Hydrogen Fluoride Solvent System VIII

A Study of the System NiF_2–HF–H_2O

A. F. CLIFFORD and A. C. TULUMELLO
Department of Chemistry, Purdue Univeristy, West Lafayette Ind.

Solubility products of three species of anhydrous nickel fluoride in liquid hydrogen fluoride at 0° C. are reported: α, $Ksp = 7 \times 10^{-9}$, generated on the surface of powdered nickel metal in anhydrous HF; B, $Ksp = 7 \times 10^{-15}$, in equilibrium with solutions of HF containing less than 2.3 molar water; γ, $Ksp = 6 \times 10^{-16}$, in equilibrium with solutions of HF containing more than 3*M* water and less than 39% water. At water concentrations greater than 0.2*M*, the nickel ion in solution is found to be predominantly hexaquonickel(II), instability constant = 4.6×10^{-10}. At a concentration of water of 39 wt. %, a transition in the solid phase in equilibrium with the solution occurs between an anhydrous form and a dihydrate. A maximum solubility of 2.56*M* is obtained in 31% HF solutions in water which corresponds to the phase change between this dihydrate and the tetrahydrate previously reported (*10*). The tetrahydrate persists to 100% water. The *Ksp* for magnesium fluoride in HF containing 0.006*M* water was found to be 2×10^{-9}.

THE SOLUBILITY of nickel fluoride in anhydrous HF has been reported by Jache and Cady (*8*) to be only 0.040 gram per 100 grams of HF at –9.7° C. However, in view of the invariable presence of small amounts of water in liquid hydrogen fluoride and of the wide-spread use of nickel or nickel-alloy equipment for handling hydrogen fluoride, the effect of water in hydrogen fluoride on nickel has been investigated through a study of the system NiF_2–H_2O–HF.

Previous studies of metal fluoride–H_2O–HF systems over essentially the whole range of HF and water concentrations have been carried out by Nickolaev *et. al.* on ZrF_4 (*18*), HfF_4 (*3*), VOF_3 (*14*), NbF_5 (*15*), TaF_5 (*2*), CrO_2F_2 (*13*), MoF_6 (*16*) and WF_6 (*12*). Phase studies have also been made on the AgF–H_2O–HF system by Thomas and Jache (*20*). These and other solubility studies have been summarized by Clifford (*4*). In Nikolaev's studies, the anionic metal fluoride, and in Thomas and Jache's study the silver fluoride, were usually present at high concentration (greater than 1 gram of metal per liter). This is not the case with nickel over much of the range of solvent concentrations. Clifford and Sargent (*5*) point out that the addition of KF and NH_4F to aqueous solutions of nickel fluoride tends to decrease the solubility, obviating the formation of an anionic species. The present work shows that the solid phases in equilibrium with HF solutions tend to become more green (characteristic of hydrated nickel (II) ion) as the concentration of water increases. The solid phases B-NiF_2, γ-NiF_2, $NiF_2 \cdot 2H_2O$ and $NiF_2 \cdot 4H_2O$ were identified as described in the discussion of results.

EXPERIMENTAL

The distillation, equilibration, and sampling of HF solutions were conducted in apparatus made entirely of Kel-F and Teflon. The design was a modification of that used by Kongpricha and Clifford (*9*). The temperature of the system under study was maintained at 0° C. by immersion of the reaction vessel in an ice bath. The platinum-lined brass bottom and internal magnetic stirrer allowed thermal equilibrium to be rapidly attained.

The HF (furnished by Blockson Chemical Division of Olin Mathieson Corp.) as received had conductivities of the order of 10^{-4} ohm^{-1} cm.$^{-1}$., this was an improvement over the electrolytically purified HF used in our previous studies. The commercial HF was used without further purification; however, determination of the conductivity on each batch before beginning an experiment allowed calculation of the water content, using the data of Fredenhagen (*7*).

The nickel was 99.7% pure nickel metal powder furnished by International Nickel Co. For preparation of anhydrous nickel fluoride, the powdered metal was dissolved in 48% HF, the solution filtered and evaporated to dryness, and the hydrated nickel fluoride obtained added to anhydrous HF and stirred for 24 hours with a magnetic stirrer. The water concentration of the solution was then determined by a Karl Fischer titration of a sample collected in a large excess of pyridine. When the water concentration was constant on repeated titration and agreed with the value expected for complete extraction of water from the solid, the solid was assumed to be anhydrous. Insufficient equilibration sometimes produced particles of nickel fluoride which were yellow outside but green within. This same technique was employed to prepare solutions saturated with nickel fluoride at various water concentrations for studying the effect of water concentration on the solubility of nickel fluoride.

Nickel was determined using a spectrophotometric method (*11, 17*) in which the nickel was oxidized by bromine water in alkaline solution, the excess bromine was decomposed by ammonia, and an orange-red color was generated by addition of a 1% solution of dimethylglyoxime in ethanol. The absorbance was measured at 445μ. Using this method we were able to determine nickel in samples more than $2 \times 10^{-5}M$ in nickel.

In addition to the conductometric method, water at low concentrations was determined by Karl Fischer titration of the sample using a potentiometric end point. The procedure employed was similar to that used by Nikolaev (*15*). For water concentrations above 15%, analysis by Karl Fischer titration became impractical. In this case, a total fluoride analysis with thorium nitrate was used instead, the HF solution being taken into ice in order to minimize loss of HF by volatilization.

Magnesium fluoride was prepared by the addition of magnesium amalgam to anhydrous HF, whereupon reaction with liberation of hydrogen produced MgF_2 in its saturated solution. This method can be used to add a quantitative amount of many metal fluorides to an HF solution.

The method used to determine magnesium concentration employed Eriochrome Black (*20*) as a colorimetric reagent.

RESULTS AND DISCUSSION

When nickel metal is placed in anhydrous HF, the nickel atoms at the surface of the metal are oxidized to nickel fluoride with the formation of elemental hydrogen. The nickel fluoride formed in this way is designated α-nickel fluoride. This reaction does not go to completion, but continues until the nickel metal is coated with a film of nickel fluoride, which separates the reacting materials (Ni^0 and HF) by a thin film which remains on the surface of the nickel. This film was equilibrated with solutions of HF containing an amount of water determined by conductivity measurements. The amount of water present was determined by comparison of the measured conductivity with conductivity data reported by Fredenhagen (*7*).

The lowest concentration of water studied by Fredenhagen was 0.003*M*. This observation fixed the lowest water concentration that could be determined in this study.

For solutions of HF containing 0.0034, 0.0058, and 0.018*M* water, the concentration of nickel in solution was 7.15×10^{-4}, 2.12×10^{-4}, and $0.184 \times 10^{-4}M$, respectively. On the basis of Kongpricha and Clifford's data (*9*) one might assume 100% ionization of the water in these solutions. These data gave an average solubility product constant for NiF_2 of $7.0 \times 10^{-9} = [Ni^{+2}][F^-]^2$.

When powdered nickel metal was used in higher concentrations of water in HF, the equilibrium solubility of nickel was too small to be observed accurately under the conditions of the experiment until the concentration of water reached approximately 0.2*M*, when the concentration of nickel in solution increased significantly. At 0.225, 0.250, and 0.300*M* water the nickel concentration was 0.84×10^{-4}, 1.9×10^{-4} and $7.7 \times 10^{-4}M$, respectively. These data are shown in Figure 1. Taking into consideration the basicity of the water at these concentrations (*9*), it was found that the maximum clustering occurred when the dissociation constant was calculated as a function of the sixth power of the free water concentration, as shown in Table I.

$$Ni(H_2O)_6^{+2} \rightleftarrows Ni^{+2} + 6H_2O \qquad (1)$$

$$Keq = \{[Ni^{+2}][H_2O]^6\}/[Ni(H_2O)_6^{+2}]$$

But it has already been shown that for the α-NiF_2:

$$[Ni^{+2}][F^-]^2 = 7.0 \times 10^{-9}$$

or

$$[Ni^{+2}] = \frac{7.0 \times 10^{-9}}{[F^-]^2} \qquad (2)$$

so that

$$Keq = \frac{7.0 \times 10^{-9}[H_2O]^6}{[F^-]^2[Ni(H_2O)_6^{+2}]} = (4.58 \pm 0.27) \times 10^{-10} \qquad (3)$$

This is remarkably close to the value of 9.8×10^{-9} given for $Ni(NH_3)_6^{+2}$ in water.

Computation of the equilibrium constant *Keq*, from these data for other powers of the water concentration, shows an ordered trend in the calculated value. This observation indicates that the hexaquonickel(II) ion is the predominant species present in solution as a result of equilibrating nickel fluoride in HF containing more than 0.2*M* water. The single datum obtained at 0.072*M* H_2O concentration indicates that at this concentration no more than four water molecules were coordinated to the nickel ion in solution.

When concentrations of water higher than 0.30*M* were used, the nickel concentration was too low to detect. Subsequent runs at concentrations lower than 0.30*M* also gave undetectably low solubilities. Coincident with the lower concentrations of nickel was observed the deposition of a fine powder on the surface of the reaction vessel. This solid could not be removed by ordinary chemical cleaning. It became apparent that nickel was reprecipitating from the solution in a more stable form than that formed initially on the surface of the metal, and that this process was being seeded by the less soluble form first obtained when the water concentration was increased above 0.30*M*. One-eighth inch of the inner surface of the reaction vessel was removed in order to free it of seed. When the surface had been renewed, a series of time studies was made, in which the nickel concentration was observed as a function of time. The data obtained in this way are reported in Table II and Figure 2. As might have been anticipated, the rate of decrease of nickel concentration in each case was found to be first order in nickel concentration. The actual rate, however, increased with each successive run (*A*, *B*, and *C*), presumably because of the increasing number of nuclei. However, when a new vessel was employed (Run *D*), the rate was again comparable to that of the initial run (*A*).

These data were extrapolated to obtain the concentration of nickel present at zero time, to obtain an estimate of the nickel concentration before the nickel entered into the precipitation reaction. When this extrapolated value was inserted into the equation for the dissociation constant of the hexaquonickel(II) ion, agreement $[7.66 \pm 3.60) \times 10^{-10}]$ was found with the previous equilibrium constant

Table I. Variation of the Cumulative Instability Constant of $Ni(H_2O)_n^{+2}$ with Variation of *n*

	"Constant" for *n* =			
Total $[H_2O]$	4	5	6	7
(0.072)	(1.31×10^{-9})	(1.44×10^{-11})	(1.59×10^{-13})	(1.75×10^{-15})
0.225	9.57×10^{-8}	6.89×10^{-9}	4.96×10^{-10}	3.57×10^{-11}
0.250	6.27×10^{-8}	5.20×10^{-9}	4.32×10^{-10}	3.59×10^{-11}
0.300	3.69×10^{-8}	4.06×10^{-9}	4.46×10^{-10}	4.91×10^{-11}
			Av. = $(4.58 \pm 0.27) \times 10^{-10}$	

Table II. Time Studies

0.265 Molar Water		0.303 Molar Water		0.260 Molar Water		0.265 Molar Water, New Vessel	
Minutes	10^4 Moles Ni/l.	Minutes	10^4 Moles Ni/l.	Minutes	10^4 Moles Ni/l.	Minutes	10^4 Moles Ni/l.
2.0	0.41	2	5.40	2	0.99	2	1.17
17.5	0.44	17	5.25	5	1.10	10	1.20
33.0	0.48	32	2.17	12	0.72	20	1.22
49.0	0.43	47	1.82	24	0.22	29	1.38
64.0	0.34	62	1.19	38	0.09	45	1.16
79.0	0.22	77	0.44	48	0.05	60	0.80
95.0	0.12	92	0.13	63	0.15	75	0.67
110.0	0.16	107	0.38	85	0.06	90	0.54
125.0	0.10	272	0.20			105	0.35
∞	0.06					120	0.30

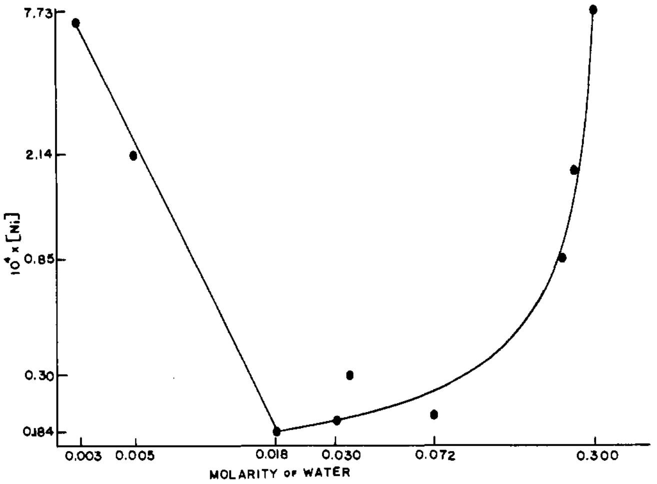

Figure 1. Solubility of α–NiF_2 as a function of water concentration

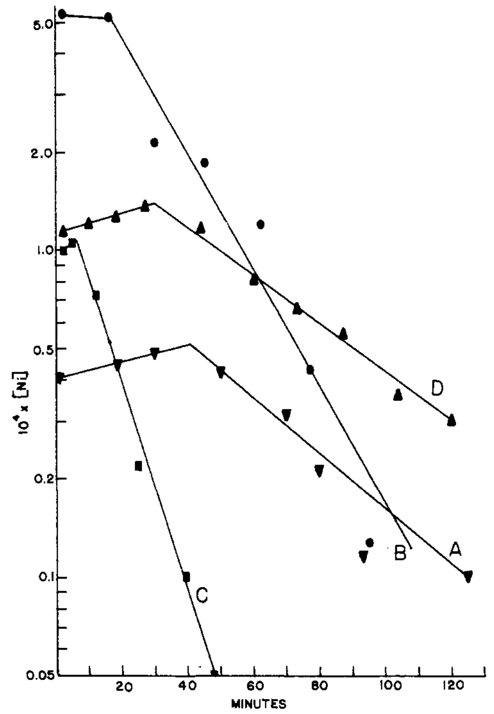

Figure 2. Concentration of nickel as a function of time

A. 1st run (0.265M H_2O)
B. 2nd run (0.303M H_2O)
C. 3rd run (0.260M H_2O)
D. 4th run (0.265M H_2O, new vessel)

(4.58×10^{-10}), providing evidence that the previous solubilities did indeed represent equilibrium conditions. The standard deviation of the mean of the extrapolated values was larger than the previous one, but this is not surprising in view of the fact that extrapolation to a somewhat arbitrary zero was necessary to obtain the second set of data.

In view of the apparent nucleation phenomenon occurring at these concentrations of water, an effort was made to identify the nucleating solid phase. Green hydrated nickel fluoride, $NiF_2 \cdot 4H_2O$, was added to anhydrous HF in such proportions as to obtain a solution of 0.30*M* water if all the water were extracted from the solid. This produced a yellow solid phase, which when dried in air gave an x-ray pattern identical with nickel fluoride prepared by the thermal decomposition of hexamminenickel(II) fluoroborate. Analysis of the HF solution in equilibrium with the yellow solid showed that all the water had been extracted from the solid, which was thus established as anhydrous.

Anhydrous nickel fluoride, produced as usually described from the hexammine fluoroborate, dissolves easily in water. That obtained by dehydration of HF did not readily dissolve in water, even in the presence of ammonia or of sodium ethylenediaminetetraacetate. Further investigation of the thermal decomposition product revealed that it usually contains considerable amounts of ammonia (*1*), but that if the decomposition were continued at 320° C. in vacuo for 2 hours after visible formation of yellow powder the product was then as difficult to dissolve as that obtained by dehydration in HF.

As the concentration of water was increased beyond 0.4*M* the solubility did not increase significantly until it reached 1.5*M*. At this concentration, there was an increase in the nickel concentration that was large and reproducible (see Table III and Figure 3).

If one assumes that all the nickel was present as the hexaquonickel(II) ion, Equation 3 may be used to calculate the solubility product of the solid phase. By taking points along the graph of Figure 3 for the concentration of hexaquonickel(II) ion, a solubility product of 7.5×10^{-15} was obtained. This species is designated as B-nickel fluoride.

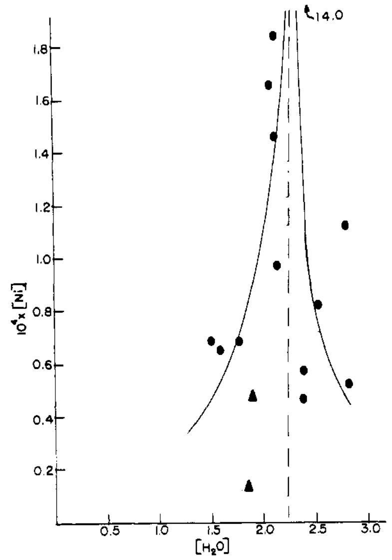

Figure 3. Solubility curve for phase change between 1.5 and 3.0M H_2O

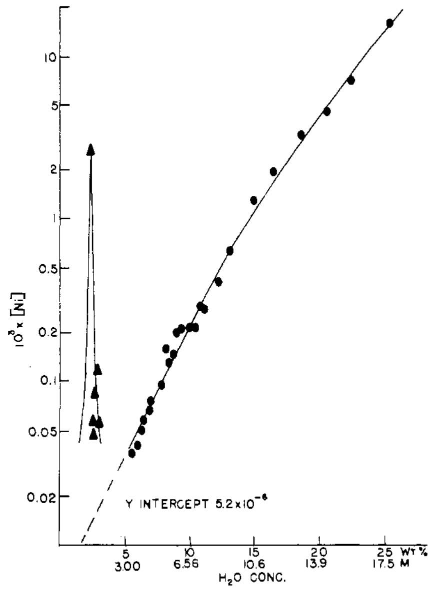

Fig. 4. Solubility curve between 5 and 25% H_2O (Δ Points from Figure 3)

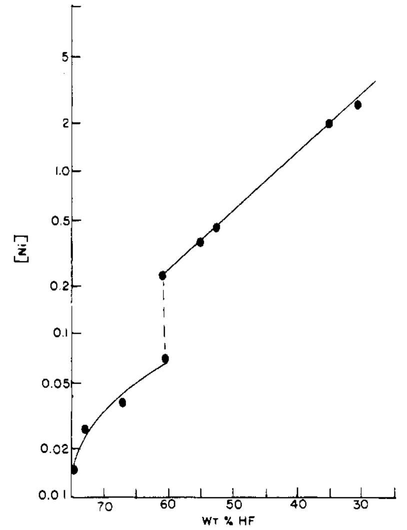

Figure 5. Solubility curve showing phase change between anhydrous NiF_2 and the dihydrate

Table III. Nickel Concentration from 1.5 to 3.0 Molar Water

Moles Water/l.	10^4 Moles Ni/l.	Moles Water/l.	10^4 Moles Ni/l.
1.51	0.73	2.15	0.97
1.58	0.68	2.31	14.0
1.69	0.13	2.43	0.48
1.76	0.68	2.47	0.57
1.89	0.46	2.54	0.82
2.08	1.66	2.88	1.14
2.12	1.46	2.89	0.54
2.12	1.84		

Most of the points in Figure 3 were obtained by adding small increments of water to solutions already in equilibrium and stirring until equilibrium was deemed to have been reestablished. The extreme difficulty of obtaining accurate values in a region of such rapidly changing solubility is exemplified by the two points (Δ) which were obtained by adding HF to solutions of higher water concentration.

To obtain this solubility product, it was necessary to know that the solid phase was anhydrous nickel fluoride. A series of studies was conducted using Karl Fischer titrations to determine the water concentrations of solutions prepared by addition of a known volume of water to a known volume of HF of known water concentration. The increase in water concentration in the solution was identical with that expected from the addition. Thus all the water added was in the liquid phase and none was absorbed by the solid phase, so that the solid phase was still anhydrous. From 2.31*M* to 3.0*M* H_2O, there was an apparent decrease in the nickel concentration. From 3*M* (5% water) to 39% water concentration, the log of the solubility of NiF_2 increased almost linearly as a function of the water concentration (see Figure 4). Using this relationship an extrapolated value was obtained for the concentration of nickel at zero water concentration. Assuming the self-ionization of the solvent as negligible compared to the ionization of nickel fluoride itself, a solubility product was calculated for the species:

$$Ksp = [Ni^{-2}][F^{-}]^2 = \frac{[Ni^{-2}]^3}{4} = 5.45 \times 10^{-16}$$

However, it should be pointed out that this is a long extrapolation. It may be postulated that this γ-nickel fluoride differs from B-nickel fluoride in that the γ-nickel fluoride has fewer molecules of HF associated with it than the beta form. The solid phase present with up to 39% water (61% HF) concentration was yellow.

Attempts to identify the equilibrium solid in this region were essentially thwarted by the above-mentioned resistance of the solid to dissolution. Since the concentrations of nickel were now much higher than in the previous phase region, the oxidative (dimethylglyoxime) method, which successfully accomplished dissolution of the solid phase, could not be used, and EDTA titration was attempted instead. In most cases, even after stirring HF-wet residues for several days in water, dissolution was obviously incomplete. In one case of two samples taken for Schreinemaker's method from 21% water-79% HF equilibrated with initially anhydrous NiF_2, analyses of 66.5% NiF_2, 28.7% HF and of 54.5% NiF_2, 38.0% HF were obtained, implying the solid phase $NiF_2 \cdot HF$. On the other hand, when hydrated NiF_2 was equilibrated with 23% water-77% HF, analyses of the residues were 42.9% NiF_2, 55.1% HF and 37.7% NiF_2, 54.9% HF, implying a solid phase $NiF_2 \cdot 4\text{-}6$ HF. At the present time, it is impossible to say which of these represents more closely the composition of the stable solid in this region.

In solutions of approximately 39% water (61% HF), the solid phase underwent a phase change (see Figure 5). Water was absorbed by the solid phase. The solid took on a greenish tinge, and the concentration of nickel ion in solution increased. As water was added to solutions containing this new phase, the solubility increased until a maximum solubility of 2.56*M* nickel ion was attained at about 31% HF. Even with the dihyrate, complete dissolution in water was difficult as evidenced by low EDTA titrations and a Tyndall effect on freshly prepared solutions. However, after several hours' stirring dissolution was complete, and by use of Schreinemaker's wet method, the solid phase present between 61% HF and 31% HF was identified as $Ni(H_2O)_2F_2$.

As a 31% solution of HF becomes more dilute in HF and approaches pure water, the concentration of nickel ion decreases. The solid phase present in solutions containing less than 31% HF has been shown by Kurternacker, Finger, and Hey (*10*) to be $Ni(H_2O)_4F_2$. This observation was confirmed in this work by use of the Schreinemaker technique.

Results represent a typical phase diagram for a mixed solvent system. The major difficulties arise from problems of handling and transferring the solvent. Problems of this kind have made relatively simple operations formidable obstacles in the progress of this work.

ACKNOWLEDGMENT

This work was supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-620. One of us (A.C.T.) is indebted to the Purdue Research Foundation for a fellowship.

LITERATURE CITED

(1) Blaz, G., Zinser, W., *Z. Anorg. Allgem. Chem.* **221**, 225 (1935).
(2) Buslaev, Y.A., Nikolaev, N.S., *Russ. J. Inorg. Chem.* (English Translation) **4**, 210 (1959).
(3) Buslaev, Y.A., Nikolaev, N.S., *Dokl. Akad. Nauk SSSR* **135**, 1385 (1960); see also *Proc. Acad. of Science* (English Translation) **135**, 1435 (1960).
(4) Clifford, A.F., "Chemie in wasserfreiem Flussäure and in anderen protonenhaltigen Solventien," Teil I Band II (in English), Friedrich Vieweg und Sohn, Braunschweig, Monograph Series, 1963.
(5) Clifford, A.F., Sargent, J.W., *J. Am. Chem. Soc.* **79**, 4041 (1957).
(6) Clifford, A.F., Zamora, E., *Trans Faraday Soc.* **57**, 1963 (1961).
(7) Fredenhagen, K., *Z. Phys. Chem.* **A146**, 257 (1929).
(8) Jache, A.W., Cady, G.H., *J. Phys. Chem.* **56**, 1066 (1952).
(9) Kongpricha, S., Clifford, A.F., *J. Inorg. Nucl. Chem.* **18**, 270 (1961).
(10) Kurtenacker, A., Finger, W., Hey, F., *Z. Anorg. Allgem. Chem.* **211**, 83 (1933).
(11) Mitchell, A.M., Mellon, M.G., *Ind. Eng., Chem. Anal. Ed.* **17**, 380 (1945).
(12) Nikolaev, N.S., *Khim. Redkikh Elementov, Akad. Nauk SSSR, Inst. Obshchei i Neorg. Khim.* **1**, 45 (1954).
(13) Nikolaev, N.S., Buslaev, Y.A., *Izvest. Sektoro. Fiz. Khim. Anal., Inst. Obschchei i Neorg. Khim. Akad. Nauk SSSR* **24**, 270 (1955).
(14) Nikolaev, N.S., Buslaev, Y.A., *Khim. Redkikh Elementov* **2**, 57 (1955).
(15) Nikolaev, N.S., Buslaev, Y.A., *Russ. J. Inorg. Chem.* (English Translation) **4**, 84 (1959).
(16) Nikolaev, N.S., Opalovskii, A.A., *Zh. Neorgan. Khim.* **4**, 1174 (1959).
(17) Sandell, E.B., "Colorimetric Determination of Traces of Metals," 2nd ed., Interscience, New York, 1950.
(18) Tananaev, I.V., Nikolaev, N.S., Buslaev, Y.A., *Zh. Neorgan. Khim.* 1, 225 (1959).
(19) Thomas, H.J., Jache, A.W., *J. Inorg. Nucl. Chem.* **13**, 54 (1960).
(20) Welcher, F.J., "Analytical Uses of Ethlenediaminetetracetic Acid," p. 237, Van Nostrand, New York, 1958.

RECEIVED for review March 1, 1962. Accepted January 28, 1963. Taken from the thesis of A.C. Tulmello, submitted to the faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Vapor Pressures of Zinc, Cadmium, Antimony, and Thallium

A. T. ALDRED[1] and J. N. PRATT
Department of Physical Metallurgy, University of Birmingham, Birmingham, England

The vapor pressures of solid zinc, cadmium, antimony, and liquid thallium in the range of 10^{-1} to 10^{-4} mm. of Hg have been remeasured using the torsion-effusion technique. The following standard latent heats of vaporization have been calculated: Zn, $\Delta H^\circ_{298} = 31.01 \pm 0.20$ kcal. per mole; Cd, $\Delta H^\circ_{298} = 26.64 \pm 0.11$ kcal. per mole; Sb, $\Delta H^\circ_{298} = 49.21 \pm 0.16$ kcal. per mole; Tl, $\Delta H^\circ_{298} = 42.85 \pm 0.20$ kcal. per mole.

DURING THE COURSE of a general series of measurements of vapor pressures over alloys, the vapor pressures of solid zinc, cadmium, antimony, and liquid thallium have been redetermined using the torsion-effusion technique (*12*). The materials used were spectroscopically pure zinc and cadmium supplied by the Imperial Smelting Co., Ltd. and spectroscopically pure antimony and thallium obtained from Johnson Matthey Ltd. The experimental method has been described in detail previously (*1, 8*) and consists basically of measuring the force exerted by vapor effusing from an orifice. A graphite effusion cell is suspended from a fine wire, and the vapor effuses in a horizontal direction from two eccentrically placed orifices thus exerting a torque. The angle through which the cell deflects is a measure of the vapor pressure.

RESULTS

Zinc. The results obtained for zinc are given in Table I. In addition, an average value of the standard latent heat of vaporization, $\Delta H^\circ_{298} = 31.01 \pm 0.20$ kcal. per mole, has been calculated by the third law method using relevant thermodynamic information given by Stull and Sinke (*10*). The vapor pressure data are compared graphically with previous results in the same pressure range in Figure 1. The values agree well with those of Vance and Whitman (*11*) but indicate somewhat higher vapor pressures than determined by Egerton (*3*) and McKinley and Vance (*5*). The average value of ΔH°_{298} for the present results agrees

---

[1] Present address, Argonne National Laboratory, Argonne, Ill.