride determined gravimetrically as AgCl. However, when it was found that the reaction was about half complete in one minute, after an initial hydrogen pressure of 19.4 cm. was admitted to the reaction vessel at the boiling point of mercury, the method was abandoned. It was evident that a sample could not be withdrawn rapidly enough to avoid a shift in the equilibrium.

A second method of using the same apparatus was devised as follows: a known quantity of nitrogen was admitted to the reaction vessel in order to determine the relationship between pressure and moles of gas as a function of temperature. This was necessary because a small part of the volume between the manometer and the reaction vessel was at lower temperatures and the exact gas volume of the vessel was unknown as a function of temperature. A measured amount of hydrogen was introduced from the gas buret and allowed to stand until equilibrium was reached. It was then assumed that

$$P_{\text{HCl}} = 2(P_{\text{equil}} - P'_{\text{H}_2}) \qquad (2)$$

and

$$P_{\text{H}_2} = 2P'_{\text{H}_2} - P_{\text{equil}} \qquad (3)$$

where P'_{H_2} represents the pressure which the hydrogen would have if none had reacted. The equilibrium constant is

$$K = P^2_{\text{HCl}}/P_{\text{H}_2} \qquad (4)$$

However, another difficulty appeared. Despite the rapidity of the initial stages of the reaction it took a long time to approach equilibrium and after the pressure attained a maximum value it began a very slow decrease. It was soon proved that the decrease was caused by diffusion of hydrogen through the walls of the Pyrex glass reaction vessel. The effect was small but was large enough to enable evaluation of the diffusion coefficients at various temperatures. The data are given in Table I. The absolute value of the diffusion coefficient was estimated from an average value of the wall thickness 2.26 mm. obtained by weighing the vessel.

In calculating the rates of diffusion of hydrogen given in Table I a small correction was applied for the shift of equilibrium pressure which accompanied hydrogen loss.

Table I

Diffusion of Hydrogen through Pyrex Glass

T, °K.	P_{H_2}, cm.	Time, hr.	Loss cm.^{3} sec.$^{-1}$ $\times 10^6$ N.T.P.	k cm.^{2} sec.$^{-1}$ (cm.)$^{-1}$ $\times 10^{11}$	$k \times 10^{11}$ calcd. by eq. 1
661.67	9.8	93	0.67	1.9	1.3
676.65	8.8	50	.54	1.7	1.6
693.00	7.7	98	.73	2.7	2.4
645.33	39.1	92	1.54	1.1	1.0
676.18	35.7	94	1.88	1.5	1.6
707.11	30.6	95	3.53	3.2	2.6
738.02	21.5	115	3.45	4.5	4.0
707.20	26.7	117	2.26	2.4	2.6
646.19	39.4	92	1.34	1.0	1.0
692.14	33.6	99	2.42	2.0	2.1
692.12	32.5	91	2.22	1.9	2.1
707.42	29.8	120	2.14	2.0	2.6
722.73	24.0	144	2.56	3.0	3.2
737.89	21.2	73	2.91	3.9	4.0
630.18	41.3	1173	1.11	0.76	0.73

A single diffusion measurement was obtained with an apparatus consisting of an evacuated bulb with a jacket containing one atmosphere of hydrogen. At the boiling point of sulfur, 717.90°K., the value of $k \times 10^{11}$ was found to be 2.5 cm.^{2} sec.$^{-1}$ (cm.)$^{-1}$. This is in satisfactory agreement with the results obtained during the equilibrium measurements and confirms quantitatively the interpretation of the pressure decrease with time. Additional measurements with the above apparatus were planned but were not obtained due to breakage and lack of time. The diffusion constant may be represented by the equation

$$\log_{10} k[\text{cm.}^2\ \text{sec.}^{-1}(\text{cm.})^{-1}] = -6.063 - 3198/T \quad (5)$$

Possible Effect of Particle Size.—After recent experience with the large effect of microscopic particle size on the equilibrium

$$Mg(OH)_2 = MgO + H_2O(g) \qquad (6)$$

in this Laboratory[9] the possibility of such an effect in the present case was considered with care. It seems rather probable that in the initial stages of the reaction

$$NiCl_2 + H_2 = Ni + 2HCl$$

that microscopic nickel particles are produced and they are a plausible explanation of the fact that equilibrium is attained very slowly.

Schutza[10] has found evidence that microscopic cobalt metal prepared by the reduction of cobalt oxide by hydrogen interferes with the true macroscopic equilibrium.

In the present case we are inclined to suspect that it would be impracticable to attain equilibrium between the macroscopic phases in any reasonable time if a mechanism for the transportation of nickel through the gas phase did not exist.

In the case of microscopic MgO produced by dehydration of the hydroxide there is no obvious mechanism by which small particles can be reconstituted into large ones. In the present case one can count on the very appreciable vapor pressure of $NiCl_2$ to transport nickel. The vapor pressure of $NiCl_2$ has been measured by Maier.[11]

The pressure of $NiCl_2$ over the range of the present measurements varies from 1.7×10^{-7} mm. at 615°K. to 2.2×10^{-4} mm. at 735°K.

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(9) W. F. Giauque, This Journal, **71**, 3192 (1949).

(10) H. Schutza, *Chem. Ing. Technik*, **21**, 177 (1949).

(11) C. G. Maier, Bur. Mines Tech. Paper No. 360 (1925).

TABLE II

DATA RELATING TO THE EQUILIBRIUM $NiCl_2 + H_2 = Ni + 2HCl$

Series	T, °K.	Gas in excess at start	P_{H_2} equil., cm.	P_{HCl} equil., cm.	Mole ratio $\frac{Ni}{NiCl_2}$ at equil.	K, atm.	$-\Delta\frac{(F^0-H_0^0)}{T}$	ΔH_0^0, cal. mole^{-1}
			0.359 mole $NiCl_2$ in reaction vessel at start of Series 1					
1	661.67	H_2	9.81	13.66	0.045	0.2503	41.186	29072
1	676.65	H_2	8.83	16.28	.045	.3949	41.128	29078
1	693.00	HCl	7.70	19.30	.045	.6365	41.065	29080
2	645.33	H_2	39.19	21.05	.069	.1488	41.251	29064
2	676.18	H_2	35.67	32.57	.072	.3913	41.130	29072
2	707.11	H_2	30.61	47.18	.078	.9568	41.011	29062
3	738.02	H_2	21.55	59.13	.134	2.135	40.893	29068
3	707.20	HCl	26.75	44.04	.130	0.9540	41.011	29069
4	646.19	H_2	39.42	21.30	.141	.1514	41.248	29079
4	692.14	H_2	33.56	39.84	.148	.6223	41.068	29077
5	692.12	H_2	32.48	39.24	.166	.6238	41.068	29073
5	707.42	H_2	29.82	46.56	.169	.9565	41.010	29066
6	722.73	H_2	24.02	50.96	.211	1.423	40.951	29090
6	737.89	H_2	21.21	58.12	.215	2.095	40.893	29090
			0.057 mole $NiCl_2$ in reaction vessel at start of Series 7					
7	630.18	H_2	41.26	16.54	0.614	0.0872	41.311	29088
							Average	29075 ± 7

0.005 mole of $NiCl_2$ was reduced between Series 1 and 2; 0.010 mole between Series 2 and 3; 0.005 mole between Series 5 and 6.

Consider an assemblage of microscopic nickel particles produced by the removal of chlorine from $NiCl_2$ during the initial irreversible stages of the reaction when there is a large excess of hydrogen and a small concentration of hydrogen chloride. The smaller nickel particles will be unstable with respect to reaction with HCl to form $NiCl_2$ with a vapor pressure in excess of that of macroscopic $NiCl_2$. Any excess pressure of $NiCl_2$ can deposit nickel on the surface of macroscopic nickel where the presence of hydrogen will form hydrogen chloride. The rate-determining step is almost certainly the diffusion of $NiCl_2(g)$ but since there is no reason to expect that the nickel in microscopic crystals needs to be transported except in the sense of joining near neighbors it was expected that the diffusion would be sufficient to eliminate the microscopic particles. The experiments indicate that this is true for the runs made in the liquid sulfur range, particularly since the first hydrogen was admitted to the nickel chloride at the boiling point of sulfur. When the apparatus was used in the mercury vapor range the equilibrium was very slow. It was not practicable to heat the reaction vessel appreciably above the boiling point of mercury and the large amount of microscopic nickel produced when hydrogen was admitted appeared to be the cause of the very slow equilibrium even at the boiling point of mercury. Several preliminary measurements made within the temperature range 600 to 645°K. gave values of the equilibrium constant which were somewhat low indicating that microscopic nickel, formed at these lower temperatures, interfered with equilibrium.

Treatment of the Data.—The data were treated by means of the equation

$$\frac{\Delta F^0}{T} = -R\ln K = \Delta\frac{(F^0 - H_0^0)}{T} + \frac{\Delta H_0^0}{T} \qquad (7)$$

Values of $(F^0 - H_0^0)/T$ for Ni[5] and $NiCl_2$[6] were taken from the work of Busey and Giauque. $(F^0 - H_0^0)/T$ values for hydrogen have been given by Giauque[12] and those for hydrogen chloride have been given by Giauque and Overstreet.[13]

Small corrections have been applied for changes in the natural constants used in the original computations for hydrogen and hydrogen chloride. The revised values of $(F^0 - H_0^0)/T$ used have been obtained from the corrections calculated by Sherman and Giauque.[14]

Data over the range 630 to 738°K. are given in Table II. Observations were limited to two or three temperatures after each introduction of hydrogen to avoid uncertainty as to the amount remaining if diffusion had occurred over longer total times. The apparatus was completely evacuated before each admission of hydrogen. The two measurements where the approach was from the hydrogen chloride side were performed by heating the reaction vessel 7 and 31 degrees, respectively, above the equilibrium temperatures before the start of the runs. The measurements are given in the order in which they were taken.

Several preliminary measurements were made in a similar apparatus over the temperature range 615 to 646°K. after the nickel chloride had been cleaned up and partially reduced at the boiling point, 630°K. of mercury. The values of ΔH_0^0 were discordant and ranged from 29186 to 29098. We believe that microscopic nickel persisted at these lower temperatures. It is probable that the nickel produced during the reduction at the boiling point of mercury remained somewhat microscopic whereas the nickel produced at the boiling point of

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[12] W. F. Giauque, THIS JOURNAL, **52**, 4816 (1930).

[13] W. F. Giauque and R. Overstreet, *ibid.*, **54**, 1731 (1932).

[14] R. H. Sherman and W. F. Giauque, *ibid.*, submitted for publication.

sulfur presented a sufficient extent of stable surface to cause the elimination of unstable nickel within the time allowed for equilibrium.

The last run given in Table II as Series 7 was made with a new sample in a mercury vapor bath after an initial reduction of nickel chloride at 645° K. In this case about 60% of the nickel chloride was reduced in order to provide a large surface in the hope that it would assist in the elimination of microscopic nickel. The system came to equilibrium in about 150 hr. and was observed for 1173 hr. The value of ΔH_0^0 = 29088 cal. mole^{-1}, agrees well with those of Series 1 to 6.

There is no evidence of a trend in the values of ΔH_0^0 with temperature. This indicates that there was no residual entropy at low temperatures when the data were obtained for evaluating the $(F^0 - H_0^0)/T$ functions for nickel and for nickel chloride. If nickel had a residual entropy of 1.0 cal. deg.$^{-1}$ mole^{-1} the values of ΔH_0^0 would show an increase of 108 cal. mole^{-1} over the 108 degree range. A similar residual entropy in nickelous chloride alone would cause a 108 cal. mole^{-1} decrease.

Aside from the cancellation of nuclear and isotopic entropy effects there is little reason to suspect that compensating residual entropies would exist in electronic systems as different as those of nickel atoms and divalent nickel ions.

We interpret the lack of trend in the values of ΔH_0^0 as indicating that metallic nickel approaches zero entropy at low temperatures within an accuracy of the order of 0.1 cal. deg.$^{-1}$ mole^{-1}.

Aside from the work of Sano[4] the previous measurements could not be expected to yield accurate results. Sano gave results at 792, 760, 738, 709 and 661°K. He used the method of observing the total pressure and the partial pressure of hydrogen by means of a palladium membrane. We have calculated the values of ΔH_0^0 corresponding to his results as 29565, 29575, 29508, 29649 and 29650 cal. mole^{-1}.

These values of ΔH_0^0 are not self consistent and average about 500 cal. mole^{-1} higher than those in the present research. This is in the direction which would be caused by microscopic nickel; however, it would be strange if this persisted at 792°K. unless the observations were taken very rapidly. Sano does not give the time allowed for equilibrium in his experiments. His temperatures were measured with a thermocouple and if one tries to account for the difference in terms of a temperature error it would be necessary to assume that his thermocouple averaged about 14° high possibly through lack of equilibrium with the reaction vessel.

The heat of formation of hydrogen chloride from the elements may be combined with the heat of reduction of nickel chloride by hydrogen to give the heat of formation of nickelous chloride. Additional data needed for 298.16° K. are

Cal. deg.$^{-1}$ mole^{-1}	H_2[14]	Cl_2[14]	HCl[14]	Ni[5]	$NiCl_2$[6]
$-F^0 - H_0^0/T$	24.420	45.933	37.718	3.300	11.803
S	31.208	53.290	44.645	7.137	23.334

$$\begin{aligned} \mathrm{Ni} + 2\mathrm{HCl} = \mathrm{NiCl_2} + \mathrm{H_2} \quad \Delta H_0^0 &= -29075 \text{ cal. mole}^{-1} \\ \Delta F_{298.16}^0 &= -16400 \qquad (8) \\ \Delta H_{298.16} &= -28888 \end{aligned}$$

The heat of formation of hydrogen chloride was calculated indirectly by Giauque and Overstreet[13] from very accurate cell data, the free energy change between aqueous and gaseous HCl, and the $\Delta(F^0 - H_0^0)/T$ value for 25°. Their calculation is subject to a minor correction for new values of the natural constants. The corrected free energy change given by Randall and Young[15] for the reaction

$$^1/_2\mathrm{H_2} + {^1/_2}\mathrm{Cl_2} = \mathrm{HCl(g)} \qquad (9)$$

is $\Delta F_{298\cdot16}$ = -22737 cal. mole^{-1} from which ΔH_{25}^0 = -22023

The heat of formation of hydrogen chloride has been measured directly by Rossini[16] who found ΔH_{25}^0 = -22063 cal. mole^{-1}. We accept the average $\Delta H_{298\cdot16}^0$ = -22043 cal. mole^{-1} from which ΔH_0^0 = -22000, $\Delta F_{298\cdot16}^0$ = -22757.

This result combined with the data relating to Equation 8 leads to

$$\begin{aligned} \mathrm{Ni} + \mathrm{Cl_2} = \mathrm{NiCl_2} \quad \Delta H_0^0 &= -73075 \text{ cal. mole}^{-1} \\ \Delta F_{298.16}^0 &= -61915 \qquad (10) \\ \Delta H_{298.16}^9 &= -72974 \end{aligned}$$

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(15) M. Randall and L. E. Young, THIS JOURNAL, **50**, 989 (1928).

(16) F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679 (1932).