

# 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

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

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

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

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

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

$V_c$  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

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

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

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

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

*The MS. of this paper was received at the Institution on 14th February, 1957.*

*This paper was presented during Session 2 of the Conference.*

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small values of  $1/V^*$ . Hirschfelder, McClure and Weeks (1942)<sup>†</sup> 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).<sup>‡</sup>

### 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).

<sup>†</sup> An alphabetical list of general references is given in Appendix 2.III.

<sup>‡</sup> 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

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

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

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

| Gas                  | $T_c$ (a)<br>deg. K. | $V_c$ (a)<br>cu. cm.<br>per mol. | Experimental<br>range of<br>$T^*$ | $\alpha$ | $\beta$ | $\gamma$ | $\delta$ |
|----------------------|----------------------|----------------------------------|-----------------------------------|----------|---------|----------|----------|
| 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 J. 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 |