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PHYSICAL PROPERTIES OF HEXAFLUOROACETONE

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SUMMARY

The vapour pressure of hexafluoroacetone has been determined from 58°C to the critical point. The critical temperature and pressure were also measured. Densities of the liquid and saturated vapour were determined between - 50°C and the critical point. Using this information the rectilinear diameter line and the heats of vaporization have been determined.

INTRODUCTION

Hexafluoroacetone has been extensively investigated with regard to its reactions, but very little has been done on its physical properties. Morse, Ayscough and Leitch [1] studied the vapour pressure of hexafluoroacetone in the temperature range - 60°C to - 28°C. Murphy [2] studied the vapour pressure in the range - 33.31°C to + 83.72°C, together with the critical properties. He also reported the density at 25°C as 1.318 g/cm^3. The purpose of this study is to measure vapour pressure data and correlate them with an equation of state. The critical properties and the densities of liquid and saturated vapour were also measured. The Clapeyron equation was used to cal-

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culate the heat of vaporization. The experimental values of the critical constants are compared with values selected by Kudchodler, Alani and Zwolinski [3] as the most reliable values reported in the literature.

EXPERIMENTAL

Hexafluoroacetone was supplied by the Pierce Chemical Company who stated that the purity is 99.1 %. The sample was further purified by placing it in contact with activated molecular sieves to absorb traces of moisture and was then degassed by subjecting the sample to a cycle of freezing, pumping, melting and freezing. The degassed sample was kept in a flask attached to a high vacuum train and surrounded by a mixture of dry ice plus acetone. The purity was checked by a determination of the pressure difference between the bubble and dew pressures. The difference was found to be negligible.

APPARATUS AND PROCEDURE

The apparatus and methods used for the measurements have been described in a previous publication [4] .

RESULTS

The experimental data on vapour pressures from 58°C to the critical temperature were tried on different forms of vapour pressure equations by the method of least squares. The equation suggested by Murphy [2] was found to be the best, with an average deviation of ± 0.16 %.

$$\begin{aligned} \mathrm{Log}_{10}\ (P_{\mathrm{abs.atm.}}) &= 11.2816 - 1183.956\ (K/T) \\ &- 0.02149103\ (T/K) \\ &+ 2.288914 \times 10^{-5}\ (T/K)^2 \end{aligned}$$

The values of the densities are shown in Table 1. The rectilinear diameter equation was found to be :

$$\frac{\text{Density (L)} + \text{Density (G)}}{2} = 0.12817 - .000\ 184\ (T/K)$$

The rectilinear diameter is shown in Fig. 1.

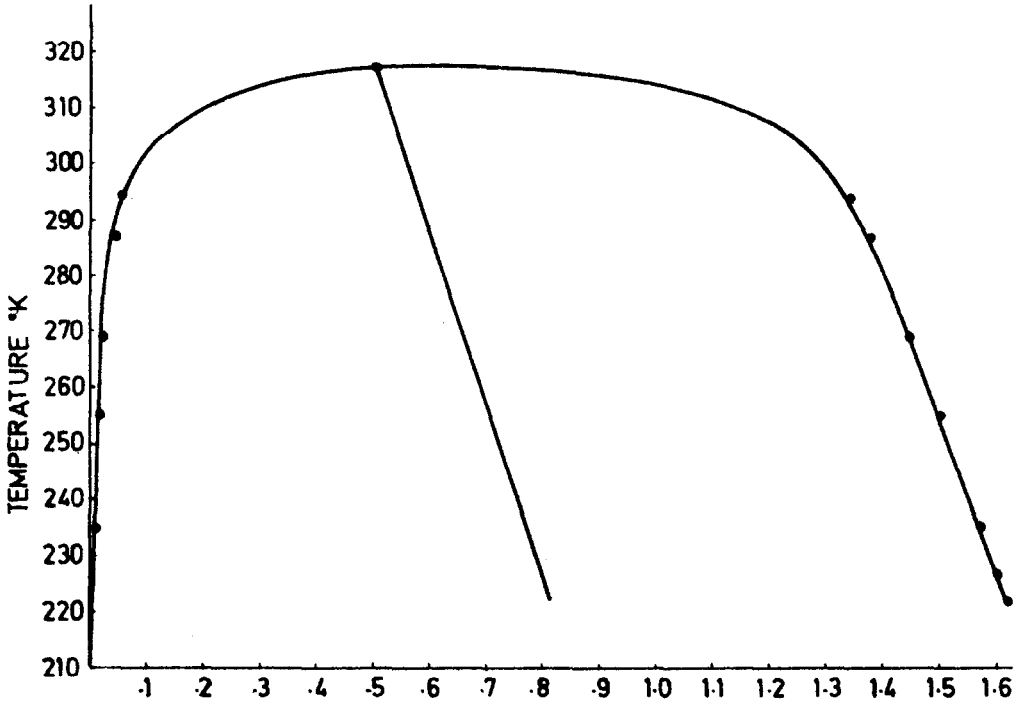

Fig. 1. Rectilinear diameter for hexafluoroacetone.

The heat of vaporization was calculated from the Clapeyron equation :

$$-\Delta H(\text{cal/g.mole}) = (dp/dt)\ T(V_L - V_G) \quad (3.77)$$

where dp/dt was found by differentiating the vapour pressure equation. The values of ΔH are shown in Table 1. The critical values are shown in Table 2.

TABLE 1

The densities (ρ) of liquid and saturated vapour and the heat of vaporization for hexafluoroacetone

T (K)	ρ(L) (g/cm^3)	ρ(G) ($g/cm^3 \times 10^{-1}$)	$-\Delta H$ (cal/g.mole)
294	1.3410	0.5400	1571340.3
287	1.3779	0.4400	1603709.9
269	1.44925	0.25560	1631026.7
255	1.50189	0.1550	1682297.9
235	1.56874	0.0690	1696312.7
227	1.6031	0.046	1750937.9
222	1.62362	0.033	1896804.1

TABLE 2

Critical Values of Hexafluoroacetone

Critical Temperature (^oC)	Critical pressure (psia)	Critical density (g/cm^3)	Reference
83.99	410.75	0.5045	This work
84.10	411.9	-	[2]

DISCUSSION

The critical properties obtained are in good agreement with those recommended by Kudchodler, Alani and Zwolinski [3]. Murphy [2] reported the liquid density at 25°C as 1.318 g/cm^3 and this fits very well in Fig. 1.

A copper-to-constantin thermocouple was used to measure the temperature. This thermocouple was calibrated against a platinum resistance thermometer, which was caliberated and certified by the National Bureau of Standards. The thermocouple was read to

0.01 K. The absolute accuracy of temperature measurements was estimated to be $\pm$ 0.2 K. The pressure gauge could be read to 0.02 lb_f in^{-2}. It was checked against a high precision dead-weight gauge with a pressure sensitivity of 0.019 lb_f in^{-2}. The absolute accuracy of the pressure measurements was estimated to be $\pm$ 0.5 lb_f in^{-2}.

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