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THE VAPOUR PRESSURES AND SATURATED VOLUMES OF BENZOTRIFLUORIDE IN THE TEMPERATURE RANGE 460-530K.

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SUMMARY

A sample of benzotrifluoride was degassed in a high vacuum train, and the vapor pressure was measured in the temperature range 460 - 530K. Also the saturated vapour and saturated liquid volumes were measured. Two simple equations were used to fit the vapour pressure data by the least square method. The heat of vaporization was calculated using Clapeyron equation.

INTRODUCTION

The vapour liquid equilibria of fluoro-compounds have not been given the great attention accorded to those of the hydrocarbons. In this laboratory, the vapour liquid equilibrium of some of fluoro-compounds was studied [1, 2, 3, 4, 5, 6] . Ambrose and Ellender [7] studied the vapour pressure of octafluorotoluene. Burger and Cady [8] , Stiles and Cady [9] and Crowder et al. [10] studied the physical properties of perfluoro-n-hexane.

Scott et al. [11] studied the vapour pressure of benzotrifluoride in the temperature range 328K to 412K. Rutledge and Smith [12] studied the densities of benzotrifluoride in the temperature range 303.15K to 353.15K.

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In a previous work, Mousa [6], it was found that the two simple vapour pressure equations :

$$\text{Log } P = A + \frac{B}{T} \qquad (1)$$

$$\text{Log } P = A + \frac{B}{t+230} \qquad (2)$$

would fit the data with great accuracy. So these equations will be used to correlate the data of benzotrifluoride.

EXPERIMENTAL

Benzotrifluoride was obtained from Koch Light Laboratories Ltd., England, with stated purity of more than 99%. Benzotrifluoride was further purified by placing it in contact with activated molecular sieves to absorb traces of moisture in a high vacuum train. The sample was then degassed by subjecting it to a cycle of freezing, pumping, melting and freezing. The freezing was done by using liquid nitrogen.

The apparatus and methods used for the measurements have been described in previous publications [1, 2]. A known amount of the degassed sample was confined over mercury in a thick-walled glass capillary tube. The volume of the tube had been determined as a function of the distance from the sealed end so that the volume occupied by the sample could be calculated at any desired condition by measuring the length of the tube filled with the sample. The length of the tube occupied by the sample was measured with a cathetometer reading to within 0.05mm. The pressure was measured with a pressure transducer calibrated against a high precision dead-weight gauge. The temperature was measured with a platinum resistance thermometer made by Fluke. The absolute accuracy of the temperature measurement was estimated to be ± 0.2K and that of the pressure to be ± 1.0 kPa.

RESULTS

The vapour pressure and saturated volumes were measured in the temperature range 460K to 530K. The results are shown in Table 1. Using the least square method the data were fitted to the previous two equations, and the constants were obtained. So the two equations become :

$$\mathrm{Log}\ (P/\mathrm{kPa}) = 6.5255 - \frac{1676.553}{(T/K)} \tag{3}$$

$$\mathrm{Log}\ (P/\mathrm{kPa}) = 6.2357 - \frac{1399.123}{230 + (t/^{\circ}C)} \tag{4}$$

The coefficient of determination (r^2) was calculated for each equation. The value of (r^2) will lie between 0 and 1.0 and will indicate how closely the equation fits the experimental data. The closer (r^2) is to 1.0 the better the fit. For equation (3), r^2 was 0.99935 and for equation (4), r^2 was 0.99927. Using the above equations, the calculated pressures are shown in Table 1. Also the percentage deviations given by

$$\%\ \mathrm{Dev.} = \left(\frac{P_{cal} - P_{exp}}{P_{exp}}\right)100$$

are shown in Table 1.

The heat of vaporization was calculated from the Clapeyron equation :

$$\Delta H(\mathrm{J/gmole}) = (dp/dT)T(V_G - V_L)$$

where dp/dT was found by differentiating the vapour pressure equation (3). The values of ΔH are shown in Table 1.

TABLE 1

The Vapour Pressure and Saturated Volumes for Benzotrifluoride and its heat of Vaporization

T (K)	P_{exp} kPa	Specific Volume cc/g		Equation (1)		Equation (2)		Heat of vaporisation H(J/gmole)
		Sat. Vap (V_G)	Sat. Liq. (V_L)	P_{cal}	%Dev.	P_{cal}	%Dev.	
468.35	882.81	44.31	1.203	882.63	-0.02	880.73	-0.24	19899.97
479.85	1089.33	36.26	1.233	1075.40	-1.28	1075.26	-1.29	19229.31
485.35	1180.96	33.12	1.262	1178.05	-0.25	1178.62	-0.20	18941.90
491.95	1292.55	30.08	1.291	1310.71	1.41	1311.93	1.50	18789.21
496.95	1415.91	26.51	1.320	1418.39	0.18	1419.93	0.28	17611.95
502.35	1517.88	23.40	1.350	1541.92	1.58	1543.59	1.69	16579.08
508.35	1698.43	19.80	1.379	1688.31	-0.60	1689.81	-0.51	14986.46
513.55	1827.33	17.43	1.408	1823.26	-0.22	1824.28	-0.17	13934.10
518.35	1970.01	14.12	1.438	1954.69	-0.78	1954.98	-0.76	11714.91
523.65	2105.13	13.15	1.467	2107.73	0.12	2106.81	0.08	11519.26
527.35	2216.11	12.04	1.496	2219.62	0.16	2217.59	0.07	10871.30
531.55	2358.12	11.13	1.525	2351.79	-0.27	2348.20	-0.42	10409.94

DISCUSSION

The above two equations gave almost the same deviation which was small enough to assume that they both represent the data with high accuracy. No data were found in the literature for benzotrifluoride, in this high temperature, so as to compare it to this work. But according to previous work carried out in this laboratory [1, 2, 3, 5, 6] it can be assumed that these equations are good enough to represent the data.

Scott *et al.* [11] reported vapour pressure data of high quality in the temperature range 328K to 412K. They correlated their data by Antoine equation

$$\mathrm{Log}(P/\mathrm{mm\ Hg}) = 6.96911 - \frac{1305.509}{t^{o}C+217.28}$$

Extrapolations using Scott's equation to the high temperature of this work do not give a good agreement. Similarly extrapolations of the equations derived in this work to the low temperature of Scott do not give a good agreement. This is not surprizing since the vapour pressure equations used are of the types which can not safely be extrapolated to temperature ranges outside the range for which they were derived. The good agreement can be seen if the two sets of data are plotted on a single graph of Log P vs T^{-1}, it is gratifying to note that all the points lie on a common straight line as shown by Fig. (1).

The densities reported by Rutledge and Smith [12] when compared to the specific volumes reported in this work lie almost on the same curve of a plot of density *vs* temperature.

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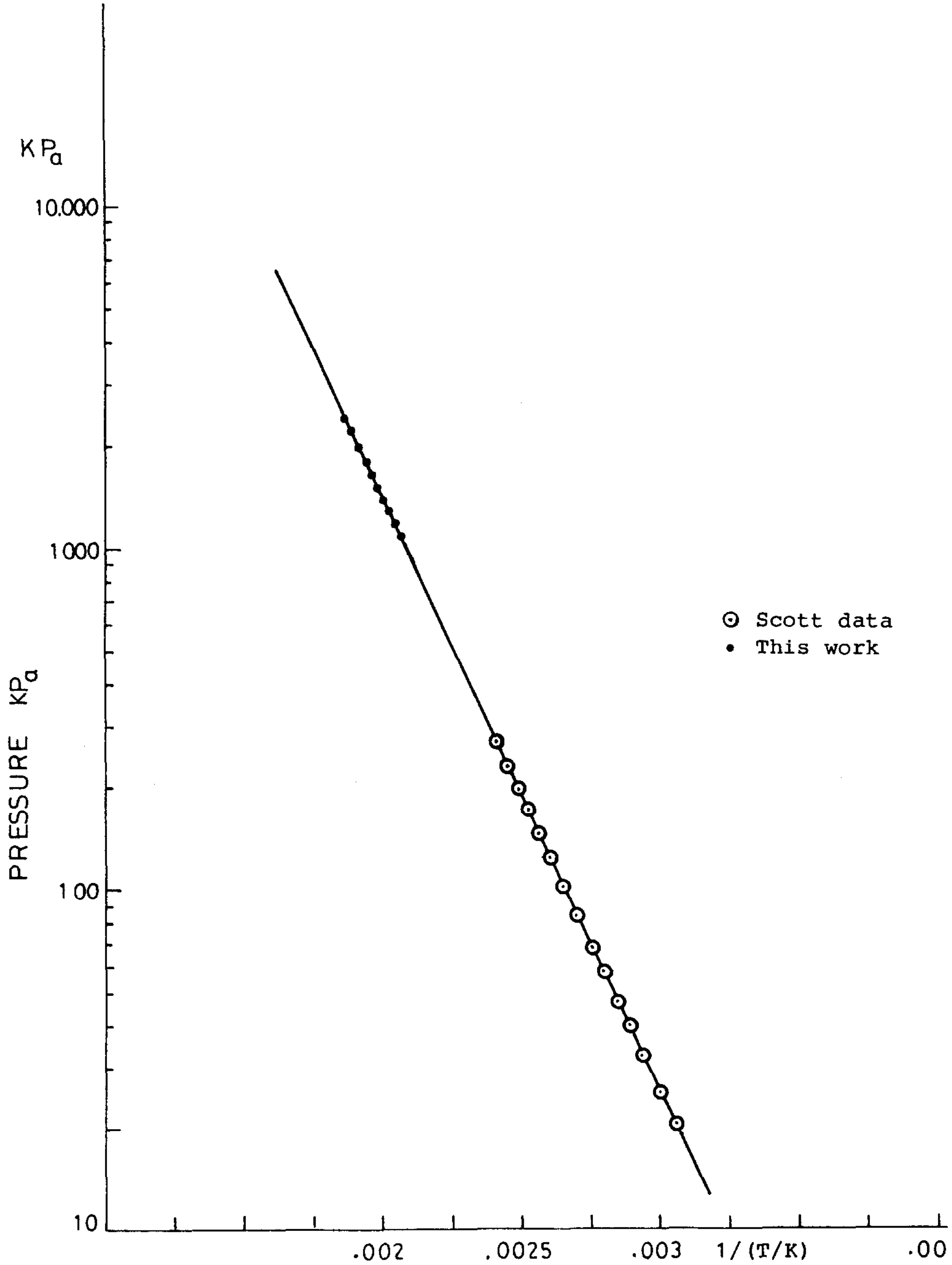

Fig. 1. Log. p vs, 1/T.

REFERENCES

1 A.H.N. Mousa, J. Fluor, Chem., 6 (1975) 221.

2 A.H.N. Mousa, J. Fluor, Chem., 8 (1976) 5

3 A.H.N. Mousa, J. Fluor, Chem., 8 (1976) 467

4 A.H.N. Mousa, J. Chem. Thermodynamics, 13 (1981) 201.

5 A.H.N. Mousa, J. Chem. Engineering Data, 26 (1981) 248.

6 A.H.N. Mousa, J. Fluor, Chem., 25 (1984) 165.

7 D. Ambrose, J.H. Ellender, J. Chem. Thermodynamics, 13 (1981) 901.

8 L.L. Burger, G.H. Cady, J. Am. Chem. Soc. 73 (1951) 4243.

9 V.E. Stiles, G.H. Cady, J. Am. Chem. Soc. 74 (1952) 3771.

10 G.A. Crowder, Z.L. Talor, T.M. Reed III, J.A. Young, J. Chem. Eng. Data 12 (1967) 481.

11 D.W. Scott, D.R. Douslin, J.F. Messerly, S.S. Todd, I.A. Hossenlopp, T.C. Kincheloe and J.P. McCullough, J. Am. Chem. Soc. 81 (1959) 1015.

12 G.P. Rutledge and W.T. Smith, Jr., J.Am. Chem. Soc., 75 (1953) 5762.