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Virial Coefficients of Pure Gases and Mixtures

SUBVOLUME A

Virial Coefficients of Pure Gases



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J. H. Dymond, K. N. Marsh, R. C. Wilhoit, K. C. Wong

Edited by M. Frenkel and K.N. Marsh

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Preface

This critical compilation of virial coefficients of pure gases is a sequel to *The Virial Coefficients of Pure Gases and Mixtures*, by J.H. Dymond and E.B. Smith (Oxford University Press, 1979). This new and enlarged edition was prepared from the virial coefficient database at the Thermodynamics Research Center, formerly at Texas A&M University, College Station, Texas and now located at the National Institute of Standards and Technology, Boulder, Colorado. The virial coefficient data in this compilation will be of interest to the theoretical chemist as it includes the many sets of accurate gas imperfection data which have been determined over the past twenty years by improved methods of gas density determination, by isochoric Burnett coupling methods and from speed of sound measurements, as well as by the more traditional techniques. The needs of the industrial chemist are met by these more reliable data and also the increased number of compounds for which data are now available.

For each compound, the second and third virial coefficient data from different published sources are tabulated in increasing order of temperature, and an estimate of the uncertainty is given. Conversion to a uniform set of units is undertaken where necessary. In the majority of cases, where the data cover a sufficiently wide range of temperature, a weighted data fit has been made for the second virial coefficients, and coefficients of the given equation are recorded. Values of the second virial coefficient given by the equation at selected temperatures are quoted.

This volume includes material published up to the end of 1998. While every effort has been made to see that the tables are free from error, it is unlikely that there will be no omissions or mistakes. We would appreciate it if corrections could be brought to our attention.

Christchurch, New Zealand and Boulder, Colorado, USA, August 2001

The Editors

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Our special thanks are due to Derek Caudwell, Barbara Clark, Christine Nichol and Ruba Vigneswaran for their assistance in formatting the text, preparing the graphs, checking the data, and composing the camera-ready copy of the manuscript. The facilities provided by the Department of Chemical and Process Engineering, University of Canterbury are gratefully acknowledged.

Christchurch, New Zealand and Boulder, Colorado, USA, August 2001

J.H. Dymond, K.N. Marsh,
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1 Introduction

The p - V - T behaviour of real gases is a topic that has concerned physicists and chemists for more than a century. Some of this interest has arisen from the importance of the study of gas imperfections in the elucidation of the forces between molecules. From a more practical point of view, knowledge of p - V - T relationships is essential for the resolution of problems in chemical engineering processes where gases are present.

1.1 Gas Imperfections

The ideal gas is characterized by the equation of state:

$$Z = pV_m / RT = 1 \quad (1.1)$$

where Z is termed the compressibility factor, or compression factor, p is the pressure, V_m the molar volume, T the absolute temperature, and R the gas constant. Real gases may show significant deviations from this equation of state even at low pressure. At low temperatures and pressures, Z is usually less than unity whereas at high temperatures and pressures the converse is true.

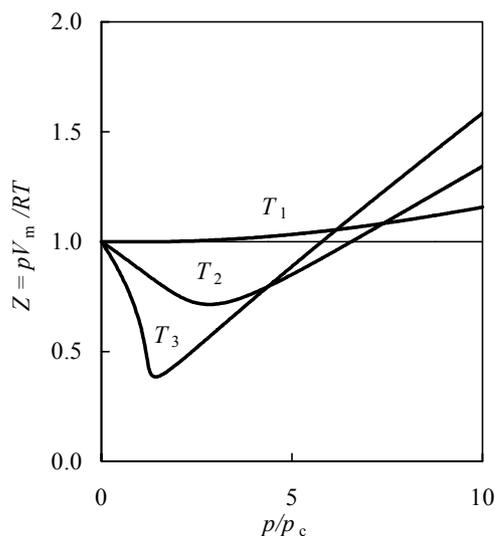


Fig. 1. The compressibility factor Z

Typical dependence of Z on p/p_c , where p_c is the critical pressure, is illustrated in Figure 1 for a series of temperatures such that $T_1 > T_2 > T_3$. The temperature T_3 is just above the critical temperature. The temperature T_1 at which the density dependence of Z is zero as $p/p_c \rightarrow$ zero is termed the Boyle temperature. For gases which are neither quantum fluids nor strongly polar, this temperature is about 2.7 times the critical temperature for monatomic substances, decreasing to around 2.3 for polyatomic fluids.

Many equations of state have been proposed to represent the p - V - T behaviour of real gases but, from a theoretical point of view, the most satisfactory form, at all but the highest pressures, is the virial equation in which the compressibility factor is expressed as a series expansion in either density (reciprocal molar volume) or pressure:

$$pV_m / RT = 1 + B/V_m + C/V_m^2 + D/V_m^3 + \dots \quad (1.2)$$

$$pV_m / RT = 1 + B^* p + C^* p^2 + D^* p^3 + \dots \quad (1.3)$$

It is normal practice to define B , C , D , ... in the density (or volume) series as the second, third, fourth, ... virial coefficients. They are all temperature dependent. The importance of these virial coefficients lies in the fact that they are related directly to the interactions between molecules. The second virial coefficient represents the departure from ideality due to interactions between pairs of molecules, the third virial coefficient gives the effects of interactions of molecular triplets, and so on. The coefficients of the two series are simply related:

$$B = B^* RT \quad (1.4)$$

$$C = (B^{*2} + C^*)(RT)^2 \quad (1.5)$$

$$D = (B^{*3} + 3B^*C^* + D^*)(RT)^3. \quad (1.6)$$

$B(T)$ is defined as follows:

$$B(T) = \lim_{1/V_m \rightarrow 0} (pV_m / RT - 1)V_m \equiv \lim_{1/V_m \rightarrow 0} A \quad (1.7)$$

and $B(T)$ is zero at the Boyle temperature. The general manner of the variation of $B(T)$ with temperature is shown in Figure 2. At low temperatures $B(T)$ is large and negative, whereas at high temperatures it has small positive values which, at very high temperatures (corresponding to twenty times the critical temperature for helium), pass through a maximum.

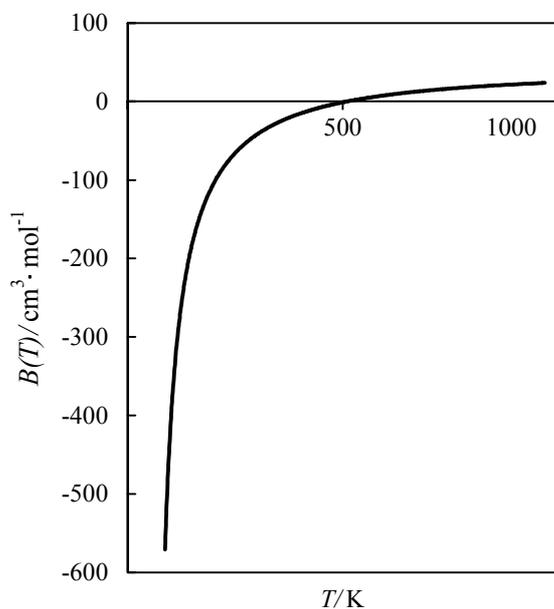


Fig. 2. Second virial coefficient of methane

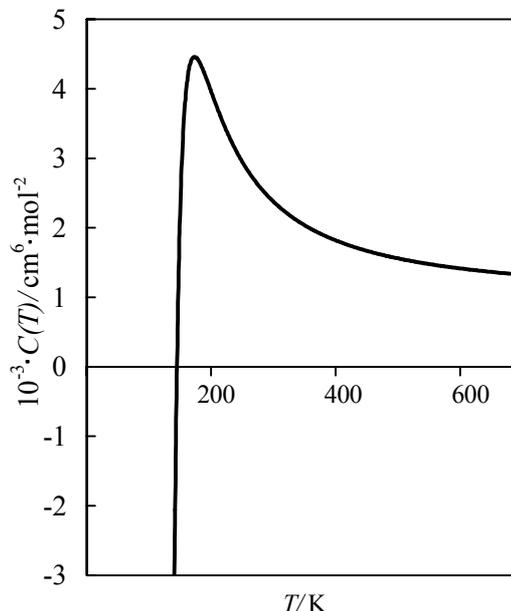


Fig. 3. Third virial coefficient of methane

The third virial coefficient is given by the following limit:

$$C = \lim_{1/V_m \rightarrow 0} (A - B)V_m. \quad (1.8)$$

However, because of the difficulty in determining p - V data at constant temperature with sufficiently high accuracy at very low densities, values for this coefficient are usually determined from gas-compressibility data by fitting the results at a given temperature to a polynomial in the reciprocal volume. The coefficients of this polynomial are then identified with the coefficients of the infinite series. The general dependence of $C(T)$ on temperature is illustrated in Figure 3.

It should be noted that values for the virial coefficients obtained in this way depend on the degree of polynomial used and on the density range of the compressibility data. The resulting uncertainties in the second virial coefficient are small, but they are much larger for the third virial coefficient, and the uncertainty in the fourth virial coefficient is such that even the sign cannot be determined with certainty from most measurements.

Table 1. Values of pV_m/RT for methane(i) at 200 K ($B = -104.64 \text{ cm}^3 \cdot \text{mol}^{-1}$; $C = 4020 \text{ cm}^6 \cdot \text{mol}^{-2}$)

p/MPa	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$1+B/V_m$	$1+B/V_m+C/V_m^2$	$Z_{\text{exp}}^{(1)}$
0.2	8209.100	0.98725	0.98731	0.98732
0.5	3219.000	0.96749	0.96788	0.96789
1	1553.700	0.93265	0.93431	0.93432
2	716.460	0.85394	0.86178	0.86170
3	431.840	0.75768	0.77924	0.77906
4	282.830		0.68028	0.68130
5	182.790		0.54785	0.54963
5.5	138.520		0.45409	0.45816
6	97.913		0.35061	0.35329

(ii) at 300 K ($B = -42.23 \text{ cm}^3 \cdot \text{mol}^{-1}$; $C = 2410 \text{ cm}^6 \cdot \text{mol}^{-2}$)

p/MPa	$V_m/\text{cm}^3 \cdot \text{mol}^{-1}$	$1+B/V_m$	$1+B/V_m+C/V_m^2$	$Z_{\text{exp}}^{(1)}$
0.2	12430.000	0.99660	0.99662	0.99662
0.5	4946.600	0.99146	0.99156	0.99157
1	2452.400	0.98278	0.98318	0.98320
2	1205.600	0.96497	0.96663	0.96667
4	582.910	0.92755	0.93465	0.93477
6	376.220	0.88775	0.90478	0.90496
8	273.820		0.87792	0.87819
10	213.400		0.85503	0.85555
15	136.870		0.82011	0.82308
20	103.320		0.81703	0.82841
25	86.125		0.83457	0.86320

⁽¹⁾ 96-wag/der

Fortunately, for calculation of gas densities up to moderate pressures it is generally necessary to include only the second and third virial coefficient terms in the virial equation. This is illustrated in Table 1 in the case of methane at 200 K (just above the critical temperature, 190.4 K) and at 300 K.

Termination of the virial equation after the second virial coefficient term gives reasonable values for Z at densities up to about 0.25 times the critical density. This can be seen from Table 1. Methane has a critical volume of $99.2 \text{ cm}^3 \cdot \text{mol}^{-1}$. Inclusion of the third virial coefficient term gives satisfactory agreement at higher densities, even approaching the critical density.

Values for the virial coefficients are derived from experimental measurements which can be conveniently classified as follows: low pressure p - V - T measurements; high pressure p - V - T measurements; speed of sound measurements; vapour pressure and enthalpy of vaporization measurements; refractive index/dielectric constant measurements and Joule-Thomson experiments. These will be discussed in Chapter 1.2, and methods of data evaluation described in Chapter 1.5. Much attention has been paid to the correlation of virial coefficient data and the more satisfactory methods are considered in Chapter 1.3, together with a brief discussion of the theoretical calculation of the second virial coefficient from pair potential energy functions which have been derived *a priori* or by consideration of other dilute gas properties. So far, this calculation is only applicable to molecules with a spherically symmetric intermolecular potential energy function, for which

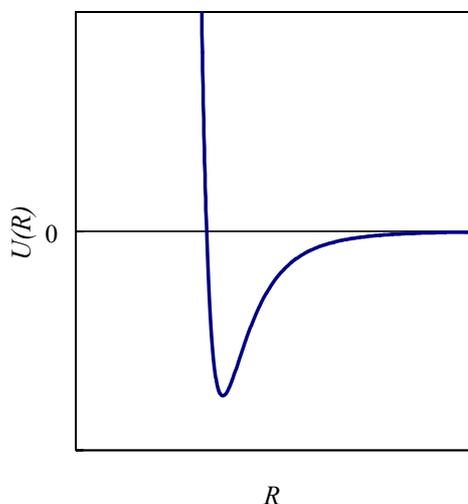


Fig. 4. Pair potential energy function

$$B(T) = -2\pi N_A \int \left(e^{-U(R)/kT} - 1 \right) R^2 dR \quad (1.9)$$

where N_A is the Avogadro number and $U(R)$ is the potential energy of a pair of molecules at separation R . The general form of the dependence of $U(R)$ on R is given in Figure 4.

1.2 Experimental Methods

Methods for the determination of virial coefficients can conveniently be classified as (a) p - V - T measurements, (b) speed of sound measurements, (c) Joule-Thomson measurements, (d) refractive index and relative permittivity measurements and (e) vapour pressure and enthalpy of vaporization measurements.

The great majority of the virial coefficient data come from a variety of experimental techniques for p - V - T measurement, both low pressure and high pressure. In principle, the results should be reliable and in agreement, and this is certainly true at temperatures above the critical temperature, but only where the high pressure measurements extend to pressures down to around 0.1 MPa. In recent years, the Burnett expansion method [36-bur] has become the favoured high-pressure technique. It has been used by many groups, including those at the National Research Council, Ottawa, Canada (W.G. Schneider), Texas A&M University, College Station, U.S.A. (J.C. Holste, K.R. Hall, K.N. Marsh and P.T. Eubank), Keio University, Yokohama, Japan (T. Sato, K. Watanabe), and the National Institute for Standards and Technology, Gaithersburg, U.S.A. (L.A. Weber and D.R. Defibaugh).

Below the critical temperature there is a major problem in all p - V - T methods, apart from achieving the required accuracy in the measured variables, which arises from adsorption and particularly from capillary condensation. This problem has been overcome by Wagner's group in Bochum using the method described in section 1.2.1.3, which is based on the buoyancy principle with two sinkers to compensate for these effects.

The alternative solution is to use a method where this problem does not arise. Of the possibilities listed under classifications (b) to (e), speed of sound measurements have the great advantage of high accuracy in the measured variable (frequency). Even for compounds where vibrational relaxation may be strong, requiring significant corrections for dispersion, there is still high precision in the measurements. Advances in the method of data analysis has led to reliable acoustic virial coefficients and derived density virial coefficients. Groups making measurements by this method include those at University College, London (M.B. Ewing), the National Institute of Standards and Technology, Gaithersburg, U.S.A. (A.R.H. Goodwin and M.R. Moldover), Imperial College, London (J.P.M. Trusler), Ruhr-Universität Bochum, Germany (W. Beckermann and F. Kohler) and Keio University (H. Sato and K. Watanabe).

Examples of the various techniques are described in the following sections. Since Mason and Spurling [69-mas/spu] have given an excellent summary of the methods employed up to 1969, attention will be focused here on the most important of those methods and on experimental work since that time.

1.2.1 p - V - T Measurements

1.2.1.1 Low Pressure Measurements

The application of the virial equation to determine values for the virial coefficients requires a knowledge of the pressure, volume, temperature and the number of moles of the gas. It is generally assumed that for pressures below 0.1 MPa, terms beyond the second virial coefficient can be neglected. For a fixed mass of gas, measurements are usually made of the pressure when the gas either occupies different known volumes at constant temperature, or is heated to different known temperatures at constant volume.

The simplest example of the first of these methods is the thermostatted Boyle's Law apparatus where a gas is confined by mercury in one side of a U-tube, which is calibrated and sealed at the upper end. The gas pressure is measured as the difference in height of the mercury menisci in the two limbs. Mercury can be added (or removed) at the bottom of the U-tube to vary the gas volume, and hence a set of p - V measurements at constant temperature can be obtained.

In order to define the gas volumes more precisely, and overcome the problems associated with the mercury in contact with the gas and the limited temperature range because gas and mercury were at the same temperature, expansion methods were later devised where the gas was allowed to expand from one vessel into another, previously evacuated, vessel (and in some cases into a series of other vessels). The volumes had previously been accurately determined by weighing with water or mercury. The gas was separated from the manometer, which can be at room temperature, by a differential pressure gauge.

Greater accuracy is obtained in relative measurements when the expansion of the test gas is compared with that of a reference gas such as nitrogen where departure from ideal-gas behaviour is small. For the two gases at identical initial pressures below 0.1 MPa, undergoing expansion between vessels of matched volumes at constant temperature, the final pressure change is related to the difference between the second virial coefficients. This method has been used by the groups at Heidelberg, Germany (B. Schramm) [82-sch/mue] and Armidale (K. N. Marsh and M. B. Ewing) [79-ewi/mar].

The quasi-isochoric method [94-mil/hen, 87-spi/gau] has been used by groups at Rostock, Germany (G. Opel and J. Millat) and Darmstadt, Germany (J. Gaube). A known mass of liquid is introduced into the cell, made of quartz in the case of the first group or stainless steel for the second group, of previously determined volume which is maintained at constant temperature. Pressures are measured with a high precision mercury manometer, with a pressure transducer between the vapour and gas above the manometer, after thermal equilibrium has been established following increases in temperature. Values for the second virial coefficient were obtained from the virial equation terminated after the third virial coefficient term by a graphical method, a surface fit of the data or by estimation of the third virial coefficients.

The isochoric method has also been used in a relative mode [91-sch/web] by the group at Heidelberg, Germany (B. Schramm). Two vessels of equal volume are filled, one with the sample of test gas and the other with a gas with well-defined volumetric behaviour, to the same pressure at the same temperature. The pressure was less than 0.1 MPa so that only the second virial term was considered necessary. The temperature was changed and the resulting pressure difference between the two gases was accurately measured. This is related to the difference between the second virial coefficients of the two gases at the original temperature and at the new temperature. Thus, it is necessary to know the values of the second virial coefficient of the reference gas at each temperature and of the test gas at the original temperature.

1.2.1.2 High Pressure Measurements

The simple and relative isothermal methods referred to just above can be used at high pressures also. The apparatus of the group at Ohio State University, Columbus, U.S.A. (W.B. Kay) [83-mar/lin] consists of a vertical tube with two volume-calibrated sections of different diameters, sealed at the upper end, in which the gas is confined by mercury. Thermal equilibrium was maintained by circulating a purified boiling liquid through an outer jacket around the tube. The weighed sample was admitted in sealed glass ampoules. Change in volume was achieved by variation in nitrogen pressure on the mercury external to the tube and the gas volume determined from measurement of the mercury height in the tube. Highest pressure (a few MPa) points were removed as necessary until the data were satisfactorily given by the virial equation with just the second virial coefficient term.

The classic apparatus for high pressure gas p - V - T studies [66-tra/was], where ‘high pressure’ now refers to pressures up to 300 MPa, was that of the group of A. Michels at the van der Waals Laboratory, Amsterdam. Known as a piezometer, the central glass gas burette consists of a series of bulbs separated by fine capillary tubing in each section of which is a contact wire of platinum. The volumes between successive contacts is accurately known. The burette is sealed at its upper end, and the gas is confined by mercury in a known volume by raising the mercury level until electrical contact is made with one of the wires. The pressure is measured at each of these points. The piezometer is surrounded by mercury or oil to reduce the pressure difference across the glass. The data are fitted to a multi-term virial equation, the number of terms depending on the pressure range of the measurements.

Another series of highly accurate virial coefficient determinations from high-pressure p - V - T studies [61-dou/har] which is worthy of note is that of the group of D.R. Douslin at the previous Bartlesville Petroleum Research Center, Oklahoma. The volume of a pre-weighed sample in a single globe is confined by mercury and the pressure is noted using a free-piston gauge after the addition of a measured volume of mercury. The highest pressures here were about 40 MPa.

The uncertainties of the effects of interaction of mercury vapour with the gas are overcome in the Burnett expansion method [36-bur]. This method has the further advantage that only pressure measurements are required - there is no need for mass or volume measurements. Here two different-sized vessels are connected *via* narrow tubing with a valve, as shown in Figure 5.

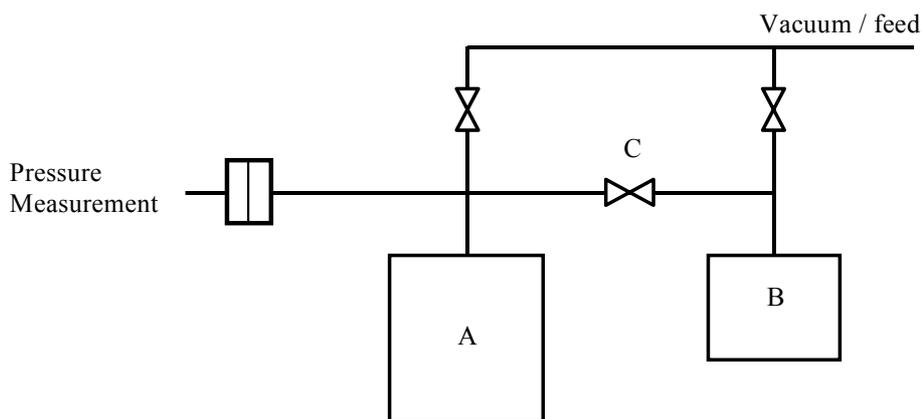


Fig. 5. Schematic Burnett apparatus

The larger vessel A contains the gas at a relatively high pressure, which is accurately measured, and the smaller vessel B is evacuated. Valve C is then opened and the gas expands into B and the new pressure is determined. By repeating the process of closing the valve, evacuating B, opening the valve and recording the new pressure, a series of pressure readings is obtained. There are various data reduction methods (88-pat/jof) for deriving values for the virial coefficients, both computational and graphical, from plots of the pressure ratios p_{i-1}/p_i , before and after the i -th expansion, versus the pressure, where

$$p_{i-1}/p_i = N_i Z_{i-1}/Z_i \quad (1.10)$$

and N_i , the cell constant, is the ratio of the total volume to the volume of A, given by the pressure ratio as the pressure tends to zero. N_i should have the same value irrespective of the sample in the cell; differences, for example with organic vapours, from the value given by a gas such as helium are evidence of adsorption.

This method has the disadvantage at temperatures below the critical temperature because of the significant decrease in the pressure range within which measurements along an isotherm can be made. As a result, it has become general practice to use a relatively high temperature Burnett expansion as a base,

and to follow this with isochoric measurements at the lower temperatures. The scheme can be explained using Figure 6.

Vessel A is initially filled to pressure p_1^1 and temperature T_1 and the temperature is lowered to T_2 (an isochoric run) and the pressure p_1^2 is measured. The temperature is then raised to the initial T_1 and a Burnett expansion is made to pressure p_2^1 . An isochoric run is made to temperatures T_2 and T_3 and the corresponding pressures measured. The temperature is then increased to T_1 and another Burnett expansion is made to pressure p_3^1 , followed by an isochoric run to temperatures T_2 , T_3 and T_4 . The Burnett-isochoric coupling procedure is repeated until the minimum measurable pressure is reached. The data for each isotherm effectively constitute other Burnett runs, and a similar analysis [88-pat/jof] can be made.

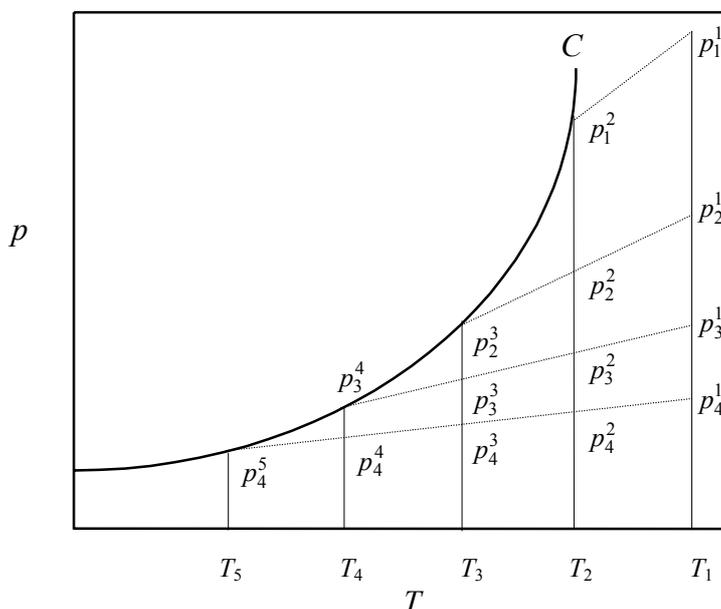


Fig. 6. $p - T$ diagram for coupled Burnett-isochoric experiments

1.2.1.3 Gas Density Determinations

This technique has been considered separately because of recent significant developments which have led to p - V - T measurements of the highest accuracy. Historically, accurate gas density measurements were made at different pressures to remove the effects of molecular interaction by extrapolation to zero pressure and hence to determine atomic weights. Second virial coefficients were derived from these data but the results for organic vapours had large uncertainties due to adsorption. Gas balances have been used specifically for second virial coefficient determination [82-zam/ste].

The development [86-kle/wag] which has led to the substantially-improved accuracy is to base the method on Archimedes' buoyancy principle but to have two sinkers of identical mass and surface area, with the same surface material (gold) but with much different volumes. This leads to compensation of all effects, including gas adsorption, which lowers the accuracy of measurements with a single sinker. The apparatus is shown schematically in Figure 7.

The measuring cell was filled with gas within the operational temperature range of 50 K to 350 K and at pressures up to 8 MPa. The sinkers were, independently, placed on the cage or removed from it. From the readings on the microbalance, which was connected to the cage by a thin bar *via* a magnetic-suspension coupling, the resulting differential buoyant force ΔF was determined.

The density was calculated from the relationship

$$\rho = (\Delta F / g) / (V_S - V_R) \quad (1.11)$$

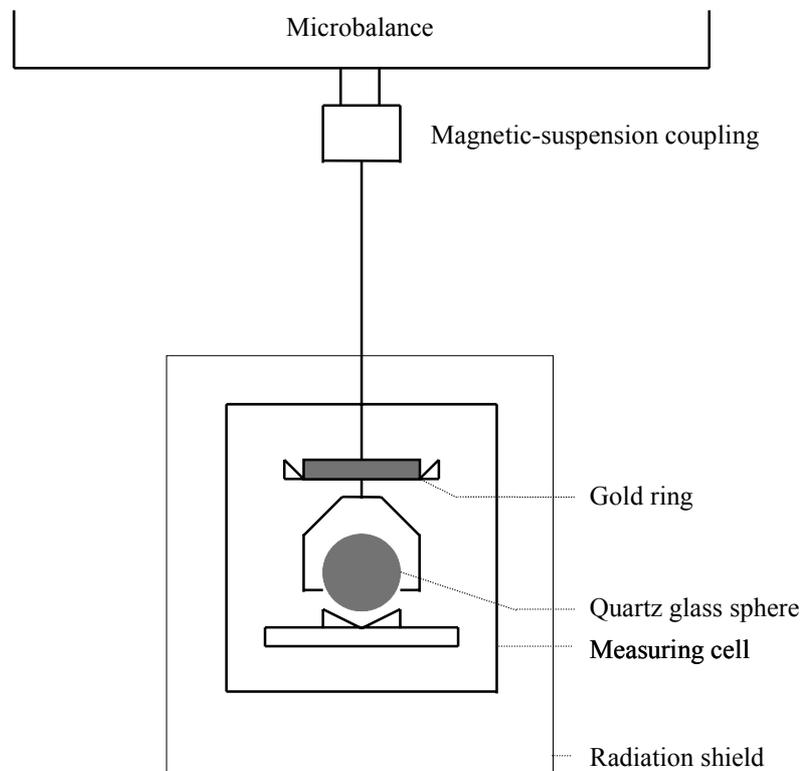


Fig. 7. Schematic drawing of the Wagner apparatus

where g is the acceleration due to gravity and V_S, V_R are the volumes of sphere and ring respectively. By measuring these volumes with an accuracy of better than 0.01 %, and the buoyant force to better than 0.01 % or 4×10^{-5} g, whichever is the greater, it is estimated that the uncertainty in the gas density is less than 0.02 % or $0.002 \text{ kg} \cdot \text{m}^{-3}$, whichever is greater. Virial coefficients derived from densities measured in this way are amongst the most accurate made.

1.2.2 Speed of Sound Measurements

The rise in importance of this method results from the high accuracy with which the speed of sound can now be measured from the spherical modes of a spherical resonator, and the fact that the results are not subject to errors from gas adsorption. One form of apparatus [89-ewi/tru] is shown schematically in Figure 8. The sealed resonator is constructed from two hemispheres of aluminium alloy, mounted on a copper support. It has two ports machined at an angle of 90° to take the electroacoustic transducers.

In the absence of dispersion, the speed of sound, u , in a gas can be expressed in terms of the temperature and molar volume:

$$u^2(T, V_m) = (RT\gamma^{\text{pg}}/M) \left\{ 1 + \beta_a/V_m + \gamma_a/V_m^2 + \dots \right\} \quad (1.12)$$

where $\gamma^{\text{pg}} = C_{p,m}/(C_{p,m} - R)$, superscript pg refers to the perfect gas state and $C_{p,m}$ is the perfect-gas molar heat capacity at constant pressure. β_a, γ_a, \dots are the second, third, ... acoustic virial coefficients which are related to coefficients in the pressure virial equation of state and their temperature derivatives:

$$\beta_a = 2B + 2(\gamma^{pg} - 1)T(dB/dT) + \left\{ (\gamma^{pg} - 1)^2 / \gamma^{pg} \right\} T^2 (d^2B/dT^2) \quad (1.13)$$

and

$$\begin{aligned} \gamma_a = & \left\{ (\gamma^{pg} - 1) / \gamma^{pg} \right\} \left\{ B + (2\gamma^{pg} - 1)T(dB/dT) + (\gamma^{pg} - 1)T^2(d^2B/dT^2) \right\}^2 \\ & + \left\{ (2\gamma^{pg} + 1)C + (\gamma^{pg2} - 1)T(dC/dT) + 0.5(\gamma^{pg} - 1)^2 T^2(dC^2/dT^2) \right\} / \gamma^{pg}. \end{aligned} \quad (1.14)$$

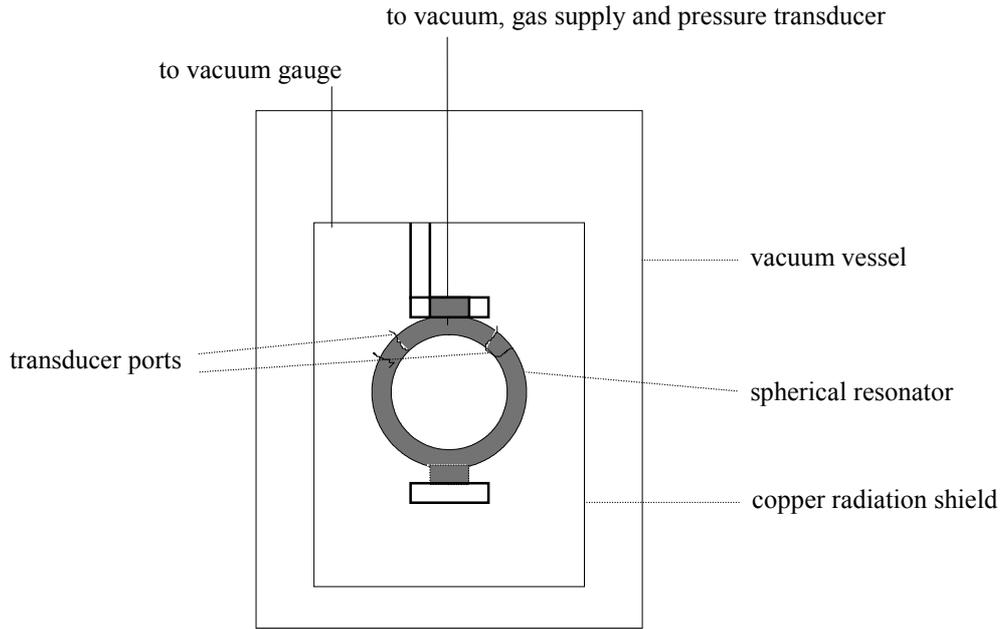


Fig. 8. Schematic diagram of a spherical resonator

The speed of sound in compressed gases is determined from the lowest-order radial modes of a spherical-resonator [89-ewi/tru, 81-meh/mol] of mean radius a_0 at the given temperature and zero pressure, since (u/a_0) is given by

$$(u/a_0) = (2\pi a/a_0)(f_{0,n} - \sum_i \Delta f_i) / v_{0,n}. \quad (1.15)$$

Here, a is the radius at pressure p , $f_{0,n}$ are the frequencies of the radial modes, $\sum_i \Delta f_i$ is the sum of small correction terms and $v_{0,n}$ is a known eigenvalue. From isothermal measurements at different pressures, the perfect gas isobaric molar heat capacity and the second and third acoustic virial coefficients can be derived by regression analysis, using an iterative procedure. Initially, molar volumes are determined from the perfect gas equation and coefficients β_a determined. By use of a model potential-energy function, such as the square-well potential, values for the molecular parameters in the expression for the second virial coefficient (see 1.3) can be determined by fitting the second acoustic virial coefficient data by the equation given above. Knowledge of the second virial coefficient gives a more accurate density and hence internal consistency can be obtained by iteration in this manner. It is not necessary to know the third virial coefficient providing the densities are sufficiently low.

For direct information on the compression factor, without any assumptions about the form of the intermolecular potential energy function, the differential equations which link the speed of sound and the virial equation of state can be numerically integrated, with known initial conditions. Specifically [96-

est/tru], the following two expressions are used to obtain Z and $C_{V,m}$ inside the (T, ρ) region where speed of sound measurements were made:

$$u^2 = (RT/M) \left[\left\{ Z + \rho_n (\partial Z / \partial \rho_n)_T \right\} + (R/C_{V,m}) \left\{ Z + T (\partial Z / \partial T)_{\rho_n} \right\}^2 \right] - (\rho_n / R) (\partial C_{V,m} / \partial \rho_n)_T \quad (1.16)$$

$$= 2T (\partial Z / \partial T)_{\rho_n} + T^2 (\partial^2 Z / \partial T^2)_{\rho_n} \quad (1.17)$$

Here, ρ_n is the amount-of-substance density, equal to the reciprocal molar volume. To carry out the numerical integration of these equations, initial values are required for two of the three quantities $C_{V,m}$, Z and $(\partial Z / \partial T)_{\rho_n}$. For example, values for Z and $(\partial Z / \partial T)_{\rho_n}$ can be determined at evenly spaced densities along an initial isotherm when accurate gas-density data are known. Then, $(\partial Z / \partial \rho_n)_T$ can be calculated and combined with speed of sound data to give values for $C_{V,m}$ at each density from the first of the equations above, and then $T^2 (\partial^2 Z / \partial T^2)_{\rho_n}$ can be determined from the second equation. A simple predictor-corrector method is then used to determine Z and $(\partial Z / \partial T)_{\rho_n}$ at a temperature ΔT from the reference isotherm. This process is then repeated to cover the range of thermodynamic states of the speed of sound measurements. Accurate coefficients in the virial equation of state can then be derived from the compression factors.

1.2.3 Joule-Thomson Measurements

Flow calorimetric measurements of the isothermal Joule-Thomson coefficient of a vapour also provide information on gas non-ideality which is free from adsorption errors. Basically, all that is required is a fixed-throttle flow calorimeter, free of heat leaks, fitted with an electric heater as shown in Figure 9 so that isothermal measurements can be made [77-alb/wor].

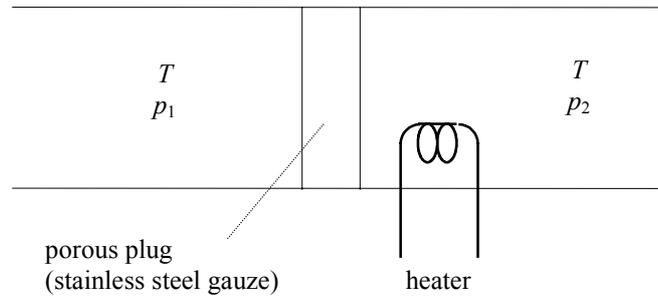


Fig. 9. Schematic diagram of an isothermal Joule-Thomson apparatus

The quantity determined in the experiments is ϕ_p , which is related to the enthalpy change, given by the electric power, P , required to maintain isothermal conditions divided by the flow rate, f , and the small pressure difference $(p_2 - p_1)$ across the stainless-steel gauze throttle:

$$\phi_p = (H_2 - H_1) / (p_2 - p_1) = P / \{f (p_2 - p_1)\} \quad (1.18)$$

since $\phi_p = (\partial H / \partial p)_T$ at the mean pressure, $p_{av} = (p_1 + p_2) / 2$ as $(p_2 - p_1) \rightarrow 0$. For vapour densities, the virial equation of state can be terminated after the third virial coefficient term, which leads to the result;

$$H_2 - H_1 = (p_2 - p_1) \{B - T(dB/dT)\} + 0.5(p_2 - p_1)(p_2 + p_1)(C' - dC'/dT) \quad (1.19)$$

where C/RT is equal to the third virial coefficient in the pressure virial series. The isothermal Joule-Thomson coefficient can then be written as

$$\phi_p = \phi_0 (1 - 2p_{av} B / RT) + 2p_{av} \{C - 0.5T(dC/dT)\} / RT \quad (1.20)$$

where the zero-pressure isothermal Joule-Thomson coefficient, ϕ_0 , which is equal to $(B - TdB/dT)$, can be obtained from the intercept of a plot of ϕ_p versus p_{av} . Since ϕ_0 depends on B and its temperature derivative, values for ϕ_0 are required over a wide temperature range for the reliable determination of second virial coefficients.

1.2.4 Refractive Index and Relative Permittivity Measurements

The dependence of the relative permittivity of a gas, ϵ , on the molar volume can be expressed by the Clausius-Mosotti equation:

$$\frac{(\epsilon - 1)V_m}{(\epsilon + 2)} = A_\epsilon + \frac{B_\epsilon}{V_m} + \frac{C_\epsilon}{V_m^2} + \dots \quad (1.21)$$

where the coefficients are dielectric virial coefficients. By introduction of the virial equation of state terminated after the second term, this becomes:

$$\frac{(\epsilon - 1)RT}{(\epsilon + 2)p} = A_\epsilon + (B_\epsilon - A_\epsilon B) \frac{p}{RT} + \dots \quad (1.22)$$

Values for $(B_\epsilon - A_\epsilon B)$ at any given temperature can be determined from measurements of the dielectric constant at different pressures. Since the second dielectric virial coefficient is very much smaller than the product $A_\epsilon B$, values for B can be determined by taking an approximate value for B_ϵ .

It was shown by Koschine and Lehrmann [92-kos/leh] that a better procedure was to use a system of two cells of matching volumes, each containing a capacitor - they had a parallel-plate type. Gas pressure and capacity were measured in one cell. The gas was then expanded into the other previously-evacuated cell, and a second set of measurements made. Finally, the first cell was evacuated and the measurements repeated after expansion into this volume. Their scheme for data analysis gives values for both the density and dielectric virial coefficients.

Measurements of the refractive index, n , of a gas at different pressures also provide information on the second virial coefficient since similar equations are obtained to the above, but with n^2 replacing ϵ . The Lorentz-Lorenz function is given by:

$$\frac{(n^2 - 1)V_m}{(n^2 + 2)} = A_1 \left\{ 1 + \frac{B_n}{V_m} + \frac{C_n}{V_m^2} + \dots \right\} \quad (1.23)$$

where A_1 is related to the polarisability α : $A_1 = 4\pi N_A \alpha / 3$ and B_n and C_n are optical, or refractivity, virial coefficients. Combination with the virial equation of state leads to the result

$$\frac{(n^2 - 1)RT}{(n^2 + 2)p} = A_1 \left\{ 1 + (B_n - B) \frac{p}{RT} + \dots \right\} \quad (1.24)$$

The second refractivity virial coefficient is usually small compared with the second density virial coefficient, and so estimates can be made for B_n . Details of the experimental method of refractive index measurement using a Michelson interferometer at temperatures from 250 K to 340 K and at pressures up to 3 MPa are given by Häusler and Kerl [88-hau/ker], who also derive values for third density virial coefficients from their results.

1.2.5 Vapour Pressure and Enthalpy of Vaporization Measurements

Second virial coefficients for a large number of organic compounds have been calculated from enthalpies of vaporization and vapour pressure data [81-hos/sco] at the former U.S. Bureau of Mines Research Center, Bartlesville by J.P. McCullough, D.W. Scott and G. Waddington. The exact Clapeyron equation can be rearranged to give

$$Z = 1 + \frac{B}{V_m} + \dots = \frac{-\Delta_{\text{vap}}H}{R\{1 - (V_L/V_m)\}\{d \ln p / d(1/T)\}} \quad (1.25)$$

where V_L is the liquid molar volume, $\Delta_{\text{vap}}H$ is the enthalpy of vaporization and p is the vapour pressure.

This group has used heat capacity measurements to check the consistency of their results from the relationship

$$\lim_{p \rightarrow 0} (\partial C_p / \partial p)_T = -T d^2 B / dT^2. \quad (1.26)$$

There is a large uncertainty in the derived virial coefficients but this method can be used for compounds where direct p - V - T methods are unsuitable.

1.3 Correlation, Prediction and Estimation of Virial Coefficients

The most satisfactory methods of data correlation are based on sound theory. In the case of the second virial coefficient, this depends on accurate knowledge of the intermolecular pair potential energy function, $U(R, \omega_1, \omega_2)$ which, in general, depends on the orientations, ω_1 and ω_2 , as well as the separation, R , of the molecules:

$$B(T) = \frac{N_A}{2V\Omega^2} \iint f_{12} d\tau_1 d\tau_2 \quad (1.27)$$

where $f_{12} = \exp\{-U(R, \omega_1, \omega_2)/kT\} - 1$. For a linear molecule:

$$d\tau_i = dr_i \sin \theta_i d\theta_i d\phi_i \quad \text{and} \quad \Omega = 4\pi$$

where θ_i and ϕ_i are the usual angles necessary to specify the orientation. For a three-dimensional rigid rotator,

$$d\tau_i = dr_i \sin \theta_i d\theta_i d\phi_i d\psi_i \quad \text{and} \quad \Omega = 8\pi^2$$

where θ_i , ϕ_i , and ψ_i are the Euler angles.

For hydrogen and helium, quantum-mechanical expressions for the second virial coefficient must be used [69-mas/spu], and even for gases with a higher relative molar mass quantum-mechanical corrections must be applied at low temperatures.

In practice, it is only for the simplest of substances that *ab initio* calculations of the pair interaction potential energy have been possible with sufficient accuracy. For helium, for example, the pair potential was determined [97-kor/wil] using infinite order symmetry adapted perturbation theory with very large orbital basis sets for intermediate separations, accurate dispersion coefficients at long range and quantum mechanical Monte Carlo calculations at short range. The results were fitted to a modified Tang-Toennies [84-tan/toe] form of potential, with no experimental input. This potential energy function was shown [97-jan/azi] to give excellent agreement with experimental second virial coefficient data.

It is more usual with closed-shell atoms to consider potential models such as the exchange-Coulomb and Hartree-Fock dispersion potentials and to determine the parameters from dilute gas properties such as the second virial coefficient and the transport properties, viscosity and thermal conductivity, together with

molecular beam data and visible-UV spectroscopic results. This approach has been most successful with monatomic gases for which $U(R)$ is now well-defined [89-azi/sla, 90-azi/sla, 94-boy, 89-dha/all, 90-dha/mea]. Analysis of the second virial coefficient data alone does not lead to a unique form for the intermolecular potential energy function, although information on parts of the curve can be obtained by inversion methods [81-mai/rig]. Once the full curve is known by inclusion of other dilute-gas properties, then the second virial coefficient values calculated from this potential function can be considered reliable. A comparison is shown in Table 1 between the present recommendations for B for argon, which were based entirely on experimental second virial coefficients, and values calculated from the potential energy function of Aziz and Slaman [90-azi/sla], for which experimental virial coefficients at temperatures above 200 K were used, with other data, to determine the potential parameters.

Table 2. Comparison of second virial coefficients for argon

T/K	$B(T)/\text{cm}^3\cdot\text{mol}^{-1}$		T/K	$B(T)/\text{cm}^3\cdot\text{mol}^{-1}$	
	This work	90-azi/sla		This work	90-azi/sla
80	-275.1 ± 4.0	-277.2	200	-47.9 ± 0.3	-48.0
85	-246.1 ± 3.0	-247.1	250	-27.7 ± 0.3	-27.8
90	-221.7 ± 2.0	-221.8	300	-15.4 ± 0.3	-15.3
95	-200.9 ± 1.5	-200.7	400	-1.2 ± 0.3	-1.0
100	-183.0 ± 1.0	-182.5	500	6.8 ± 0.5	6.8
110	-153.8 ± 1.0	-153.3	600	11.8 ± 0.5	11.7
125	-121.7 ± 0.5	-121.3	700	15.3 ± 0.5	14.9
150	-86.3 ± 0.3	-86.3	800	17.8 ± 0.5	17.2

For diatomic (and higher polyatomic) molecules, the angle-dependence of the pair intermolecular potential energy function makes the determination of $U(R, \omega_1, \omega_2)$ very difficult. For this reason, it has been customary to correlate second virial coefficient data on the basis of a function which is dependent just on intermolecular separation. Furthermore, although the form of the interaction energy curve will differ from substance to substance, lack of knowledge of the detailed form has led to the wide-spread use of generalised forms of intermolecular potential functions. Specific molecular parameters are then derived from fitting second virial coefficient data.

The simplest potential form which exhibits the necessary properties of a core repulsion and an attractive interaction energy at larger separations is the square-well (SW) potential energy function, illustrated in Figure 10.

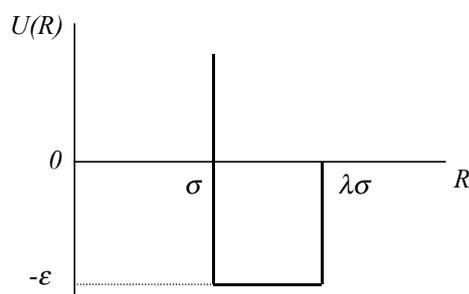


Fig. 10. Square-well potential energy function.

For SW molecules with core diameter σ , attractive energy $-\epsilon$ and well-width $(\lambda-1)\sigma$, the second virial coefficient is given by [81-mai/rig]

$$B(T) = b_0 \left[1 - (\lambda^3 - 1) \{ \exp(\varepsilon/kT) - 1 \} \right] \quad (1.28)$$

where $b_0 = 2\pi N_A \sigma^3/3$.

This three-parameter equation gives a very reasonable fit to the recommended data for most compounds except alcohols. The agreement is generally within experimental uncertainty over the whole temperature range although for some compounds the calculated $B - T$ plots show a slightly different curvature to the experimental results. Different sets of parameters often give equally satisfactory fits, which means that no physical significance should be given to the results. The SW potential energy function is unsatisfactory in not giving the maximum at high reduced temperature which is found experimentally for gases such as helium.

A more realistic form of $U(R)$ will have a soft repulsive part and a longer range attractive part to the curve, with the theoretical R^{-6} dependence at large separations. The repulsive interaction is theoretically given by an exponential term, but inverse-power forms give a similar degree of 'softness'. Taken together, these results give the ($n-6$) potentials:

$$U(R) = a/R^n - b/R^6 \quad (1.29)$$

of which the most widely-used is the Lennard-Jones (12-6) potential (24-len):

$$U(R) = 4\varepsilon \left\{ (\sigma/R)^{12} - (\sigma/R)^6 \right\} \quad (1.30)$$

where σ is the molecular separation at zero potential energy, and $-\varepsilon$ is the maximum attractive energy. Second virial coefficients are given for this potential by analytical integration which gives

$$B(T)/b_0 = \sum_{j=0}^{\infty} a_j / T^{(2j+1/4)}. \quad (1.31)$$

Expressions were given [24-len] for the coefficients a_j and tabulations of the reduced second virial coefficient $B(T)/b_0$ at a series of reduced temperatures kT/ε from 0.3 to 100 are available [81-mai/rig], together with molecular parameters for a number of substances. Laesecke [2000-lae] has investigated the significance of the individual terms in a series with temperature exponents $(1-i)/4$ where $i = 1$ to 80 and found by structural optimization methods that the $B(T)$ values were best fitted by an eight term series with $i = 1$ to 8. This corresponds to the first four terms of the theoretical infinite series, plus an additional four terms to account for all the remaining contributions. Where experimental data are available over a wide temperature range, it is found that they cannot be satisfactorily correlated within the estimated uncertainty on the basis of this potential.

Other, more complex forms of $U(R)$ have been proposed [81-mai/rig] which have proved very satisfactory for the representation of specific rare gas interactions, for example. However, for the correlation and prediction of second virial coefficient data, empirical methods are generally used. Those methods which are based on the corresponding states principle usually represent the second virial coefficient by a series of terms in inverse powers of temperature, as suggested by results for the ($n-6$) potentials, but usually with integer powers.

For non-polar molecules, Tsonopoulos [74-tso] modified the Pitzer and Curl [57-pit/cur] relationship for the reduced second virial coefficient in terms of T_r , the temperature reduced by the critical temperature, and a third parameter, the acentric factor ω , which had been introduced to extend the application to non-spherical non-polar molecules, to give:

$$\begin{aligned} \frac{Bp_c}{RT_c} = & 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \\ & + \omega \left\{ 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \right\}. \end{aligned} \quad (1.32)$$

This gave a very reasonable fit to the second virial coefficient data then available, but more recent, accurate values from Burnett and speed of sound measurements indicate that the coefficients need to be re-determined. Even so, this method is very valuable for estimating second virial coefficients where data are lacking.

For polar molecules, the temperature dependence of $B(T)$ is different. One way to account for this [74-tso] is to add another term, $a/T_r^6 - b/T_r^8$, where a is related to the reduced dipole moment. b is zero for molecules such as aldehydes, ethers, ketones and nitriles which do not hydrogen-bond. Values for a and b have been given [74-tso, 75-tso] for a number of polar substances, but where these parameters are not available it is not possible to predict the second virial coefficient.

An alternative approach [75-hay/oco, 77-tar/dan] is to use the mean radius of gyration instead of the acentric factor as the third parameter. Hayden and O'Connell [75-hay/oco], for example, use the radius of gyration to determine an effective non-polar acentric factor, in terms of which the molecular energy parameter ε and size parameter σ are expressed. An equation is given for the second virial coefficient for non-polar substances in terms of these three parameters; for polar non-associating substances additional terms involving the reduced dipole moment are given, and for polar-associating substances the association contribution is added. This approach gives a better fit than the Tsonopoulos method for some halogenated and oxygenated compounds, and for some compounds containing nitrogen or sulphur. However, for associating compounds, the additional parameter is determined specifically for the compound considered and there is no procedure for estimating it for other compounds.

More recently, a method has been described [84-mcc/dan], based on group-additivity, which does not depend on a knowledge of molecular properties or on empirical parameters. Each group contribution was derived by analysis of available second virial coefficient data, and represented by the equation

$$\Delta B_i = a_i + b_i/T_r + c_i/T_r^3 + d_i/T_r^7 + e_i/T_r^9. \quad (1.33)$$

For most groups, only the first four terms were required. Second virial coefficients for any organic compound (except acids for which the contributions are not available) can be calculated from these group contributions, and critical temperatures, for reduced temperatures from 0.5 to 5, by summing up the products of the group contribution and their respective number of occurrences. The method compares favourably with other estimation methods, and is more generally applicable.

The third virial coefficient is given [69-mas/spu] by the sum of a pairwise additive term plus a term arising from departure from pairwise additivity:

$$C(T) = C_{\text{add}} + \Delta C_{\text{non-add}} \quad (1.34)$$

where

$$C_{\text{add}} = \frac{N_A^2}{3V\Omega^3} \iiint f_{12} f_{23} f_{31} d\tau_1 d\tau_2 d\tau_3 \quad (1.35)$$

$$\Delta C_{\text{non-add}} = \frac{N_A^2}{3V\Omega^3} - \iiint \left[\exp\{-(\Delta U/kT) - 1\} \exp\{-(U_{12} + U_{23} + U_{31})/kT\} \right] d\tau_1 d\tau_2 d\tau_3. \quad (1.36)$$

The non-additive contribution to the total energy, ΔU , is given by $U_{123} - \sum U_{ij}$. For the square-well potential with well width $< \sigma$, C_{add} is given in reduced form by

$$\begin{aligned} C_{\text{add}} = & 5/8 - (\lambda^6 - 18\lambda^4 + 32\lambda^3 - 15) \{ \exp(\varepsilon/kT) - 1 \} \\ & - (2\lambda^6 - 36\lambda^4 + 32\lambda^3 + 18\lambda^2 - 16) \{ \exp(\varepsilon/kT) - 1 \}^2 \\ & - (6\lambda^6 - 18\lambda^4 + 18\lambda^2 - 6) \{ \exp(\varepsilon/kT) - 1 \}^3. \end{aligned} \quad (1.37)$$

The square-well expressions for $B(T)$ and $C(T)$ have been used [96-gil/mol] to represent the temperature dependence of these virial coefficients for real gases in the analysis of speed of sound measurements to