Vapor Pressures of BeF_2 and NiF_2

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Manometric methods were used to measure the vapor pressures of BeF_2 and NiF_2. The measurements for BeF_2, taken in the temperature range, 872° to 1099° C., are given by $\log p(\text{mm.}) = 10.487 - 10,967/T(^\circ\text{K.})$. From this equation, the enthalpy of vaporization and extrapolated normal boiling point are: 50.2 kcal. per mole and 1169° C. For NiF_2, measured between 1077 and 1283° C., the vapor pressures are given by $\log p(\text{mm.}) = 11.385 - 14,860/T(^\circ\text{K.})$. The NiF_2 had not melted at 1283° C. The calculated enthalpy of sublimation and extrapolated normal sublimation point are 68.0 kcal. per mole and 1474° C.

THE VAPOR pressures of BeF_2 and NiF_2 were measured as part of a study of physical chemical properties of fluorides which are of importance to Oak Ridge National Laboratory's molten salt reactor program. The vapor pressures of both compounds have been previously determined (*2–7, 9, 10*), but only by vapor transport techniques. In the present work, the vapor pressures were measured by direct, manometric methods.

EXPERIMENTAL

Materials. NiF_2 was obtained from batches previously prepared at Oak Ridge National Laboratory by passing anhydrous HF over the chloride at 500° C. Spectrochemical analysis (all chemical analyses were performed by the Analytical Chemistry Division of Oak Ridge National Laboratory) of this product indicated that Fe was the only metallic impurity present to a concentration greater than 0.01%. Spectrophotometric determination of Fe showed 0.058%. Other analyses: Ni, 60.6 wt.% (theoretical for NiF_2, 60.7); F, 38.9 (theoretical, 39.3); Cl, 0.011; O, 0.126.

Commercial BeF_2, at least 99% pure according to the supplier, Brush Beryllium Co., was treated with a HF-H_2 gas mixture at 500° C. to decrease the oxide and sulfate content. (The supplier believed these anions were the major impurities.) This hydrofluorinated product contained in weight %: O, 0.38; S, 0.058. Spectrochemical analysis showed that the only relatively large metallic impurities were Mg, 0.01% and Fe, 0.005%.

Temperature Measurements and Control. Temperatures of the samples were measured with Pt and Pt–10% Rh thermocouples in a thermowell extending approximately 2 cm. into the condensed salt phase. The thermal e.m.f.s were measured with a Rubicon High Precision Type-B Potentiometer. The measuring thermocouples were calibrated against NBS calibrated thermocouples. The standard thermocouples were stated to be accurate within $\pm 0.5°$ up to 1100° C. and within $\pm 2°$ beyond 1100° C.

Temperatures of the samples were controlled to within 0.2° C. by regulating the furnace with a Wheelco Capacitrol, Model 401.

Vapor Pressure Measurements. Most of the vapor pressures were measured by the Rodebush-Dixon quasi-static technique (*8*). The experimental procedure and details of apparatus (for this study the vapor pressure vessels were made of nickel) are given in an earlier publication by the author (*1*). For BeF_2 vapor pressures above 50 mm., boiling points were measured in the same apparatus. For these determinations, the system was brought to a total pressure (of argon gas) greater than the expected vapor pressure. The system pressure was then reduced very slowly (approximately 0.1 mm. per minute) at constant temperature. When the BeF_2 began to boil, a slight cooling of the liquid was "seen" by the deflection in the sensitive galvanometer (Leeds and Northrup, Model 2430C) connected to the potentiometer. The pressure-reducing stopcock was then immediately shut; the system pressure, now very slightly less than the vapor pressure, was read on a mercury manometer. Vapor pressures, obtained by boiling point measurements were virtually identical with those obtained by the Rodebush-Dixon method.

For NiF_2, all of the vapor pressures were measured by the Rodebush-Dixon method. Some of the measurements were made in vessels where the condensed salt was in contact with platinum only. For these measurements, the nickel vessel was suitably altered to include a platinum crucible to contain the salts and a thin-walled platinum cup to cover the nickel thermowell. For those measurements where the salt was to be in contact with nickel only, the NiF_2 was first intimately mixed with Ni powder. These differing containment conditions were used to determine if the reaction $NiF_2(c) + Ni(c) = 2NiF(g)$ made a significant contribution to the observed vapor pressures.

RESULTS

The pressure-temperature data are given in Tables I and II.

Table I. Vapor Pressures of BeF_2

Temperature, ° C.	Observed Pressure, Mm. of Hg	Method Used
872.4	8.05	RD[a]
896.7	13.0	RD
912.5	17.1	RD
917.6	19.2	RD
936.9	26.5	RD
958.5	38.4	RD
978.1	53.7	BP[b]
982.4	57.2	RD and BP
1000	76.2	RD and BP
1009	86.8	BP
1024	108.6	BP
1026	112.5	BP
1038	133.4	BP
1050	156.3	BP
1061	182.9	BP
1070	210.9	BP
1081	245.8	BP
1088	267.5	BP
1099	305.2	BP

[a] Rodebush-Dixon (*8*). [b] Boiling point measurement.

Table II. Vapor Pressures of NiF_2

Temperature, ° C.	Observed Pressure, Mm. of Hg	Container
1077	2.45	Ni
1083	2.55	Ni
1110	4.30	Ni
1132	6.70	Ni
1163	10.8	Pt
1173	12.8	Pt
1193	18.6	Ni
1205	21.3	Pt
1219	27.3	Pt
1228	30.2	Ni
1247	40.7	Ni
1253	43.6	Pt
1268	55.0	Ni
1283	67.9	Pt

Table III. Thermodynamic Properties

BeF_2	
Enthalpy of vaporization (from 872 to 1099° C.)	50.2 kcal. per mole
Extrapolated boiling point (1 atm. pressure)	1169° C.
Entropy of vaporization	34.8 cal. per (mole ° K.)
NiF_2	
Enthalpy of sublimation (from 1077 to 1283° C.)	68.0 kcal. per mole
Extrapolated sublimation point (1 atm. pressure)	1474° C.
Entropy of sublimation	38.9 cal. per (mole ° K.)

After each run with NiF_2, the vessel was opened and the contents were examined. In every case, the NiF_2 appeared to be sintered. The melting point of NiF_2 is, therefore, greater than 1283° C. Nickel surfaces, which were exposed to the vapor did not appear to have corroded. Furthermore, microscopic examination of the small amount of sublimate deposited on the tubes of the vessels revealed pure crystalline NiF_2 only.

DISCUSSION

The pressure-temperature data can be represented by the following equations

$$BeF_2: \quad \log p(\text{mm.}) = 10.487 \pm 0.024 - \frac{10{,}967 \pm 31}{T}$$

$$NiF_2: \quad \log p(\text{mm.}) = 11.385 \pm 0.021 - \frac{14{,}860 \pm 30}{T}$$

The dispersion values given in these equations are standard deviations from least square solutions of these constants.

During these measurements, vapor from the sample solidified in the cooler parts of the apparatus. However, the vapor pressure was never a function of time—i.e., the $\log p$ *vs.* $1/T$ plot for a sample did not change with temperature recycle. Hence, the effect of impurities on the observed vapor pressures was negligible.

For BeF_2, these data virtually coincide with Sense's redetermination of the vapor pressures (*10*).

For NiF_2, the measured pressures are lower than those obtained by linear extrapolation of the data of Ehlert and coworkers (2) but higher than the extrapolated pressures of Faber and coworkers (*3*).

The NiF_2 samples, whether in contact with nickel or platinum, yielded vapor pressures that were concordant—i.e., both sets of data fit the same $\log p - 1/T$ equation. This concordance together with the post-experimental examinations of the vessels lead to conclusions that the observed vapor pressure was due to the reaction $NiF_2(c) = NiF_2(g)$ and not due to NiF_2 (c or g) + Ni(c) = 2NiF(g).

Pressures from dissociation reactions—e.g., $NiF_2(c) = Ni(c) + F_2(g)$ or $NiF_2(c) = NiF(g) + \frac{1}{2}F_2(g)$— estimated from appropriate thermochemical properties are several orders of magnitude less than the observed vapor pressures. Therefore, dissociation reactions are of negligible significance to the vapor pressure of NiF_2 at temperatures up to 1283° C.

From the data, some thermodynamic properties of these compounds were calculated. These properties are given in Table III.

The entropies of vaporization and sublimation given in Table III were estimated by dividing the listed enthalpies of vaporization and sublimation by the extrapolated boiling and sublimation temperatures.

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