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3 THE VIRIAL EQUATION OF STATE

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3.1 INTRODUCTION

3.1.1 The Volumetric Behaviour of Real Fluids

The virial equation of state is a relation between pressure p, temperature T and amount-of-substance density ρ_n which may be applied to real gases. For a perfect gas, these quantities are related by the well known equation

$$p = \rho_n RT \tag{3.1}$$

or simply

$$Z = 1 \tag{3.2}$$

where R is the universal gas constant and $Z = p/\rho_n RT$ is called the compression factor.

For real fluids, the compression factor is found to behave in a rather more complicated way than Equation (3.1) predicts. Such behaviour is illustrated in Figure 3.1 where experimentally determined values of Z are plotted as a function of ρ_n along a number of isotherms for fluid methane (1,2). At temperatures above the critical, the isotherms are smooth continuous functions of density but, at subcritical temperatures, they are split into two branches which each terminate on the vapour-liquid coexistence curve. At low densities, the isotherms converge in accordance with the experimentally proven result that
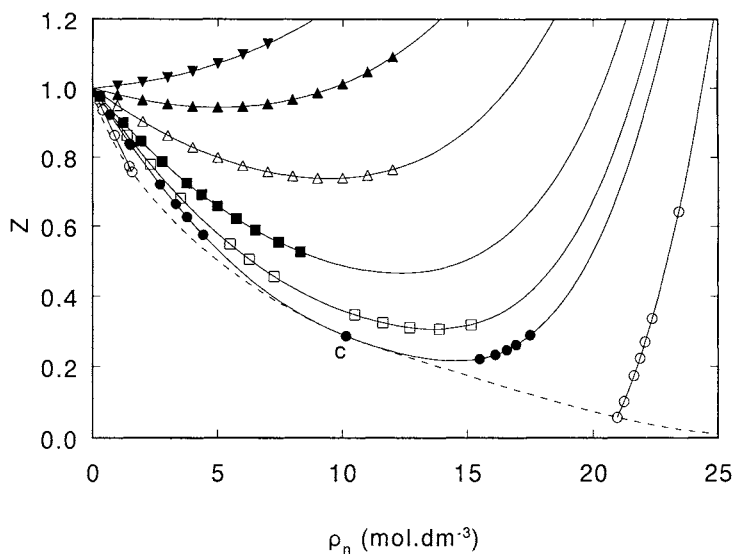

Figure 3.1 Compression factors of fluid methane as a function of density (1,2). - - - - - - -, saturation curve; ——— isotherms calculated from the equation of state of Setzmann and Wagner (3); c, critical point. O, 160 K; ●, 190.555 K; □, 200 K; ■, 220 K; △, 273.15 K; ▲, 373.15 K; ▼, 573.15 K.

$$Z(T, \rho_n \to 0) = 1 \tag{3.3}$$

for all non-reacting gases. This behaviour will be referred to as the perfect-gas limit. At the other extreme of high densities, the isotherms adopt positive slopes and Z starts to increase rapidly as the fluid becomes nearly incompressible. It is also instructive to examine the same experimental isotherms as a function of pressure as in Figure 3.2. Here, one can see that both branches of a subcritical isotherm terminate on the coexistence curve at the saturated vapour pressure. The high compressibility of the fluid in the near-critical state is also apparent.
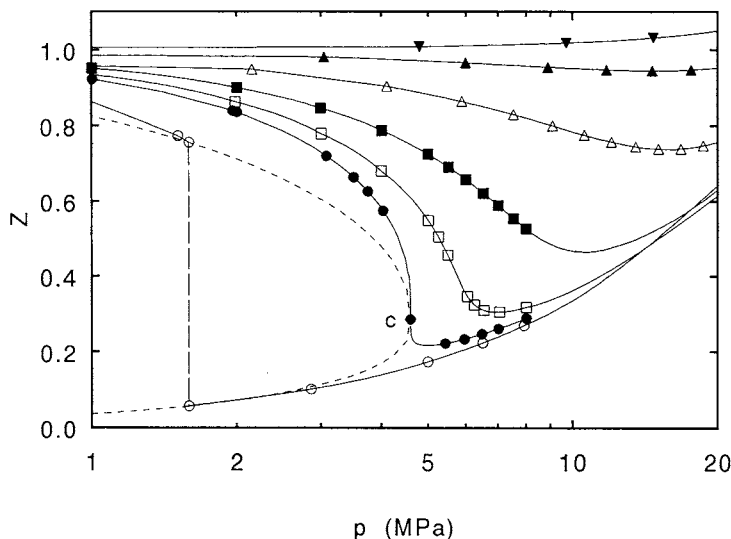
Figure 3.2 Compression factors of fluid methane as a function of pressure (1-3). Symbols and curves as for figure 1 except — — — —, tie line.

3.1.2 The Virial Equation of State

The accurate representation of $p(T, \rho_n)$ over wide ranges of temperature and density is a problem of great practical importance to which there is no simple solution. The virial equation of state

$$p = \rho_n RT \{1 + B\rho_n + C\rho_n^2 + D\rho_n^3 + \cdots\} \tag{3.4}$$

is one of the many hundreds of equations which have been proposed in an attempt to obtain a more accurate description of the behaviour of real fluids than is given by Equation (3.1). This equation may be viewed as a MacLaurin series in which (p/RT) is expanded in powers of ρ_n about the perfect-gas limit with density-independent coefficients B, C, D $\cdots$ known as virial

coefficients. Conventionally, B is called the second viral coefficient, C the third virial coefficient, D the fourth and so on. Since it is an experimentally proven fact that Z is a function of both T and ρ_n, one must expect B, C, D, $\cdots$ to be functions of the temperature and, as $Z(T, \rho_n)$ is not generally the same function for all gases, the virial coefficients for mixtures must also be functions of the composition.

If the virial equation of state had no better foundation than the empirical arguments introduced above, it is doubtful that it would have received the attention that it has. Indeed, some modern empirical equations of state (see, *e.g.,* reference 3) are of much wider applicability and their greater complexity is not usually a real disadvantage. However, the importance of the virial equation is that it has a rigorous theoretical foundation in statistical thermodynamics which provides exact analytic relations between the virial coefficients and the interactions between molecules in isolated clusters. One finds that B depends upon interactions between pairs of molecules, C upon interactions in a cluster of three molecules, D upon interactions in a cluster of four molecules, and so on.

3.1.3 Temperature Dependence of the Virial Coefficients

One of the significant advantages of the virial equation of state is the existence of a very large database of experimentally determined virial coefficients (4). The second virial coefficient is by far the most well studied but C is known with some accuracy for a number of fluids and a few values of D have been reported. In view of this situation, the temperature dependence of the virial coefficients will be discussed first in the light of the experimental results. Figure 3.3 shows values of the second and third virial coefficients of methane over a wide range of temperature. The critical temperature T^c and the Boyle temperature T^B (at which $B = 0$) are also indicated in this figure. At high temperatures, B is positive and varies only slowly with temperature while, at lower temperatures, it becomes large and negative. Like B, C is a slowly varying positive quantity at high temperatures and a rapidly varying negative one at low temperatures; in between these extremes it passes through a maximum. The curves shown in Figure 3.3 were calculated from intermolecular pair and triplet potential-energy functions determined for methane from speed-of-sound measurements (5). The behaviour shown in Figure 3.3 is typical of almost all gases although, of course, the magnitude of the virial coefficients and the characteristic temperatures such as T^B vary from substance to substance.

The temperature dependence of the higher virial coefficients is not well established experimentally but theoretical evaluations for model systems (see Section 3.3.6) indicate that these virial coefficients too are positive at high temperatures with a rapid divergence towards large negative values at temperatures below the critical (6).

3.1.4 Composition Dependence of the Virial Coefficients

For a pure gas, the phase rule requires that the pressure be a function of the two variables T and ρ_n only. Similarly, in the case of a mixture composed of v components, with amounts of substance n_1, n_2, $n_3 \cdots n_v$ present in volume V, the pressure must be a function of the $(v+1)$ variables T, n_1/V, n_2/V, $n_3/V \cdots n_v/V$ and an expansion of p, at constant temperature, in powers of n_1/V, n_2/V, $n_3/V \cdots n_v/V$ should exist. Carrying out this expansion, one again arrives at the
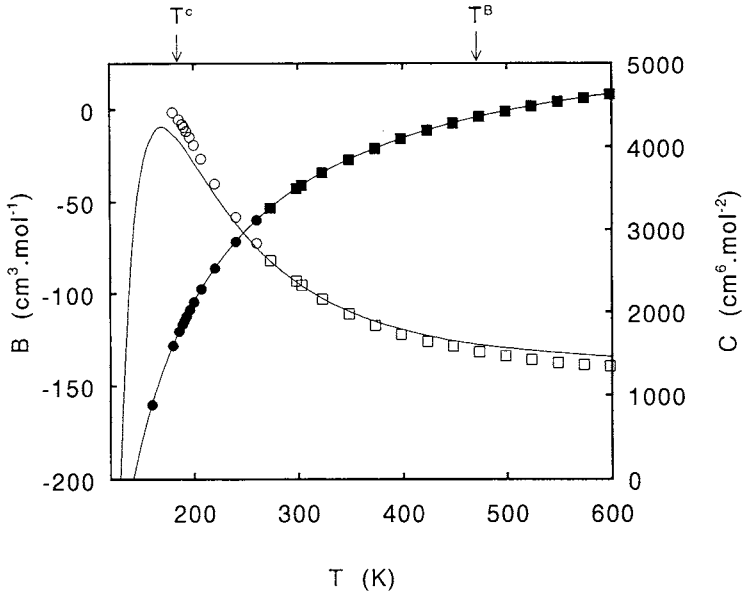
Figure 3.3 Second and third virial coefficients of methane (1,2). ●, ■ B ; ○, □ C. Curves are calculated from intermolecular pair and triplet potentials determined from speed of sound measurements (5).

virial equation of state with $\rho_n = (\Sigma_{i=1}^{\nu} n_i)/V$ but with virial coefficients that depend upon composition as follows:

$$
\left.
\begin{aligned}
B_{\mathrm{mix}} &= \sum_{i=1}^{\nu}\sum_{j=1}^{\nu} x_i x_j B_{ij} \\
C_{\mathrm{mix}} &= \sum_{i=1}^{\nu}\sum_{j=1}^{\nu}\sum_{k=1}^{\nu} x_i x_j x_k C_{ijk} \\
D_{\mathrm{mix}} &= \sum_{i=1}^{\nu}\sum_{j=1}^{\nu}\sum_{k=1}^{\nu}\sum_{l=1}^{\nu} x_i x_j x_k x_l D_{ijkl} \\
&\quad etc.
\end{aligned}
\right\}
\qquad (3.5)
$$

Here, $x_s = n_s/(\Sigma_{i=1}^{\nu} n_i)$ denotes the mole fraction of substance s in the mixture and B_{ij}, C_{ijk}, D_{ijkl}, ⋯ denote a set of virial coefficients which depend only on T. Clearly, B_{ss}, C_{sss}, D_{ssss} ⋯ are the virial coefficients of pure s. The remaining coefficients are known as interaction virial coefficients and are related by the theory to interactions within clusters of dissimilar molecules. It is notable however that the composition dependence of the mixture virial coefficients (quadratic, cubic, quartic, *etc.* in the mole fractions) was arrived at without

recourse to molecular theory. Interaction second virial coefficients B_{ij} have been measured for many systems and the results collated by Dymond and Smith (4) but there are few experimental results for the higher-order terms.

3.1.5 The Pressure Series

In both experimental work and practical applications it is sometimes convenient to use (T, p) as the independent variables in place of (T, ρ_n). For this purpose, an expansion of Z in p is used which may be written as:

$$Z = 1 + B'p + C'p^2 + D'p^3 + \cdots \tag{3.6}$$

The coefficients of this series are uniquely related to the virial coefficients as may be shown by eliminating p from the right hand side of Equation (3.6) using Equation (3.4) and collecting terms. The first few such relations are given in Table 3.1. The composition dependence of the coefficients B', C', $D' \cdots$ in a mixture may be determined by combining these relations with Equations (3.5).

Table 3.1 Relations between coefficients in the density and pressure-explicit expansions of Z.

Pressure Series	Density Series
$B' = B / RT$	$B = RTB'$
$C' = (C - B^2) / (RT)^2$	$C = (RT)^2 (C' + B'^2)$
$D' = (D - 3BC + 2B^3) / (RT)^3$	$D = (RT)^3 (D' + 3B'C' + B'^3)$

3.1.6 Convergence of the Virial Series

It is important to recognize that the virial series might not converge for all experimentally realisable densities. The true radius of convergence is unknown in general and the experimental evidence is somewhat ambiguous. It is certainly possible to fit experimental compression-factor isotherms that extend over a wide range of densities to a truncated form of Equation (3.4). At supercritical temperatures, such representations appear to be satisfactory at densities of up to two or three times the critical (see, e.g., reference 7) while, at subcritical temperatures, good results may be obtained up to the density of the saturated vapour. However, it is often argued that the coefficients obtained in this way are not the true virial coefficients (8); indeed, the value of B determined in a fit to high-density data may differ noticeably from that obtained by analysis of precise low-density data (9). Whether or not such differences should be attributed solely to experimental uncertainties, or to the limitations of Equation (3.4) itself, is really not clear. On the other hand, it is known that the equation of

state is non-analytic at the critical point and it is therefore certain that some fluid states exist in the neighbourhood of the critical point at which the virial series fails to converge. Some theoretical results pertaining to the issue of convergence will be mentioned later in connection with model systems (see Section 3.3.6).

Whatever the ultimate radius of convergence might be, the question of real practical importance is to establish the region in which the series is rapidly convergent. Often, the virial series is truncated after the term in C; we are then interested in the associated truncation error. Provided that sufficiently accurate values of B and C are available, compression factors may be obtained with an accuracy of order 10^{-4} at supercritical temperatures for densities up to roughly one sixth of the critical and the truncation error may be expected to rise to 10^{-2} at about three quarters of the critical density. These estimates of truncation error are based largely on theoretical expectations of the magnitude of D and higher virial coefficients (6). The predicted divergence of these coefficients at low temperatures suggests that there might be a range of temperatures around the critical in which somewhat larger truncation errors occur. At lower temperatures still, the rapid decline in the saturated vapour density is such that the series converges rapidly for all accessible states of the gas.

3.2 THERMODYNAMIC PROPERTIES OF GASES

In this section, a general prescription is presented by means of which the thermodynamic properties of a fluid may be expressed in terms of an equation of state. Explicit results are presented for the virial equation of state.

3.2.1 Perfect-gas and Residual Properties

It is often convenient to express the thermodynamic properties of a fluid as the sum of a perfect-gas term and a residual term (10). The utility of this separation lies first in the availability of widely-applicable theory for the prediction, estimation and correlation of perfect-gas properties (11); and second in the dearth of such theory to account exactly for the effects of molecular interactions with the consequent need for some measure of empiricism.

For generality, consider a mixture of v components characterised by amounts of substance n_1, n_2, $n_3 \cdots n_v$ (denoted by the vector $\boldsymbol{n}^v$), temperature T, pressure p and volume V. If $(T,V,\boldsymbol{n}^v)$ are taken as the independent variables, a thermodynamic property $X(T,V,\boldsymbol{n}^v)$ may be written in the form

$$X(T,V,\boldsymbol{n}^v) = X^{\mathrm{pg}}(T,V,\boldsymbol{n}^v) + X^{\mathrm{res}}(T,V,\boldsymbol{n}^v) \tag{3.7}$$

where $X^{\mathrm{pg}}(T,V,\boldsymbol{n}^v)$ denotes the property of a hypothetical perfect gas with the specified values of $(T,V,\boldsymbol{n}^v)$ and where $X^{\mathrm{res}}(T,V,\boldsymbol{n}^v)$ is the residual term. A similar decomposition may be applied with $(T,p,\boldsymbol{n}^v)$ as the independent variables

$$X(T,p,\boldsymbol{n}^v) = X^{\mathrm{pg}}(T,p,\boldsymbol{n}^v) + X^{\mathrm{res}}(T,p,\boldsymbol{n}^v) \tag{3.8}$$

but one should note that, although $X(T,V,\boldsymbol{n}^v) = X(T,p,\boldsymbol{n}^v)$, the perfect-gas terms and the residual terms in Equations (3.7) and (3.8) generally differ. This is a consequence of the fact that, while $(T,V,p,\boldsymbol{n}^v)$ characterise the state of the real fluid, the state of the hypothetical

perfect gas depends upon whether $(T,V,\boldsymbol{n}^{\mathrm{v}})$ or $(T,p,\boldsymbol{n}^{\mathrm{v}})$ are specified. The difference between $X^{\mathrm{pg}}(T,p,\boldsymbol{n}^{\mathrm{v}})$ and $X^{\mathrm{pg}}(T,V,\boldsymbol{n}^{\mathrm{v}})$ may be obtained by noting that the volume of the hypothetical perfect gas is nRT/p in the one case, where $n = \sum_{i=1}^{\mathrm{v}} n_i$, but V in the other so that

$$X^{\mathrm{pg}}(T,V,\boldsymbol{n}^{\mathrm{v}}) = X^{\mathrm{pg}}(T,p,\boldsymbol{n}^{\mathrm{v}}) + \int_{nRT/p}^{V} (\partial X^{\mathrm{pg}} / \partial V)_{T,n^{\mathrm{v}}} \, dV \tag{3.9}$$

and

$$X^{\mathrm{res}}(T,V,\boldsymbol{n}^{\mathrm{v}}) = X^{\mathrm{res}}(T,p,\boldsymbol{n}^{\mathrm{v}}) - \int_{nRT/p}^{V} (\partial X^{\mathrm{pg}} / \partial V)_{T,n^{\mathrm{v}}} \, dV \tag{3.10}$$

In the case of properties for which the perfect-gas term depends only on $(T,\boldsymbol{n}^{\mathrm{v}})$, one then has $X^{\mathrm{pg}}(T,V,\boldsymbol{n}^{\mathrm{v}}) = X^{\mathrm{pg}}(T,p,\boldsymbol{n}^{\mathrm{v}})$.

3.2.2 Helmholtz Energy and Gibbs Energy

All of the thermodynamic properties of a homogeneous phase may be obtained from the Helmholtz energy or from the Gibbs energy, as discussed in Chapter 2. When $(T,V,\boldsymbol{n}^{\mathrm{v}})$ are the independent variables, the Helmholtz energy $A(T,V,\boldsymbol{n}^{\mathrm{v}})$ is the appropriate choice and the fundamental thermodynamic equation for the phase is

$$dA = -SdT - pdV + \sum_{i=1}^{\mathrm{v}} \mu_i dn_i \tag{3.11}$$

where S is the entropy and μ_i is the chemical potential of component i. The partial derivatives of A with respect to T, V or n_i then give $-S$, $-p$ or μ_i respectively. Once these quantities are obtained, the other state functions such as enthalpy H, energy U and Gibbs energy G follow from the appropriate combinations of A, TS and pV. Quantities such as heat capacity and compressibility may be obtained from second derivatives of the Helmholtz energy combined, where necessary, with the Maxwell relations (12).

When $(T,p,\boldsymbol{n}^{\mathrm{v}})$ are the independent variables, the properties of a homogeneous phase are best obtained from the Gibbs energy $G(T,p,\boldsymbol{n}^{\mathrm{v}})$ and the fundamental equation in the form

$$dG = -SdT + Vdp + \sum_{i=1}^{\mathrm{v}} \mu_i dn_i \tag{3.12}$$

S, V and μ_i are then obtained from the first-order partial derivatives, other state functions from combinations of G, TS and pV, and the remaining properties from second-order partial derivatives of G.

Equations (3.11) and (3.12) are, of course, quite general and apply to any homogeneous phase. In the following sections, these relations are applied to obtain, first, expressions for the properties of the perfect gas and, second, expressions for the residual properties of a real gas in terms of either the virial coefficients or the coefficients of Equation (3.6).

3.2.3 Perfect-Gas Properties

The molar Helmholtz energy $A_{\mathrm{m}}^{\mathrm{pg}} = A^{\mathrm{pg}}/n$ of a pure perfect gas is a function only of (T, ρ_n) and may conveniently be written

$$A_{\mathrm{m}}^{\mathrm{pg}}(T, \rho_n) = A_{\mathrm{m}}^{\circ} + \int_{T^{\circ}}^{T}(\partial A_{\mathrm{m}}^{\mathrm{pg}}/\partial T)_{\rho_n} dT + \int_{\rho_n^{\circ}}^{\rho_n}(\partial A_{\mathrm{m}}^{\mathrm{pg}}/\partial \rho_n)_T d\rho_n \qquad (3.13)$$

where T° and ρ_n° are reference values of the temperature and density at which $A_{\mathrm{m}}^{\mathrm{pg}}$ takes the value A_{m}°. A_{m}° is often specified in terms of reference values of molar energy and molar entropy: $A_{\mathrm{m}}^{\circ} = U_{\mathrm{m}}^{\circ} - T^{\circ}S_{\mathrm{m}}^{\circ}$. The integration with respect to temperature is best carried out after noting that

$$(\partial A_{\mathrm{m}}^{\mathrm{pg}}/\partial T)_{\rho_n} = -S_{\mathrm{m}}^{\mathrm{pg}} = -\int_{T^{\circ}}^{T}(C_{V,\mathrm{m}}^{\mathrm{pg}}/T)dT - S_{\mathrm{m}}^{\circ} \qquad (3.14)$$

where $C_{V,\mathrm{m}}^{\mathrm{pg}}$ is the isochoric perfect-gas heat capacity and is a function only of temperature. For the integration over density, it is also convenient to note that

$$(\partial A_{\mathrm{m}}^{\mathrm{pg}}/\partial \rho_n)_T = p/\rho_n^2 = RT/\rho_n \qquad (3.15)$$

Then, carrying out the integrations in Equation (3.13), one obtains the molar Helmholtz energy of the perfect gas as

$$A_{\mathrm{m}}^{\mathrm{pg}} = \int_{T^{\circ}}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} dT - T\int_{T^{\circ}}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} d\ln T + RT\ln(\rho_n/\rho_n^{\circ}) + U_{\mathrm{m}}^{\circ} - TS_{\mathrm{m}}^{\circ} \qquad (3.16)$$

Provided that $C_{V,\mathrm{m}}^{\mathrm{pg}}(T)$ is known and that T°, ρ_n°, $U_{\mathrm{m}}^{\cup}$ and S_{m}° are defined, all of the thermodynamic properties of the pure perfect gas may then be obtained through Equations (3.11) and (3.16). Typically in the construction of an equation of state, the perfect-gas heat capacity is correlated by means of a suitable function which may then be integrated to obtain an analytic approximation to $A_{\mathrm{m}}^{\mathrm{pg}}(T, \rho_n)$.

For a mixture of v components, the molar Helmholtz energy is given by (11)

$$A_{\mathrm{mix}}^{\mathrm{pg}}(T, \rho_n, \boldsymbol{x}^v) = \sum_{i=1}^{v} x_i A_i^{\mathrm{pg}} + RT\sum_{i=1}^{v} x_i \ln x_i \qquad (3.17)$$

where A_i^{pg} is the molar Helmholtz energy of pure i and $\boldsymbol{x}^v$ denotes the set of mole fractions x_1, $x_2, x_3 \cdots x_v$.

The principal perfect-gas thermodynamic properties of pure substances and multi-component mixtures determined from Equations (3.11), (3.16) and (3.17) with $(T, \rho_n, \boldsymbol{x}^v)$ as the independent variables are summarised in Table 3.2.

An equivalent set of equations to describe the properties of the perfect gas may also be obtained in terms of the Gibbs energy. Following arguments similar to those used to derive Equation (3.16), one may show that

$$G_{\mathrm{m}}^{\mathrm{pg}} = \int_{T^\circ}^{T} C_{p,\mathrm{m}}^{\mathrm{pg}}\, dT - T\int_{T^\circ}^{T} C_{p,\mathrm{m}}^{\mathrm{pg}}\, d\ln T + RT\ln(p/p^\circ) + H_{\mathrm{m}}^\circ - TS_{\mathrm{m}}^\circ \qquad (3.18)$$

Here, $C_{p,\mathrm{m}}^{\mathrm{pg}} = C_{V,\mathrm{m}}^{\mathrm{pg}} + R$ is the isobaric perfect-gas heat capacity and T°, p°, H_{m}° and S_{m}° are reference values of temperature, pressure, molar enthalpy and molar entropy. In order to make Equations (3.16) and (3.18) consistent, one must choose the same reference states; this requires that $p^\circ = RT^\circ\rho_n^\circ$ and $H_{\mathrm{m}}^\circ = U_{\mathrm{m}}^\circ + RT$. Mixture properties may be obtained by means of the equation

$$G_{\mathrm{mix}}^{\mathrm{pg}}(T,p,\mathbf{x}^v) = \sum_{i=1}^{v} x_i G_i^{\mathrm{pg}} + RT\sum_{i=1}^{v} x_i \ln x_i \qquad (3.19)$$

The perfect-gas thermodynamic properties determined from Equations (3.12), (3.18) and (3.19) with $(T,p,\mathbf{x}^v)$ as the independent variables are summarised in Table 3.3.

It should be emphasised that the relations in Tables 3.2 and 3.3 give identical values of the thermodynamic properties when the reference states are defined as above and when ρ_n and p are related by $p = \rho_n RT$. However, as indicated in Section 3.2.2, when these relations are applied to obtain the perfect-gas component of the thermodynamic properties of a *real* fluid, the results generally depend upon the choice of the independent variables. This completes the discussion of perfect-gas properties.

Table 3.2 Thermodynamic properties of pure gases and gaseous mixtures with $(T, \rho_n, \boldsymbol{x}^\upsilon)$ as the independent variables.

Perfect-Gas Properties		Residual Properties
Pure gas	Mixture	Pure gas or mixture*
$A_{\mathrm{m}}^{\mathrm{pg}} = \int_{T^\circ}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} dT - T \int_{T^\circ}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} d\ln T$ $+ RT\ln(\rho_n/\rho_n^\circ) + U_{\mathrm{m}}^\circ - TS_{\mathrm{m}}^\circ$	$A_{\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i A_i^{\mathrm{pg}} + RT \sum_{i=1}^{\upsilon} x_i \ln x_i$	$A_{\mathrm{m}}^{\mathrm{res}} = RT\{B\rho_n + \tfrac{1}{2} C\rho_n^2 + \tfrac{1}{3} D\rho_n^3 + \cdots\}$
$S_{\mathrm{m}}^{\mathrm{pg}} = S_{\mathrm{m}}^\circ + \int_{T^\circ}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} d\ln T - R\ln(\rho_n/\rho_n^\circ)$	$S_{\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i S_i^{\mathrm{pg}} - R \sum_{i=1}^{\upsilon} x_i \ln x_i$	$S_{\mathrm{m}}^{\mathrm{res}} = -R\{(B+B_1)\rho_n + \tfrac{1}{2}(C+C_1)\rho_n^2 + \tfrac{1}{3}(D+D_1)\rho_n^3 + \cdots\}$
$U_{\mathrm{m}}^{\mathrm{pg}} = U_{\mathrm{m}}^\circ + \int_{T^\circ}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} dT$	$U_{\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i U_i^{\mathrm{pg}}$	$U_{\mathrm{m}}^{\mathrm{res}} = -RT\{B_1\rho_n + \tfrac{1}{2} C_1\rho_n^2 + \tfrac{1}{3} D_1\rho_n^3 + \cdots\}$
$C_{V,\mathrm{m}}^{\mathrm{pg}} = C_{V,\mathrm{m}}^{\mathrm{pg}}(T)$	$C_{V,\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i C_{V,i}^{\mathrm{pg}}(T)$	$C_{V,\mathrm{m}}^{\mathrm{res}} = -R\{(2B_1+B_2)\rho_n + \tfrac{1}{2}(2C_1+C_2)\rho_n^2 + \tfrac{1}{3}(2D_1+D_2)\rho_n^3 + \cdots\}$
$H_{\mathrm{m}}^{\mathrm{pg}} = U_{\mathrm{m}}^\circ + RT + \int_{T^\circ}^{T} C_{V,\mathrm{m}}^{\mathrm{pg}} dT$	$H_{\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i H_i^{\mathrm{pg}}$	$H_{\mathrm{m}}^{\mathrm{res}} = RT\{(B-B_1)\rho_n + (C-\tfrac{1}{2}C_1)\rho_n^2 + (D-\tfrac{1}{3}D_1)\rho_n^3 + \cdots\}$
$G_{\mathrm{m}}^{\mathrm{pg}} = A_{\mathrm{m}}^{\mathrm{pg}} + RT$	$G_{\mathrm{mix}}^{\mathrm{pg}} = \sum_{i=1}^{\upsilon} x_i G_i^{\mathrm{pg}} + RT \sum_{i=1}^{\upsilon} x_i \ln x_i$	$G_{\mathrm{m}}^{\mathrm{res}} = RT\{2B\rho_n + \tfrac{3}{2} C\rho_n^2 + \tfrac{4}{3} D\rho_n^3 + \cdots\}$
$\mu_s^{\mathrm{pg}} \equiv \mu_s^{*\mathrm{pg}} = G_{\mathrm{m}}^{\mathrm{pg}}$	$\mu_s = \mu_s^{*\mathrm{pg}} + RT \ln x_s$	$\mu_s^{\mathrm{res}} = RT\{2(\sum_i x_i B_{is})\rho_n + \tfrac{3}{2}(\sum_i \sum_j x_i x_j C_{ijs})\rho_n^2$ $+ \tfrac{4}{3}(\sum_i \sum_j \sum_k x_i x_j x_k D_{ijks})\rho_n^3) + \cdots\}$

* Here $B_1 = T(dB/dT)$, $B_2 = T^2(d^2B/dT^2)$ *etc.* for a pure gas, and $B = B_{\mathrm{mix}}$, $B_1 = T(dB_{\mathrm{mix}}/dT)$, *etc.* for a mixture.

Table 3.3 Thermodynamic properties of pure gases and gaseous mixtures with $(T, p, \boldsymbol{x}^\upsilon)$ as the independent variables.

Perfect-Gas Properties		Residual Properties
Pure gas	Mixture	Pure gas or mixture*
$G_\mathrm{m}^\mathrm{pg} = \int_{T^\circ}^{T} C_{p,\mathrm{m}}^\mathrm{pg}\,dT - T\int_{T^\circ}^{T} C_{p,\mathrm{m}}^\mathrm{pg}\,d\ln T$ $+ RT\ln(p/p^\circ)\ + H_\mathrm{m}^\circ - TS_\mathrm{m}^\circ$	$G_\mathrm{mix}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i G_i^\mathrm{pg} + RT\sum_{i=1}^{\upsilon} x_i \ln x_i$	$G_\mathrm{m}^\mathrm{res} = RT\{B'p + \tfrac{1}{2}C'p^2 + \tfrac{1}{3}D'p^3 + \cdots\}$
$S_\mathrm{m}^\mathrm{pg} = S_\mathrm{m}^\circ + \int_{T^\circ}^{T} C_{p,\mathrm{m}}^\mathrm{pg}\,d\ln T + R\ln(p/p^\circ)$	$S_\mathrm{mix}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i S_i^\mathrm{pg} - R\sum_{i=1}^{\upsilon} x_i \ln x_i$	$S_\mathrm{m}^\mathrm{res} = -R\{(B' + B_1')p + \tfrac{1}{2}(C' + C_1')p^2 + \tfrac{1}{3}(D' + D_1')p^3 + \cdots\}$
$H_\mathrm{m}^\mathrm{pg} = H_\mathrm{m}^0 + \int_{T^\circ}^{T} C_{p,\mathrm{m}}^\mathrm{pg}\,dT$	$H_\mathrm{mix}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i H_i^\mathrm{pg}$	$H_\mathrm{m}^\mathrm{res} = -RT\{B_1'p + \tfrac{1}{2}C_1'p^2 + \tfrac{1}{3}D_1'p^3 + \cdots\}$
$C_{p,\mathrm{m}}^\mathrm{pg} = C_{p,\mathrm{m}}^\mathrm{pg}(T)$	$C_{p,\mathrm{mix}}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i C_{V,i}^\mathrm{pg}(T)$	$C_{p,\mathrm{m}}^\mathrm{res} = -R\{(2B_1' + B_2')p + \tfrac{1}{2}(2C_1' + C_2')p^2 + \tfrac{1}{3}(2D_1' + D_2')p^3 + \cdots\}$
$U_\mathrm{m}^\mathrm{pg} = H_\mathrm{m}^0 + \int_{T^\circ}^{T} C_{p,\mathrm{m}}^\mathrm{pg}\,dT - RT$	$U_\mathrm{mix}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i U_i^\mathrm{pg}$	$U_\mathrm{m}^\mathrm{res} = -RT\{(B' + B_1')p + (C' + \tfrac{1}{2}C_1')p^2 + (D' + \tfrac{1}{3}D_1')p^3 + \cdots\}$
$A_\mathrm{m}^\mathrm{pg} = G_\mathrm{m}^\mathrm{pg} - RT$	$A_\mathrm{mix}^\mathrm{pg} = \sum_{i=1}^{\upsilon} x_i A_i^\mathrm{pg} + RT\sum_{i=1}^{\upsilon} x_i \ln x_i$	$A_\mathrm{m}^\mathrm{res} = -RT\{\tfrac{1}{2}C'p^2 + \tfrac{3}{2}D'p^3 + \cdots\}$
$\mu_s^\mathrm{pg} \equiv \mu_s^{*\mathrm{pg}} = G_\mathrm{m}^\mathrm{pg}$	$\mu_s = \mu_s^{*\mathrm{pg}} + RT\ln x_s$	$\mu_s^\mathrm{res} = RT[\{2\sum_i x_i B_{is} - B\}(p/RT)$ $+ \{\tfrac{3}{2}\sum_i\sum_j x_i x_j C_{ijs} - 2B\sum_i x_i B_{is} + \tfrac{3}{2}B^2 - C\}(p/RT)^2$ $+ \{\tfrac{3}{2}\sum_i\sum_j\sum_k x_i x_j x_k D_{ijks} - 3B\sum_i\sum_j x_i x_j C_{ijs}$ $+ (4B^2 - 2C)\sum_i x_i B_{is} - D + 4BC - \tfrac{10}{3}B^3\}(p/RT)^3 + \cdots]$

* Here $B_1' = T(dB'/dT)$, $B_2' = T^2(d^2B'/dT^2)$ *etc.* for a pure gas, and $B' = B_\mathrm{mix}'$, $B_1' = T(dB_\mathrm{mix}'/dT)$, *etc.* for a mixture. μ_s^res is given in terms of the interaction virial coefficients defined in Equation (3.5) with $B = B_\mathrm{mix}$, *etc.*

3.2.4 Residual Properties

All residual thermodynamic properties may be expressed in terms of an equation of state of the form $p = p(T, \rho_n)$ or $\rho_n = \rho_n(T, p)$; Equation (3.4) is an example of the former and Equation (3.6) of the latter. The residual part of the Helmholtz energy for a phase of constant composition may be obtained by combining the identity

$$A_m^{res}(T, \rho_n) = \int_0^{\rho_n} \{(\partial A_m / \partial \rho_n)_T - (\partial A_m^{pg} / \partial \rho_n)_T\} d\rho_n \qquad (3.20)$$

in which $(\partial A_m / \partial \rho_n)_T = p / \rho_n^2$, with Equation (3.4) for the pressure. All other residual properties may then be derived by manipulation of the result. Table 3.2 gives expressions for A_m^{res} and for the other five common residual thermodynamic functions S_m^{res}, U_m^{res}, $C_{V,m}^{res}$, H_m^{res} and G_m^{res} in terms of the virial coefficients and with (T, ρ_n, x^v) as the independent variables.

Also given in Table 3.2 is the expansion of the residual part of the chemical potential μ_s of component s in a multi-component mixture. This is useful in a vapour-liquid equilibrium calculation where the virial equation of state is used for the vapour phase.[*] Such calculations are usually carried out for conditions of constant temperature and pressure and, to evaluate the chemical potential for specified values of (T, p, x^v), one must first solve Equation (3.4) for ρ_n. The partial fugacity f_s of component s in a mixture is often used in place of the chemical potential to determine the equilibrium condition between phases. This quantity may be defined by the relation

$$\ln(f_s / p) = (\mu_s - \mu_s^{*pg}) / RT \qquad (3.21)$$

where μ_s^{*pg} is the perfect-gas chemical potential of pure s at the temperature and pressure in question. In turn, f_s may be conveniently expressed in terms of the dimensionless partial fugacity coefficient $\phi_s = (f_s / x_s p)$ which, in view of Equations (3.19) and (3.21), is most closely related to the residual chemical potential at specified (T, p, x^v):

$$\begin{aligned} RT \ln \phi_s(T, \rho_n, x^v) &= \mu_s^{res}(T, p, x^v) \\ &= \mu_s^{res}(T, \rho_n, x^v) - RT \ln Z(T, \rho_n, x^v) \end{aligned} \qquad (3.22)$$

The second part of Equation (3.22) may be obtained by using Equation (3.10). The residual part of the Gibbs energy may be obtained in a manner analogous to that used to obtain A_m^{res}. Table 3.3 gives the expansions of G_m^{res}, S_m^{res}, H_m^{res}, $C_{p,m}^{res}$, U_m^{res}, A_m^{res} and μ_s^{res} in terms of the coefficients of Equation (3.6) with (T, p, x^v) as the independent variables. Other thermodynamic properties may be obtained through standard manipulations of the relations given in Tables 3.2 and 3.3.

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[*] The chemical potential of components in the coexisting liquid cannot be obtained from the virial equation but may be deduced from, for example, an activity coefficient model.

3.3 THEORY

In this section, the theoretical basis of the virial equation of state will be outlined and the relationships between the virial coefficients B, C, D, $\cdots$ and intermolecular potential energies will be derived. Although the virial equation derives its name from the virial theorem of Clausius, only the more powerful statistical-mechanical development based on the grand canonical ensemble will be considered here (8,13,14). The development is carried out in both classical and quantum mechanics and the results are compared with experiment.

3.3.1 Properties of the Grand Canonical Partition Function

The ensemble methods of statistical mechanics have been discussed by many authors (11,13,15) and the well known results which form the starting point in the derivation of the virial equation are therefore reviewed here only briefly. The grand canonical ensemble is a hypothetical isolated assembly of some large number of systems of volume V each separated from its neighbours by walls which are permeable to both matter and energy. Since the entire ensemble is isolated it must be isothermal and each of its systems is therefore a replica on a macroscopic scale of a single open isothermal system with volume V, temperature T and absolute activity λ_i for molecules of type i ($\lambda_i \equiv e^{\mu_i / RT}$).

The number N_i of molecules of type i in each system of the ensemble is not fixed but may fluctuate about mean values $\overline{N}_i$ which, according to the postulates of statistical mechanics, are taken to be identical with the observable value of this property in the real system. The value of $\overline{N}_i$ and of all the other thermodynamic properties of the open isothermal system may be obtained from a single function Ξ called the grand canonical partition function.

For the general case of a mixture containing v components, the grand canonical partition function is given by

$$\Xi = \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \cdots \sum_{N_v=0}^{\infty} \Theta_{N_1 N_2 \cdots N_v} \prod_{c=1}^{v} \lambda_c^{N_c} \tag{3.23}$$

The quantity $\Theta_{N_1 N_2 \cdots N_v}$ which appears as a coefficient in Equation (3.23) is the canonical-ensemble partition function for a closed system containing the specified numbers of molecules in volume V at temperature T. This quantity is given by

$$\Theta_{N_1 N_2 \cdots N_v} = \sum_{J} \exp(-E_J / kT) \tag{3.24}$$

where E_J is the energy of quantum state J and the summation is performed over all possible states of the system with the given volume and numbers of molecules.

The grand partition function is related to thermodynamic properties of the system by the equation

$$\Xi = \exp(pV / kT) \tag{3.25}$$

This may be combined with the fundamental thermodynamic equation for the system with (T, V, λ^v) as the independent variables (11)

$$d(pV) = SdT + pdV + RT\sum_i n_i d\ln\lambda_i \qquad (3.26)$$

to obtain all of the other thermodynamic properties. In particular, the amount of substance n_i of component i in the system is given by

$$Ln_i = \overline{N}_i = (\partial\ln\Xi / \partial\ln\lambda_i)_{T,V,\lambda_{j\neq i}} \qquad (3.27)$$

where $L = R/k$ is Avogadro's constant. In the following sections, these relations are applied to derive the virial equation of state.

3.3.2 The Virial Equation of State from the Grand Partition Function

In principle, the thermodynamic properties of the system may be obtained directly from the grand partition function through Equations (3.23) and (3.25). Unfortunately, this requires computation of $\Theta_{N_1 N_2 \cdots N_\nu}$ for all possible values of N_1, N_2, $\cdots$; this is an impossible task. A practical alternative which leads to the virial equation is to develop Ξ as a power series in some suitably chosen set of variables which are then eliminated in favour of the number densities $\overline{N}_i / V$. Several authors have given derivations of the virial series for one-component (8,11,13,15), two-component (16) and multi-component systems (17,18). Here, the general case of the multi-component system is considered in outline.

It is first convenient to make two definitions. An 'active number density' z_i is defined for each component in the mixture by the equation

$$z_i = (\Theta_1^{(i)}/V)\lambda_i \qquad (3.28)$$

This quantity has the property that $z_i \to \overline{N}_i / V$ as $\lambda_i \to 0$. A configurational partition function $Q_N^{(ij\cdots)}$ is also defined for the system when it contains a total of N molecules of types $(i,j, \cdots)$ by means of the relation

$$Q_N^{(ij\cdots)} = \Theta_N^{(ij\cdots)}\left(\prod_{c=1}^\nu (V/\Theta_1^{(c)})^{N_c} N_c!\right) \qquad (3.29)$$

In these equations, the partition functions Θ and Q are labelled in the same notation; thus $\Theta_N^{(ij\cdots)} \equiv \Theta_{N_1 N_2 \cdots N_\nu}$, $N = \Sigma_{c=1}^\nu N_c$ and $(i,j, \cdots)$ lists the type (species) of each molecule in turn. In terms of these new variables, the grand partition function is given by

$$\Xi = 1 + \sum_{i=1}^\nu Q_1^{(i)} z_i + \sum_{i=1}^\nu\sum_{j=1}^\nu (Q_2^{(ij)}/2!) z_i z_j + \sum_{i=1}^\nu\sum_{j=1}^\nu\sum_{k=1}^\nu (Q_3^{(ijk)}/3!) z_i z_j z_k + \cdots \qquad (3.30)$$

and takes the form of a power series in the z_i in which the Nth group of terms pertains to a system of $N-1$ molecules. It is then *assumed* that an analogous expansion of p in powers of the z_i exists:

$$p/kT = \sum_{i=1}^{v} b_1^{(i)} z_i + \sum_{i=1}^{v} \sum_{j=1}^{v} b_2^{(ij)} z_i z_j + \sum_{i=1}^{v} \sum_{j=1}^{v} \sum_{k=1}^{v} b_3^{(ijk)} z_i z_j z_k + \cdots \qquad (3.31)$$

The coefficients $b_N^{(ij\cdots)}$ of this series may be related to the $Q_N^{(ij\cdots)}$ by means of a simultaneous expansion of $\exp(pV/kT)$ in powers of the z_i and term-by-term comparison with Equation (3.30). The results of that operation are:

$$\left.\begin{aligned}
b_1^{(i)} &= Q_1^{(i)}/(1!V) = 1 \\
b_2^{(ij)} &= (Q_2^{(ij)} - V^2)/(2!V) \\
b_3^{(ijk)} &= (Q_3^{(ijk)} - VQ_2^{(ij)} - VQ_2^{(ik)} - VQ_2^{(jk)} + 2V^3)/(3!V) \\
&\quad etc.
\end{aligned}\right\} \qquad (3.32)$$

Incidentally, the quantities $b_N^{(ij\cdots)}$, known as cluster integrals, which appear here play an important role in some formulations of statistical thermodynamics (15). They have the property that $b_N^{(ij\cdots)} \to 0$ when any one or more members of the group of N molecules is remote from the others.

The final step in the derivation is to eliminate the z_i from Equation (3.31) in favour of the number densities $\overline{N}_i/V$. This may be done by noting that $\overline{N}_i/V$ is given according to Equations (3.27) and (3.28) by

$$\begin{aligned}
\overline{N}_i/V &= (z_i/V)(\partial \ln \Xi/\partial z_i)_{T,V,z_{j\neq i}} \\
&= (z_i/kT)(\partial p/\partial z_i)_{T,V,z_{j\neq i}},
\end{aligned} \qquad (3.33)$$

from which it follows that,

$$\overline{N}_i/V = z_i \left(b_1^{(i)} + 2\sum_{j=1}^{v} b_2^{(ij)} z_j + 3\sum_{j=1}^{v} \sum_{k=1}^{v} b_3^{(ijk)} z_j z_k + \cdots \right) \qquad (3.34)$$

Equation (3.34) may be inverted to obtain a power series for z_i in the number densities $\overline{N}_i/V$,

$$z_i = (\overline{N}_i/V) \left(a_1^{(i)} + \sum_{j=1}^{v} a_2^{(ij)} (\overline{N}_j/V) + \sum_{j=1}^{v} \sum_{k=1}^{v} a_3^{(ijk)} (\overline{N}_j \overline{N}_k/V^2) + \cdots \right) \qquad (3.35)$$

with coefficients:

$$\left.\begin{aligned}
a_1^{(i)} &= 1 \\
a_2^{(ij)} &= -2b_2^{(ij)} \\
a_3^{(ijk)} &= -3b_3^{(ijk)} + 2b_2^{(ij)}(b_2^{(ij)} + b_2^{(ik)}) + 2b_2^{(ik)}(b_2^{(ik)} + b_2^{(ij)}) \\
&\quad etc.
\end{aligned}\right\} \qquad (3.36)$$

Finally, combining Equation (3.31) with Equations (3.36) and collecting coefficients of $(\overline{N}_i/V)^\alpha$, one obtains the virial equation of state with $\rho_n = (\Sigma_i \overline{N}_i / LV)$ and with virial coefficients which are related to the cluster integrals as follows:

$$
\left.\begin{aligned}
B_{ij} &= -Lb_2^{(ij)} \\
C_{ijk} &= -L^2 \{2b_3^{(ijk)} - \tfrac{4}{3}(b_2^{(ij)}b_2^{(ik)} + b_2^{(ij)}b_2^{(jk)} + b_2^{(ik)}b_2^{(jk)})\} \\
&\quad etc.
\end{aligned}\right\}
\tag{3.37}
$$

These equations apply to any combination of like and unlike molecules and, by combination with Equations (3.32), the virial coefficients may be calculated from configurational partition functions. In the case of a one-component gas, the results simplify to $B = -Lb_2$ and $C = -L^2(2b_3 - 4b_2^2)$. General relationships have been derived for the one-component gas by which any virial coefficient may be expressed in terms of a set of cluster integrals and by which each cluster integral may be expressed in terms of configurational partition functions (14,19).

In the following sections, the evaluation of $Q_N^{(ij\cdots)}$ will be considered in both classical and quantum mechanics for $N = 1, 2, 3, \cdots$. However, one can see already that, in making the virial expansion, the intractable N-body problem posed by Equations (3.23) and (3.25) has been converted into a series of one-body, two-body, three-body $\cdots$ problems the first few of which one may expect to solve with relative ease.

3.3.3 The Virial Coefficients in Classical Mechanics

For almost all substances at accessible temperatures a classical treatment, augmented at low temperatures by small quantum 'corrections', may be used to obtain the configurational partition function and thus the virial coefficients with great accuracy. Only at low temperatures for the isotopes of hydrogen and helium is a fully quantum-mechanical treatment required. A fully classical treatment of $Q_N^{(ij\cdots)}$ will therefore be considered first.

We begin by returning to Equation (3.24) for the canonical partition function. The energy levels over which the summation in that equation extends are those of the entire system and it is usual to make the assumption that they may be separated into two entirely independent sets. The first is associated with the internal degrees of freedom of the molecules and the second with the position, orientation and momentum of the molecules. With this assumption, which is amply justified for small rigid molecules, the partition function factorises into the product of two terms, the one ($\Gamma_N^{(ij\cdots)}$) for the internal degrees of freedom and the other ($\Phi_N^{(ij\cdots)}$) for the motion of the centres of mass:

$$
\Theta_N^{(ij\cdots)} = \Gamma_N^{(ij\cdots)}\Phi_N^{(ij\cdots)}
\tag{3.38}
$$

By essentially the same assumption, $\Gamma_N^{(ij\cdots)}$ for $N > 1$ factorises into the product of N one-molecule partition functions with one term for each molecule. The configurational partition function is then entirely independent of the internal degrees of freedom and is given by

$$Q_N^{(ij\cdots)} = \Phi_N^{(ij\cdots)} \prod_{c=1}^{v} (V/\Phi_1^{(c)})^{N_c} N_c! \tag{3.39}$$

The centre-of-mass term is given in quantum mechanics by the sum

$$\Phi_N^{(ij\cdots)} = \sum_J \exp(-H_J/kT) \tag{3.40}$$

over all allowed (and distinguishable) translational quantum states of the N-molecule system. The quantity H_J which appears in this expression is the total (kinetic + potential) energy of the N centres of mass when the system is in the quantum state labeled J. The classical limit of $\Phi_N^{(ij\cdots)}$ is obtained by replacing the discrete spectrum of translational states by a continuum and the summation by integrals over the position, orientation and momentum of the molecules (20):

$$\Phi_N^{(ij\cdots)} = \left(h^{3N} \prod_{c=1}^{v} \Omega_c^{N_c} N_c! \right)^{-1} \int \exp(-H/kT)\, d\mathbf{P}^N d\mathbf{r}^N d\omega^N \tag{3.41}$$

Here, $H = \Sigma_{i=1}^{N}(\mathbf{P}_i \cdot \mathbf{P}_i/2m_i) + U_N^{(ij\cdots)}$ is the classical equivalent of H_J, $\mathbf{P}_i$ is the momentum and m_i the mass of molecule i, $U_N^{(ij\cdots)}$ is the total potential energy stored in the intermolecular forces, and $\mathbf{r}^N$ and ω^N denote the set of position and orientation vectors of the N molecules. In addition, Ω_c is a normalisation constant equal to the integral $\int d\omega$ over all possible orientations in space of one molecule of component c.* The integration in Equation (3.41) is carried out over all possible values of linear momentum, over all positions of the molecules within the volume V and over all possible orientations of the molecules. The integration over momentum is easily carried out, yielding a factor $(2\pi m_i kT)^{3/2}$ for each molecule, so that

$$\Phi_N^{(ij\cdots)} = \left(\prod_{c=1}^{v} \Lambda_c^{3N_c} \Omega_c^{N_c} N_c! \right)^{-1} \int \exp(-U_N^{(ij\cdots)}/kT)\, d\mathbf{r}^N d\omega^N \tag{3.42}$$

where

$$\Lambda_i = h/(2\pi m_i kT)^{1/2} \tag{3.43}$$

is a de Broglie wavelength. Since, for a system containing only one molecule, there is no intermolecular potential energy, $\Phi_1^{(c)}$ is given by

---

* The appearance of the remaining terms in the prefactor of Equation (3.41) is explained as follows. Since molecules of the same species are indistinguishable, configurations which differ only by the assignments of labels to the individual molecules are actually identical and should not be counted separately. It is therefore necessary to divide by the $N_c!$ possible assignments of labels amongst the N_c molecules for each component c in the system. h^{3N} is a normalisation factor for the integrations over position and momentum chosen such that the classical and quantum treatments of the partition function converge in the limit of high temperatures.

$$\Phi_1^{(c)} = (V/\Lambda_c^3) \tag{3.44}$$

and, finally, the configurational partition function is

$$Q_N^{(ij\cdots)} = \left(\prod_{c=1}^{\nu}\Omega_c^{N_c}\right)^{-1}\int\exp(-U_N^{(ij\cdots)}/kT)d\mathbf{r}^N d\omega^N \tag{3.45}$$

Note that, while $\Phi_N^{(ij\cdots)}$ is dimensionless, $Q_N^{(ij\cdots)}$ has the dimensions of V^N.

In order to evaluate the virial coefficients, knowledge is required of the potential energy of clusters of N molecules with $N = 2, 3, \cdots$. For $N = 2$, the situation is comparatively simple and $U_2 = u(r_{12}, \omega_{12})$ is just the intermolecular potential-energy function for a pair of molecules with separation $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ and relative orientation given by a set of (body-fixed) coordinates denoted by ω_{12}. The precise quantitative determination of $u(r_{12}, \omega_{12})$ for a range of interesting molecules remains one of the most resilient problems in chemical physics and our present knowledge is quite restricted. The pair potential is however known with considerable accuracy for several monatomic substances, especially He, Ne, Ar, Kr, Xe and their mixtures, and for a number of simple systems containing molecular hydrogen (21,22). Considerable progress has been made for other diatomic gases, for mixtures of diatomic and monatomic components, and for a few other systems such as water (22). For other polyatomic systems, it has so far proved impossible to establish the multi-dimensional potential energy surface in any precise way. In these cases only crude models are available, many of which neglect completely the orientational dependence of the pair potential. The origin and determination of the intermolecular pair potential has been reviewed by several authors (21-23).

For virial coefficients above the second, U_N is required for $N \geq 3$ and the question therefore arises as to whether or not this may be expressed simply as a sum of pair interaction energies. It is now well established that the approximation of pair-wise additivity is in fact fairly poor (24) and that one should write

$$U_N = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}u_{ij} + \Delta u_N \tag{3.46}$$

where $u_{ij} = u(r_{ij}, \omega_j)$ and Δu_N represents the deviations from pair-wise additivity in a cluster of N molecules (8). Some information is available on the behaviour of Δu_3 and, in particular, the asymptotic long-range form of the potential for atoms and spherical-top molecules is known from the theory of dispersion forces to be (25)

$$\Delta u_3 = \upsilon_3(1 + 3\cos\vartheta_i\cos\vartheta_j\cos\vartheta_k)/(r_{ij}r_{ik}r_{jk})^3 \tag{3.47}$$

Here, υ_3 is a dispersion coefficient and ϑ_i is the angle subtended at molecule i by molecules j and k. υ_3 is related approximately to the coefficient C_6 of r^{-6} in the asymptotic long-range expansion of the two-body potential by $\upsilon_3 = \frac{3}{4}\alpha C_6$, where α is the polarizability. The corresponding result for linear molecules is also known (26).

The cluster integrals $b_2^{(ij)}$ and $b_3^{(ijk)}$ may now be evaluated from Equations (3.32) and (3.45) and the results are

$$b_2^{(ij)} = (2!V\Omega^2)^{-1} \int f_{ij} \ d\mathbf{r}_i d\mathbf{r}_j d\omega_i d\omega_j$$

$$b_3^{(ijk)} = (3!V\Omega^3)^{-1} \int [f_{ij}f_{ik}f_{jk} + f_{ij}f_{ik} + f_{ij}f_{jk} + f_{ik}f_{jk}] d\mathbf{r}_i d\mathbf{r}_j d\mathbf{r}_k d\omega_i d\omega_j d\omega_k$$

$$+ (3!V\Omega^3)^{-1} \int (1+f_{ij})(1+f_{ik})(1+f_{jk})f_{ijk} \ d\mathbf{r}_i d\mathbf{r}_j d\mathbf{r}_k d\omega_i d\omega_j d\omega_k . \tag{3.48}$$

Here use has been made of the Mayer function f_{ij}, defined by

$$f_{ij} = \exp(-u_{ij}/kT) - 1 \tag{3.49}$$

and of an analogous function of the three-body potential:

$$f_{ijk} = \exp(-\Delta u_3 / kT) - 1 \tag{3.50}$$

For neutral molecules, both f_{ij} and f_{ijk} approach zero rapidly as the separation of the molecules is increased thus ensuring that the integrals converge. Notice that, if Δu_3 is zero, f_{ijk} vanishes.

Since the intermolecular potential energy depends only on the relative position and orientation of the molecules, it is convenient to transform the integration variables from the space-fixed to the body-fixed frame. In the case of the position vectors, the transformations are

$$V^{-1} d\mathbf{r}_i d\mathbf{r}_j = 4\pi r_{ij}^2 dr_{ij}$$

$$V^{-1} d\mathbf{r}_i d\mathbf{r}_j d\mathbf{r}_k = 8\pi^2 r_{ij} r_{ik} r_{jk} dr_{ij} dr_{ik} dr_{jk} \tag{3.51}$$

and the integrations for $b_3^{(ijk)}$ then extend over all values of (r_{ij}, r_{ik}, r_{jk}) which form a triangle. It is also convenient to extend formally the range of integrations over molecular separations to infinity, rather than just to the walls of the container, and this is justified by the rapid convergence of the integrals. For the orientation vectors, one may adopt any convenient set of angular coordinates provided that the appropriate normalisation constant is used. Equations (3.37), (3.48) and (3.51) are now combined to determine B and C.

The second virial coefficient corresponding to the interaction of molecules 1 and 2 is given in body-fixed coordinates as

$$B_{12} = -(2\pi L/\Omega_{12}) \int_0^\infty \int_{(\omega_{12})} f_{12} r_{12}^2 dr_{12} d\omega_{12} \tag{3.52}$$

where Ω_{12} is a new normalisation factor equal to the integral $\int d\omega_{12}$ over all possible relative orientations.

In the case of the third virial coefficient corresponding to the interaction of molecules 1, 2 and 3, the effects of additive and non-additive intermolecular potential energies separate so that

$$C_{123} = C_{123}^{add} + \Delta C_{123} \tag{3.53}$$

The additive and non-additive contributions are given by

$$C_{123}^{add} = -(8\pi^2 L^2/3\Omega_{23}) \int f_{12}f_{13}f_{23} \; r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23}d\omega_1 d\omega_2 d\omega_3 \tag{3.54}$$

and

$$\Delta C_{123} = -(8\pi^2 L^2/3\Omega_{23}) \int (1+f_{12})(1+f_{13})(1+f_{23})f_{123} \; r_{12}r_{13}r_{23}dr_{12}dr_{13}dr_{23}d\omega_1 d\omega_2 d\omega_3 \tag{3.55}$$

where $\Omega_{123} = \int d\omega_1 d\omega_2 d\omega_3$. Explicit expressions for the additive and non-additive parts of D have been given by Mason and Spurling (8); for higher virial coefficients it is preferable to use graphical notation to simplify the otherwise complicated expressions (15).

As a practical consideration, evaluation of B is easy by quadrature even for non-linear molecules (a six-dimensional integral is required). Similarly, evaluation of C, D or E for monatomic molecules is quite easy but, as soon as orientational dependence of the intermolecular potential is included, one is faced with a significant computational task. For example, to evaluate C for three linear molecules, one must integrate over nine coordinates and it is then probably necessary to resort to Monte-Carlo methods at least for the angular variables.

In the few cases where the intermolecular pair potential is accurately known, and quantum effects are unimportant, values of B calculated from Equation (3.52) are in close agreement with experiment. This situation is illustrated in Figure 3.4 by the example of krypton. The experimental third virial coefficients of krypton (28-30) are also shown in Figure 3.4 together with values calculated by means of Equations (3.54) and (3.55) on the assumption that Δu_3 is given by Equation (3.49) with the theoretical value of υ_3 (23). In view of the considerable scatter amongst the experimental results, the agreement is satisfactory and certainly much better than when ΔC is neglected.

3.3.4 Quantum Corrections

Except for hydrogen and helium at low temperatures, quantum effects may be accounted for rather accurately by the addition to the results of the previous section of small quantum corrections. It turns out that these terms may be obtained by expansion of the quantum-mechanical partition function about the classical limit in powers of $\hbar^2$ (31). At the low temperatures where these corrections are significant, it is safe to treat the molecules as rigid rotators. Only translational and rotational terms will then be present in the expansion.

The treatment is most complete for monatomic systems where B is known correct to $O(\hbar^6)$ (32) and C is known, including the effects of non-additive intermolecular forces, correct to $O(\hbar^4)$ (33,34). In the case of polyatomic molecules, the expansion of B is less well developed and there appears to have been no calculations for C. The translational and rotational quantum corrections to B were worked out for linear molecules to $O(\hbar^2)$ by Kirkwood (35) and later to $O(\hbar^4)$ by Wang Chang (36). However, Pack (37) has pointed out that, in the derivation presented by Wang Chang, the transformation from space-fixed coordinates to body-fixed coordinates was made incorrectly with the consequence that a
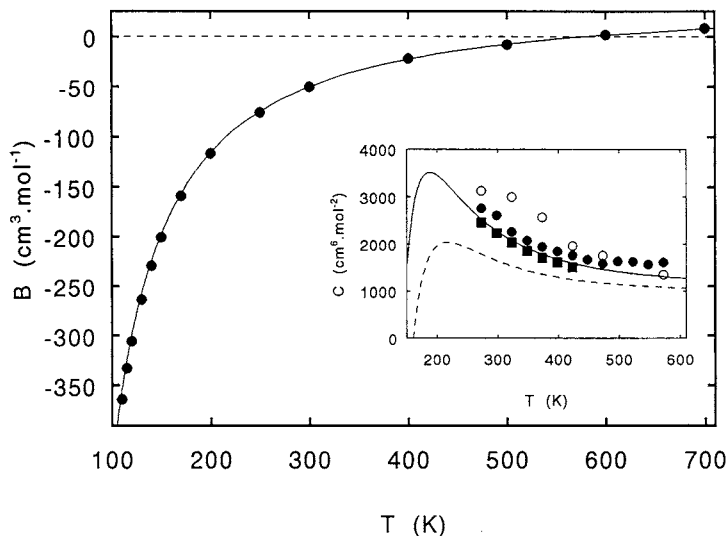
Figure 3.4 Second virial coefficients of krypton. ●, recommended (experimental) values from reference 4; ———, calculated from the interatomic potential of Aziz and Slaman (27). Insert: third virial coefficients. ●, (28); ■, (29); O, (30); ———, $C^{add} + \Delta C$; - - - - - -, C^{add}.

coriolis-type rotation-translation coupling term was neglected. It has also been observed that some terms of $O(\hbar^4)$ are missing from Wang Chang's formulae (38). A revised semi-classical expression for B,

$$B = B_{class} + (\hbar^2/2\mu)B_{tl} + (\hbar^2/2I_1)B_{rl}^{(1)} + (\hbar^2/2I_2)B_{rl}^{(2)} + (\hbar^2/2\mu)B_{cl} \tag{3.56}$$

correct to $O(\hbar^2)$ has been derived and may be applied to all rigid molecules (both like and unlike) except asymmetric tops. In Equation (3.56), B_{class} is the classical second virial coefficient, μ is the reduced mass and I_1, I_2 are the moments of inertia of the two molecules. The coefficients B_{tl}, $B_{rl}^{(i)}$ and B_{cl} determine respectively the leading translational, rotational and coriolis contributions to the quantum corrections. Pack (37) gives a general formula in space-fixed coordinates that relates the leading quantum corrections to the translation-rotation Hamiltonian. Specific expressions were also given in body-frame coordinates for linear molecules and for the interaction between an atom and either a linear molecule or a spherical top molecule. Here, only the results for a system of linear molecules are given:*

---

* Alternative expressions for B_r and B_c are given in reference 37 for the case in which the intermolecular potential is expanded in spherical harmonics.

$$B_{class} = -\frac{2\pi L}{\Omega_{12}} \int\limits_{0}^{\infty} \int\limits_{(\omega_{12})} \{\exp(-u/kT) - 1\} \, r_{12}^2 dr_{12} d\omega_{12} \tag{3.57}$$

$$B_{t1} = \frac{\pi L}{6(kT)^3 \Omega_{12}} \int\limits_{0}^{\infty} \int\limits_{(\omega_{12})} \exp(-u/kT)(\partial u/\partial r)^2 \, r_{12}^2 dr_{12} \, d\omega_{12} \tag{3.58}$$

$$B_{r1}^{(i)} = \frac{\pi L}{6(kT)^3 \Omega_{12}} \int\limits_{0}^{\infty} \int\limits_{(\omega_{12})} \exp(-u/kT)\{(\partial u/\partial \theta_i)^2 + (\partial u/\partial \phi_i)^2 \csc^2\theta_i\} \, r_{12}^2 dr_{12} d\omega_{12} \tag{3.59}$$

$$B_{c1} = \frac{\pi L}{6(kT)^3 \Omega_{12}} \int\limits_{0}^{\infty} \int\limits_{(\omega_{12})} \exp(-u/kT) F(r,\theta_1,\theta_2,\phi_{12}) \, dr_{12} d\omega_{12} \tag{3.60}$$

where (39)

$$\begin{aligned}
F(r,\theta_1,\theta_2,\phi_{12}) &= (\partial u/\partial \theta_1)^2 + (\partial u/\partial \theta_2)^2 + \{\csc^2\theta_1 + \csc^2\theta_2 - 2\}(\partial u/\partial \phi_{12})^2 \\
&- 2(\partial u/\partial \phi_{12})\sin\phi_{12}\{(\partial u/\partial \theta_1)\cot\theta_2 + (\partial u/\partial \theta_2)\cot\theta_1\} \\
&+ 2\cos\phi_{12}\{(\partial u/\partial \theta_1)(\partial u/\partial \theta_2) - \cot\theta_1 \cot\theta_2 (\partial u/\partial \phi_{12})^2\}
\end{aligned} \tag{3.61}$$

Here, θ_i and ϕ_i are body-fixed polar and azimuthal angles, $\phi_{12} = (\phi_2 - \phi_1)$, and

$$\int\limits_{(\omega_{12})} d\omega_{12} = \int\limits_{-1}^{1} d(\cos\theta_1) \int\limits_{-1}^{1} d(\cos\theta_2) \int\limits_{0}^{2} d\phi_{12} = \Omega_{12} = 8\pi \tag{3.62}$$

Equations (3.57) – (3.60) are easily specialised to atom-linear molecule systems, where u no longer depends upon θ_2 and ϕ_{12}. B_{t1} further reduces to the corresponding monatomic result when u is a function only of r. These formulae may also be applied to the interaction second virial coefficient B_{12}.

An important theoretical result is that B_{class} always gives a lower bound for B itself so that the quantum effects are always positive (37). It appears that the semi-classical expansion of B in $\hbar^2$ converges satisfactorily for neon and for heavier monatomic systems at all temperatures above the normal boiling temperature. This is illustrated in Figure 3.5 where B and, on an expanded scale, the first two translational quantum corrections are plotted for neon. For helium, the series converges satisfactorily only at temperatures above about 40 K. Except for the isotopes of hydrogen, molecular gases are generally sufficiently heavy that translational quantum effects are given with sufficient accuracy at temperatures of interest by the correction of $O(\hbar^2)$. Whether or not this is also true of the rotational term depends upon the moment of inertia and the degree of anisotropy of the intermolecular potential. For non-polar molecules, the rotational and coriolis terms together are generally smaller than the translational term but for polar molecules, especially polar hydrides, the reverse is true. It appears that B_c is always significantly smaller than B_r. These points are illustrated in Figures 3.6 and 3.7, where B, B_{t1}
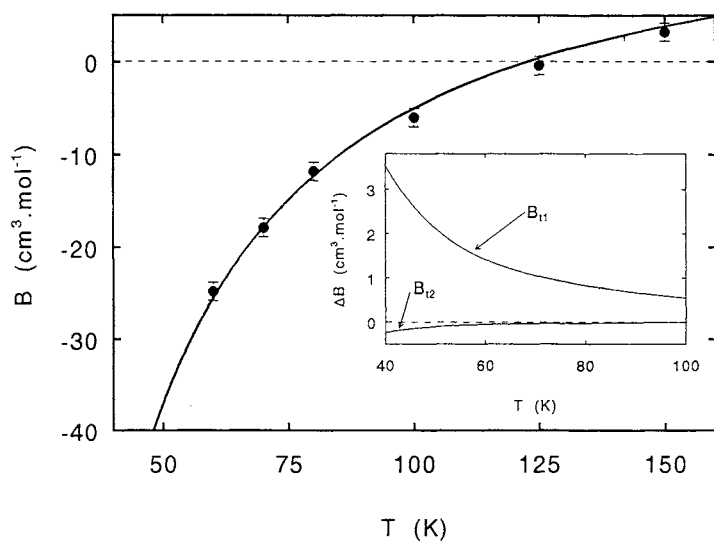
Figure 3.5. Second virial coefficients of neon. ●, recommended (experimental) values from reference 4; ————, calculated correct to the second quantum correction from the interatomic potential of Aziz and Slaman (40). Insert: B_{t1} and B_{t2}.
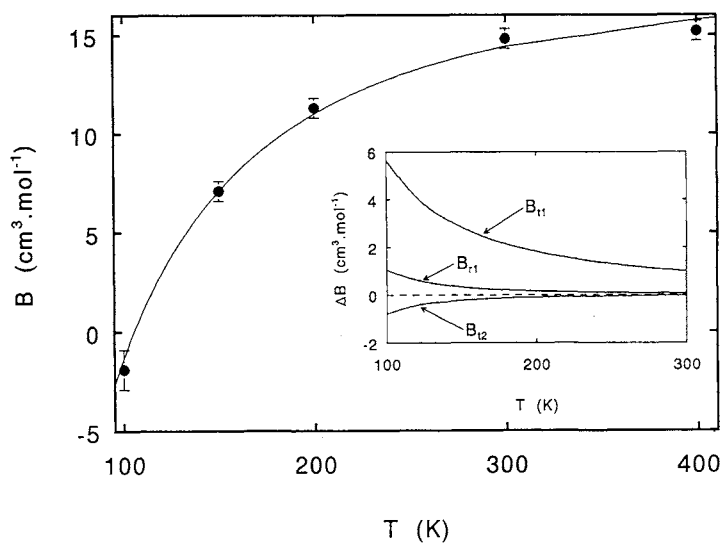

Figure 3.6. Second virial coefficients of hydrogen. ●, recommended (experimental) values from reference 4; ————, calculated correct to the first quantum corrections from an anisotropic intermolecular potential model. Insert: B_{t1}, B_{r1} and B_{t2}.
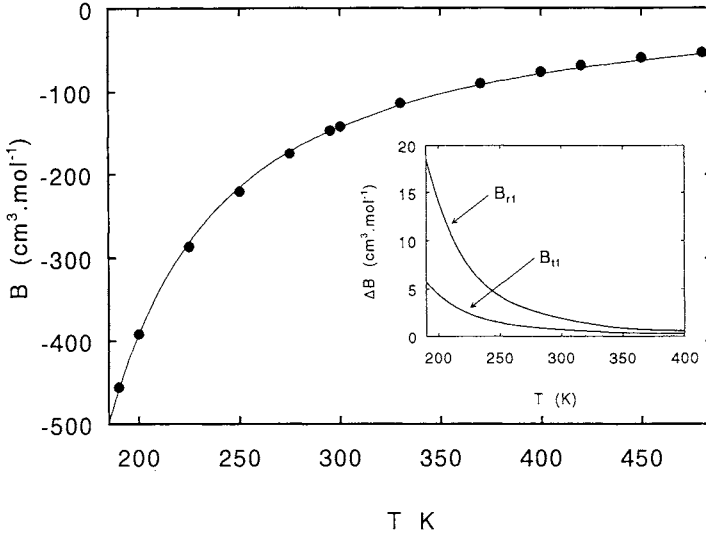
Figure 3.7 Second virial coefficients of hydrogen chloride. ●, experimental results of Schramm and Leuchs (42); ——————, calculated correct to the first quantum correction from the Stockmayer potential (43) with ε/k = 413 K and σ = 0.2591 nm, where ε and σ are the scaling parameters for energy and length in the isotropic part of the potential. The dipole moment was taken as 3.53×10^{-30} C·m (22). Insert: B_{t1} and B_{r1}.

and B_{r1} are plotted for H_2 and for HCl; in these cases, B_{c1} is negligible. For hydrogen *, the second translational quantum correction is also shown.

---

* The potential model used here is given by:

$$U(r,\theta_1,\theta_2,\phi_{12}) = A\exp(-Br)[1 + C\{P_2(c_1) + P_2(c_2)\}] - F(r)\left[C_6 r^{-6} f_1 - \tfrac{3}{4}(\theta^2/4\pi\varepsilon_0)r^{-5} f_2 + \tfrac{9}{8}(\theta^2\bar{\alpha}/4\pi\varepsilon_0)f_3\right]$$

where

$$f_1 = 1 - \kappa - \tfrac{3}{2}\kappa(1-\kappa)(c_1^2 + c_2^2) - \tfrac{3}{2}\kappa^2(s_1 s_2 c - 2c_1 c_2)^2, \quad f_2 = 1 - 5(c_1^2 + c_2^2) - 15c_1^2 c_2^2 + 2(s_1 s_2 c - 4c_1 c_2)^2,$$

$$f_3 = s_1^4 + s_2^4 + 4c_1^4 + 4c_2^4, \quad \kappa = (\alpha_\parallel - \alpha_\perp)/3\bar{\alpha}, \quad \bar{\alpha} = \tfrac{2}{3}\alpha_\perp + \tfrac{1}{3}\alpha_\parallel, \quad c_i = \cos\theta_i, \quad s_i = \sin\theta_i, \quad c = \cos\phi_{12},$$

and

$$F(r) = \exp[-\{(r_0/r)-1\}^2] \qquad r < r_0$$
$$= 1 \qquad r \geq r_0$$

A and B were fitted to the high-temperature second virial coefficients while C and C_6 were taken from (41): $A/k = 3.545\times10^7$ K, $B = 38.27$ nm^{-1}, $C = 0.14$, $C_6/k = 0.0899$ K·nm^6, $r_0 = 0.3$ nm. Polarisabilities $\alpha_\parallel$ and $\alpha_\perp$ and the quadrupole moment Θ where taken from reference 24.

3.3.5 The Virial Coefficients in Quantum Mechanics: Helium and Hydrogen

For the isotopes of helium and hydrogen, the semi-classical expansion of the virial coefficients does not converge at low temperatures and, to obtain reliable results, a fully quantum-mechanical evaluation is then required. Although the relations given in Section 3.3.2 between the virial coefficients and the configurational partition function remain formally valid, the evaluation and treatment of the energy levels from which Q_N may be calculated is different in the full quantum treatment. The origin of these differences lies primarily in quantisation of the angular momentum.

It is important to recognise that we should observe quantum statistics as well as quantum mechanics in a correct treatment. It turns out that the statistical restrictions on the allowed states of a system become important at very low temperatures, and this aspect of the problem will be examined first. The essential limitations imposed by quantum statistics are well known and may be stated as follows. When a system is composed of two or more *indistinguishable* molecules, the only allowed states of the system are those which are either symmetrical or anti-symmetrical with respect to the interchange of two particles. Only symmetrical states are found for systems composed of indistinguishable atoms or molecules which contain an even number of elementary particles; such systems are said to observe Bose-Einstein quantum statistics. For systems composed of indistinguishable atoms or molecules which contain an odd number of elementary particles, Fermi-Dirac quantum statistics apply and only anti-symmetrical states are allowed. The adoption of correct quantum statistics restricts the number of quantum states from which the canonical partition function of a system of indistinguishable molecules is constructed. In the case of distinguishable molecules, no statistical restrictions apply.

The symmetry of a quantum state is determined by the parity of the wavefunction Ψ which describes it.* For indistinguishable atoms, the parity of Ψ is determined by the nuclear-spin and translational states of the system and, in the case of non-zero nuclear spin, a number of degenerate nuclear-spin states is available. For molecules, the parity of Ψ is determined by nuclear-spin, translational, rotational and vibrational states. However, the isotopes of hydrogen are the only molecular systems where statistical quantum restrictions have a significant influence on the virial coefficients and, even then, the effects are restricted to temperatures below about 10 K. Under those conditions, only the lowest accessible vibrational and rotational states will be populated in the gas and the treatment of internal modes is thereby greatly simplified. It is however necessary to recognise the existence of (distinguishable) ortho and para H_2 and D_2 molecules.

In view of the forgoing remarks, only a single (but possibly degenerate) internal energy level need be considered for an isolated atom or molecule at temperatures where statistical effects are of significance. The internal partition function Γ_1 is therefore given by

$$\Gamma_1 = g_0 \exp(-\varepsilon_0 / kT) \tag{3.63}$$

---

* A symmetric (or even-parity) state is characterised by a wavefunction which is invariant under the operation of exhanging the co-ordinates of any two molecules. Conversely, an antisymmetric (or odd-parity) state has a wavefunction which, under the same operation, changes sign.

where ε_0 and g_0 are the energy and degeneracy. Since the zero of energy may be defined at will, one might as well measure all energies relative to that of the isolated molecule in the lowest allowed energy level. In that case, $\varepsilon_0 = 0$ and

$$\Gamma_1 = g_0 \tag{3.64}$$

In the case of an atom with nuclear-spin quantum number s, $g_0 = (2s+1)$ while, for a diatomic molecule, $g_0 = (2s+1)(2j+1)$, where j is the rotational quantum number of the lowest allowed energy level. Since, for a system containing just a single molecule, the question of parity does not arise, the overall partition function Θ_1 is simply the product $\Gamma_1 \Phi_1$, where Φ_1 is given by Equation (3.40) with its unrestricted sum over translational states. For all cases of practical importance, the sum over the translational quantum states may be approximated by an integral giving $\Phi_1 = (V/\Lambda^3)$ and thence

$$\Theta_1 = g_0 (V/\Lambda^3) \tag{3.65}$$

When the system contains two or more molecules, the calculation of the partition function is more involved. In the following treatment, attention will be restricted to the second virial coefficient and at first to the case of a one-component gas. The discussion starts with spherically-symmetric systems and proceeds to the case of linear molecules. The corresponding results for unlike atoms or molecules are also obtained rather easily by dropping the symmetry constraints.

In the case where the intermolecular potential is (or is assumed to be) spherically symmetric, it is still convenient to treat the translational and internal degrees of freedom of the molecules separately. However, in order to satisfy the symmetry constraints, both the internal and translational parts of the partition function should be separated into terms arising from quantum states of given parity. Φ_2 is therefore split into two terms, Φ_2^+ and Φ_2^-, which are obtained by summing only over translational states of the specified parity (+ or -). Similarly, the $(g_0)^2$ degenerate internal states are separated into symmetric and anti-symmetric terms and the overall partition function Θ_2 is then formed from products of internal and translational terms which have the required parity:

$$\Theta_2 = (g_0)^2 \left(W_2^+ \Phi_2^+ + W_2^- \Phi_2^- \right) \tag{3.66}$$

In this equation, W_2^+ and W_2^- are statistical weights which are determined as follows. For indistinguishable atoms or molecules which obey Bose-Einstein statistics, $(g_0)^2 W_2^+$ is the number of symmetric internal states and $(g_0)^2 W_2^-$ is the number of anti-symmetric internal states of the two molecules each in its lowest allowed internal-energy level. In the case of Fermi-Dirac statistics, the situation is reversed while, for distinguishable molecules, Boltzmann statistics apply and $W_2^+ = W_2^- = 1/2!$. The statistical weights W_2^+ and W_2^- for the isotopes of helium and molecular hydrogen are given in Table 3.4. Consistent with the assumption of a spherical intermolecular potential, hydrogen molecules are treated as spherical particles with spin equal to the vector sum of the spins of the constituent nuclei.

Table 3.4. Statistical weights for the isotopes of helium and hydrogen (44,45).

System	j	s	g_0	W_2^+	W_2^-	System	j	s	g_0	W_2^+	W_2^-
^{3}He		$\frac{1}{2}$	2	1/4	3/4	o-D$_2$	0	0,2	6	7/12	5/12
^{4}He		0	1	1	0	p-D$_2$	1	1	9	5/9	4/9
p-H$_2$	0	0	1	1	0	HD	0	$\frac{1}{2},\frac{3}{2}$	6	5/12	7/12
o-H$_2$	1	1	9	5/9	4/9						

In view of Equation (3.66), the configurational partition function of a pure gas is given by

$$Q_2 = 2(V/\Theta_1)^2\Theta_2 = 2\Lambda^6(W_2^+\Phi_2^+ + W_2^-\Phi_2^-) \tag{3.67}$$

and the second virial coefficient becomes

$$B = W_2^+B^+ + W_2^-B^- \tag{3.68}$$

Here, B^+ and B^- involve only translational partition functions and are given by

$$B^\pm = -(L\Lambda^6/V)(\Phi_2^\pm - \tfrac{1}{2}\Phi_1^2) \tag{3.69}$$

An important theoretical consequence of the adoption of quantum statistics is that B does not vanish in the absence of intermolecular forces. Indeed one can show that, for non-interacting indistinguishable atoms or molecules (14),

$$\Phi_2^\pm - \tfrac{1}{2}\Phi_1^2 = \pm 2^{-5/2}(V/\Lambda^3) \tag{3.70}$$

so that the second virial coefficient, $B_{\text{exch}}^{(0)}$, is given by

$$\begin{aligned} B_{\text{exch}}^{(0)} &= W_2^+B^{(0)+} + W_2^-B^{(0)-} \\ &= -2^{-\frac{5}{2}}L\Lambda^3(W_2^+ - W_2^-) \end{aligned} \tag{3.71}$$

with

$$B^{(0)\pm} = \mp 2^{-\frac{5}{2}}L\Lambda^3 \tag{3.72}$$

In view of the existence of an exchange term even for non-interacting molecules, it is convenient for real systems to deal with that part of $B^\pm$ which arises from the intermolecular forces:

$$B^{\pm} - B^{(0)\pm} = -(L\Lambda^6/V)(\Phi_2^{\pm} - \Phi_2^{(0)\pm}) \tag{3.73}$$

The partition functions $\Phi_2^{\pm}$ and $\Phi_2^{(0)\pm}$ which appear here are given by

$$\left. \begin{array}{l} \Phi_2^{\pm} = \displaystyle\sum_{\sigma} \exp(-H_{\sigma}/kT) \\[2mm] \Phi_2^{(0)\pm} = \displaystyle\sum_{\sigma} \exp(-H_{\sigma}^{(0)}/kT) \end{array} \right\} \tag{3.74}$$

where σ represents the full set of six translational quantum numbers for the two-molecule system (subject to the implied symmetry restrictions) and H_{σ} and $H_{\sigma}^{(0)}$ are the translational (kinetic + potential) energy of the system with and without intermolecular forces. Both H_{σ} and $H_{\sigma}^{(0)}$ may be separated into the sum of two terms each associated with three quantum numbers, the one term for the translational kinetic energy of the centre of mass, and the other for the (kinetic + potential) energy of the relative motion. Integration over the former yields a common factor of $2^{3/2}(V/\Lambda^3)$ so that

$$B^{\pm} - B^{(0)\pm} = -2^{3/2} L\Lambda^3 \left(\sum_{\sigma'} \exp(-H_{\sigma'}/kT) - \sum_{\sigma'} \exp(-H_{\sigma'}^{(0)}/kT) \right) \tag{3.75}$$

where σ' indicates that the summations now exclude the centre-of-mass terms.

In the present case, with an isotropic intermolecular potential, the possible states of relative motion are characterised by the quantum numbers (l, m_l, n). Here, l is the quantum number for the orbital angular momentum 1, m_l gives the orientation of 1 in space, and n determines the energy. It is convenient to divide these states into bound levels, with discrete energy levels ε_{nl}, and states with a continuum of positive energy levels H_{nl}^{c}; each such state is $(2l+1)$ fold degenerate corresponding to the $(2l+1)$ allowed values of m_l. The summation over n for positive energies may be replaced by an integral over the continuous variable κ,

$$\sum_{n} \exp(-H_{nl}^{c}/kT) = \int_0^{\infty} \exp(-\beta\kappa^2)(dn/d\kappa)\, d\kappa \tag{3.76}$$

where κ is defined such that $H_{nl}^{c} = \hbar^2\kappa^2/2\mu$, μ is the reduced mass, $\beta = \hbar^2/2\mu kT$, and $(dn/d\kappa)$ is the density of quantum states in the continuum. A similar equation holds for the summation over the energy levels $H_{nl}^{(0)}$ but with a different density of states: $(dn/d\kappa)^{(0)}$. The quantity $(dn/d\kappa) - (dn/d\kappa)^{(0)}$ is known as the excess density of states and may be related rather easily to the quantum-mechanical phase shifts $\eta_l(\kappa)$ of atom-atom scattering theory (46):

$$(1/\pi)(d\eta_l/d\kappa) = (dn/d\kappa) - (dn/d\kappa)^{(0)} \tag{3.77}$$

Equation (3.75) then becomes

$$
\left.
\begin{aligned}
B^+ - B^{(0)+} &= -2^{3/2} L\Lambda^3 \sum_{l\,\text{even}} (2l+1)B_l \\
B^- - B^{(0)-} &= -2^{3/2} L\Lambda^3 \sum_{l\,\text{odd}} (2l+1)B_l
\end{aligned}
\right\}
\tag{3.78}
$$

where*

$$
B_l = \sum_n [\exp(-\varepsilon_{nl}/kT) - 1] + (2\beta/\pi)\int_0^\infty \eta_l(\kappa)\exp(-\beta\kappa^2)\kappa\,d\kappa
\tag{3.79}
$$

One can therefore write the complete second virial coefficient as

$$
B = B_{\text{direct}} + B_{\text{exch}}
\tag{3.80}
$$

where

$$
B_{\text{direct}} = -2^{1/2} L\Lambda^3 \sum_l (2l+1)B_l
\tag{3.81}
$$

and

$$
B_{\text{exch}} = -2^{1/2} L\Lambda^3 (W_2^+ - W_2^-)\left(\sum_l (-1)^l (2l+1)B_l + \tfrac{1}{8}\right)
\tag{3.82}
$$

In the case of unlike atoms of types 1 and 2, $B_{\text{exch}} = 0$ and it is easy to show that

$$
B_{12} = -(L\Lambda_{12}^3/2)\sum_l (2l+1)B_l
\tag{3.83}
$$

where $\Lambda_{12} = (h^2/2\pi\mu kT)^{1/2}$.

In order to evaluate the second virial coefficient, one must calculate from Equation (3.79) the quantity B_l for $l = 0, 1, 2, \cdots$. ε_{nl} and η_l are required for this purpose and both may be obtained by numerical solution of the radial Schrödinger equation for the two atom system. Although once considered to be a computationally demanding procedure, such calculations are today routine and may be performed for helium over a wide range of temperatures. Numerical methods for the precise evaluation of the phase shifts have been described by Boyd et al. (47), while Cooley (48) and Cashion (49) have described methods of calculating the bound-state energies. In practise, numerical calculation of the sums over l are usually truncated at some value $l = l_{\max}$ and the remaining contribution of terms with $l > l_{\max}$ are estimated using the Born approximation. Similarly, the integrals over κ may be truncated at some upper limit and appropriate choices, together with some highly accurate calculations, have been reported by Aziz and Slaman for ³He and ⁴He (50). It appears that the intermolecular potential of helium

---

* The form of this equation is arrived at after integration by parts and noting that, according to Levinson's theorem, $\eta_l(0)/\pi$ is equal to the number of bound states in the well for the given l.

supports only one bound state for ^{4}He ($l = n = 0$) with an energy given by $E_{00}/k = -0.0016$ K (50). In the case of ^{3}He, there are no bound states.

The results of full quantum-mechanical calculations of B for the isotopes of helium, based on an accurate intermolecular potential (50), are compared with experiment in Figure 3.8. Remarkably, the agreement is within a few tenths of a cm^3/mol over the entire temperature range. For comparison, the semi-classical results for ^{4}He are also shown. It is interesting to note that, while the contribution of $B_{exch}^{(0)}$ appears to be significant up to temperatures of order 100 K, the total $|B_{exch}|$ given by Equation (3.82) drops off very rapidly with increasing temperature and is negligible (< 0.01 cm$^3 \cdot$mol^{-1}) for ^{4}He above 5 K and for ^{3}He above 6 K (47). At higher temperatures, quantum effects are confined to the difference between B_{direct} and the classical second virial coefficient; the origin of such differences lies is the quantisation of angular momentum. At temperatures where the semi-classical treatment of B is valid, these differences are accounted for correctly by the quantum corrections and it would therefore be incorrect to then add $B_{exch}^{(0)}$ to the result.
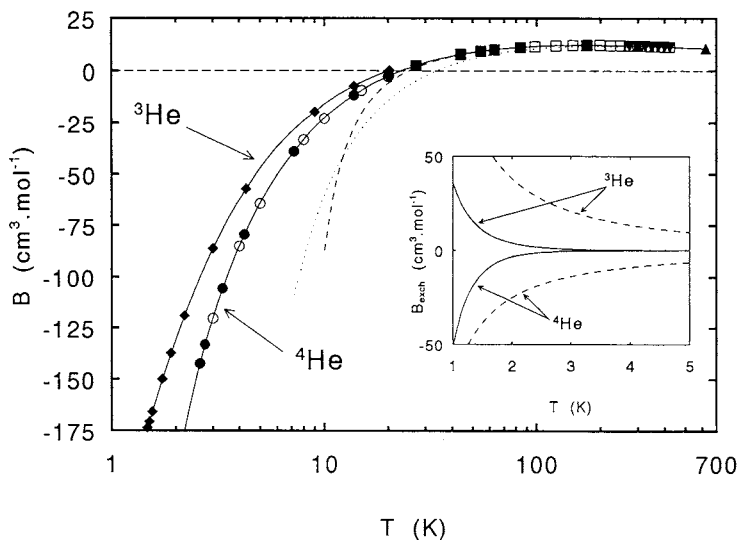

Figure 3.8 Second virial coefficients of ^{3}He and ^{4}He. $\bullet$, (51); $\bigcirc$, (52); $\blacksquare$, (53); $\square$, (54); $\blacktriangle$, (55); $\blacktriangledown$, (56); $\blacklozenge$, (57). ————, quantum-mechanical calculation of B (50); ·············, semi-classical B for ^{4}He to O($\hbar^2$); - - - - - - -, semi-classical B for ^{4}He to O($\hbar^4$).
Insert: ————, B_{exch}; - - - - - - -, $B_{exch}^{(0)}$ (47).

Apart from ^{3}He and ^{4}He, a fully-quantum mechanical treatment is required only for the isotopes of hydrogen. For H$_2$ and D$_2$, but not for HD, the molecules exist in distinguishable ortho (o) and para (p) forms and the gas is best considered as a mixture with second virial coefficient

$$B = x_o^2 B_{oo} + 2x_o x_p B_{op} + x_p^2 B_{pp} \tag{3.84}$$

Since calculations indicate that B_{exch} is completely negligible in all cases at temperatures above 10 K, only B_{direct} will be considered further here.

Molecular systems are characterised by the presence of angular-dependent intermolecular forces. These have the effect of coupling the angular momentum of the individual molecules to the intermolecular axis and thereby lifting the degeneracy of the states of relative motion. Strictly, only the total angular momentum **J** is a rigorous constant of motion but, in systems containing H_2, HD or D_2, the anisotropy is weak and the angular momenta $\mathbf{j}_1$ and $\mathbf{j}_2$ of the individual molecules are very nearly conserved. Each state with orbital angular momentum **l** is associated with sub-states characterised by the quantum numbers J and K. Here, J is the quantum number for **J** and K is the quantum number for the internal rotation angular momentum $\mathbf{K} = \mathbf{j}_1 + \mathbf{j}_2$.

In view of the coupling of rotational and translational states, one must return to Equation (3.67) and proceed with the full partition function. In the case where only the lowest allowed rotational energy level is populated, the development is rather simple and parallels closely that given above. The bound-state energies of the two-molecule system are now characterised by (n, l, K, J) and written ε_{nlK}^J. Considering for generality the case of unlike molecules with rotational quantum numbers j_1 and j_2, the result is

$$
B_{1,2\,\text{direct}} = \frac{-L\Lambda_{12}^3}{2(2j_1+1)(2j_2+1)}
$$
$$
\times \left(\sum_{K=|j_1-j_2|}^{j_1+j_2} \sum_{l=0}^{\infty} \sum_{J=|l-K|}^{l+K} (2J+1) \sum_n \exp(-\varepsilon_{nlK}^J/kT) + \int_0^\infty [(dn/d\kappa) - (dn/d\kappa)^{(0)}] \exp(-\beta\kappa^2) d\kappa \right) \tag{3.85}
$$

The excess density of states in the continuum is given by (41,58)

$$(dn/d\kappa) - (dn/d\kappa)^{(0)} = (i/2\pi)\, \text{Tr}\, (S\, dS^\dagger/d\kappa) \tag{3.86}$$

where $S = S(\kappa)$ is the S-matrix of molecule-molecule scattering theory, $S^\dagger$ is the adjoint of S, and Tr denotes the trace operation over the full set of quantum numbers (l, K, J). The result of this operation may be expressed in terms of a set of generalised phase shifts $\eta_{lK}^J(\kappa)$ and, for each l, $(2j_1+1)(2j_2+1)$ such terms appear.

These last two equations may be applied to obtain B_{direct} for any combination of like or unlike molecules or atoms. In the case of an atom-molecule interaction, the sum over K drops out while, for atom-atom systems, $J = l$ and the sums over both K and J drop out. In the latter case, only the diagonal elements of the S matrix are non-zero and they are related to the scattering phase shifts by $S_{ll}(\kappa) = \exp[2i\eta_l(\kappa)]$. Equation (3.86) then reduces to Equation (3.77) and Equation (3.85) reduces to Equation (3.81).

Determination of ε_{nlK}^J and $S(\kappa)$ again involves solution of Schrödinger's equation for the system and such calculations are tractable for the low temperatures at which the quantum treatment is required. The S-matrix may be determined to high accuracy in the close-coupled approximation while the bound-state energies may be obtained by the same general method

(59) or by the more efficient secular equation method (60). It is also possible to rely on spectroscopically determined values of ε_{nlK}^{J} and it is worth remarking that, for the systems of interest, only $n = 0$ states have been observed and there is little evidence of splitting of the l states due to anisotropy of the intermolecular potential (61). The sums over K and J in Equation (3.85) could therefore reasonably be collapsed leaving a bound-state contribution to B_{direct} identical in form with that of a monatomic system.

Although Equation (3.85) is restricted to molecules in a single rotational level, it is clearly possible to derive a more general expression in which the full set of molecular rotational energy levels is retained. Alternatively, the gas may be treated as a mixture of species having different values of j. Unfortunately, close-coupling calculations become very time consuming once more than a few rotational levels are populated. It is notable however that, for p-H_2, the j = 2 level only reaches 1 per cent occupancy at about 75 K while, for o-H_2, the temperature must reach 145 K before the $j = 3$ level reaches the same occupancy. For purposes of comparison, the semi-classical formula, including the translational corrections to $O(\hbar^4)$, should be of sufficient accuracy at temperatures above about 100 K (see Figure 3.6).

3.4 CALCULATION AND ESTIMATION OF VIRIAL COEFFICIENTS

Although an extensive database of experimental virial coefficients is available (4), methods for the calculation and estimation of virial coefficients are important for a number of reasons. In the first place, there are still many systems (especially mixtures) for which B and C are not known at the temperatures of interest and, in these cases, estimation methods can be very useful. Even when experimental data are available, in may be desirable to establish a soundly-based correlation and, for that purpose, a model intermolecular potential with appropriately chosen parameters can be very powerful. Finally, it is sometimes useful (for example, in thermodynamic perturbation theory) to have essentially exact virial coefficients for some simple model potential.

3.4.1 The Virial Coefficients of Model Systems

Virial coefficients have been evaluated for several isotropic model intermolecular potential-energy functions including the square-well, Lennard-Jones (n,6), exponential-six and Maitland-Smith functions.* A number of tabulations of B, C , D and E are available (6,21,62,63) and, as mentioned above, the evaluation of B and C by quadrature is quite routine. The parameters of such a model may be optimised fairly easily in a fit to virial coefficients or related quantities such as the Joule-Thomson coefficient or acoustic virial coefficients. The model may then permit extrapolation or the estimation of other properties, often with high accuracy. It appears that simple isotropic potential models can offer a very good account of the second and third virial coefficients of non-polar molecules provided that non-additive three-body forces are included in the calculation of C (5,64). Equation (3.47), with υ_3 treated as an empirical parameter, appears to be quite adequate (64).

Although the importance of analytical and tabulated results has been greatly diminished by the speed of modern computers, there is one class of model systems, namely the convex hard bodies, which are of special importance as reference systems in statistical

---

* Descriptions of these models may be found in, for example, reference 21.

thermodynamics and for which the existence of tabulated results is important. The virial coefficients of such systems are independent of temperature and some of the results are mentioned here.

The simplest of the convex hard bodies is the hard sphere. Analytical expressions for B, C and D, and precise numerical results up to the eighth virial coefficient, are available for a gas composed of such molecules (13,65). Estimates of the ninth and tenth virial coefficients have also been made (65) and the results are given in Table 3.5. A considerable amount of work has also been done on non-spherical convex hard cores for which the second virial coefficient is given by $B = Lv(1 + \gamma)$, where v is the volume of one molecule and γ is a shape factor which may be determined from the mean radius of curvature, the surface area and v (66). For spherical hard cores, $\gamma = 3$ while, for other shapes, $\gamma > 3$ and increases with the eccentricity of the molecule. Virial coefficients up to the fifth have been computed numerically for hard ellipsoids of revolution (67), spherocylinders (68) and chains of fused hard spheres (69). Except for highly eccentric molecules, the results are found to correlate rather well with the shape factor γ (67).

Table 3.5 Virial coefficients of hard spheres of diameter d (13,65).

$$B = 2\pi L d^3/3 = b_0$$
$$C = (5/8)\, b_0^2$$
$$D = 0.2869495\, b_0^3$$
$$E = (0.110252 \pm 0.000001)\, b_0^4$$
$$F = (0.038808 \pm 0.000055)\, b_0^5$$
$$G = (0.013071 \pm 0.000070)\, b_0^6$$
$$H = (0.00432 \pm 0.00010)\, b_0^7$$
$$I \approx 0.00142\, b_0^8$$
$$J \approx 0.00047\, b_0^9$$

It appears that the virial series for hard spheres is convergent up to the density at which computer simulations indicate that solidification occurs (70). For non-spherical hard cores, Padé approximants to the compression factor formed from the available virial coefficients also agree closely with the results of computer simulations up to very high densities (71). These observations suggest that the virial equation is valid for all fluid states of this class of system.

Hard bodies do not exhibit a vapour-liquid phase transition but the addition to the intermolecular potential of an attractive field outside the hard core does give rise to this phenomenon. A simple and very interesting model of that kind is the one considered by van der Waals (72) in which the molecules are treated as spherical hard cores of diameter d with a weak but long-range attractive interaction such that the intermolecular potential is:

$$\underset{\delta \to \infty}{\text{Lim}} \begin{cases} u(r) = +\infty & r < d \\ = -\varepsilon/\delta^3 & d \le r < \delta d \\ = 0 & r \ge \delta d \end{cases} \qquad (3.87)$$

The second virial coefficient for this system is $b_0\{1-(\varepsilon/kT)\}$ but the dimensionality of the cluster integrals is such that all higher virial coefficients are identical with those of the corresponding hard sphere system. Consequently, for this model system the virial series is also convergent for all fluid states, both gas and liquid, and the equation of state is analytic everywhere including at the critical point. However, for systems with an intermolecular potential of *finite* range, it is known that the equation of state is non-analytic at the critical point and that the virial series must, therefore, have a finite radius of convergence on isotherms close to the critical temperature. The convergence of the virial series elsewhere for this class of system is not established theoretically owing, at least in part, to the absence of a complete set of virial coefficients. For Lennard-Jones molecules, virial coefficients up to the fifth have been computed (6) and found to diverge towards -∞ as $T \to 0$; the results are plotted in Figure 3.9. This behaviour is usually taken as evidence that the virial series does not converge for such molecules in the liquid state. However, a satisfactory virial expansion might exist for both gas and liquid branches below the critical temperature if the higher virial coefficients adopt finite positive values (73). The question therefore remains open.
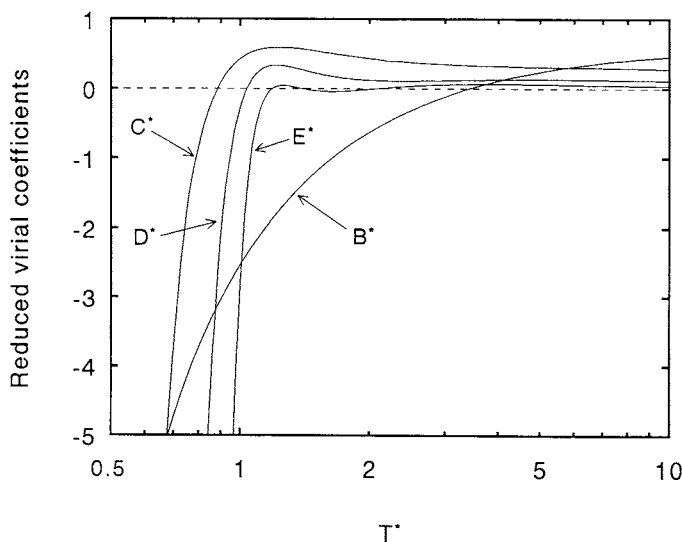

Figure 3.9 Reduced virial coefficients for the Lennard-Jones (12,6) potential (6). $T^* = kT/\varepsilon$, $B^* = C/b_0$, $C^* = C/b_0^2$, $D^* = D/b_0^3$ and $E^* = E/b_0^4$.

3.4.2 Estimation of Virial Coefficients

For cases in which experimental values of B and C are unavailable, some method of prediction is required and for this purpose the principle of corresponding states is usually applied. In its simplest form, the principle applies to systems whose intermolecular pair potentials may be written in the form $u(r) = \varepsilon \ F(r \ / \ \sigma)$, where ε and σ are scaling parameters which characterise a particular substance and F is a universal function. Systems which obey this relation are said to be conformal. In all conformal systems to which classical statistical mechanics applies, the reduced second virial coefficient, $B^* = B/(\frac{2}{3}\pi L\sigma^3)$, is a universal function of $T^* = kT/\varepsilon$. Thus, the second virial coefficient of one conformal substance (labeled i) may be estimated from that of another (labeled 0) if the ratios $\varepsilon_i/\varepsilon_0$ and σ_i/σ_0 are known. From a theoretical point of view, the most satisfactory way of relating the scaling parameters to measurable properties is by means of the Boyle temperature and the so-called Boyle volume V^B, equal to $T(dB/dT)$ at $T = T^B$. In terms of these quantities, B/V^B is, according to the principle, a universal function of T/T^B and, if pair-wise additivity of the intermolecular forces is assumed, $C/(V^B)^2$ is another universal function of T/T^B. This method of selecting the scaling parameters has the disadvantage of requiring some measurements of $B(T)$ in the first place. Furthermore, T^B is inconveniently high for most substances.

Practical correlations of virial coefficients employ as scaling parameters the critical temperature T^c and the characteristic molar volume RT^c/p^c, where p^c is the critical pressure, and seek to represent $B(p^c/RT^c)$ and $C(p^c/RT^c)^2$ as universal functions of the new reduced temperature $T_r = T/T^c$. Although the principle, as stated above, applies to only a small number of simple fluids, Pitzer (74) was able to show that many different kinds of molecular complexity may be accounted for by the inclusion of a third parameter ω which he called the acentric factor. This parameter is defined in terms of the vapour pressure p^σ, by the equation

$$\omega = -1 - \log_{10}\{p^\sigma(T_r = 0.7)/p^c\} \tag{3.88}$$

such that it is essentially zero for the simple fluids Ar, Kr and Xe. For other fluids, values between 0 and about 0.4 are usually found. The second virial coefficient is given in this extended principle of corresponding states by

$$B(p^c/RT^c) = B_0 + \omega B_1 \tag{3.89}$$

where B_0 and B_1 are dimensionless functions of T_r. Expressions for B_0 and B_1 were given by Pitzer and Curl (75) in their original formulation but here the more recent correlations proposed by Tsonopoulos (76) for non-polar gases are given:

$$\left. \begin{array}{l} B_0 = 0.1445 - 0.3300/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 - 0.000607/T_r^8 \\ B_1 = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8 \end{array} \right\} \tag{3.90}$$

As it stands, Equation (3.89) is useful only for essentially non-polar gases, but Tsonopoulos showed (76) that the addition of the term a/T_r^6 to the right-hand side of that equation

permitted the results for polar gases to be correlated also. A further term b/T_r^8 is necessary for associating compounds. While there seems to be no simple universal correlation for the additional parameters a and b, correlations of the former in terms of the dipole moment may be established within certain classes of compounds such as ketones or ethers (76).

In order to apply these formulae to mixtures, some method is required for determining the acentric factor ω_{ij} and the pseudo-critical constants T_{ij}^c and p_{ij}^c for the unlike interactions. In the present case, extended van der Waals one-fluid mixing rules are applied (76) in terms of which

$$
\left.
\begin{aligned}
\omega_{ij} &= \tfrac{1}{2}(\omega_i + \omega_j) \\
T_{ij}^c &= (1 - k_{ij})\sqrt{T_i^c T_j^c} \\
p_{ij}^c &= 4T_{ij}^c \{(p_i^c V_i^c / T_i^c) + (p_j^c V_j^c / T_j^c)\} / \{(V_i^c)^{1/3} + (V_j^c)^{1/3}\}
\end{aligned}
\right\}
\tag{3.91}
$$

where k_{ij} is a binary interaction parameter, which may be optimised against experimental data, and V_i^c is the critical molar volume of pure i. When an experimental value is unavailable, $V_i^c = (RT_i^c Z_i^c / p_i^c)$ may be estimated from the correlation of the critical compression factor proposed by Lee and Kesler (77): $Z_i^c = 0.2905 - 0.085\omega_i$. For interactions between polar and non-polar molecules, the polar term a/T_r^6 is dropped while for polar-polar interactions an arithmetic-mean combining rule is recommended for a.

The third virial coefficients of pure non-polar gases have also been correlated using a similar model by Orbey and Vera (78) and the results are:

$$
\left.
\begin{aligned}
C(p^c/RT^c)^2 &= C_0 + \omega C_1 \\
C_0 &= 0.01407 + 0.02432 / T_r^{2.8} - 0.00313 / T_r^{10.5} \\
C_1 &= -0.02676 + 0.0177 / T_r^{2.8} + 0.040 / T_r^3 - 0.003 / T_r^6 - 0.00228 / T_r^{10.5}
\end{aligned}
\right\}
\tag{3.92}
$$

Several methods have been proposed for the estimation of the interaction third virial coefficients C_{ijk} in mixtures. Orbey and Vera (78) follow Chueh and Prausnitz (79) in proposing the relation

$$
C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3}
\tag{3.93}
$$

in which C_{ij} is evaluated from Equations (3.92) with the acentric factor and pseudo-critical constants pertaining to the binary pair i and j. In a recent test against accurate experimental results for binary mixtures (80), this method was found to give satisfactory estimates.

Although none of the formulae discussed in this section are very accurate, gas densities and partial fugacity coefficients estimated by such methods for non-polar and slightly-polar pure gases and mixtures may be accurate enough for many engineering purposes up to about two thirds of the critical density (78,80). Furthermore, as the method may be applied knowing only the critical constants and the acentric factor for each component, it is very easy to apply.

3.5 SUMMARY

In one sense, being restricted to gases at low and moderate densities, the virial equation of state is of rather limited application. Nevertheless, it has the merits of a sound theoretical basis, a large database of experimentally-determined virial coefficients, and the ability to describe mixtures exactly. The relations set out in Table 3.2 may be used to express a wide range of thermodynamic properties of pure gases and mixtures in terms of the virial coefficients, their temperature derivatives and the heat capacity of the ideal gas. The virial coefficients may be obtained from experiment, from knowledge of the intermolecular potential-energy functions or from the principle of corresponding states.

The relations between the virial coefficients and intermolecular forces is of real importance and has therefore been explored in detail. Equations (3.52), (3.54), and (3.55) may be used to determine B and C from u_{12} and Δu_3 at temperatures where quantum corrections are unimportant. Quantum effects have also been considered above in sufficient detail to permit their calculation for the atomic and molecular systems of interest. Because such calculations can now be performed routinely, even for non-spherical molecules, it is perfectly feasible to represent the equation of state correct at least to the third virial coefficient by means of prescribed pair and triplet potentials.

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