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THE VAPOUR PRESSURES AND EXCESS FREE ENERGIES OF MIXING OF THE SYSTEMS  
HEXAFLUOROBENZENE-CARBON TETRACHLORIDE AND HEXAFLUOROBENZENE-  
PERFLUOROMETHYLCYCLOHEXANE

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SUMMARY

The vapour pressures of liquid mixtures of hexafluorobenzene with carbon tetrachloride and of hexafluorobenzene with perfluoromethylcyclohexane (tetradecafluoromethylcyclohexane) have been measured in the range of temperature 20-50 °C, in a static system. These have been used to obtain the excess free energies of the mixtures. Both mixtures show large positive deviations from thermodynamic ideality, and also show azeotropic behaviour.

INTRODUCTION

In a recent paper [1] we have reported some of the excess properties of mixing for the systems hexafluorobenzene-carbon tetrachloride and hexafluorobenzene-perfluoromethylcyclohexane, and have discussed these in relation to some theories of liquid mixtures. In this paper we present the experimental measurements of the vapour pressures together with more details of the obtaining of the excess free energies of mixing and derived quantities.

EXPERIMENTAL

A static manometric system was used to measure the vapour pressures of the pure components and of the liquid mixtures. The arms of the simple U-tube manometer were constructed from 'Pyrex' tubing of internal diameter 12 mm. To one arm was attached a small bulb in which the sample of liquid under investigation could be trapped by the mercury in the manometer.

The other arm was connected to a vacuum line which was evacuated to high vacuum when vapour pressures were being measured. At the bottom of the U of the manometer was a T-junction through which mercury could be admitted from a reservoir. Samples of liquid were introduced to the manometer bulb from the vacuum line by distillation through the U-tube of the manometer whilst the mercury was withdrawn from it. The whole manometer system was immersed in water contained in a large tank (of capacity 500 l) fitted with windows to allow the viewing of the manometer. To ensure uniformity of the temperature of the water within the tank, the water was circulated by two pumps. The water was heated by heating elements immersed in the tank and operated by a thermo-regulator. A copper coil, for the circulation of cold water, was also immersed in the tank. This facilitated the regulation of the temperatures below 35 °C. Temperatures were measured using thermometers certified by the National Physical Laboratory, and showed a maximum fluctuation of  $\pm 0.004$  °C at any set temperature.

A thoroughly degassed sample, either of pure component or of a mixture, was distilled into the cooled manometer bulb under high vacuum. There it was allowed to melt, and about 20% of the sample was distilled off under vacuum (at a low temperature) before mercury was introduced into the manometer to enclose the remainder of the sample. In the cases of mixtures the boiling-off procedure may change the composition of the mixture. Because of this the compositions of mixtures were determined after the pressures had been measured. After measurement of the vapour pressures the mixture enclosed in the manometer bulb was frozen in liquid air before removing the mercury from the arms of the manometer. The mixture was then removed by distillation, distilled *in vacuo*, and its composition was determined by refractometry.

Values of the vapour pressures were corrected to the standard value of g and to 0 °C, and are reported here as p/Torr (1 Torr = 101 325/760 Pa).

### Materials

Hexafluorobenzene. Two batches of hexafluorobenzene were used. Both were supplied by the Imperial Smelting Corporation (Avonmouth). The first batch, which was prepared from normal commercial material,

was purified by fractional crystallisation. From freezing behaviour and by gas chromatography, its purity appeared greater than 99.9%. The second batch was a highly purified anaesthetic grade of purity greater than 99.91%. The vapour pressures of the two batches were in excellent agreement with published values (see below).

Carbon Tetrachloride. Two batches of material were used. Both were prepared from 'Analar' grade carbon tetrachloride using a purification procedure given by Weissberger [6], followed by fractional distillation. The vapour pressures of the two batches agreed well with one another and with published values (see below).

Perfluoromethylcyclohexane. The material was prepared in this Department by Dr A. E. Pedler from the products of fluorination of methylbenzene with cobalt trifluoride. The crude perfluoromethylcyclohexane was purified by distillation (at 40 °C) of the azeotrope which it forms with acetone (propan-3-one). The azeotrope was washed with water to remove the acetone. The perfluoromethylcyclohexane was separated from the aqueous solution, dried ( $MgSO_4$ ) and distilled through a fractionating column. The constant boiling fraction was collected for use. No impurity could be detected using gas chromatography. The vapour pressures were consistent with published values (see below).

## RESULTS

### Vapour pressures of pure components

The vapour pressures of the pure substances were fitted to Antoine equations:

$$\log(p/\text{Torr}) = A - B/(C + t/^\circ\text{C})$$

using the least square procedure [12,14].

A summary of the vapour pressures measured for the two batches of hexafluorobenzene is shown in Table 1. These are compared with the values given by (or interpolated from) work of other authors. The concordance between the measurements for the two samples and with the values reported by Counsell *et al.* [2], and by Gaw and Swinton [3], is good and justifies the experimental procedure. The agreement with the

TABLE 1.

Vapour Pressures of  $C_6F_6$ .

t/°C	p/Torr				
	Counsell <i>et al.</i> [2]	Gaw and Swinton [3]	Findlay [4]	This work Sample 1    Sample 2	
20	65.75*		66.22	65.60	65.62
25	84.42*		84.88	84.27	84.29
30	107.29*	107.34	107.68	107.14	107.15
35	135.05*		135.28	134.91	134.92
40	168.46	168.45	168.39	168.34	168.35
45	208.34		207.82	208.28	208.29
50	255.62	255.64	254.39	255.61	255.63

\* extrapolated beyond experimental range.

values of Findlay [4] is less good, but satisfactory. The latter results are probably less precise than the others quoted. The values reported by Patrick and Prosser [10] are now recognised as less precise.

The results obtained for carbon tetrachloride (Table 2) need some comment. For many years the results reported by Young [13] for the vapour pressures of carbon tetrachloride have been widely accepted, even in selected compilations [12]. The present results are more consistent with those reported more recently by Marsh [11], by Barker *et al.* [5], and by McGlashan *et al.* [16]. Our results, if extrapolated, are consistent with values reported by Smith and Bonner [7]. The values given by Young [13] differ from more recent values by 2-3 mmHg at 50 °C, and by about 0.5 mmHg at 20 °C. There is good reason, therefore, to prefer values close to those reported here.

The coefficients of the Antoine equations fitted to the combined results for the respective substances are as follows:

Hexafluorobenzene:            A = 7.018420    B = 1218.218    C = 214.208  
(n = 60,  $\sigma$  = 0.03)

Carbon tetrachloride:        A = 8.866834    B = 1201.934    C = 224.876  
(n = 57,  $\sigma$  = 0.04)

Perfluoromethylcyclohexane: A = 6.786720    B = 1113.194    C = 208.716  
(n = 55,  $\sigma$  = 0.04)

$$(\sigma^2 = \Sigma(\Delta p)^2 / (n-3), \text{ where } n \text{ is the number of observations})$$

TABLE 2.

Vapour pressures of  $\text{CCl}_4$ 

t/°C	p/Torr			
	McGlashan [16]	Marsh [11]	Barker <i>et al.</i> [5]	This work Sample 1      Sample 2
20		91.13		90.89      90.87
25	113.96	114.21		113.95      113.96
30		141.87		141.60      141.62
35		174.76		174.49      174.53
40	213.34	213.60	213.42	213.35      213.39
45		259.12	258.84	258.93      258.95
50		312.14	312.23	312.04      312.00

TABLE 3.

Vapour pressures of  $\text{C}_6\text{F}_{11}\text{C F}_3$ 

t/°C	p/Torr		
	Rowlinson [8]	Good [17]	This work Sample 1      Sample 2
25	107.05	105.80*	106.78      106.75
30	132.96	133.04*	132.74      132.77
35		165.75	165.45      165.52
40	205.58	204.69	204.41      204.52
45		250.71	250.45      250.57
50	304.48	304.71	304.44      304.58

\* Extrapolated beyond range of observation

The vapour pressures of two batches of perfluoromethylcyclohexane are in good agreement with one another and with values reported previously [8] (Table 3).

Vapour pressures of mixtures

Tables 4 and 5 present the vapour pressures of the mixtures, the number (n) of measurements and their deviations ( $\sigma$ ) from the equations to which they have been fitted.

Ignoring a small term for the volume change on mixing the molar excess free energy of mixing to give a liquid mixture containing mole fractions  $x_1$  and  $x_2$  of 1 and 2 is [12]

$$g^E = x_1 RT \ln \gamma_1 + x_2 RT \ln \gamma_2$$

where  $\gamma_1, \gamma_2$ , are the activity coefficients of components 1 and 2. Also

$$RT \ln \gamma_1 = RT \ln (y_1 p / x_1 p_1^\circ) - (p - p_1^\circ)(V_1^\circ - B_{11}) + 2p(\delta B)_{12} y_2^2$$

where  $y_1$  and  $y_2$  are the mole fractions of 1 and 2 in the vapour,  $p$  the total vapour pressure at equilibrium,  $p_1^\circ$  the saturation vapour pressure, and  $V_1^\circ$  the molar volume, of pure liquid 1, and  $B_{11}$  is the second virial coefficient of 1.  $(\delta B)_{12} = B_{12} - \frac{1}{2}(B_{11} + B_{22})$ , where  $B_{12}$  is the cross-virial coefficient and  $B_{22}$  is the virial coefficient of 2. An analogous expression holds for  $RT \ln \gamma_2$ . In the subsequent working  $(\delta B)_{12}$  was set equal to zero. Although not strictly correct [15], this assumption should cause little relative error in the values of  $g^E$  that are obtained.

Compositions of the vapour were not measured. Vapour pressures were treated by the method of Barker [9]. Setting

$$g^E = x_1 x_2 [A_g + B_g (x_1 - x_2) + C_g (x_1 - x_2)^2] \text{ then}$$

$$RT \ln \gamma_1 = x_2^2 [A_g + B_g (3 - 4x_2) + C_g (5 - 16x_2 + 12x_2^2)]$$

A similar expression holds for  $RT \ln \gamma_2$ . The Scatchard parameters,  $A_g$ ,  $B_g$  and  $C_g$ , are obtained by iteration, so as to give a best fit, in the least squares sense, to the vapour pressures for mixtures at a temperature of interest.

Second virial coefficients of hexafluorobenzene were calculated from the expression of Counsell *et al.* [2] to represent experimental results. Pitzer's equation for second virial coefficients in terms of the reduced temperature ( $T_r = T/T_c$ ), critical temperature ( $T_c$ ), critical pressure ( $p_c$ ), and acentric factor, ( $\omega$ ), obtainable from reduced vapour pressures, ( $p/p_c$ ), of the substance is

$$B_{p_c} / RT_c = (0.1445 + 0.073\omega) - (0.330 - 0.46\omega) T_r^{-1} - (0.1385 + 0.50\omega) T_r^{-2} - (0.0121 + 0.097\omega) T_r^{-3} - 0.0073\omega T_r^{-8}$$

Calculations of  $B$  for hexafluorobenzene, ( $\omega = 0.4$ ), are in poor agreement with experimental results. A larger value of  $\omega$ , (0.6), gives better agreement.

TABLE 4.

Experimental results for mixtures of  $C_6F_6$  +  $CCl_4$ .

$x(C_6F_6)$	$t/^\circ C$	p/Torr							
		20	25	30	35	40.08	45	49.92	
0.095	93.16	116.66	145.17	179.24	219.68	265.83	319.40		
0.201	93.75	117.60	145.98	180.23	221.19	268.10	322.27		
0.318	92.20	115.80	144.19	178.24	219.38	267.76	320.03		
0.427	90.81	114.13	142.04	175.81	216.21	262.61	316.19		
0.525	87.76	110.39	137.20	169.85	210.55	255.32	308.88		
0.662	83.59	104.90	131.38	163.40	201.80	245.70	297.08		
0.700	81.35	103.09	129.33	160.97	199.15	242.56	293.85		
0.824	75.04	95.66	120.44	150.50	186.92	228.81	278.14		
0.938	69.74	88.72	112.28	141.13	176.22	216.66	264.73		
$n$	38	48	42	41	43	43	40		
$\sigma/Torr$	0.22	0.29	0.38	0.34	0.35	0.46	0.46		

$$\sigma^2 = \frac{\sum (\Delta p)^2}{(n-3)}$$

TABLE 5  
 Experimental results for mixtures of  $C_6F_6$  +  $C_6F_{11}C F_3$

$x(C_6F_6)$	p/Torr									
	t/°C	20	25	30	35	40	45	50		
0.077		87.95	110.95	138.94	172.28	212.22	259.71	314.61		
0.153		90.12	113.23	141.94	176.18	217.23	265.35	321.55		
0.264		-	116.14	145.02	180.27	221.86	270.53	327.81		
0.338		91.35	115.65	144.87	180.27	222.52	271.50	329.33		
0.442		90.66	114.92	144.32	179.83	221.90	271.26	329.12		
0.518		90.28	114.11	144.10	178.21	219.67	268.95	326.20		
0.590		88.73	112.28	141.15	175.90	217.41	265.77	322.64		
0.707		85.82	108.62	137.98	171.04	210.69	258.05	313.14		
0.850		79.78	101.87	127.90	159.10	196.22	239.68	291.20		
0.906		75.32	96.14	120.83	152.32	188.23	231.61	282.05		
n		25	33	35	33	32	32	35		
$\sigma$ /Torr		0.33	0.36	0.50	0.25	0.21	0.46	0.55		

$$\sigma^2 = \Sigma(\Delta p)^2 / (n-3)$$



Second virial coefficients of carbon tetrachloride were taken from values given by McGlashan *et al.* [16] which are about 5% greater than estimates from Pitzer's equation, using  $\omega = 0.19$ , from vapour pressures. Second virial coefficients of perfluoromethylcyclohexane have been measured. Estimates used were ( $\text{cm}^3\text{mol}^{-1}$ ): -3400, -3200, -3100, -2900, -2800, -2600 and -2500, at temperatures ( $^{\circ}\text{C}$ ): 20, 25, 30, 35, 40, 45 and 50, respectively. These are larger by 10-20% than values from Pitzer's relationship. The corrections were based upon experience with hexafluorobenzene. There are doubts about these values. Since the mixtures show large deviations from thermodynamic ideality, the effects of uncertainties in the virial coefficients will be relatively small, but not negligible. (The accepted critical pressure of perfluoromethylcyclohexane (23 atm. [8]) may be too large. Taken with the vapour pressures reported here, this critical pressure requires that  $\omega = 0.49$ . If the critical pressure were 18 to 20 atm., smaller values of  $\omega$ , (0.40 to 0.43), would be required. The different combinations of values, when used in Pitzer's equation, give estimates of the second virial equation which may differ by up to about 15%.)

Molar volumes of the pure liquids were determined from densities measured in these laboratories, which were consistent with values in the literature ( $\text{C}_6\text{F}_6$  [2],  $\text{CCl}_4$  [16],  $\text{CF}_3\text{C}_6\text{F}_{11}$  [8]). Values of  $p_c$  and  $T_c$  for use in Pitzer calculations were taken from the references, as follows: for  $\text{C}_6\text{F}_6$  [2], for  $\text{CCl}_4$  [12], for  $\text{CF}_3\text{C}_6\text{F}_{11}$  [8].

Values of  $A_g$ ,  $B_g$  and  $C_g$ , obtained by application of Barker's method to the experimental results, are given in Tables 6 and 7.

TABLE 6  
Scatchard parameters,  $A_g$ ,  $B_g$ ,  $C_g$  ( $\text{J mol}^{-1}$ ) for mixtures of  $\text{C}_6\text{F}_6 + \text{CCl}_4$

$t/^{\circ}\text{C}$	$A_g$	$B_g$	$C_g$
20.00	1114	-365.1	217.6
25.00	1080	-424.9	71.6
30.00	1038	-408.8	89.2
35.00	1034	-410.2	86.1
40.08	989.3	-409.5	121.6
45.00	969.2	-400.5	152.1
49.92	946.4	-380.6	132.2

TABLE 7

Scatchard parameters,  $A_g$ ,  $B_g$ ,  $C_g$  ( $/J \text{ mol}^{-1}$ ) for mixtures of  $C_6F_6 + CF_3C_6F_{11}$

$t/^\circ\text{C}$	$A_g$	$B_g$	$C_g$
20.00	1882	28.0	398.0
25.00	1824	69.4	337.4
30.00	1811	112.4	160.5
35.00	1762	149.0	184.7
40.00	1713	103.6	83.0
45.00	1668	94.7	49.5
50.00	1621	72.0	42.2

Values of  $g^E$  calculated from the Scatchard coefficients at 25 °C and 50 °C were given in the earlier paper [1], together with values of the excess heat of mixing,  $h^E$ , and  $Ts^E$ , where  $s^E$  is the excess entropy of mixing obtained by taking account of the variation of  $g^E$  with temperature. The significance of these quantities has been discussed [1].

Both mixtures show positive deviations from thermodynamic ideality. They also display positive azeotropy at the temperatures studied. The self-consistency of the derived enthalpies of mixing may be confirmed from observations upon the azeotropic behaviour. The variation of the vapour pressures of azeotropes with temperature obeys the Clapeyron equation:

$$dp_{az}/dT = \Delta H_{v,az}/T \Delta V$$

where  $\Delta H_{v,az}$  is the heat of vaporization of the azeotrope, and  $\Delta V$  is the change in volume accompanying vaporization. The heat of vaporization

of the azeotrope is related to the excess heat of mixing, ( $h_{az}^E$ ), to give a mixture of the azeotropic composition. To an adequate approximation

$$h_{az}^E = x_{1,az} \Delta H_{v,1} + x_{2,az} \Delta H_{v,2} - \Delta H_{v,az}$$

The heats of vaporization of the azeotropes were calculated from Antoine equations fitted to the appropriate vapour pressures. Since the vapour pressures were obtained by interpolation of vapour pressures of the chosen mixtures, the Antoine equations are less precise than those fitted to pure substances. The Antoine coefficients are, for the mixture  $C_6F_6$ - $CCl_4$ :  $A = 6.93072$ ,  $B = 1214.97$ ,  $C = 224.93$ ; and for the mixture  $C_6F_6$ - $CF_3C_6F_{11}$ :  $A = 6.85075$ ,  $B = 1141.73$ ,  $C = 213.53$ .

Values of  $x_{1,az}$  were estimated graphically from the ratios of the activity coefficients,  $\gamma_1$  and  $\gamma_2$ , as a function of composition, using the condition,  $p_1^o/p_2^o = \gamma_2/\gamma_1$ , for azeotropy, where  $p_1^o$  and  $p_2^o$  are the vapour pressures of the pure components. For this purpose  $\gamma_1$  and  $\gamma_2$  were calculated using the Scatchard coefficients reported in Tables 9 and 10. For the mixture  $C_6F_6$ - $CCl_4$ , the azeotropic composition is given by

$$x(C_6F_6) = 0.3146 + 1.520 \times 10^{-3} t/^\circ C$$

and for the mixture  $C_6F_6$ - $CF_3C_6F_{11}$ , the azeotropic composition is given by

$$x(C_6F_6) = 0.3126 + 1.170 \times 10^{-3} t/^\circ C.$$

For the first mixture,  $x(C_6F_6)$  was 0.173 at 25 °C, and  $h^E$  from observations on the azeotrope was 500 J mol<sup>-1</sup>, compared with 460 J mol<sup>-1</sup> from the values of  $g^E$  using the Scatchard parameters. At 50 °C the corresponding quantities are 0.2108, 555 and 520 J mol<sup>-1</sup>. For the second mixture at 25 °C,  $x(C_6F_6)$  is 0.3418,  $h^E$  from azeotropic behaviour 1140 J mol<sup>-1</sup>, and from the Scatchard coefficients, 1080 J mol<sup>-1</sup>. The corresponding quantities are 0.3720, 1090 and 1110 J mol<sup>-1</sup>, at 50 °C.

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