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).
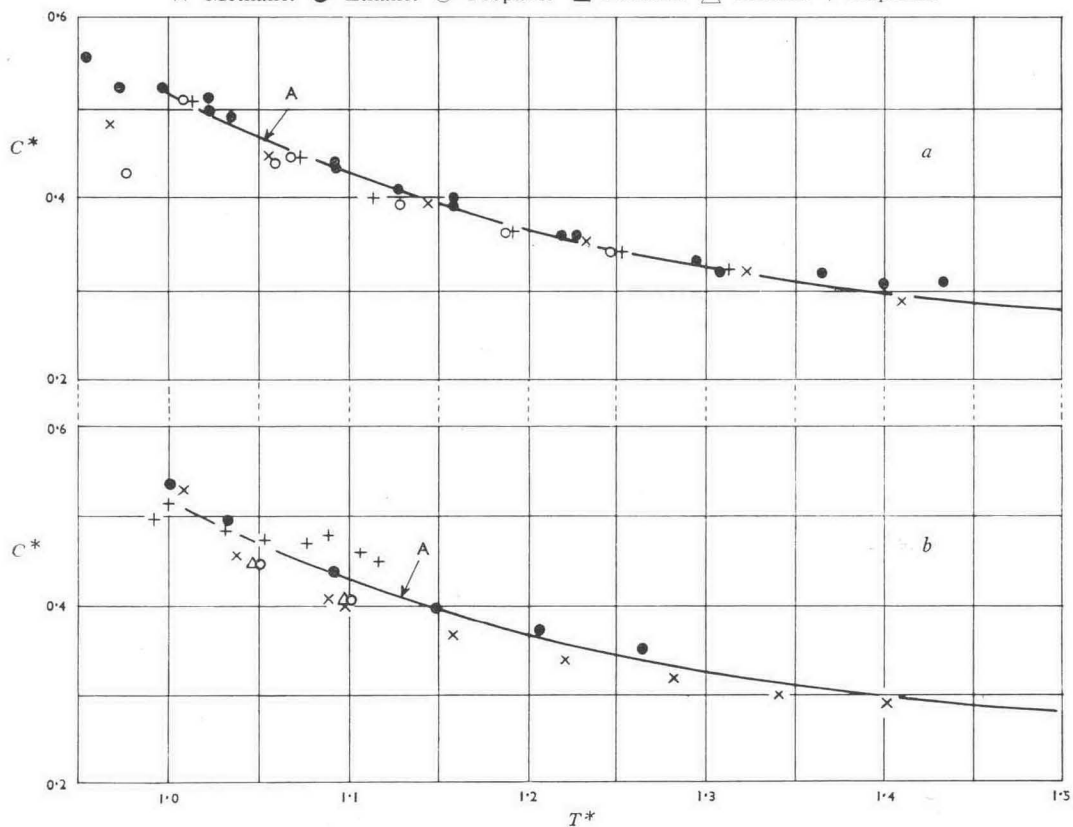× Methane. ● Ethane. ○ Propane. ■ Pentane. △ Butane. + Heptane.

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*) × Ethene. ● Propene. ○ 1-butene. + 2-methyl propene. (*b*) × 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).

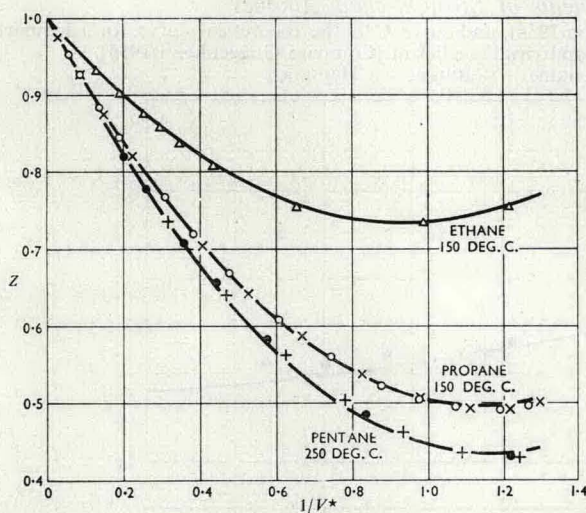In Fig. 2.3 three experimental isotherms are compared,

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
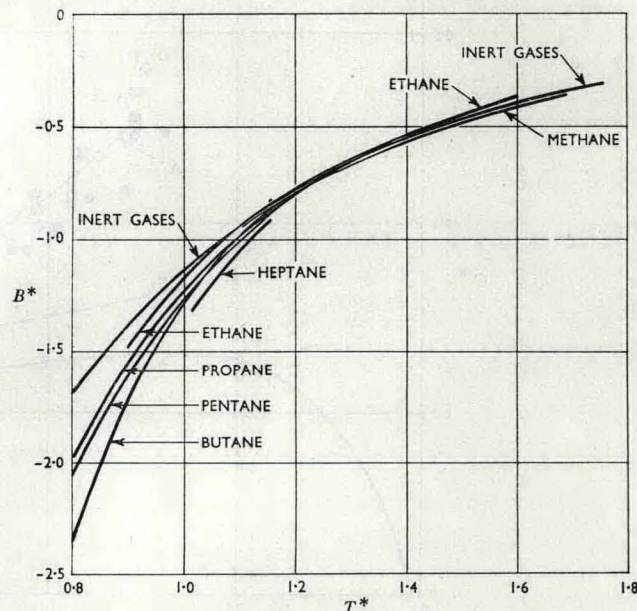

Fig. 2.4. The Reduced Second Virial Coefficients of Some Straight-chain Alkanes

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