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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 ±0.1° at critical temperature measurements and ±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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Table I. Critical Constants of XeF_2 and XeF_4

	t_c, °C	Rate of change, deg/min	No. of tubes	P_c, atm	ρ_c, g/cm^3	V_c, cm^3/mol	Z_c
XeF_2	358 ± 2	−1	8	92 ± 1	1.14 ± 0.01	149 ± 2	0.265
XeF_4	339 ± 1	−0.1	3	69.5 ± 0.5	1.10 ± 0.01	189 ± 2	0.262

cepted value of 358°C. The third column of Table I gives the number of experimental tubes, where the meniscus disappeared in the middle third of the tube. Only these tubes were used in the determination of the critical temperature of a fluoride.

The critical pressures and critical densities of both fluorides were estimated by the method of Hakuta and Hirata (*2*) and are given in Table I. In this estimation the experimental critical temperatures and the liquid densities extrapolated to the sublimation points (P = 1 atm) were used. Sublimation point temperatures were calculated from vapor-pressure equations (*7*) as 114.3°C for xenon difluoride and 115.7°C for xenon tetrafluoride. Accuracies given were estimated from the accuracies of experimental critical temperatures and liquid densities.

Values of the critical ratios Z_c of both fluorides were calculated from the defining equation $Z_c = P_cV_c/RT_c$ by using the values of critical constants given in Table I with T_c in K.

Liquid Densities. Only one set of density measurements was made with a particular fluoride. The exception is an independent measurement at 189°C for XeF_2. The values for undercooled liquids were also obtained.

Estimated uncertainty in the experimental densities is ±0.01 g/cm^3 based mainly on checking with water at room temperature after the experiments.

The vapor corrections, assuming ideal gas behavior, were from 0.2–0.5% on xenon difluoride and 0.1–0.2% on xenon tetrafluoride. The larger corrections for xenon difluoride are mainly due to the larger volume of vapor because of an additional enlargement in the upper part of the tube. To the authors' knowledge, the vapor pressures of both liquid fluorides had not been published and were therefore estimated by the Riedel-Plank-Miller method (*6*). In the estimation, the experimental critical temperatures, the estimated critical pressures, the triple point temperatures and pressures (*7*) of both fluorides were used.

The measured density values of both fluorides were fitted by the method of unweighted least squares to the following equations:

$$XeF_2 \quad \rho = 3.641 - 3.96 \times 10^{-3}\, t \qquad (115\text{–}90°\mathrm{C})\ \mathrm{g/cm^3}$$

or in terms of molar volume:

$$V_m = 44.76 + 0.0723\, t \qquad (115\text{–}90°\mathrm{C})\ \mathrm{cm^3/mol}$$

and for XeF_4:

$$\rho = 3.500 - 4.05 \times 10^{-3}\, t \qquad (110\text{–}50°\mathrm{C})\ \mathrm{g/cm^3}$$

or

$$V_m = 57.38 + 0.0950\, t \qquad (110\text{–}50°\mathrm{C})\ \mathrm{cm^3/mol}$$

Relative standard deviation of the calculated values from the observed ones is ±0.05%.

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