the accuracy of the relative measurements given above and the reported accuracy (better than 1%) of Ziebland's equation for the k of toluene (*23*), the values of Tables III and IV are considered accurate to within about 2.5%. Any future changes in the k of toluene can be used to correct the k values reported here.

The apparatus and experimental measurements have been validated by comparing the values of k of a number of compounds at 20°C and B, the temperature coefficient of thermal conductivity, with values as evaluated by Jamieson and Tudhope (*10*) to be accurate to within ±2%. For example, the values of k at 20°C agree to within about 1.5% for ethanol and carbon tetrachloride. The values of B reported (*10*) vary considerably, but the present values fall within their range.

Each petroleum fraction is identified further by experimental viscosity–temperature data and the specific gravity at 15.5°C. Limited data indicate that the density-temperature relationship can be represented satisfactorily by the nomograph of Ritter et al. (*16*). The characterization factor "K" is commonly used in the petroleum industry as an index of the paraffinicity of various oils. It is defined as the ratio of the cube root of the average boiling point (°R) at atmospheric pressure to the specific gravity at 60°F.

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Vapor Pressures Over NdI_3 and PrI_3

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The sublimation pressures of neodymium and praseodymium triiodides have been measured. The heats of sublimation, $\Delta H_{S_{298}}{}^\circ$, for NdI_3 and PrI_3 are 77.8 ± 0.6 and 78.6 ± 1.5 kcal/mol, respectively.

Except for samarium, europium, ytterbium, and lutetium, the trivalent salt is the normally stable state for the lanthanides. The divalent salt is the normally stable state for the former four lanthanides. It has been reported by Hastie et al. (*7*), that $EuCl_3$ and $LuCl_3$, for example, would be stabilized only by mixing these lanthanide salts with KCl.

The solid trihalides of the lanthanides, except those of Sm, Eu, Yb, and Lu, are generally believed to vaporize as the monomeric lanthanide trihalide. The trihalides of Sm, Eu, Yb, and Lu are known to disproportionate to the dihalide and the halogen gas. Mass spectrometric evidences have been obtained for a number of stable trifluorides (*17*) and trichlorides (*7*), and also over some stable dichlorides and dibromides (*6, 7*). Extensive vapor pressure measurements over the liquid trichlorides and dichlorides of the lanthanides have been reported by Russian workers (*12*). Some vapor pressure measurements over solid halides have also been reported (*13*). However, there has been a paucity of data on the vapor pressures over the lanthanide iodides. Shimazaki and Niwa (*13*) reported the vapor pressures over solid LaI_3, PrI_3, and NdI_3. These workers, however, did their measurements using fused silica torsion effusion cells. It is known that the lanthanide halides react with fused silica.

We here report the vapor pressures over solid NdI_3 and PrI_3 using tantalum effusion cells to compare against the results of Shimazaki and Niwa. This metal is nonreactive with the lanthanide iodides in the temperature range measured. Subsequently, we will report on the mass spectra over these iodides (*8*).

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EXPERIMENTAL

Materials Preparation. The NdI_3 was prepared by the method of Asprey et al. (*1*), and also by direct reaction of neodymium metal with iodine (*3*). The latter material was purified by sublimation. Products from both methods of preparation gave materials with identical vapor pressures. The PrI_3 was prepared by the method of Asprey et al. by reacting the pure metal with HgI_2 vapor in a sealed, evacuated silica tube. The product mercury and excess HgI_2 were subsequently removed by distillation. The lanthanide materials were 99.9% purity from American Potash and Chemicals; the HgI_2 was Fisher Scientific ACS Certified Grade; and the iodine was 99.99% purity from Alfa Inorganic. The rare earth metals and their iodides were handled in a polyethylene glove bag in a helium or argon atmosphere. All precautions were taken to prevent the formation of oxyiodides in the preparation.

Measurements. The effusion measurements were made on a Cahn microbalance, Model RH, with a sensitivity of two micrograms. The Knudsen cell was hung from the balance into the fused silica furnace tube by a 3-mil tungsten wire. A dummy tantalum rod, with a Chromel-Alumel thermocouple in contact, was hung adjacent to the Knudsen cell for temperature control and measurement. A split-tube electric furnace, controlled by a Wheelco controller to within ±2°C, was used for heating the sample. The weight loss by effusion as a function of time was recorded on a Speedomax strip chart recorder.

The tantalum Kundsen cell had internal dimensions of $^5/_{16}$ in. i.d. × $^9/_{16}$ in. depth with a screw cap. A 3-mil thick disc, with an appropriate orifice in its center, was placed over the mouth of the bottom piece of the cell, then the threaded cap was fitted tightly so that there was no leakage of vapor around the edge of the disc. The cap had an opening of $^1/_4$ in. in the center. The orifice diameters used in these measurements were 0.020 and 0.040 in. The Clausing factor of each orifice was determined by calibration with zinc by using the vapor pressure data reported by Nesmeyanov (*11*). The Clausing factors determined in this manner were all near unity.

Approximately 0.2–0.45 gram of sample was used in the measurements. The material was loaded into the cell under a helium or argon atmosphere, and a drop of mineral oil (Nujol) was placed over the orifice to protect the sample from air during the rapid transfer of the cell to the microbalance. This technique was adopted from Hascke and Eick (*6*). The oil was evaporated under vacuum at 250°C, and the sample was generally heated at 400°C overnight under vacuum. The measurements were made at increasing and at decreasing temperatures with each orifice. The measurement at each temperature was made over a sufficiently long time to assure a linearity of weight loss as a function of time.

RESULTS

Table I. Vapor Pressure, in Torr, over NdI_3 and PrI_3

NdI_3 Orifice diam, in.	NdI_3 K	NdI_3 $p \times 10^3$	PrI_3 Orifice diam, in.	PrI_3 K	PrI_3 $p \times 10^3$
0.020	937	3.32	0.020	983	18.8
0.020	959	6.83	0.020	1007	50.9
0.020	979	14.2	0.020	1032	152
0.020	996	25.3	0.020	987	20.0
0.020	1013	44.9	0.020	947	4.56
0.020	1030	83.0	0.020	907	1.03
0.020	1012	43.4	0.040	908	1.02
0.020	985	15.5	0.040	925	1.89
0.020	966	8.50	0.040	940	3.18
0.020	951	5.52	0.040	955	4.84
0.020	933	2.59	0.040	972	8.95
0.020	917	1.55	0.040	989	17.6
0.020	902	0.693	0.040	1006	37.7
0.020	887	0.324	0.040	975	11.2
0.040	921	1.96	0.040	937	2.33
0.040	936	3.26	0.040	900	0.583
0.040	951	5.17	0.040	865	0.134
0.040	964	8.17	0.040	841	0.0566
0.040	980	15.3	0.040	869	0.176
0.040	998	26.0	0.040	895	0.450
0.040	1009	41.1	0.040	923	1.20
0.040	1022	63.5	0.040	948	2.99
0.040	1037	104.0	0.040	974	8.35
0.040	1013	42.4	0.040	1000	29.9
0.040	987	17.8	0.040	983	15.3
0.040	965	7.78	0.040	955	5.01
0.040	950	4.29	0.040	927	1.60
0.040	912	1.02	0.040	911	0.870
0.040	899	0.565	0.040	884	0.259
0.040	888	0.344	0.040	861	0.0820
0.040	870	0.166			
0.040	857	0.0820			

The vapor pressures of NdI_3 and PrI_3 were calculated from the effusion rates of the monomeric triiodides; i.e., $LnI_3(c) \rightarrow LnI_3(g)$, where Ln is the lanthanide. Mass spectrometric measurements, to be reported later (*8*), of these salts have ascertained the vapor compositions over the temperature ranges measured herein to be the monomer only. The vapor pressures of NdI_3 and PrI_3 are presented in Table I. A semilog plot of vapor pressure against $1/T$ gave a straight line with all three iodides, with no dependence on orifice dimensions.

The usual vapor pressure equations fitted to the data of Table I by a least-squares analysis were as follows:

$$NdI_3\text{: } \log p_{\text{mm}} = -(15037 \pm 125)/T + 13.51 \pm 0.13 \quad (1)$$

$$PrI_3\text{: } \log p_{\text{mm}} = -(15281 \pm 302)/\text{T} + 13.75 \pm 0.32 \quad (2)$$

The linear equations in $1/T$ are also plotted in Figure 1, together with those of Shimazaki and Niwa (*13*) for NdI_3 and PrI_3. Although the slopes for the latter iodides are nearly the same in both works, our vapor pressures are appreciably higher than those of Shimazaki and Niwa.

NdI_3. For the process, $NdI_3(c) \rightarrow NdI_3(g)$, the heat of sublimation at the median temperature of 943K is 68.81 ± 0.58 kcal/mol. This value was extrapolated to 298K by using $\Delta C_p = -14$ cal/deg, as suggested by Brewer (*2*), to give $\Delta H_{s_{298}}{}^\circ = 77.9 \pm 0.6$ kcal/mol. Shimazaki and Niwa report a

Table II. Thermodynamic Properties of NdI_3 and PrI_3 at 298K

	Heat of formation, $-\Delta H_f{}^\circ$, kcal/mol	Heat of sublimation, $\Delta H_s{}^\circ$, kcal/mol	Free energy of formation, $-\Delta G_f{}^\circ$, kcal/mol	Entropy of formation, $\Delta S_f{}^\circ$, eu	Entropy, S°, eu
$NdI_3(c)$	152[a]	77.8 ± 0.6	151	−3.4	56.0
$NdI_3(g)$	74		91	57.2	116.6
$PrI_3(c)$	157[a]	78.9 ± 1.5	156	−3.7	55.7
$PrI_3(g)$	78		94	54.1	113.5

[a] Feber (*5*).

Table III. Heat of Reaction, Free Energy, and Entropy Changes for Reactions at $T°$ and 298K
ΔH and ΔG in kcal, ΔS in EU

Reaction	T, K	ΔH_T	ΔG_T	ΔS_T	298K ΔH	298K ΔG	298K ΔS
$NdI_3(c) \rightarrow NdI_3(g)$	943	68.81	22.9	48.6	77.8	59.7	60.6
$PrI_3(c) \rightarrow PrI_3(g)$	937	69.93	23.3	49.7	78.9	61.6	57.8

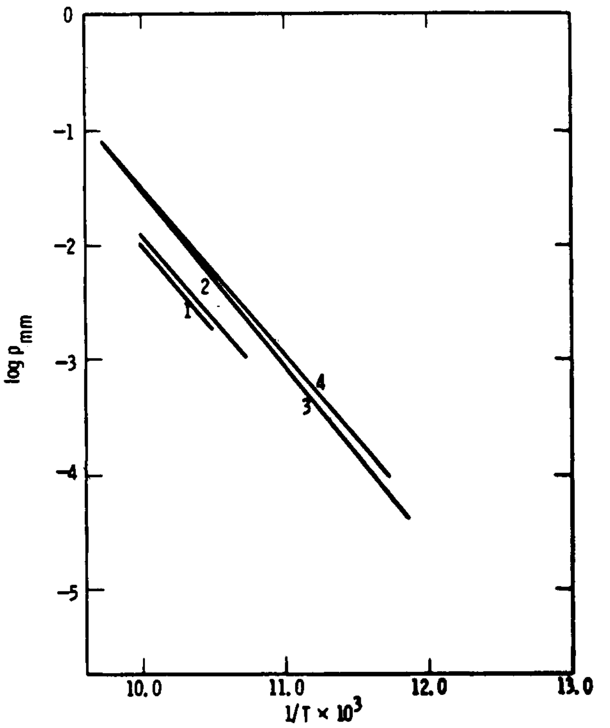

Figure 1. Log p_{mm} vs. 1/T for NdI_3 and PrI_3

(1) NdI_3, Shimazaki and Niwa; (2) PrI_3, same authors; (3) PrI_3, this work; (4) NdI_3, this work

value of 75.8 kcal/mol for $\Delta H_{s_{298}}°$. All of the extrapolated thermochemical data reported in this paper will be by the second law method, since there are no adequate third-law free-energy function values, including the recent ones by Krasnov and Danilova (*9*). All third-law extrapolations of the heats for these materials resulted in values that differed by 10–15 kcal from those of the second-law extrapolations.

The thermodynamic properties for the formation of NdI_3 at 298K are summarized in Table II. The heat of formation of $NdI_3(c)$ is that estimated by Feber (*5*). His heats of formation for the crystalline iodides are probably accurate to within ±5 kcal/mol.

The free energy of sublimation of NdI_3 may be represented in terms of the vapor pressure by $\Delta G_T = -RT \ln K_p = 68.81 - 48.64T \times 10^{-3}$ over the measured temperature range. At 943K, $\Delta G = 22.94 \pm 0.59$ kcal/mol. When we combine this value with the heat of sublimation at this temperature, the entropy of sublimation, ΔS_{943}, is 48.6 ± 0.6 entropy units (eu). The entropy of $NdI_3(c)$ at 298K, estimated by Latimer's data (*10*) and corrected for magnetic contributions from Westrum (*16*), is $S_{298}° = 56.0$ eu. From the $S_T - S_{298}$ data of Dworkin and Bredig (*4*) for $NdI_3(c)$, $\Delta S_{943} = 90.2$ eu. The entropy of $NdI_3(g)$ at 943K is therefore 138.8 eu. The latter entropy of the gas was combined with the $S_T - S_{298}$ values of $LaI_3(g)$, reported by Krasnov and Danilova (*9*), to give $S_{298}° = 116.6$ eu for $NdI_3(g)$. The free energies and entropies of formation of the crystalline and gaseous neodymium triiodide at 298K, shown in Table II, were then obtained by utilizing the entropy data for neodymium and iodine from Stull and Sinke (*14*). Table III summarizes the heats of reactions at 298K and at the median of the temperature ranges.

PrI_3. The thermodynamic properties of praseodymium triiodide, recorded in Tables II and III, were computed in a similar manner to those for NdI_3. The heat of sublimation at 937K was 69.93 ± 1.38 kcal/mol. A $\Delta H_{s_{298}}°$ of 78.9 ± 1.5 was obtained by assuming $\Delta C_p = -14$ cal/deg. Shimazaki and Niwa obtained a $\Delta H_{s_{298}}°$ of 75.7 kcal/mol for $PrI_3(c)$. From Feber's $\Delta H_{f_{298}}°$ of −157 kcal/mol, and our heat of sublimation, we obtain $\Delta H_{f_{298}}°$ of −78 kcal/mol for $PrI_3(g)$.

The free energy of sublimation of PrI_3 at 937K, from the equation $\Delta G_T = 69.93 - 49.74\ T \times 10^{-3}$, is 23.32 ± 1.4 kcal/mol. The ΔS_{937} is therefore 49.7 ± 1.5 eu. From Latimer's and Westrum's data, $S_{298}°$ is 55.7 eu for $PrI_3(c)$. The entropy at 937K for the solid, 85.8 eu, was obtained by utilizing the $S_T - S_{298}$ data of Dworkin and Bredig for $NdI_3(c)$ after subtracting the entropy of transition for the neodymium iodide. The entropy of $PrI_3(g)$ at 937K was therefore 135.5 eu. This value was extrapolated to 298K by using Krasnov and Danilova's $S_T - S_{298}$ data for $LaI_3(g)$ to obtain $S_{298}°$ of 113.5 eu for $PrI_3(g)$. The entropies and free energies of formation shown in Table II were obtained by combining the above data with those of praseodymium and iodine given in Stull and Sinke (*15*).

DISCUSSION

The extrapolated thermodynamic data at 298K presented here should be taken as tentative until improved spectroscopic data for the gaseous lanthanide triiodides and heats of formation for the solid iodides are obtained. A satisfactory fit of third-law extrapolations is still needed.

The higher vapor pressures for NdI_3 and PrI_3 in this work, compared to those of Shimazaki and Niwa, are attributed to the material used for the effusion cell. It is not known at present the exact nature of the reaction between silica and the lanthanide iodides, but there is no doubt that a reaction does take place. However, our heats of sublimation for NdI_3 and PrI_3 are in good agreement with those of Shimazaki and Niwa.

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Critical Constants and Liquid Densities of Xenon Difluoride and Xenon Tetrafluoride

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The measured critical temperatures and liquid densities of XeF_2 (115–89°C) and XeF_4 (110–50°C) and the estimated critical pressures and critical densities are reported.

The critical temperature of XeF_2 can be measured by the sealed-tube method when the compound is sealed in quartz tubes (5). However, because of the reaction of XeF_2 with quartz at elevated temperatures and possible thermal dissociation, the measured critical temperature varied with the time of measurement. To minimize these two effects, the measurements were repeated by heating the tubes rapidly in a liquid bath. The new series of experiments included XeF_4.

Since there is no general and accurate method of estimating the critical temperature of inorganic compounds, the experimental work seemed to be justified.

We also estimated the critical pressures and critical densities of both fluorides. Since, for this purpose, the saturated liquid densities of both fluorides were needed but not known, we determined them also.

EXPERIMENTAL

Materials. Xenon difluoride was prepared by photosynthesis at room temperature (3, 9). It was purified by pumping off the volatiles in vacuo at −78°C and then it was stored in a nickel container. Infrared spectra of its vapor showed no bands of possible impurities. The triple point temperature of the purified sample was determined visually as 129.3°C, whereas the published value was 129.02°C (7).

Xenon tetrafluoride was prepared by thermal dissociation of xenon hexafluoride (8). The remaining xenon hexafluoride was absorbed on uranium tetrafluoride. The infrared spectra of vapors showed, besides the strong XeF_4 band, traces of XeF_2. The triple point temperature of the sample was 116.8°C, whereas the published value amounted to 117.10°C (7). The product was judged sufficiently pure for our critical temperature and liquid density measurements.

Procedure. Both fluorides were sublimed under a high vacuum into quartz tubes previously baked at 750°C for 12 or more hr. They were sealed off while the lower parts with fluoride samples were at the liquid nitrogen temperature and stored at this temperature until the measurements were made.

In the critical temperature determinations, the tubes (i.d., 2 mm; o.d., 7 mm, 40 mm long) were heated rapidly by immersing in a liquid bath. The range of temperatures between 351° and 359°C for XeF_2 and between 337° and 341°C for XeF_4 was more carefully examined in steps of 1°. The temperature of the bath was set to the temperature within this range, the tube was immersed, and after the initial disappearance of the meniscus, the change in the critical temperature with time was explored.

In the measurements of densities of liquid fluorides, the height of the meniscus in the quartz tubes (volume, 0.15 cm^3, i.d. of a capillary 1 mm), calibrated with mercury, was first measured at the melting point. Subsequently, readings were taken, while the temperature was raised stepwise, followed by stepwise cooling, and for undercooled liquid. The amounts of fluoride (usually about 0.4 gram) in the tubes were determined from the weighings of full and empty broken ampuls after the experiments. No etching of quartz was observed.

The temperature of the bath in a transparent Dewar vessel was measured by a mercury-in-glass thermometer (1/10°) up to 350°C and by an iron-constantan thermocouple at higher temperatures. The temperature was constant to $\pm 0.1°$ at critical temperature measurements and $\pm 0.02°$ at density measurements. The whole apparatus, including thermometers, was calibrated against the critical temperature of toluene at 318.6°C (1) and against the triple point temperature of benzoic acid at 122.37°C (4). The heights of the menisci were measured with a cathetometer graduated to 0.01 mm.

RESULTS

Critical Constants. Values for the critical temperatures of both fluorides are given in Table I. These values were determined by the extrapolation of the measured critical temperatures to the beginning of the experiment. Estimated accuracy of the results is thus the accuracy of the extrapolation.

The second data column gives the rates of change of the measured critical temperatures with time of heating. Applying this rate to the previously measured critical temperature of xenon difluoride at 335°C (5), where the time of heating was 20–25 min results in approximately the now ac-

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