



precautions were taken to avoid photochemical change as the laboratory was illuminated only by subdued artificial lighting. It was necessary to eliminate traces of non-condensable gases (nitrogen, oxygen, inert gases) and carbon dioxide, because of their effect on the density. 1 Part in 2500 of nitrogen in the cyclohexane was equivalent to a 5% error in the virial coefficient. The materials were repeatedly distilled from trap to trap at  $-180^{\circ}$  and  $-80^{\circ}$  with frequent evacuation on the diffusion pump. No permanent gas could be detected at the tip of a 0.1 mm. bore tube when about 2 ml. of the vapour was compressed by an advancing surface of the condensed vapour (Young's test).

*Nitrogen.* This was a special sample in a cylinder provided by The British Oxygen Co. Ltd. from liquid-air fractionation. Details of its composition are given by Reeves and Whytlaw-Gray.<sup>2</sup>

*Determination of the Balancing Pressures.*—The gaseous pressures bringing the balance to equilibrium were determined by a Rayleigh manometer in which the uncertain setting of a cathetometer cross-wire on the vertex of a 40 mm. diam. mercury meniscus was replaced by a series of operations in which mercury surfaces were set to tungsten reference points. The reproducibility of the pressure measurements in this fashion was considerably better than the 0.01 mm. of conventional cathetometry. The gases and vapours were contaminated by mercury vapour because they were handled by mercury cut-offs or similar methods. To maintain a mercury-free condition in the balance case the entrance line was protected by a trap containing gold foil and granules and the interior of the balance case, with the exception of the portions required for observation, was covered with fired-on gold film. The balance case was never kept evacuated overnight, but when left unattended was always filled with nitrogen to near the balancing pressure to reduce the diffusion of mercury towards the balance.

If  $R$ ,  $T$ ,  $M_1$ , and  $M_2$  are regarded as exactly specified constants, then by numerical substitution into eqn. (2) it can be seen that the absolute density of the mercury, the gravitational and altitude corrections, and the absolute value of the length scale of the manometric system do not warrant consideration. In the conditions of the present experiments it is believed that the quantity  $(M_2P_2/M_1P_1)$ , which is necessarily close to unity, is known to about 0.0001, corresponding to an error of some 2% on the final value of  $B$ .

*The Microbalance and Adsorption.*—The balance used was of greater sensitivity than that employed for benzene, partly because a larger buoyancy bulb was used, and partly because of a more critical adjustment of the centre of gravity and the use of suspension fibres of smaller diameter. [Time of swing, 24 sec. Weight sensitivity,  $1.038 \times 10^{-5}$  g./mm. of point movement. Pressure sensitivity, 0.0231 mm. of point movement/0.01 mm. of nitrogen pressure change.] With the optical system used, the balance could be adjusted to within 0.003 mm. The limiting factors in the manipulations were the determination of the balancing pressure and the inability to define and position the balance relative to an arbitrary zero.

Since the silica surface of the balance acquires an equilibrium state of adsorbed vapour whose mass contributes to the displacement torques, correction to the hypothetical state of no adsorption is required. The balance and bulb used in the density work were converted into an adsorption balance by puncturing the bulb and readjusting ( $\pm 2 \times 10^{-5}$  g.) the silica weights, so that the inner and the outer surface of the bulb acted as the adsorbing area when exposed to various pressures and temperatures of the experimental vapours. Some isotherms so determined have been reported.<sup>3</sup> The deflection of the density balance due to adsorption on the outer surface of the closed bulb is assumed to be half that of the deflection of the adsorption balance by the adsorption on the open bulb under comparable vapour conditions. The following well-defined corrections (to be subtracted from the observed balancing pressure) were obtained: cyclohexane, 0.022 mm. at  $22^{\circ}$ , 0.013 mm. at  $35^{\circ}$ ; carbon disulphide, 0.003 mm. at  $22^{\circ}$ , 0.001 mm. at  $35^{\circ}$ ; carbon tetrachloride, 0.011 mm. at  $22^{\circ}$ .

*Results.*—The Table summarises the accepted observations on each substance. Each pressure entry represents a separate filling and balancing operation. From the quoted mean pressures and pressure ratios, together with the standard values of the atomic weights C, 12.011; H, 1.0080; Cl, 35.457; N, 14.008; S, 32.066; the gas constant  $R$ , 82.057 cm.<sup>3</sup> atm. ( $T$  mole<sup>-1</sup>); and the virial coefficients of nitrogen,  $-5.3$  cm.<sup>3</sup>/mole at  $22^{\circ}$  and  $-2.9$  cm.<sup>3</sup>/mole at  $35^{\circ}$  C, the following final values for the second virial coefficients (cm.<sup>3</sup>/mole) can be deduced: cyclohexane  $-1600$  at  $22^{\circ}$ ,  $-1515$  at  $35^{\circ}$ ; carbon disulphide  $-646$  at  $22^{\circ}$ ,  $-582$  at  $35^{\circ}$ ; carbon

<sup>2</sup> Reeves and Whytlaw-Gray, *Proc. Roy. Soc.*, 1955, A, **232**, 173.

<sup>3</sup> Remington and Whytlaw-Gray, *Trans. Faraday Soc.*, in the press.

tetrachloride — 1283 at 22°. (These values include the necessary Rayleigh correction for the volume change of the buoyancy bulb when exposed to various pressures.)

Com- pound	Temp. (° c)	Nitrogen pressure (mm. Hg at 0°)	Vapour pressure (mm. Hg at 0°) *	Ratio	Com- pound	Temp. (° c)	Nitrogen pressure (mm. Hg at 0°)	Vapour pressure (mm. Hg at 0°) *	Ratio	
C <sub>6</sub> H <sub>12</sub>	22	164-954	54-647	3-01852	CS <sub>2</sub>	35	172-184	63-227	2-72324	
		164-952	54-643	3-01870			172-159	63-207	2-72375	
		164-917	54-626	3-01900			172-134	63-206	2-72340	
		164-896	54-634	3-01818			172-147	63-226	2-72275	
		164-931	54-644	3-01826			172-219	63-251	2-72277	
	(Mean	164-930	54-639	3-01853)		(Mean	172-169	63-223	2-72318)	
	35	172-133	57-036	3-01798		CCl <sub>4</sub>	22	164-995	29-988	5-50203
		172-124	57-038	3-01770				164-998	29-980	5-50359
		172-127	57-030	3-01819				164-993	29-983	5-50287
		172-051	57-024	3-01716				164-939	29-979	5-50181
	172-109	57-032	3-01776)	165-034	29-985			5-50390		
CS <sub>2</sub>	22	164-968	60-575	2-72338	(Mean		164-999	29-985	5-50279)	
		164-972	60-561	2-72408						
		164-926	60-567	2-72305						
		164-975	60-567	2-72386						
		164-986	60-574	2-72372						
(Mean	164-965	60-569	2-72362)							

\* Includes adsorption correction.

Judged from the self-consistency of the separate ratios there appears to be good ground for assessing the error in  $B$  as about 2% .

#### DISCUSSION

*Comparison with Other Work.*—cycloHexane. The present values are consistent ( $\pm 100$  cm.<sup>3</sup>/mole) with the data in the range 42—75° c by Waelbroeck<sup>4</sup> and 50—130° c by Lambert, Roberts, Rowlinson, and Wilkinson.<sup>5</sup> The precision of all the data is limited and an exhaustive re-examination of cyclohexane over a wide temperature range is urgently required. With a different balance, probably less reliable, we obtained —1523 cm.<sup>3</sup>/mole at 35°, but —1663 at 22°, from 18 ratio determinations of the same self-consistency as those shown in the Table.

*Carbon disulphide.* Bottomley and Reeves,<sup>6</sup> using our material, determined the second virial coefficient at several temperatures with a precision differential compressibility apparatus and quote —849 and —748 cm.<sup>3</sup>/mole at 22° and 35°. It is impossible to disguise the gross discrepancy between the current work and these figures. Casado, Massie, and Whytlaw-Gray<sup>7</sup> by the microbalance method found  $B$  at 22° to be —658 cm.<sup>3</sup>/mole. The direct compressibility method is relatively insensitive to the absolute purity of the substance: 5% of nitrogen is required to produce a 5% error in  $B$ , in contrast to 0.04% in the microbalance method. It is possible that the samples are not free from carbon dioxide, but we have not yet devised a satisfactory chemical method of removing it.

*Carbon tetrachloride.* Casado, Massie, and Whytlaw-Gray<sup>7</sup> with the microbalance method gave  $A_2$  as 0.0457 at 22°, and hence  $B = -1107$  cm.<sup>3</sup>/mole. Lambert, Roberts, Rowlinson, and Wilkinson<sup>5</sup> studied the virial coefficient between 44° and 80°, but commented that it was impossible to make measurements with carbon tetrachloride above 80° c, as the vapour attacked the mercury in the burette, and that the measurements at lower temperatures may be in error for the same reason. Francis and McGlashan<sup>8</sup> carried out further measurements at 42—70°, obtaining results largely concordant with those of

<sup>4</sup> Waelbroeck, *J. Chim. phys.*, 1957, **54**, 710.

<sup>5</sup> Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113.

<sup>6</sup> Bottomley and Reeves, preceding paper.

<sup>7</sup> Casado, Massie, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1952, *A*, **214**, 466.

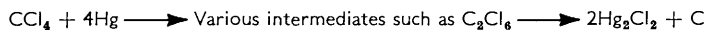
<sup>8</sup> Francis and McGlashan, *Trans. Faraday Soc.*, 1955, **51**, 593.

Lambert and his co-workers, but markedly divergent at the higher temperatures from the earlier work of Eucken and Meyer.<sup>9</sup> The value suggested by an extrapolation of the results at 40—80° is  $-1780 \text{ cm.}^3/\text{mole}$ .

*Static Electricity.*—The involuntary generation of static electricity by the movement of the gases in the apparatus and the mercury surfaces in the various cut-offs causes considerable difficulty because the microbalance, being of highly insulating silica, acquires and retains charges for long periods and assumes spurious equilibria due to the electrical interactions. To minimise the errors from this cause, the gas, vapour, and mercury manipulations were carried out very slowly and the approach of the balance to equilibrium was followed for several hours before a final setting was attempted. The gold-plated interior of the balance case provided a high conductance and a large capacitance, but did not prevent trouble with static electricity.

Various suggestions have been made to reduce the trouble: a small radioactive source in the balance case to maintain an ionising atmosphere; radioactive  $^{203}\text{Hg}$  at low concentration in the ordinary mercury and therefore in the gas phase; the provision of nearly transparent but electrically conducting films on all the glass interior surfaces by either chemical deposition of lead sulphide or treatment when hot with stannous chloride fumes. Trial experiments along these lines have been made.

With carbon tetrachloride vapour<sup>10</sup> there is also a chemical change due to the rupture of  $\text{CCl}_4$  in the presence of mercury:



Manifestations of this reactivity are seen in annular "tide-marks" in mercury manometers and the tendency of McLeod gauges to show "sticking mercury." Bottomley and Reeves<sup>6</sup> were unable to measure the virial coefficient of carbon tetrachloride over mercury because of this interference. The loss of vapour in an expansion amounted to 20—30% of the effect sought. This behaviour casts doubt on the accuracy of the measurements reported by Lambert *et al.* and Francis and McGlashan.

*General Discussion.*—The microbalance values for the present three substances, whilst evidently of the correct magnitude, do not warrant reliability as great as that suggested by the reproducibility of the balancing ratios. Two factors play a considerable part in this indefiniteness, the purity of the material, and the adsorption corrections. Because of the extraordinary sensitivity of the density balance, the purification of the working materials becomes a major research in itself, and we suggest that such discrepancies as do occur between different balances and different workers represent minor differences in purity of the working materials rather than any defect of the method as such. With carbon disulphide the isotopic variation of sulphur may be significant because of its effect on the assumed molecular weight. Though every care has been taken in the assessment of the adsorption effects, it still remains possible that the basic assumption, equal adsorption on the inner and outer surfaces of the silica bulb, is to some degree unjustified. Given adequate time and facilities there is no reason to doubt that the density balance method could be made considerably more reliable: as a practical proposition the direct measurement method, when it is carried out with suitable refinements to obtain a precision of  $10 \text{ cm.}^3/\text{mole}$  or better, is superior. With benzene, which has been examined<sup>11</sup> by both microbalance and compressibility methods in several laboratories, there is substantial agreement amongst all the data.

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<sup>9</sup> Eucken and Meyer, *Z. phys. Chem.*, 1929, B, 5, 452.

<sup>10</sup> Bottomley and Reeves, *Trans. Faraday Soc.*, 1957, 53, 1455.

<sup>11</sup> Bottomley, Reeves, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1958, A, 246, 504.