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SESSION 2: P.V.T. PROPERTIES—COMPILATION

The Gas Imperfections of Hydrocarbons

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THIS PAPER summarizes the results of a large number of computations of the reduced second and third virial coefficients of hydrocarbon gases. The complete data will later be collected in the form of cyclostyled tables.

There is a brief discussion of the physical significance of some trends in the virial coefficients.

INTRODUCTION

IN THE PAST TWENTY YEARS there have been a large number of measurements of the P–V–T properties of hydrocarbon gases. Since the results have a theoretical as well as a practical value we have considered it worth while to review the field and reduce the data to a convenient form which eliminates the multiplicity of units used in the original papers.

The present authors have chosen to fit the experimental isotherms to the relation

$$PV/RT = z = 1 + B/V + C/V^2, \qquad (2.45)$$

where P denotes the pressure, V the molar volume, and T the absolute temperature of the gas; R is the gas constant, and B and C are constants for each isotherm. Equation (2.45) can be rewritten

$$z = 1 + B^*/V^* + C^*/V^{*2}, \qquad (2.46)$$

where B^*, C^* and V^* are defined by

$$B^* = \frac{B}{V_c}, \; C^* = \frac{C}{V_c^2}, \; V^* = \frac{V}{V_c}, \qquad (2.47)$$

V_c being the critical volume of the gas. They have found that the quadratic equation (2.46) gives an adequate representation of the behaviour of the lower hydrocarbon gases so long as V^* is greater than 1·3. In these circumstances B^* and C^* can be identified with the second and third virial coefficients in the infinite series

$$z = 1 + B^*/V^* + C^*/V^{*2} + D^*/V^{*3} + E^*/V^{*4} + (2.48)$$

By the principle of corresponding states they should be universal functions of the reduced temperature T^* ($= T/T_c$).

Equation (2.46) can be rearranged to

$$(z - 1)V^* = B^* + C^*/V^*, \qquad (2.49)$$

so that a plot of $(z - 1)V^*$ against $1/V^*$ should be a straight line of slope C^* and intercept B^*. Most of the experimental data satisfy these requirements when $1/V^*$ is less than 0·8, but a few give plots that curve badly at small values of $1/V^*$. Hirschfelder, McClure and Weeks (1942)[†] have pointed out that this behaviour must arise from experimental inaccuracies and in their analysis the authors have rejected any isotherms of this sort.

With the exception of heptane (Table 2.2) the authors have fitted the experimental values of $(z - 1)V^*$ to equation (2.49) by the method of least squares, giving to each point a weight $1/V^*$. This procedure is equivalent to fitting the values of z to equation (2.46), each point being given equal weight. The analyses were limited to values of $1/V^*$ less than 0·8. Some of the calculations were made on a desk calculator, using the Doolittle (1878) method of analysis, but the majority were carried out on the Sydney University Electronic Computer, 'Silliac'.

Altogether about 200 isotherms were analysed and it is hoped soon to prepare tables of the complete results. Here the data are summarized in one table and some diagrams.

SOURCES OF DATA

Inert gases
The values of B^* and C^* for these gases have been taken from the tables of Rowlinson (51).[‡]

Methane
B^*: references (22, 32, 34, 39, 44).
C^*: references (32, 34, 39, 44).

Ethane
B^*: references (25, 40, 41, 48). The authors have left out the values of Eucken and Parts (19) because they are evidently too low (compare Rowlinson 1954), and those of Lambert, Roberts, Rowlinson and Wilkinson (35) because they are too widely scattered. The data of Beattie (3, 10), have also been omitted for the reasons given in reference (24).
C^*: references (40, 41, 48).

Propane
B^*: references (5, 14, 17, 27, 31, 49, 58).

† An alphabetical list of general references is given in Appendix 2.III.
‡ An alphabetical list of source references is given in Appendix 2.II. For convenience these have been numbered.

C^*: references (5, 14, 49). The data of Deschner and Brown (17) have also been used, with the exception of those for the two highest temperatures, where C^* shows an abnormal increase with increasing temperature.

Butane

B^*: references (9, 11, 26, 45, 47). The data of Kay (28) are too inaccurate for our purpose.
C^*: references (9, 45).

Pentane

B^* and C^*: references (6, 33, 53).

Hexane

There seem to be no accurate $P-V-T$ data for this gas. The two isotherms of Kelso and Felsing (29) are dubious, the results of Vines (35) are scattered, and those of Watson and Dodge (57) give plots of $(z - 1)V^*$ against $1/V^*$ which curve badly at low densities.

Heptane

B^* and C^*: reference (54).

Ethene

B^*: references (13, 15, 38). The authors have left out the data of Eucken and Parts (19) since there is some doubt about their reliability (compare Rowlinson 1954), and those of Masson and Dolley (37) and of Danneel and Stoltzenberg (16) because the plots of $(z - 1)V^*$ curve violently at low densities. They have also left out the results of Roper (50) since his data on the higher alkenes generally disagree with the results of other workers.
C^*: reference (38).

Propene

B^*: references (20, 36, 42). The values of B^* given by the data of Vaughan and Graves (55) appear to be much too high.

1-Butene

B^* and C^*: references (7, 46).

2-Methyl Propene (iso-butylene)

B^* and C^*: reference (4).

Benzene

B^*: references (12, 21, 23, 35, 56). The authors have left out the values of Eucken and Meyer (18) and Baxendale and Enüstün (1) because they are clearly wrong (compare reference 21).
C^*: reference (23).

2-Methyl Propane (iso-butane)

B^* and C^*: references (8, 43).

2:2 Di-methyl Propane (neo-pentane)

B^*: references (2, 25).
C^*: reference (2).

2-Methyl Pentane

B^* and C^*: reference (29).

2:3 Di-methyl butane

B^* and C^*: reference (30).

RESULTS

Second virial coefficients

For most of the gases the experimental reduced virial coefficients were fitted to the arbitrary relation

$$B^* = \alpha + \frac{\beta}{T^*} + \frac{\gamma}{T^{*2}} + \frac{\delta}{T^{*3}}, \qquad (2.50)$$

where T^* denotes the reduced temperature. The coefficients $\alpha \ldots \delta$ were computed by the method of least squares and the results are given in Table 2.2.

Table 2.2. Coefficients in the Formula $B^* = \alpha + \dfrac{\beta}{T^*} + \dfrac{\gamma}{T^{*2}} + \dfrac{\delta}{T^{*3}}$

Gas	T_c (a) deg. K.	V_c (a) cu. cm. per mol.	Experimental range of T^*	α	β	γ	δ
Inert gases	—	—	0·8 – 2·70	+0·3867	−0·7104	−0·9768	+0·1706
Methane	191·1	99·0	1·06 – 2·67	+0·4042	−0·7517	−1·0553	+0·2714
Ethane	305·5	148	0·89 – 1·67	+1·612	−5·416	+5·099	−2·461
Propane	370·0	200	0·74 – 1·65	−0·7073	+2·7609	+4·3019	+1·0213
Butane	425·2	255	0·64 – 1·35	−5·0620	+15·277	−15·608	+4·1136
Pentane	469·8	311	0·66 – 1·22	+1·5881	−3·5783	+1·5122	−0·7831
Heptane (b)	540·2	426	1·01 – 1·15	—	—	—	—
2-methyl propane	408·1	263	1·01 – 1·40	+3·6915	−13·032	+14·652	−6·5373
2:2-dimethyl propane	433·8	303	0·75 – 1·26	+0·1226	+0·2519	−1·7169	+0·0874
Ethene	282·4	129	0·96 – 1·50	+4·912	−18·575	+23·892	−8·975
Propene	365·0	181	0·76 – 1·43	−0·8060	+3·1860	−4·8766	+1·2500
1-butene	419·6	240	0·90 – 1·25	+6·3190	−20·220	+20·609	−7·9224
2-methyl propene	417·9	239	1·01 – 1·31	+0·0489	+0·1094	−1·1562	−0·2422
Benzene	562	260	0·53 – 1·12	−1·5770	+4·5248	−4·9866	+0·7948

(a) The critical constants have been taken from the review of Kobe and Lynn, 1953, Chemical Reviews, vol. 52, p. 117, with the exception of the critical volume of ethene, for which their value of 124 cu. cm./per mol. appears to be wrong. The figure adopted here is the mean of the value, 129·9 cu. cm. per mol., given by Mathias, Crommelin and Watts, 1927, Comptes Rendus, Vol. 185, p. 1240, and a value, 128·1 cu. cm. per mol., calculated by the method of rectilinear diameters from the coexistence curve of Naldrett and Maass, 1940, Canadian Jl. of Research, vol. 18B, p. 118.

(b) Equation (2.46) was inadequate for heptane, and therefore the isotherms were fitted to the relation $z = 1 + B^*/V^* + C^*/V^{*2} + E^*/V^{*4}$. The values of B^* are

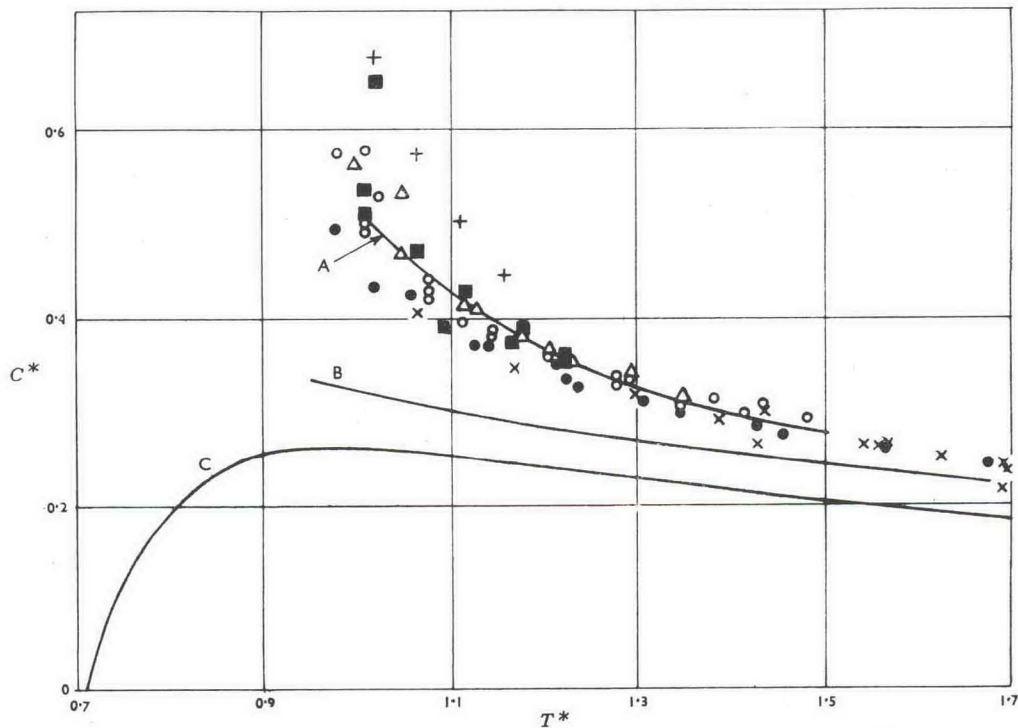| T^*	1·015	1·061	1·107	1·154
B^*	−1·31	−1·16	−1·03	−0·91

Fig. 2.1. The Reduced Third Virial Coefficients of Straight-chain Alkanes

Curve A is defined by equation (2.51); curve B is for the inert gases (Rowlinson 1954), and curve C is the theoretical curve for a Lennard-Jones 12:6 gas with the same potential parameters as for the second virial coefficient (Compare Guggenheim 1953).
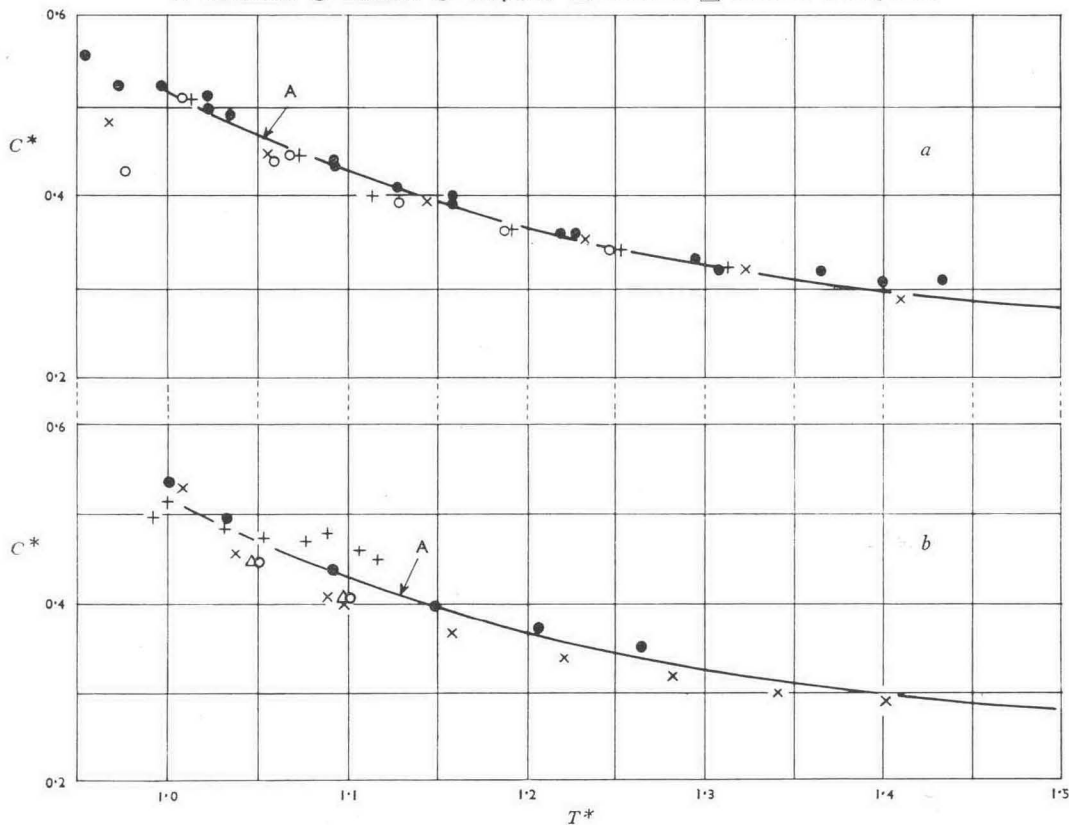$\times$ Methane. ● Ethane. ○ Propane. ■ Pentane. △ Butane. + Heptane.

Fig. 2.2. The Reduced Third Virial Coefficients of Alkenes (upper) and Branched-chain Alkanes and Benzene (lower)

The curves A are defined by equation (2.51). (a) $\times$ Ethene. ● Propene. ○ 1-butene. + 2-methyl propene. (b) $\times$ 2-methyl propane ● 2-2 dimethyl propane. ○ 2-methyl pentane. △ 2-3 dimethyl butane. + Benzene.

There should be no need to emphasize that the co-efficients $\alpha \ldots \delta$ in Table 2.2. are only valid within the limited range of temperatures indicated in the table, and that they have no significance beyond their ability to represent the experimental data.

Third virial coefficients

Figs. 2.1 and 2.2 give plots of the reduced third virial coefficients for three homologous series of hydrocarbons. The curve A in each figure is a fitted one, represented by the equation

$$C^* = 0.5419 - \frac{1.1249}{T^*} + \frac{1.0973}{T^{*2}} \qquad (2.51)$$

In these diagrams we have plotted only the values of C^* above or close to the critical temperature, the reason being that it is very difficult to make accurate measurements of C^* below the critical temperature and the data in that region are widely scattered. Nevertheless, there is evidence in several papers (17, 20, 36, 41, 42, 49, 53), that with decreasing temperature C^* passes through a maximum value and becomes negative at a reduced temperature of about 0.7. This behaviour is to be expected theoretically (compare curve C in Fig. 2.1).

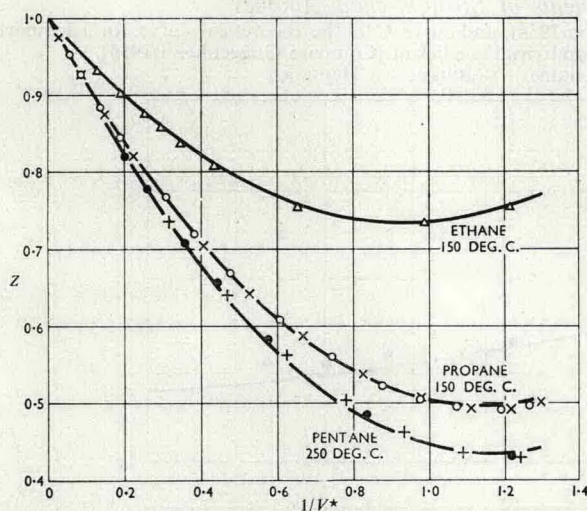In Fig. 2.3 three experimental isotherms are compared,

Fig. 2.3. A Comparison of Some Experimental and Fitted Isotherms

The curves are based on second virial coefficients calculated from Table 2.2, and third virial coefficients from equation (2.51). △ Michels, van Straaten and Dawson (1954). ○ Michels and others (1953). × Marchman, Prengle and Motard (1949). + Beattie, Levine and Douslin (1952). ● Kun Li and Canjar (1953).

selected at random, with the values of z calculated from equations (2.46), (2.50), (2.51), and using the coefficients in Table 2.1. Clearly the fitted curves give a good representation of the experiments.

DISCUSSION

Second virial coefficients

The reduced second virial coefficients of the straight chain alkanes are shown as functions of the reduced

temperature in Fig. 2.4, where the curves have been calculated from the coefficients in Table 2.2. Apart from
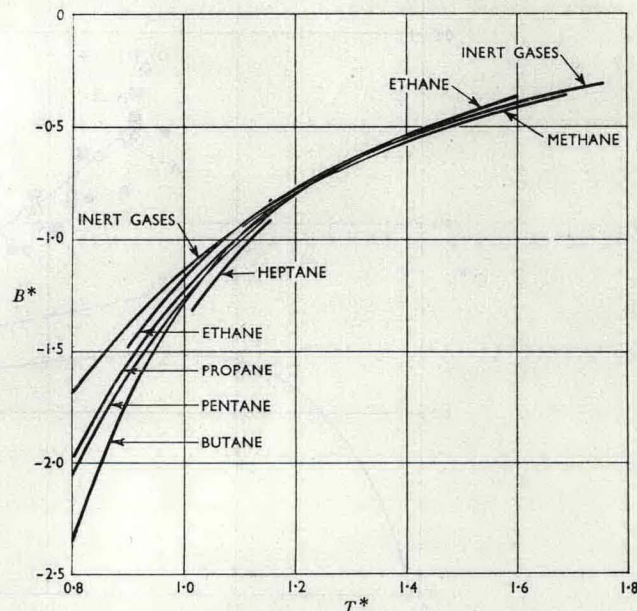

Fig. 2.4. The Reduced Second Virial Coefficients of Some Straight-chain Alkanes

the anomalous position of the curve for pentane the results show steadily increasing deviations from the behaviour of the inert gases as the chain length increases. This trend was predicted by Rowlinson's (1954) theory of the behaviour of gases with non-spherical molecules. The abnormal position of pentane suggests that Sage and Lacey's (53) values of B^* at low temperatures are too high, and it is significant that a single low temperature measurement by Jessen and Lightfoot (27) lies well below Sage and Lacey's results.

In contrast to those of the alkanes, the values of B^* for the straight-chain alkenes show no regular trend with increasing chain length. In fact the curves for ethene, propene and 1-butene are all nearly coincident with the curve for propane in Fig. 2.4. The behaviour of propene and 1-butene may be complicated by the fact that their molecules have small dipole moments.

Third virial coefficients

The most remarkable feature of the reduced third virial coefficients is the uniformity of their values at temperatures above the critical. Figs. 2.1 and 2.2 show that they all lie close to the curve A, although there is perhaps a slight upward trend with increasing molecular weight. The values are always higher than those for the inert gases, which in turn are higher than those to be expected for a Lennard-Jones 12:6 gas on the assumption that the potential parameters determining C^* are the same as those determining B^*. These trends could mean that the inert gases and the hydrocarbon gases have intermolecular potentials which deviate progressively from the 12:6 form. But from the absence of any clear-cut structural effects

the present authors are inclined to think that the higher values of C^* arise mainly from the failure of the principle of additivity of intermolecular forces. It is believed (Axilrod 1949, 1951) that the average attractive forces are weaker in 3-body interactions than in 2-body interactions, and this change will have the effect of increasing the effective molecular volume and shifting C^* to higher values. The hydrocarbons would deviate more than the inert gases because the collision of their molecules involves a greater number of simultaneous atomic interactions.

APPENDIX 2.II

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APPENDIX 2.III

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