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Density of Liquid Hydrogen Fluoride between 258 K and 373 K at Pressures up to 200 MPa

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Densities of pure liquid hydrogen fluoride were measured in a piston-cylinder type densimeter. The HF was contained in a bellow made of tetrafluormethylene, which was surrounded by methanol. This arrangement allowed measurements to be performed over a temperature range from 258 K to 373 K, at pressures up to 200 MPa. The results could be well-described by the Tait equation, where both fit parameters show a systematic temperature dependence. When compared to other simple liquids, HF shows an unusually high compressibility over the whole temperature and pressure range studied.

Introduction

The hydrides of the elements of the first row of the periodic system are a group of compounds with exceptional chemical and physical properties. Best known is the unique behavior of liquid and solid water (Franks, 1972), but NH_3 and HF also present many unusual properties that all ultimately derive from their ability to form hydrogen-bonded structures.

The liquids of these hydrides find many applications in industry and science. Among these hydrides HF forms the strongest hydrogen bonds (Honda et al., 1992).

In complementation to our studies on the molecular mobility in water and aqueous solutions (Lang and Lüdemann, 1991), we measured the self-diffusion in neat ammonia and hydrogen fluoride (Gross et al., 1997; Karger et al., 1994; Karger and Lüdemann, 1998) as a function of temperature and pressure. For the quantitative evaluation of these results, the knowledge of the density ρ is necessary. No pressure dependence of ρ for the temperature range between 250 K and 370 K could be found in the literature. It was thus decided to modify a densimeter used in our previous studies on inert liquids (Wappmann et al., 1995) to permit the pVT measurements on highly aggressive pure hydrogen fluoride. An additional motivation for this study is the many unusual properties of liquid HF at atmospheric pressure, especially the unusually high isothermal compressibility.

Experimental Section

Liquid water-free hydrogen fluoride (>99.9% purity, Merck-Schuchardt, Hohenbrunn, FRG) was used as supplied.

Apparatus. The densimeter used is of the piston-cylinder type, where the cylinder has a bore of 22 mm and an outer diameter of 70 mm. The movable piston and the front and back stamps, which close the bore, are sealed by O-rings. For the low-temperature measurements ($T < T_{\mathrm{amb}}$), the O-rings employed were made from silicone, while for higher temperatures Viton was used. The low-temperature, high-pressure limit of the measurements was set by the embrittlement of the silicone. The position of the piston can be determined to ±0.05 mm by detecting the magnetic field of a ferromagnet that is connected to the piston by a rigid steel rod. This gives an error in the volume determination of 20 mm^3.

The pressure was determined with two precision Bourdon gauges (Heise, New Haven, CT) with ranges of 100 MPa and 400 MPa. It was measured in the pressure liquid circle, and hence the measured values had to be corrected for the friction of the piston. This was done by moving the piston forward and backward to a defined position and determining the pressure difference. This correction was applied to the pressures given below. The accuracy of the pressure data is judged to ±0.2 MPa below 100 MPa and ±1 MPa above 100 MPa.

Thermostating of the cell is achieved by pumping thermostated silicone oil through a jacket around the cylinder. The temperature inside the sample volume is measured with a metal-sheathed chromel/alumel thermocouple, which had been soldered into a high-pressure plug. The thermocouple and display unit were calibrated to ±0.2 K. Details of the construction and operation of the densimeter have been published previously (Wappmann et al., 1995).

HF Sample. Owing to the extremely corrosive nature of HF, the liquid was contained in a bellow made of TFM (tetrafluormethylene; Berghof, Eningen, FRG), which is shown in Figure 1. This material is, at least up to temperatures of 100 °C, resistant to HF and has a comparatively small porosity.

To fill the bellow, it was fixed in a stretched position and put in a glovebox, through which a stream of cool (0 °C) nitrogen was flowing. The HF was taken directly from a lecture bottle and transferred to the bellow via a small Teflon hose. When the bellow was filled completely, the hose was removed and the bellow sealed with a Teflon cone seal.

By weighing the bellow before and after the filling, the amount of HF could be determined accurately (±0.5 mg).

After the bellow was checked for leaks, it was inserted into the cylinder of the densimeter. About 25 g of methanol p.a. were then added from a syringe, which was also weighed before and after the filling. The methanol serves as a pressure transmitter, and it dissolves and dilutes the extremely corrosive neat HF in case of leaks.

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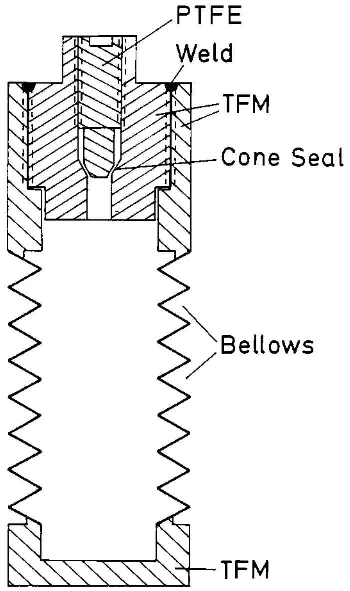

Figure 1. Bellow made of TFM (tetrafluormethylene), and Teflon (PTFE) cone seal used for the measurements; it contains ca. 10 g HF.

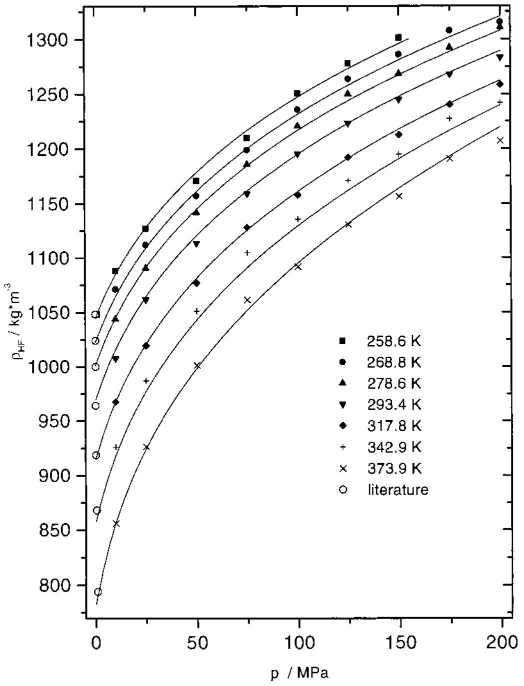

Figure 2. Measured densities of HF, together with saturated liquid densities from Franck and Spalthoff (1957) and Sheft et al. (1973); the lines are fits of the combined experimental data to the Tait equation (eq 1); the vapor pressure of HF between 253 K and 373 K can be calculated by the empirical equation (obtained by fitting the data of Vanderzee and Rodenburg (1970): ρ_V/MPa = $-10.99 + 0.1233T - 4.658 \times 10^{-4}\mathrm{T}^2 + 5.943 \times 10^{-7}T^3$.

Table 1. Measured Densities, ρ/kg m^{-3}, of HF

	T/K						
p/MPa	258.6	268.8	278.7	293.5	317.8	342.9	373.9
10	1088	1071	1044	1008	967.5	926.4	856.1
25	1127	1112	1091	1062	1020	987.1	926.7
50	1171	1157	1142	1113	1077	1051	1002
75	1210	1199	1186	1159	1128	1105	1061
100	1251	1236	1221	1195	1158	1136	1092
125	1278	1264	1250	1223	1192	1171	1131
150	1301	1286	1269	1245	1212	1195	1156
175		1308	1293	1268	1240	1227	1191
200		1315	1311	1283	1258	1242	1207

Table 2. Fit Parameters for the Tait Equation (Eq 1); $A(T) = a_0 + a_1T + a_2T^2$, $B(T) = b_0 + b_1T + b_2T^2$, $\rho_0(T) = \rho_{00} + \rho_{01}T$

i	a_i	b_i	ρ_{0i}
0	0.09867	53.94 MPa	1594 kg m^{-3}
1	2.016×10^{-4} K^{-1}	-0.1541 MPa K^{-1}	-1.97 kg m^{-3} K^{-1}
2	7.065×10^{-7} K^{-2}	8.541×10^{-5} MPa K^{-2}	

Table 3. Density of HF: Fit Parameters for the Tait Equation 1; ρ_0 Is the Measured Density at the Lowest Pressure Studied, i.e., 10 MPa

T/K	ρ_0 (=ρ(10 MPa))/ kg m^{-3}	*A*	*B*/MPa	standard deviation/%
258.6	1088	0.0935	20.44	0.5
268.8	1071	0.0935	19.03	0.5
278.7	1044	0.0991	17.74	0.2
293.5	1008	0.1028	15.92	0.3
317.8	967.5	0.1046	13.28	0.3
342.9	926.4	0.1112	11.02	0.3
373.9	856.1	0.1229	8.86	0.7

Table 4. Isothermal Compressibilities k_T of HF at Saturated Vapor Pressure and at 100 MPa

	T/K						
	258.6	268.8	278.7	293.5	317.8	342.9	373.9
k_T(SVP)/ 10^{-10} Pa^{-1}	43.8	46.9	53.1	61.0	73.6	93.0	125.0
k_T(100 MPa)/ 10^{-10} Pa^{-1}	8.90	9.04	9.82	10.5	11.1	12.3	14.4

The measurements were performed by keeping the temperature constant and varying the pressure. The total volume of the three components, HF, Teflon, and methanol, was determined by measuring the position of the piston, and the density of HF was calculated by subtracting the known volumes of Teflon and methanol. The density of methanol was taken from the literature (Goodwin, 1987). The density of the bellow was measured in the same densimeter, over the same temperature and pressure range as the measurements of HF, with a bellow filled with methanol. After the measurements, the mass of the HF-filled bellow was checked. The maximal weight loss after measuring several isotherms was 0.05 g.

Accuracy. The calibration of the densimeter (Wappmann et al., 1995) showed the error in density to be less than ±0.2% for pure liquids. This includes the errors in pressure, temperature, volumetric measurement, and weighing. Since HF occupies about 20% of the sample volume, the accuracy of our results is better than ±1%. This includes the error in the density of the used methanol values (<0.1%). With different bellows, the density data derived for HF were reproducible to ±0.6%.

Results

The measured density values of HF are compiled in Table 1. They are plotted in Figure 2, together with literature data along the saturation curve (Simons and Bouknight, 1932; Franck and Spalthoff, 1957; Sheft et al., 1973). The lines are results of fits to the Tait equation (Tait, 1900)

$$\frac{\rho_0(p_0)}{\rho} = 1 - A \ln\left(\frac{B + p}{B + p_0}\right) \qquad (1)$$

The fits show a maximal standard deviation of 1%, when $A(T)$ and $B(T)$ were fitted to a quadratic temperature

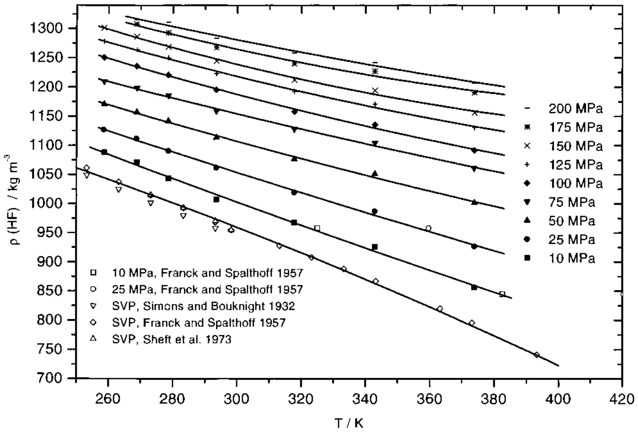

Figure 3. Isobaric densities of HF and polynomial fits ($n = 2$) of the data; literature values are included for comparison.

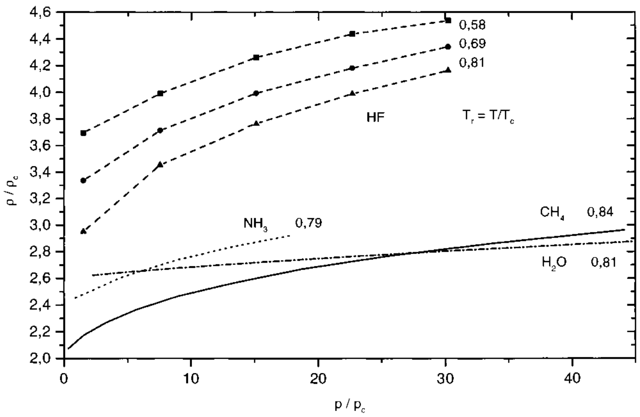

Figure 4. Reduced densities as a function of reduced pressure at various reduced temperatures; values for the critical point (T_c, p_c, ρ_c): HF, 461 K, 6.62 MPa, 290 kg/m^3; NH_3, 405 K, 11.25 MPa, 235 kg/m^3; CH_4, 191 K, 4.64 MPa, 162 kg/m^3; H_2O, 647 K, 2.22 MPa, 305 kg/m^3.

dependence, and ρ_0 was assumed to depend linearly on temperature. The parameters a_i, b_i, and ρ_{0i}, which are useful for the interpolation of our data, are given in Table 2.

A better fit could be obtained by using the measured values for ρ_0 (10 MPa) and by fitting $A(T)$ and $B(T)$ (see Table 3). Here, the isotherms ρ(HF) could be described with a standard deviation between 0.2 and 0.7%.

Comparison with Literature Values. Except for three data points at 10 and 25 MPa (Franck and Spalthoff, 1957), only saturation pressure densities were found in the literature (Simons and Bouknight, 1932; Franck and Spalthoff, 1957; Sheft et al., 1973). The high-pressure data by Franck and Spalthoff (1957) are part of a *pVT* study that extends to considerably higher temperatures and pressures. In the region of overlap, the agreement with our data is well within experimental error (cf. Figure 3). Our experimental data extrapolate to saturated liquid densities published by Franck and Spalthoff (1957) and Sheft et al. (1973). The data set given by Simons and Bouknight (1932) shows a systematic deviation from the other data by −1.2%. These data were therefore not used in the fitting of the Tait equation.

Discussion

The unusual properties of liquid hydrogen fluoride become obvious from a comparison of the reduced densities of CH_4 (Harris and Trappeniers, 1980), NH_3 (Mills et al., 1984), H_2O (Rosner and Straub, 1980), and HF, presented in Figure 4 in the same region of the reduced temperature $T_r = T/T_c$ and reduced pressure $p_r = p/p_c$. Here, liquid hydrogen fluoride shows by far the largest changes as function of pressure.

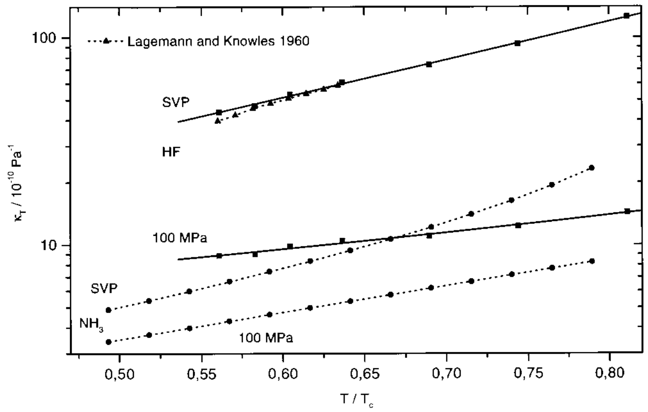

Figure 5. Isothermal compressibilities k_T at saturated vapor pressure and 100 MPa obtained in this work (Table 4), compared to the data of Lagemann and Knowles (1960); the literature data were calculated from measured sound velocities, combined with the unreliable density data of Simons and Bouknight (1932); also included are values of NH_3, calculated from Mills et al. (1984).

In Figure 5 the isothermal compressibilities as derived from the density data of Figure 2 are given at saturation vapor pressure and at 100 MPa. When compared to NH_3 at similar reduced temperatures, they reveal the exceptional properties of HF. This unusually high compressibility is still observable in the k_T(100 MPa) data.

Note Added in Proof. High-pressure, high-temperature density data for HF have appeared recently (Franck et al., 1998). The data extend from 473 K to 973 K at pressures up to 200 MPa. These data could also be described by the Tait equation.

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