

**774.** *The Virial Coefficients of Carbon Disulphide, Diethyl Ether, and n-Hexane.*

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The virial coefficients of carbon disulphide, diethyl ether, and *n*-hexane have been determined to very high precision in the reduced temperature range 0.53 to 0.74 by differential compressibility. The experimental work demonstrates very clearly that the  $PV$ - $P$  isotherms are linear up to 70% of the saturation pressure. Details of the manometric apparatus are discussed.

THE  $PVT$  behaviour [where  $P$  is the pressure (atm.),  $V$  the volume (cm.<sup>3</sup>) occupied by 1 mole, and  $T$  the absolute temperature] of three vapours was examined with the same method and differential compressibility apparatus as for benzene.<sup>1</sup> A sample of the vapour confined over grease-free mercury in a Pyrex apparatus is brought to the same pressure ( $\pm 0.0002$  mm.) as a similarly confined reference sample of nitrogen. The separate volumes of the vapour and the reference gas are determined to 1 in 100,000 by methods involving only the weighing of mercury. The pressures of the vapour and nitrogen are

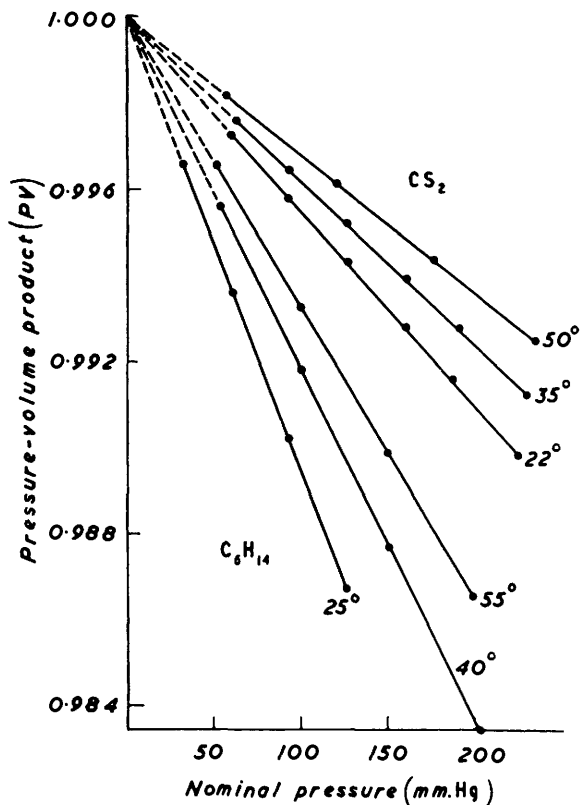
<sup>1</sup> Bottomley, Reeves, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1958, *A*, **246**, 504.

changed and re-balanced; the volume determinations are then repeated. After making the very slight allowance for the non-ideality of the reference gas these measurements permit the calculation of  $PV$  as a function of pressure for the vapour and so lead to the enumeration of virial coefficients.

## EXPERIMENTAL

*Materials.—Carbon disulphide.* "AnalaR" material was repeatedly agitated with clean mercury until no further fouling of the interface occurred and then fractionally distilled in nitrogen from phosphoric oxide and mercury.

*Diethyl ether.* "AnalaR" material was shaken at intervals with 10% aqueous potassium hydroxide containing a small amount of potassium permanganate, washed with water, agitated

FIG. 1. *Pressure-volume product as function of pressure.*

with 10% aqueous ferrous sulphate slightly acidified, dried ( $\text{Na}_2\text{SO}_4$ ), and fractionally distilled from sodium.

*n-Hexane.* Used as supplied by the Chemical Research Laboratories, Teddington, Middlesex (99.81 moles %).

The samples were then separately sealed without decomposition into vapour preparation lines controlled by mercury cut-offs. The carbon disulphide and *n*-hexane were dried by long-continued cycling over phosphoric oxide; the ether was stored as liquid over vacuum-distilled metallic sodium. Before use each sample was freed from entrained gases by repeated vacuum distillation at both  $-180^\circ$  and  $-80^\circ$  until Young's test (see following paper) was negative. Care is needed when carbon disulphide is solidified as the solid can easily shatter the glass container unless the crystals are grown upwards from the bottom of the specimen bulb. The vapour

pressures of the purified materials were measured to  $\pm 0.05$  mm. Hg with a wide-bore manometer to provide the following comparison with values in the literature.<sup>2</sup>

Material	Obs. vapour pressure (mm.)	Reported vapour pressure (mm.)
CS <sub>2</sub> .....	128.0 at 0°	127.3, 127.9, 128.0, 126.4, 127.0, 127.25
C <sub>4</sub> H <sub>10</sub> O .....	186.3 at 0°	186.1, 184.9, 185.3
C <sub>6</sub> H <sub>14</sub> .....	46.2 at 0°	45.45, 45.4

*Conduct of an Isothermal Measurement.*—The vapour, purified and degassed, was transferred to one side of the differential apparatus and opposed by nitrogen dried at  $-180^\circ$ .<sup>1</sup> The individual  $PV$  products are reliable to 2 in  $10^5$  at all pressures used. As in the previous work,<sup>1</sup> the pressure of the nitrogen was measured at the highest pressure and then deduced for the subsequent lower pressures from the successive volumes of the nitrogen phase.

*Results.*—The virial coefficients ( $B$ ) were computed from the slope of the  $PV$ - $P$  line best fitting the observations after making the usual allowances for non-ideality of the nitrogen and the reduction of the pressure to standard conditions. Each expansion included measurements at four or more equally spaced pressures. The individual  $PV$  values differed from the mean lines by no more than 2 in  $10^5$ : typical differences were: CS<sub>2</sub> ( $-0.2$ ,  $-0.3$ ,  $+0.8$ ,  $-0.5$ ), C<sub>4</sub>H<sub>10</sub>O ( $+1.0$ ,  $-2.0$ ,  $+1.1$ ,  $-0.7$ ), C<sub>6</sub>H<sub>14</sub> ( $+0.9$ ,  $-1.3$ ,  $-0.2$ ,  $+0.5$ ) in parts per  $10^5$  of the  $PV$  value.

The final values of  $-B$  (cm.<sup>3</sup>/mole), with a probable error of  $\pm 3$  cm.<sup>3</sup>/mole, were:

CS <sub>2</sub> .....	849 at 22.0°	748 at 35.0°	661 at 50.0°
C <sub>4</sub> H <sub>10</sub> O .....	1226 at 22.0°	1084 at 35.0°	950 at 50.0°
C <sub>6</sub> H <sub>14</sub> .....	1984 at 25.0°	1620 at 40.0°	1406 at 55.0°

Fig. 1 shows the working range of pressure used.

## DISCUSSION

*Comparison with Related Work.*—*Direct PVT measurement.* The values reported here for *n*-hexane and for diethyl ether at the highest temperatures overlap with the lowest temperature values reported by Lambert, Roberts, Rowlinson, and Wilkinson.<sup>3</sup> Though these authors estimate the probable error of their results as  $\pm 20$  to  $\pm 100$  cm.<sup>3</sup>/mole and the values at various temperatures show considerable scatter, our values and theirs agree within these limits.

The higher-temperature values for *n*-hexane just overlap with the experiments of McGlashan and Potter;<sup>4</sup> if allowance is made for the alternative notations in use, our values clearly are distinctly less negative than theirs.

*Values deduced from density.* Much pioneer work has been done by R. Whytlaw-Gray and his collaborators on the possibility of obtaining virial coefficients by determining densities with the microbalance. This method has advantages in special cases, though it is far more sensitive to the purity of the material than the direct method. Casado, Massie, and Whytlaw-Gray<sup>5</sup> present work which leads to  $B$  values: diethyl ether  $-1211$ , carbon disulphide  $-658$  cm.<sup>3</sup>/mole at  $22^\circ$ . The agreement with ether is as perfect as the errors permit; the value for carbon disulphide (which is at present under re-examination by the microbalance method in these laboratories) is markedly anomalous. A similar disparity for benzene was resolved when adsorption errors were studied systematically in the two methods.

*Values by indirect method.* The second virial coefficient of a vapour can be deduced from the molar volume of the liquid, the calorimetric latent heat of vaporisation, and

<sup>2</sup> Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

<sup>3</sup> Lambert, Roberts, Rowlinson, and Wilkinson, *Proc. Roy. Soc.*, 1949, *A*, **196**, 113.

<sup>4</sup> McGlashan and Potter, Joint Conference of Thermodynamic and Transport Properties of Fluids. The Institution of Mechanical Engineers and the International Union of Pure and Applied Chemistry, July 1957.

<sup>5</sup> Casado, Massie, and Whytlaw-Gray, *Proc. Roy. Soc.*, 1952, *A*, **214**, 466.

vapour pressure as a function of temperature, if sufficiently accurate data are available.<sup>6</sup> Waddington and Douslin<sup>7</sup> have applied this method to *n*-hexane and give

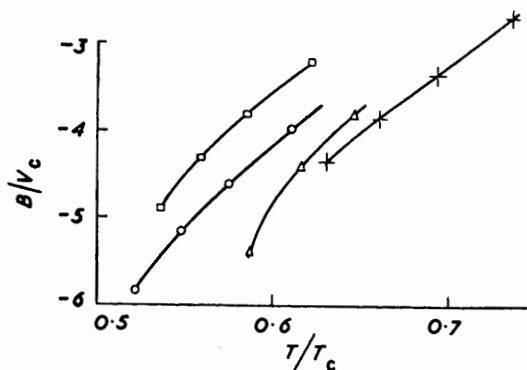
$$B = -2270 + 6.25 \times 10^5 T^{-1} - 1.306 \times 10^{13} T^{-4}$$

as the relation between the second virial coefficient and the absolute temperature. The values from this equation at the temperatures of our experiments with *n*-hexane are  $-1825$ ,  $-1634$ , and  $-1492$ ; the agreement is far from impressive.

The results quoted above have been obtained at lower reduced temperatures ( $T/T_c$ ), where the subscript *c* denotes a critical-point parameter, than those commonly employed. Fig. 2 shows reduced virial coefficients as a function of reduced temperature; the critical

FIG. 2. Reduced virial coefficient ( $B/V_c$ ) as function of reduced temperature ( $T/T_c$ ).

- Carbon disulphide.
- Benzene, previous work (ref. 1).
- △ *n*-Hexane.
- + Diethyl ether.



data used are taken from Kobe and Lynn.<sup>8</sup> It is obvious that  $B/V_c$  is not a unique function for all substances and that errors of 20% can easily arise if it is assumed that a particular substance follows the general trend.

In the present work the  $PV$ - $P$  line is linear to high accuracy, justifying the use of the equation

$$PV = RT + BP/M$$

to represent the data, where  $M$  is the molecular weight. Some authors<sup>4</sup> recommend

$$PV = RT + B'(1/V)/M$$

as being of greater theoretical significance. The present experimental data can equally well be handled on this basis since the volume of the system is determined at various pressures in each expansion.  $PV$  versus  $1/V$  plots drawn from the observations appear very nearly linear when drawn on quarto graph paper.

If  $PV = 1 + bP$ , then  $PV = 1 + (b/V)/(1 - b/V)$

and by binomial expansion

$$PV = 1 + b(1/V) + b^2(1/V)^2 + b^3(1/V)^3 \dots$$

A typical value of  $b$  is  $-0.00006$ ; over the working range of  $(1/V)$  the term  $(1/V)^2$  contributes some 0—4 parts per  $10^5$  to the  $PV$  values. At a nominal vapour pressure of 200 mm.,  $PV = 0.988$  and  $1/V = 202.429$ , so it follows that  $B'$  is smaller than  $B$  by

<sup>6</sup> Allen, Everett, and Penney, *Proc. Roy. Soc.*, 1952, *A*, **212**, 149.

<sup>7</sup> Waddington and Douslin, *J. Amer. Chem. Soc.*, 1947, **69**, 2275.

<sup>8</sup> Kobe and Lynn, *Chem. Rev.*, 1953, **52**, 117.

1.2%. We state firmly that the relative merits of  $PV-P$  and  $PV-(1/V)$  plots cannot be established unless the experimental results and the reports include measurements of  $PV$  at several widely spaced pressures for each expansion.

*Adsorption.*—The mass of vapour contributing to the gas phase varied slightly with pressure because of the adsorption on the glass walls of the apparatus and on the mercury. The necessary slight allowances for the glass adsorption were made from Bottomley and Reeves's data,<sup>9</sup> but there is unfortunately no information on the adsorption of these vapours on mercury. The adsorption corrections are less serious than with benzene; the uncertainty cannot exceed 5 cm.<sup>3</sup>/mole at most with the present apparatus.

*Dilation of Apparatus.*—During an experiment the apparatus was subjected to various pressure differences between interior and exterior which cause slight changes in the effective volume. No significant error arose in this way. Over the normal pressure range the volume change did not exceed 6 parts in 10<sup>5</sup> of the gas or vapour volume; the apparatus was symmetrical, so that volume changes and their consequences on one side were paralleled on the other; the rate of change of volume with pressure on the two sides has been measure accurately and found identical within satisfactory limits.

*Static Electricity.*—Some difficulty was caused by the unavoidable generation of static electricity through the movement of mercury over the Pyrex glassware which had been very thoroughly dried by repeated evacuation with the diffusion pump and by rinsing with nitrogen dried at  $-180^{\circ}$ . The static electricity prevents the attainment of a stable pressure balance until some hours have elapsed after the movement of substantial amounts of mercury. If the observed anomalous pressures are due to static electricity producing electrostriction in the volume of the nitrogen or the vapour (though this is not the only possible explanation) then our apparatus with one gas phase subjected to an electrical potential gradient should prove a very direct method of investigation. None of the vapours examined showed any change in  $PV$  at constant pressure with time, so that under our conditions the materials are stable towards mercury, light, and static electricity. This apparently self-evident point is mentioned because it had been planned to study carbon tetrachloride. It was found that  $PV$  of a sample of highly purified carbon tetrachloride showed a steady fall of 10 parts per 10<sup>5</sup> for each redetermination at fixed pressure, and the mercury meniscus in the null manometer became foul at the contact with the glass. This behaviour is undoubtedly due to the rupture of the carbon tetrachloride molecule by static electricity to form carbon and mercurous chloride.

*Capillarity.*—The key operation of the experiments was the adjustment of the pressures on the two sides of a null manometer fitted with tungsten reference points. The setting of a mercury surface to a tungsten point can be made reproducible<sup>10</sup> to within 0.0002 mm., but this does not guarantee that the pressure equality of the two sides is so good. The reference points were first brought to the same horizontal plane by tilting the null manometer until, with both sides highly evacuated, the mercury surfaces set simultaneously to each tungsten point. With 35 mm. tubing it is certain that no possible variation of meniscus height and capillary depression can adversely influence the setting operation. When, as in the working experiments, the null manometer contains nitrogen on one side and a vapour at perhaps 70% saturation on the other, various possibilities for error exist. The vapour is adsorbed on the mercury surface, lowers the surface tension, and reduces the capillary depression, but cannot affect the depression by more than 0.001 mm. with 35 mm. bore tubes even if the meniscus is made horizontal. Above room temperature the vapour pressure of the mercury is appreciably higher than the permissible error in manometry, so it must be ensured that both the vapour and the nitrogen, in which diffusion proceeds at different rates, become fully saturated with mercury vapour before a pressure balance is attempted. Because of the need to allow 24 hr. to elapse to disperse static electricity, we have not found any evidence of difficulty from this potential error.

<sup>9</sup> Bottomley and Reeves, *Trans. Faraday Soc.*, 1957, **53**, 1455.

<sup>10</sup> Bottomley, *J. Sci. Instr.*, 1958, **35**, 254.

*Manometric Errors.*—Rowlinson and his co-workers<sup>11,12</sup> have drawn attention to the possible detrimental effect of mercury vapour in substances under *PVT* examination at moderate and high pressures and have shown experimentally that the presence of a vapour enhances the solubility of mercury in the gas phase by as much as 35% in certain circumstances. That this effect does not influence our experiments has been demonstrated as follows: with the thermostat at 22° (mercury-vapour pressure 0.0014 mm.) nitrogen was admitted to one side of the null manometer and diethyl ether to the other, the two gas phases being connected by a long capillary tube. The manometer system was then tilted until the tungsten points set simultaneously to the mercury surfaces. This setting does not occur with the points horizontal because of the slightly different hydrostatic heads of the vapour and nitrogen in the dead spaces, a fact which demonstrates the extreme sensitivity of the point settings. The null manometer was maintained at the same level, the thermostat temperature raised to 57° (mercury-vapour pressure 0.020 mm.) and the filling repeated. The null manometer showed no pressure difference. It follows that the vapour pressures of mercury in the two gas phases at 57° are identical to  $\pm 0.001$  mm. at worst, and that the enhanced solubility effect does not amount to more than 5% of the vapour pressure of mercury.

There is another manometric error. The null manometer system permits adjustment to pressure equality at the level of the tungsten points but not at the level of the centre of gravity of the gas phase. The hydrostatic head between the level of the tungsten points and the centres of gravity is not the same because the gases have different density. Furthermore, as the gas phases are expanded during an experiment the disparity between the level of the null manometer and the centre of gravity changes. Elementary calculation from the vertical distribution of a gas in a gravitational field shows that the effects are just at the limit of precision of our experimental technique; with a vapour as dense as perfluoromethylcyclohexane the corrections would be significant.

The capillary effect of the tungsten rod which protrudes through the mercury meniscus (within 1 mm. of the dead-space wall) was of some practical importance. To test the "figure" of a meniscus of 35 mm. diameter interference fringes were formed with sodium light between the mercury and an optical flat partially obscured with chemically deposited lead sulphide to increase the contrast. An obstacle corresponding to the tungsten rod was then inserted through the meniscus and the limits of distortion of the fringes observed visually. The capillary disturbance extended from the rod much further than might be supposed but did not materially affect the centre of the 35 mm. diameter meniscus. By the same test it was clear that the curvature of the central 10 mm. of the meniscus was little more than 1 wavelength, so that exact centering of the tungsten reference point was not required.

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<sup>11</sup> Jepson and Rowlinson, *J. Chem. Phys.*, 1955, **23**, 1599.

<sup>12</sup> Jepson, Richardson, and Rowlinson, *Trans. Faraday Soc.*, 1957, **53**, 1586.