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Interactions of Metals with their Molten Salts. I. The Nickel–Nickel Chloride System

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NICKEL-NICKEL CHLORIDE SYSTEM*

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Nickel metal has been found to have appreciable solubility in molten nickel chloride. The depression of the freezing point of nickel chloride (1009.1°) by the dissolved metal was measured and a eutectic point found at 977.5° and 9 mole % Ni. The constitution of the solution is discussed in the light of the freezing point depression.

Introduction

The phenomenon of metals dissolving in their molten salts has received considerable attention in recent years.¹⁻³ These studies have been largely

confined to the metals of Groups I and II of the periodic table, with some excursions into Groups III, IV, V and the rare earths. Existing hypotheses designed to explain the nature of metal-metal salt solutions have, in general, been specifically directed toward a given group or class of elements. Thus, they do not lend themselves to predictions or explanations of systems outside these groups or classes.

The present investigation of the nickel-nickel chloride system had its inception in a survey of other metal-metal halide systems for appreciable solubility of the metal. It is hoped that data on new systems will provide some elements of an

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(1) D. D. Cubicciotti and C. D. Thurmond, *J. Am. Chem. Soc.*, **71**, 2149, 4119 (1949); **74**, 1198 (1952).

(2) M. A. Bredig, J. W. Johnson and Wm. T. Smith, Jr., *ibid.*, **77**, 307 (1955); M. A. Bredig, H. R. Bronstein and Wm. T. Smith, Jr., *ibid.*, **77**, 1454 (1955).

(3) J. D. Corbett and S. von Winbush, *ibid.*, **77**, 3964 (1955); J. D. Corbett, S. von Winbush and F. C. Albers, *ibid.*, **79**, 3020 (1957); J. D. Corbett and R. K. McMullan, *ibid.*, **77**, 4217 (1955).

explanation and reveal useful applications of this effect.

Experimental

Materials.—Analytical reagent grade $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and high purity nickel metal fragments were used in this investigation.

The nickel chloride was dehydrated by heating in a Vycor tube through which a stream of dry HCl was passing. The temperature was raised gradually to 550° and held for several hours. After cooling to room temperature, the anhydrous salt containing adsorbed HCl was stored in a desiccator for future use. The nickel metal fragments were immersed in a 50–50 mixture of concd. nitric acid and glacial acetic acid and gently heated for 15 minutes. This treatment resulted in a clean surface on the nickel fragments which were then rinsed in distilled water several times, dried under vacuum and stored in a desiccator.

Apparatus and Procedure.—Thermal analysis of samples of known composition was employed to determine the solubility limits of the Ni-NiCl_2 system in the salt-rich region. For this purpose, 20 mm. bore Vycor tubes 3 in. long were sealed at one end and a thermocouple well blown in to a distance of $1\frac{1}{2}$ in. above the bottom. A 4 in. piece of 7 mm. bore Vycor tubing was sealed to the other end for use in loading, evacuation and subsequent sealing under vacuum. The use of Vycor as a container material was dictated by the reactivity of NiCl_2 with iron or steel. Nickel was obviously not suitable in this study. Sealed tubes were required because of the high vapor pressure of NiCl_2 which has a sublimation pressure of 1 atmosphere some 30° below the melting point.

A platinum-platinum 10% rhodium thermocouple (calibrated at the melting points of NBS standard samples of tin, lead, zinc, aluminum and copper metals) was used to determine the sample temperature. The maximum correction to be applied occurred at the melting point of copper, 1083.3° where the couple read 1081.5. The e.m.f. of the couple was measured with a Rubicon precision potentiometer.

Heating of the samples was accomplished with a 16 in. Marshall furnace having a 3 in. bore and equipped with external taps to which resistances could be attached to reduce temperature gradients.

The procedure employed was to load the Vycor tube with approximately 20 g. of anhydrous NiCl_2 , containing adsorbed HCl gas, and then to attach the tube to the vacuum line. Pumping was continued at room temperature until the pressure was reduced to 5×10^{-6} mm. then a clam shell heater was placed around the sample and the temperature slowly raised to 550° maintaining the pressure at the above value. The sample was held for one hour at this temperature and pressure, and then allowed to cool to room temperature while still under vacuum. This treatment was judged adequate to remove the last traces of HCl from the NiCl_2 . The tube was detached from the vacuum line, a weighed amount of nickel metal added corresponding to the composition desired, and the tube reattached to the vacuum line and the pressure again reduced to 5×10^{-6} mm. At this point, the portion of the tube containing the charge was sealed off under vacuum with a hand torch leaving a small hook at the top.

The sealed tube was weighed and hooked to the end of a heavy Chromel wire, the thermocouple was inserted in the well, and the whole assembly lowered into the furnace. The temperature was raised slowly to approximately 1050° and held for one hour to allow complete solution of the metal in the molten salt. At the end of the hour the furnace current was reduced to allow the sample to cool through the desired temperature range. Readings of the e.m.f. of the couple were recorded every minute to determine thermal inflections and halts corresponding to initial precipitation of NiCl_2 and solidification at the eutectic temperature and composition. At least two cooling curves were taken for each composition to ensure reproducibility of the thermal effects observed.

After the cooling curves were obtained on each sample, the tube was weighed, opened, and the NiCl_2 dissolved in distilled water. The nickel, which remained as a finely divided precipitate in the beaker, was dried and weighed. The weights of the Vycor, the finely divided nickel metal, and the sealed tube allowed the composition to be calculated. The absence of any traces of the original nickel

fragments together with the absence of temperature gradients along the tube (thus eliminating the possibility of mass transfer) was taken as evidence that complete solution of the nickel metal had occurred.

Results and Discussion

The data obtained in this study are summarized in the first three columns of Table I. These solutions supercooled about 1° in some cases and it was necessary to obtain the temperature at which the break occurred by extrapolation. This introduces an uncertainty in the tabulated temperatures estimated at $\pm 0.3^\circ$.

TABLE I
MELTING POINT DEPRESSION OF NiCl_2 BY NICKEL

Comp., mole % Ni	Temp., Initial break, $^\circ\text{C}$.	Eutectic halt	Activity NiCl_2 (calcd.)	Caled. for Ni ^o	
				Mole fraction NiCl_2	Act. coef. NiCl_2
0.00	1009.1	...	1.000	1.000	1.000
0.92	1006.1	...	0.983	0.9908	0.992
1.84	1002.2962	.9816	.980
4.25	994.3	976.0	.918	.9575	.959
6.10	988.1	977.4	.886	.9390	.944
7.42	983.5	977.6	.862	.9258	.929

The melting point of anhydrous NiCl_2 was found to be $1009.1 \pm 0.3^\circ$, which is to be compared with 1001° obtained by Fischer and Gewehr,⁴ 1007 – 1010° by Jones,⁵ and 1030° derived by Coughlin⁶ from heat content measurements. The value of 1030° is somewhat disconcerting in view of the high purity NiCl_2 used and the careful experimentation involved in its determination. However, alleviating factors exist in that: (1) the measurement of heat content is not a sensitive method for the determination of the melting point; (2) so-called "premelting effects" were observed in the temperature range of 1008 to 1013° which encompasses the values found by Jones⁵ and the present work; and (3) impurities present in concentrations of at least 5 mole % would be required to lower the melting point from 1030 to 1009° . Our analysis showed impurities could not have been present in excess of 0.3 mole per cent.

The portion of the Ni-NiCl_2 system examined in the course of this work represents about the limit of information obtainable by the method since the solubility curve rises very steeply to the right of the eutectic point, which occurs at 9.1 mole % metal and at a temperature of $977.5 \pm 0.3^\circ$.

The form of the metallic nickel recovered from the solidified melt by dissolving the NiCl_2 in water is of considerable interest. The metal was in the form of fibers 300 – 400μ long and having a diameter of 1 to 1.5μ . Microscopic examination revealed most of the fibers to be made up of two or three straight sections attached to each other at sharp angles while some were straight throughout their entire length. The angularity may be a function of the cooling conditions or possibly of the anion of the salt since preliminary tests on NiBr_2 resulted in fibers with a high proportion of single straight sec-

(4) W. Fischer and R. Gewehr, *Z. anorg. allgem. Chem.*, **222**, 303 (1935).

(5) G. P. Jones, Royal School of Mines, London, private communication.

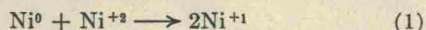
(6) J. P. Coughlin, *J. Am. Chem. Soc.*, **73**, 5314 (1951).

tions. The conspicuous absence of branched fibers in the samples examined may be significant. In addition to the fibers, a small portion of the metal was in the form of hexagonal platelets; however, these were not present in all of the melts.

The freezing point depressions of NiCl_2 and the experimental heat of fusion of the pure salt provide a basis for speculation concerning the constitution of the melt. The data can be interpreted in two ways and both of these are discussed below: (1) a standard cryoscopic calculation of the number of moles of particles formed per g. atom of nickel metal dissolved has been made; (2) the nickel metal was assumed to be monatomically dispersed in solution and the deviation of the activity of nickel chloride from Raoult's law was calculated.

For the calculation of the number of moles of particles formed per g. atom of nickel dissolved the usual assumptions were made: (a) Raoult's law is obeyed by NiCl_2 ; (b) no solid solution occurs; (c) the heat of fusion is constant over the range of interest. The latter assumption is valid to within 1% from Coughlin's heat content data on liquid and solid NiCl_2 . The heat of fusion of NiCl_2 calculated from the concentration of dissolved nickel and attendant freezing point depressions results in a value of 9,150 cal./mole, while the experimental heat of fusion of NiCl_2 reported by Coughlin⁶ is 18,450 cal./mole.

The calculated value of the heat of fusion of NiCl_2 being very nearly one-half that of the experimental value strongly suggests the existence of two particles in solution per atom of nickel dissolved. A reasonable inference is that univalent nickel ion is formed by the reaction



The chemistry of nickel indicates that univalent compounds are not unlikely and this probably foreshadows the transition to copper, which is commonly unipositive. At least one compound containing +1 nickel has been characterized.⁷ The existence of the nickel in the metallic state in the solidified melt at room temperature requires that

(7) H. Remy, "Treatise on Inorganic Chemistry," translated by J. S. Anderson and edited by J. Kleinberg, Elsevier Publ. Co., 1956, Vol. II, p. 311.

the +1 state be unstable with respect to Ni^0 and Ni^{+2} at some intermediate temperature. Such disproportionation could occur in the transition from liquid to solid.

Recalling the controversy engendered by some previous reports of subhalide formation in metal-metal salt systems, it is pertinent to examine the possibility of an interpretation on a physical basis. The activities and the activity coefficients of NiCl_2 consistent with the experimental data were calculated using the relation

$$\ln a_1 = \ln \gamma_1 x_1 = - \frac{\Delta H_f}{R} \left(\frac{T_m - T}{T_m T} \right) \quad (2)$$

where the subscript 1 refers to NiCl_2 , a_1 is activity, γ_1 activity coefficients and x_1 mole fraction. $\Delta H_f = 18,450$ cal./mole, T is the experimentally determined freezing point and $T_m = 1282.1^\circ\text{K}$, the melting point of NiCl_2 . The results of these calculations appear in Table I.

As is to be expected from the experimental results, the activity coefficients of NiCl_2 are less than unity reflecting the negative deviation from Raoult's law. It must be emphasized that these activity coefficients, which are very nearly equal to the mole fraction of NiCl_2 , are not referred to the same temperature but to the freezing point of the particular solution in question. The activity coefficients of NiCl_2 do not fall below 0.92 in the range examined. Thus, in the absence of information concerning activity coefficients in such systems, a physical interpretation cannot be ruled out.

Therefore despite a factor of 2 in the heat of fusion corresponding to an absolute difference of 9,000 cal./mole, obtained from the two assumptions, it seems the physical picture is not unduly strained to explain the data. It must be admitted that sub-halide formation is an appealing explanation and exhibits positive deviations at the higher concentrations, in accord with other metal-salt systems, but this cannot be considered confirmation.

In the opinion of the authors a decision cannot be made concerning the state of the dissolved nickel in nickel chloride with the available data. Extreme caution must be observed when using freezing point depression measurements to determine the nature of dissolved species in these systems.

