775. The Virial Coefficients of cycloHexane, Carbon Disulphide, and Carbon Tetrachloride Vapours.

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The densities of the vapours of *cyclohexane*, carbon disulphide, and carbon tetrachloride relative to that of nitrogen have been determined by the silicasuspension microbalance. The virial coefficients have been deduced by a comparison between the observed density and that calculated from the atomic weights. Pressures were measured on a manometer with an internal reference grid: experimentally determined corrections for adsorption were applied. Purification of the materials limited the precision.

THE microbalance technique for the determination of virial coefficients previously used for benzene¹ has been applied to three other vapours. The separate pressures are determined at which the vapour and nitrogen cause a quartz-fibre suspension microbalance to take up a particular balancing position equivalent to a definite density (g./ml.). If the equation of state for the vapour be represented by

[where P is the pressure (atm.), V the volume (cm.³) occupied by 1 mole, and T the absolute temperature], then the corresponding density is $M/(\mathbf{R}T/P + B)$ g./ml. For two different gases (1 and 2) brought to the same density

$$B_2 = \frac{\mathbf{R}T}{P_2} \left[\left(\frac{M_2 P_2}{M_1 P_1} \right) \left(1 + \frac{P_1 B_1}{\mathbf{R}T} \right) - 1 \right] \quad . \quad . \quad . \quad (2)$$

so that the virial coefficient of the vapour (B_2) can be deduced from the exact molecular weights $(M_1 \text{ and } M_2)$, the balancing pressures $(P_1 \text{ and } P_2)$ (atm.) and the virial coefficient of the reference gas, B_1 . Though the determination of the virial coefficient is thus reduced to the measurement of two pressures, there remain formidable difficulties of technique.

EXPERIMENTAL

Materials.—cyclo*Hexane.* Used as obtained from Bureau International des Étalons physico-chimiques, Brussels.

Carbon disulphide. "AnalaR" material was repeatedly shaken with clean mercury until no further darkening of the interface occurred, then distilled from mercury. The product was refluxed over phosphoric oxide and mercury in nitrogen and then slowly fractionated through a Dixon-ring column. The middle fraction was selected, though the boiling point was constant $(\pm 0.05^\circ)$ throughout.

Carbon tetrachloride. Chlorine from a cylinder was bubbled into the "AnalaR" reagent until a strong yellow colour was present; the system was irradiated by direct sunshine for 8 hr. and left for 100 hr. in the dark. Excess of chlorine was removed with 10% potassium hydroxide, and then distilled water. The sample was then refluxed with 10% potassium hydroxide for several hours in a nitrogen atmosphere, washed with distilled water, and dried (Na₂SO₄, then P₂O₅). Finally it was fractionated from phosphoric oxide. The middle eight cuts boiled at 76.5° \pm 0.05°, and gave indistinguishable refractive indices on a Pulfrich refractometer (\pm 0.00002).

The purified samples were individually admitted to the nitrogen-purged lines of the apparatus, frozen in liquid nitrogen, and sealed with precautions to avoid contamination. For precautions with carbon disulphide see preceding paper (their neglect led to loss of the sample used in the density work with which it had been intended to determine the isotopic composition). The samples were desiccated *in situ* by phosphoric oxide. No special

¹ Bottomley, Remmington, and Whytlaw-Gray, Proc. Roy. Soc., 1958, A, 246, 514.

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 *cyclo*hexane was equivalent to a 5% error in the virial coefficient. The materials were repeatedly distilled from trap to trap at -180° and -80° 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.²

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 \mathbf{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, 1.038×10^{-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 $(\pm 2 \times 10^{-5} \text{ g.})$ 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.³ 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: *cyclo*hexane, 0.022 mm. at 22°, 0.013 mm. at 35°; carbon disulphide, 0.003 mm. at 22°.

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.³ atm. (T mole⁻¹); and the virial coefficients of nitrogen, -5.3 cm.³/mole at 22° and -2.9 cm.³/mole at 35° c, the following final values for the second virial coefficients (cm.³/mole) can be deduced: cyclohexane -1600 at 22°, -1515 at 35°; carbon disulphide -646 at 22°, -582 at 35°; carbon

² Reeves and Whytlaw-Gray, Proc. Roy. Soc., 1955, A, 232, 173.

³ Remmington 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 C ₆ H ₁₂	Temp. (° c) 22 (Mean 35 (Mean 22	Nitrogen pressure (mm. Hg at 0°) 164:954 164:952 164:917 164:896 164:930 172:133 172:124 172:127 172:051 172:051 172:109 164:968 164:972	Vapour pressure (mm. Hg at 0°) * 54.647 54.643 54.626 54.634 54.639 57.036 57.038 57.038 57.038 57.032 60.575 60.561	Ratio 3.01852 3.01870 3.01900 3.01818 3.01826 3.01853) 3.01798 3.01770 3.01819 3.01716 3.01776) 2.72338 2.72408	Com- pound CS ₂ CCl ₄	Temp. (° c) 35 (Mean 22	Nitrogen pressure (mm. Hg at 0°) 172:184 172:159 172:134 172:147 172:219 172:169 164:995 164:993 164:993 164:939 165:034 165:037 164:099	Vapour pressure (mm. Hg at 0°) * 63·227 63·207 63·206 63·226 63·226 63·223 29·988 29·980 29·983 29·983 29·983 29·993 29·993	Ratio 2.72324 2.72375 2.72275 2.72275 2.72277 2.72218) 5.50203 5.50359 5.50287 5.50181 5.50390 5.50254 5.50254
U32	22	$164.968 \\ 164.972 \\ 164.926 \\ 164.975 \\ 164.986$	$ \begin{array}{r} 80.575 \\ 60.561 \\ 60.567 \\ 60.567 \\ 60.574 \\ \end{array} $	2·72338 2·72408 2·72305 2·72386 2·72372		(Mean	164·999	29·993 29·985	5·50279)
	(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 .-- cyclo Hexane. The present values are consistent $(\pm 100 \text{ cm}^3/\text{mole})$ with the data in the range $42-75^\circ$ c by Waelbroeck ⁴ and $50-130^\circ$ c by Lambert, Roberts, Rowlinson, and Wilkinson.⁵ The precision of all the data is limited and an exhaustive re-examination of *cyclo*hexane over a wide temperature range is urgently required. With a different balance, probably less reliable, we obtained -1523 cm.³/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,⁶ using our material, determined the second virial coefficient at several temperatures with a precision differential compressibility apparatus and quote -849 and -748 cm.³/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 7 by the microbalance method found B at 22° to be -658 cm.³/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 7 with the microbalance method gave A_2 as 0.0457 at 22°, and hence B = -1107 cm.³/mole. Lambert, Roberts, Rowlinson, and Wilkinson⁵ 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 ⁸ carried out further measurements at $42-70^{\circ}$, obtaining results largely concordant with those of

- ⁴ Waelbroeck, J. Chim. phys., 1957, **54**, 710. ⁵ Lambert, Roberts, Rowlinson, and Wilkinson, Proc. Roy. Soc., 1949, A, **196**, 113.
- ⁶ Bottomley and Reeves, preceding paper.

⁷ Casado, Massie, and Whytlaw-Gray, Proc. Roy. Soc., 1952, A, 214, 466.

⁸ 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.⁹ The value suggested by an extrapolation of the results at $40-80^{\circ}$ is -1780 cm.³/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 ²⁰³Hg 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 ¹⁰ there is also a chemical change due to the rupture of CCl_4 in the presence of mercury:

$$CCl_4 + 4Hg \longrightarrow Various intermediates such as $C_2Cl_6 \longrightarrow 2Hg_2Cl_2 + C$$$

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 ⁶ 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 cm. 3 /mole or better, is superior. With benzene, which has been examined 11 by both microbalance and compressibility methods in several laboratories, there is substantial agreement amongst all the data.

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⁹ Eucken and Meyer, Z. phys. Chem., 1929, B, 5, 452.

¹⁰ Bottomley and Reeves, Trans. Faraday Soc., 1957, 53, 1455.

¹¹ Bottomley, Reeves, and Whytlaw-Gray, Proc. Roy. Soc., 1958, A, 246, 504.