

Vapour Pressures of Some Liquids of Quasi-spherical Molecules Near Their Critical Points and the Applicability of the Principle of Corresponding States

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Abstract

Vapour pressures of some liquids of quasi-spherical molecules (CCl_4 , SiCl_4 and GeCl_4) near their critical points are reported. The deviations from the principle of corresponding states obeyed by the inert gases are calculated by using Rowlinson's analysis. The magnitudes of the deviations for the tetrachlorides studied are similar.

One of the assumptions made when current theories of liquid mixtures are applied is that both components obey the same principle of corresponding states. The inert gases, nitrogen, oxygen, methane and carbon monoxide obey almost the same principle of corresponding states within experimental error. There are relatively few experimental results to establish the behaviour of other quasi-spherical molecules.¹ Young has calculated deviations for the globular molecules, octamethylcyclotetrasiloxane² and the cycloalkanes.³ Dickinson and McLure have calculated the deviations of a number of dimethylsiloxane oligomers.^{4,5} It is of interest therefore to establish how other quasi-spherical molecules deviate from the principle of corresponding states obeyed by the inert gases (called 'simple corresponding states' hereafter). In this work we consider the Group 4 tetrachlorides as these form a simply related group of quasi-spherical molecules.

Experimental

The critical temperatures were measured by the sealed-tube technique described elsewhere.⁶ The vapour pressures and critical pressures were measured with apparatus similar to that described previously.² Some modifications of the apparatus and procedure were necessary for the studies on silicon tetrachloride and germanium tetrachloride because of their reaction with water vapour. Precautions were taken so that neither the compounds nor the apparatus in which they were studied came in contact with moist air throughout the experiment.

¹ Rowlinson, J. S., 'Liquids and Liquid Mixtures' (Butterworths: London 1969).

² Young, C. L., *J. Chem. Thermodyn.*, 1972, 4, 65.

³ Young, C. L., *Aust. J. Chem.*, 1972, 25, 1625.

⁴ Dickinson, E., and McLure, I. A., *J. Chem. Thermodyn.*, 1976, 8, 93.

⁵ Dickinson, E., and McLure, I. A., *J. Chem. Soc., Faraday Trans. 1*, 1974, 70, 2313.

⁶ Hicks, C. P., and Young, C. L., *Trans. Faraday Soc.*, 1970, 66, 1340.

Chemicals

Carbon tetrachloride was an analytical reagent grade sample obtained from B.D.H. Silicon tetrachloride and germanium tetrachloride were Ventron samples with stated purities of 99.999 mole %.

Results and Discussion

The vapour pressures in the reduced temperature range $0.88 < T/T^\circ \leq 1$ of carbon, silicon and germanium tetrachlorides are given in Table 1.

Table 1. Vapour pressures of carbon, silicon and germanium tetrachlorides

CCl ₄		SiCl ₄		GeCl ₄	
T/K	10 ⁻⁵ p/Pa ^{A,B}	T/K	10 ⁻⁵ p/Pa	T/K	10 ⁻⁵ p/Pa
478.8	15.38	455.4	17.28	492.2	16.71
483.0	16.38	459.9	18.59	496.2	18.12
498.9	18.58	464.8	19.79	499.8	18.91
495.3	20.07	469.1	21.30	503.3	20.01
498.7	21.27	475.3	23.60	506.2	21.11
504.6	22.57	473.6	24.41	509.5	22.31
508.1	23.57	482.3	26.31	513.9	23.41
510.5	24.57	486.6	27.61	516.9	23.91
512.2	25.67	488.5	28.11	520.7	24.80
515.6	26.47	490.5	29.12	525.4	26.50
519.0	27.57	493.6	29.82	528.7	28.11
524.5	29.47	495.7	30.82	532.6	29.00
528.4	31.47	497.8	32.12	537.6	31.20
531.6	32.77	500.6	33.33	541.9	32.61
536.2	34.56	504.9	35.24	545.6	34.90
540.6	36.96	508.1 ^C	35.93 ^C	553.2 ^C	38.61 ^C
543.4	38.06				
550.8	43.06				
556.6 ^C	45.16 ^C				

^A Corrected for variation in the earth's gravitational acceleration [979.979 gal (1 gal = 10⁻² m s⁻²) at Melbourne].

^B Estimated error $\pm 0.05 \times 10^5$ Pa in p .

^C Critical point.

Using the method of analysis described by Rowlinson^{7,8} we have calculated the deviation parameter, δ° , for some of the Group 4 tetrachlorides and tetramethyls. The vapour pressures which were used in the calculation of δ° have been reported for stannic tetrachloride,⁹ neopentane¹⁰ and tetramethylsilane.¹¹ The calculated values of δ° are as follows:

CCl ₄	SiCl ₄	GeCl ₄	SnCl ₄	C(CH ₃) ₄	Si(CH ₃) ₄
0.10	0.11	0.12	0.10	0.10	0.10

⁷ Rowlinson, J. S., *Trans. Faraday Soc.*, 1954, **50**, 647.

⁸ Cook, D., and Rowlinson, J. S., *Proc. R. Soc. London*, 1953, **219**, 405.

⁹ Young, S., *Sci. Proc. R. Dublin Soc.*, 1909, **12**, 374.

¹⁰ Beattie, J. A., Douslin, D. R., and Levine, S. W., *J. Chem. Phys.*, 1951, **19**, 948.

¹¹ Hicks, C. P., and Young, C. L., *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 122.

All the compounds deviate slightly from 'simple corresponding states' and obey, almost within experimental error, the same principle of corresponding states given by the equation proposed by Rowlinson with $\delta^e = 0.11$. We attempted to study tetramethyltin but suspect that this decomposes slightly near the critical point.

Acknowledgment

This work is part of a project, supported by the Australian Research Grants Committee, on the phase behaviour of mixtures.

Manuscript received 16 February 1977