

An Equation for Predicting Third Virial Coefficients of Nonpolar Gases

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An empirical correlation for calculating third virial coefficients of nonpolar gases is developed in agreement with the corresponding states theorem. This equation requires the use of a third parameter which can be estimated from molecular parameters. The method is reliable, even for systems where no experimental data are available. The extension to mixtures involves one interaction constant for all possible binary sets.

SCOPE

Volumetric and thermodynamic properties of gases and vapors can be conveniently estimated by the virial equation of state. The virial equation is normally used up to moderate pressures, since only data of second virial coefficients are plentiful in the literature. Indeed, several analytical methods have been developed for calculating second virial coefficients (Tsonopoulos, 1974; Hayden and O'Connell, 1975; Tarakad and Danner, 1977). However, the advantages of the virial equation could be increased if quantitative information were available on the third virial coefficient.

Calculations of the third virial coefficients with intermolecular potential functions cannot be carried out with sufficient accuracy because of the present uncertainties on the real potential functions and on their nonpairwise additivity corrections. Empirical correlations are more useful. The only one available is that of Chueh and Prausnitz (1967) which, however, does not allow calculations in the absence of data.

This work provides a predictive method based on the available data and on recent advances in the theoretical estimates of the third virial coefficient.

CONCLUSIONS AND SIGNIFICANCE

A successful correlation for predicting the third virial coefficients of pure and mixed nonpolar gases in temperature ranges of practical interest has been developed. The equation is in agreement with the corresponding states theorem and requires a knowledge of the critical volume and temperature, acentric factor, dipole polarizability, and molecular volume of the compounds involved. A binary interaction constant is also required to extend the method

to mixtures. The correlation is a reliable predictive method of the third virial coefficients as shown by comparisons with experimental data.

The main significance of this work concerns the possibility of extending the virial equation up to about three-fourths of the critical density to calculate fugacity coefficients. These are required to interpret multicomponent vapor-liquid and gas-liquid equilibria at high pressures.

The virial equation is

$$z = \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (1)$$

where B , the second virial coefficient, is related to the potential energy between two molecules; C , the third virial coefficient, is related to the interaction energy among three molecules, etc. The theoretical calculations of C for various gases are hindered by the uncertainties about the real form of binary intermolecular potentials and about the nonpairwise additivity contributions. Simple potential functions with two or three parameters do not allow accurate calculations, even if several three-body contributions are taken into account (De Santis and Grande, 1979).

In order to estimate third virial coefficients with accuracy, empirical correlations are more useful. Two reasons have caused chemical engineers to neglect this approach. First, data of C obtained from p-v-T measurements are scarce and not completely reliable, and, second, the limitations of the corresponding states theorem (CST) for the calculation of C are not precisely known.

The Chueh and Prausnitz correlation (1967) is the only method available in the framework of CST; however, this equation makes use of a third parameter which cannot be estimated in the absence of data. Another correlation, presented by Pope et al. (1973), is of limited utility because its validity is restricted to compounds with acentric factors up to 0.1 (ethane) in narrow temperature ranges.

THEORETICAL REMARKS

It can be shown that C can be written in the form

$$C = C_{add} + \Delta C \quad (2)$$

where C_{add} is the contribution of the pairwise additivity of intermolecular potential and ΔC the contribution of nonpairwise additivity. The second term is the sum of several contributions, each accounting for a type of three-body interaction:

$$\Delta C = \Delta C_{ddd} + \Delta C_{ddq} + \Delta C_{dq q} + \Delta C_{qq q} + \dots + \Delta C_{ddd_4} + \dots \quad (3)$$

In Equation (3), the first four terms are contributions of the third-order interactions of the multipolar expansion [dipole-dipole-dipole (ΔC_{ddd}), dipole-dipole-quadrupole (ΔC_{ddq}), dipole-quadrupole-quadrupole ($\Delta C_{dq q}$), quadrupole-quadrupole-quadrupole ($\Delta C_{qq q}$)], and the last term is the first contribution of the fourth-order interaction among three molecules. The overlap nonadditivity can be neglected (Present, 1967).

Analytical expressions for the various contributions of the three-body interactions are known (De Santis and Grande, 1979). Once an intermolecular potential function is chosen, such expressions can be numerically integrated. Calculations of this type, based on various highly accurate multiparameter potentials of simple gases, all originating from the work of Barker and Pompe (1968), have been carried out recently by various authors (Johnson and Spurling, 1971; Barker et al., 1972; Caligaris, 1973; Caligaris and Henderson, 1975). These calculations show that the main contribution to the nonpairwise additivity is the term ΔC_{ddd} , the multipolar expansion is rapidly convergent, ΔC_{ddq} and $\Delta C_{qq q}$ are uncertain and irrelevant, and ΔC_{ddd_4} is negative and of the same order of magnitude of ΔC_{ddq} . The sum of ΔC_{ddq} and ΔC_{ddd_4} never exceeds 10% of ΔC_{ddd} . The tables of Caligaris and Henderson (1975), which report the calculated C_{add} , ΔC_{ddd} , ΔC_{ddq} , ΔC_{ddd_4} of argon, krypton, and xenon, are the most reliable results available today. These calculations, which cannot be carried out for many fluids because their intermolecular potential is not known, can be useful to develop an empirical correlation.

Restricting the analysis to argon and krypton (the intermolecular potential of xenon is not sufficiently reliable), we observe that reduced third virial coefficients (C/v_c^2) of argon and krypton from the tables of Caligaris and Henderson exhibit differences of 6% at reduced temperatures of 0.9. The differences between C/v_c^2 of argon and krypton are due mainly to ΔC_{ddd} and, therefore, to the different polarizabilities (De Santis and Grande, 1979); however, they are of the same order of magnitude of experimental uncertainties and larger than the observed differences.

Differences are very slight at high temperatures where the CST is fully validated by the negligible influence of the nonadditivity effects. It seems convenient, therefore, to assume the validity of CST for $T_R > 0.9$. In addition, third virial coefficients calculated by Caligaris and Henderson agree rather well with experimental data for $T_R > 2.5$.

At any rate, calculations of C of practical interest for reduced temperatures lower than 0.8 are seldom important, since saturation pressures are low, and the virial equation can be truncated to the second coefficient.

EXPERIMENTAL DATA

The values of C , obtained from p-v-T measurements, are strongly dependent on the degree of the polynomial (1) used to fit the data. Michels et al. (1960) and Hall

and Canfield (1967) have suggested statistical criteria for truncating the virial equation to obtain values of coefficients close to the theoretical, that is, included in the series of infinite terms.

The problem was also studied by Levelt Sengers (1968), who suggested correlating p-v-T data by a polynomial of degree $(m-1)$ up to densities such that the $(m+1)^{\text{th}}$ coefficient does not contribute to the compressibility factor for more than the experimental error. This method requires evaluating the order of magnitude of the $(m+1)^{\text{th}}$ coefficient with an intermolecular potential function. In any case, it seems assured that the coefficient C from a six- or seven-term polynomial cannot be identified with the third virial coefficient on statistical grounds.

Using the Hall and Canfield cutoff criterion, Righter and Hall (1975) and Lee et al. (1978) presented generalized plots for selecting the optimal truncation based on the maximum density or pressure of data at a reduced temperature. These charts can be guidelines to analyze critically sets of virial coefficients obtained from the p-v-T data.

Few reliable experimental C 's exist in the literature. Even with accurate volumetric data, the uncertainty on C is generally one order of magnitude greater than that on B . Table 1 indicates the sources of data used for the development of our correlation. Many of these data are taken from the compilation of Dymond and Smith (1969), which covers the literature until 1968. Data relative to common gases are also reported by Levelt Sengers et al. (1972).

Tests have been carried out to verify the validity of the truncation for a given set of data by the plots of Lee et al. (1978). The truncations, generally of low degree, appear quite correct. In some cases, however, the optimal number of virial coefficients varies with temperature at the same maximum pressure, whereas our truncations are temperature independent.

The reduced C data exhibit a maximum for all the nonpolar fluids near $T_R = 0.91$. This maximum increases with molecular dimensions. At $T_R > 1.8$, data are scarcer and their scatter is higher than differences among different fluids; therefore, in the limits of the experimental uncertainties, it can be assumed that reduced C of all the fluids converge in a single curve.

DEVELOPMENT OF THE CORRELATION

The previous discussion leads to the development of a correlation in the framework of three-parameter CST and to the assignment of a fair reliability to experimental data. In addition, reduced C of all nonpolar fluids are universal functions of T_R at high temperatures. This function can be obtained from the calculations of Caligaris and Henderson for $T_R > 2.5$.

The influence of the molecular shape and dimensions on the deviations from the two-parameter CST is generally characterized by the acentric factor. Chueh and Prausnitz (1967) noted that differences between reduced C of argon and that of other gases are not simply related to the acentric factor. Their third parameter, in fact, can be calculated only when data are available. Calling d the third parameter, one can write

$$\frac{C}{v_c^2} = f(T_R, d) \quad (4)$$

Expanding in series around $d = 0$ and truncating after the quadratic term, one obtains

TABLE 1. DATA SOURCES FOR THIRD VIRIAL COEFFICIENTS

Substance	Temperature range, °K	Sources
Argon	116-573	Michels et al. (1949), Michels et al. (1958), Crain and Sonntag (1966), Kalfoglou and Miller (1967), Blancett et al. (1970), Provine and Canfield (1971), Levelt Sengers et al. (1972), Pope et al. (1973).
Fluorine	80-300	Prydz and Straty (1970).
Sulfur hexafluoride	271-404	Mears et al. (1969), Sigmund et al. (1972).
Krypton	273-873	Beattie et al. (1952), Whalley and Schneider (1954), Trappeniers et al. (1966), Levelt Sengers et al. (1972).
Nitrogen	133-423	Michels et al. (1934), Canfield et al. (1963), Hoover et al. (1964), Crain and Sonntag (1966), Ku and Dodge (1967), Levelt Sengers et al. (1972).
Oxygen	85-323	Michels et al. (1954), Weber (1970), Levelt Sengers et al. (1972).
Xenon	273-773	Beattie et al. (1951), Michels et al. (1954), Whalley et al. (1955), Levelt Sengers et al. (1972).
Dichlorodifluoromethane	323-423	Michels et al. (1966).
Carbon tetrafluoride	203-773	MacCormack and Schneider (1951), Kalfoglou and Miller (1967), Douslin et al. (1967), Lange and Stein (1970), Sigmund et al. (1972).
Carbon monoxide	273-423	Michels et al. (1952).
Carbon dioxide	262-773	Michels and Michels (1935), MacCormack and Schneider (1950), Pfefferle et al. (1955), Butcher and Dadson (1964), Vukalovich and Masalov (1966), Levelt Sengers et al. (1972).
Methane	147-623	Schamp et al. (1958), Douslin et al. (1967), McMath and Edmister (1969), Lee and Edmister (1970), Pope et al. (1973).
Ethylene	238-448	Michels and Geldermans (1942), Butcher and Dadson (1964), McMath and Edmister (1969), Lee and Edmister (1970), Pope et al. (1973), Douslin and Harrison (1976).
Ethane	209-623	Reamer et al. (1944), Michels et al. (1954), Douslin and Harrison (1973), Pope et al. (1973).
Propyne	348-473	Vohra et al. (1962).
Propylene	298-423	Michels et al. (1953), Warowny et al. (1978).
Propane	373-423	Warowny et al. (1978).
<i>i</i> -butane	344-444	Connolly (1962).
<i>n</i> -butane	344-444	Connolly (1962).
Neopentane	348-548	Beattie et al. (1952), Dawson et al. (1973).
Benzene	493-573	Connolly and Kandalic (1960).
Cyclohexane	423-523	Kerns et al. (1974).
Octane	493-573	Connolly and Kandalic (1960).
Helium	10-573	Keesom (1942), Michels and Wouters (1941), Pfefferle et al. (1955), Canfield et al. (1963), Hoover et al. (1964), Ku and Dodge (1967), Kalfoglou and Miller (1967), Hall and Canfield (1970), Blancett et al. (1970), Provine and Canfield (1971).
Hydrogen	16-423	Michels and Goudekot (1941), Goodwin (1964), Levelt Sengers et al. (1972), Mihara et al. (1977).
Neon	44-423	Nicholson and Schneider (1955), Michels et al. (1960), Gibbons (1969), Levelt Sengers et al. (1972).

Sources not reported in the Literature Cited are taken from the compilation of Dymond and Smith (1969).

$$\frac{C}{v_c^2} = C^0(T_R) + dC'(T_R) + d^2C''(T_R) \quad (5)$$

The function C^0 has been obtained by fitting the C data of argon up to $T_R = 2.5$ and the calculated values of Caligaris and Henderson above $T_R = 2.5$. The following expression is proposed:

$$C^0 = \frac{0.1961}{T_R^{1/4}} + \frac{0.3972}{T_R^5}$$

$$+ \left(0.06684 T_R^4 - \frac{0.5428}{T_R^6} \right) \exp(-T_R^2) \quad (6)$$

Equation (6) was derived by giving more weight to the data of Crain and Sonntag (1966) and Pope et al. (1973) than to data of Michels et al. (1960) around the maximum of C . Figure 1 shows the experimental and calculated C of argon. The equation predicts a maximum of 0.44 at $T_R = 0.91$. Figure 2 shows data of C/v_c^2 of various fluids compared with Equation (6) and the cor-

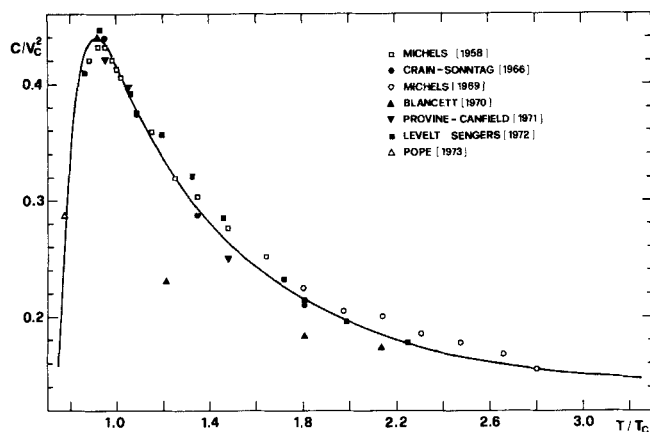


Figure 1. Third virial coefficients of argon.

relation of Chueh and Prausnitz. The effect of C' and C'' is negligible for the fluids and the temperatures reported in Figure 2.

A rough analysis of data cited in Table 1 suggests that, to a first approximation, d can be evaluated as

$$d = \frac{\omega \alpha N}{b} \quad (7)$$

where ω is the acentric factor, α the dipole polarizability, and b the molecular volume calculated, as done by Bondi (1968), from atomic radii and bond distances. A comprehensive tabulation of b is reported by Nothnagel et al. (1973). Pure component parameters are indicated in Table 2. Equation (7) allows an a priori estimation of d . This third parameter accounts empirically for the influence of molecular shape and dimensions and for the non-additivity effects on the deviations from the two-parameter CST. In fact, the total nonadditivity is, as a first approximation, linear with the reduced polarizability α/b because of the practical cancellation of contributions ddq and ddd_4 (De Santis and Grande, 1979).

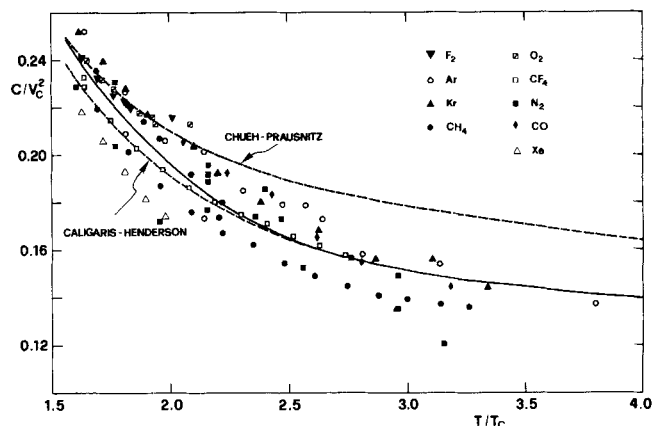


Figure 2. Third virial coefficients at high temperatures.

Functions C' and C'' have been obtained by fitting the data of fluids in the range of acentric factors $0.1 \div 0.4$. The following expressions are proposed:

$$C' = \frac{64.5}{T_R^9} [1 - 2.085 \exp(-T_R^2)] \quad (8)$$

$$C'' = \frac{801.7}{T_R^7} \quad (9)$$

The weight of functions C' and C'' is significant up to $T_R = 2$, at the most. Equations (8) and (9) are simple because the scarcity of data does not justify more complicated formulations. However, these equations provide a good estimate of the effect of molecular shape and dimensions.

Figure 3 shows the agreement obtained with data of various fluids. Reduced C of gases like krypton, xenon, fluorine, nitrogen, oxygen, and methane turn out to be nearly equal or slightly greater than those of argon. The maximum of carbon dioxide is 0.56, whereas the data of Michels and Michels (1935) indicate a value of 0.63 and

TABLE 2. PURE COMPONENT PARAMETERS

Substance	ω	$\alpha 10^{24}, \text{cm}^3$	$b, \text{cm}^3/\text{mole}$	$v_c, \text{cm}^3/\text{mole}$	$T_c, ^\circ\text{K}$
Argon	-0.004	1.59	48.7	74.9	150.8
Fluorine	0.048	1.25	61.7	66.2	144.3
Sulfur hexafluoride	0.257	6.21	140.0	194	318.7
Krypton	-0.002	2.36	58.4	91.2	209.4
Nitrogen	0.035	1.73	56.9	89.5	126.2
Oxygen	0.021	1.57	47.2	74.4	154.6
Xenon	0.002	3.94	75.1	118	289.7
Dichlorodifluoromethane	0.176	7.15	155	217	385
Carbon tetrafluoride	0.169	3.85	108.0	140	227.6
Carbon monoxide	0.049	1.93	21.6	93.1	132.9
Carbon dioxide	0.225	2.65	70.1	94	304.2
Methane	0.013	2.70	68.5	99.0	190.6
Ethylene	0.101	4.26	86.2	129	282.4
Ethane	0.105	4.47	109.5	148	305.4
Propyne	0.276	5.27	133	164	402.4
Propylene	0.148	6.19	136.5	181	365.0
Propane	0.152	6.29	142.2	203	369.8
<i>i</i> -butane	0.176	8.23	195.5	263	408.1
<i>n</i> -butane	0.193	8.23	191.5	255	425.2
Neopentane	0.197	10.36	232.5	303	433.8
Benzene	0.215	10.32	193.5	260	562.1
Ciclohexane	0.213	10.9	246	308	553.4
Octane	0.394	15.5	354.5	492	568.8
Helium				37.5	10.47
Hydrogen				51.5	43.6
Neon				40.3	45.5

data of Butcher and Dadson (1964) a value of 0.50. A disagreement appears for SF₆ (nonhydrocarbon compound) with an observed maximum of the order of 0.53, whereas calculations give 0.60. Predictions are poor for cyclohexane. However, the data used to test the correlation (Kerns et al., 1974) are strongly negative even for $T_R \approx 0.95$. The equation correctly predicts reduced C 's for n -butane larger than those for isobutane, even if the data indicate slightly greater differences.

Uncertainties still remain at $T_R > 1.2$ for fluids with high values of d . Lacking data in this region, their C are obtained by extrapolating the behavior of simpler fluids. The reduced C of octane, for example, from the above equations coincides with that of argon for $T_R \approx 2.0$; such a prediction is largely arbitrary.

For $0.8 < T_R < 0.9$, the reliability of the equation is within the limits of uncertainty in the data and in the validity of CST. For reduced temperatures less than 0.85, it predicts a cross effect which depends on the weight given to measurements of Pope et al., who observed this phenomenon for argon, methane, and ethane. The Chueh and Prausnitz correlation does not predict it. However, as stated above, a very precise representation of C at these temperatures is not important.

The method can be used also for quantum fluids, provided temperature dependent reducing parameters are used instead of the real critical constants (Gunn et al., 1966). These effective critical constants are expressed by

$$T_c = \frac{T_c^0}{1 + \frac{21.8}{mT}} \quad (10)$$

$$v_c = \frac{v_c^0}{1 - \frac{9.91}{mT}} \quad (11)$$

where m is the molecular weight, and T_c^0 , v_c^0 are the classical critical constants with values for hydrogen, helium, and neon reported in Table 2. The third parameter d must be assumed equal to zero for quantum gases. Virial coefficients data of quantum fluids of various authors were not deemed accurate and consistent with one another; therefore, they were not included in the fitting. However, Equation (6) with temperature dependent reducing parameters gives fair estimates. Using effective constants at low temperatures, that is, in the region close to the root of the denominator of Equation (11), generates erroneous results.

Unfortunately, discrepancies still exist in the literature on the values of the critical constants and the acentric factors, limiting the reliability of the equation. In particular, the critical volumes are the most uncertain, and, being present with an exponent of two, their weight on the calculated C is high.

In line with the theoretical arguments discussed above, it would be more nearly correct to develop a correlation of the type

$$\frac{C}{v_c^2} = f^0(T_R) + \omega f'(T_R) + \frac{\alpha}{b} f''(T_R) \quad (12)$$

where the first addendum indicates the contribution of pairwise additivity of rare gases, the second the contribution of molecular shape and dimensions on additivity, and the third the contribution of nonadditivity.

The first term is known today with a good accuracy from the tabulations of Caligaris and Henderson. The third term can be calculated from the observed C of gases

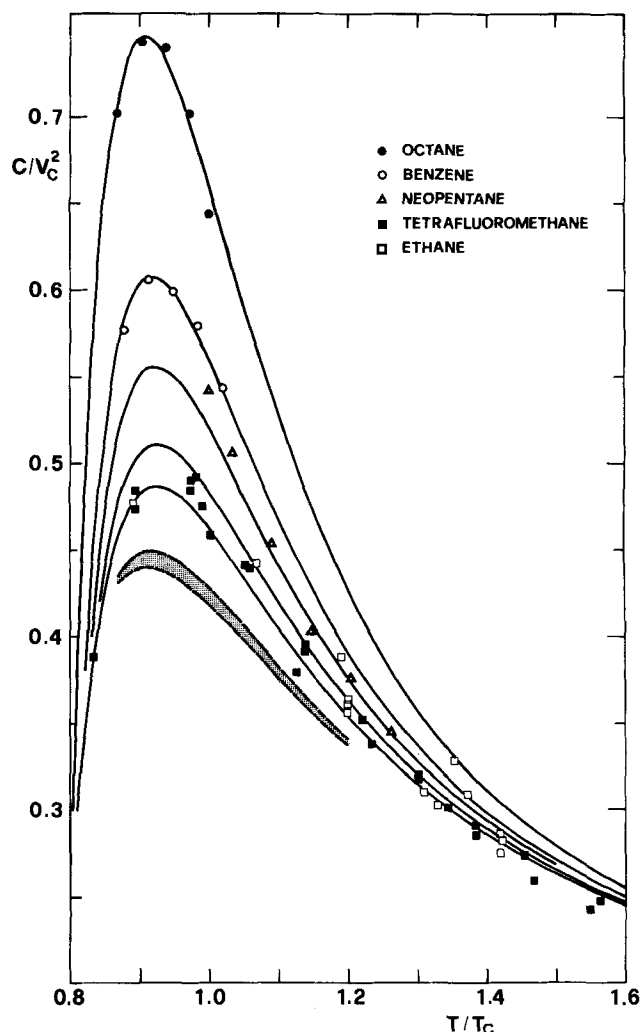


Figure 3. Third virial coefficients of some nonpolar gases. The dotted region comprehends C of fluids like krypton, xenon, methane, fluorine, nitrogen, oxygen.

like argon, krypton, xenon, methane, nitrogen, and oxygen since the second term is zero for such fluids. Finally, the second addendum could be obtained by fitting the data for Pitzer's fluids. This simple approach, however, did not lead to significant results, even taking into account the uncertainties of the data.

EXTENSION TO MIXTURES

The third virial coefficient of a mixture is rigorously expressed by

$$C = \sum_{i=1}^n \sum_{j=1}^n \sum_{k=1}^n y_i y_j y_k C_{ijk} \quad (13)$$

The correlation proposed above can be extended to the calculation of the mixture coefficients by following the same criterion used by Chueh and Prausnitz. The cross coefficients are expressed by

$$C_{ijk} = (C_{ij} C_{ik} C_{jk})^{1/3} \quad (14)$$

where C_{ij} , C_{ik} , C_{jk} can be evaluated with the same relationship as that for pure components:

$$C_{ij} = v_{cij}^2 f\left(\frac{T}{T_{cij}}, d_{ij}\right) \quad (15)$$

Binary parameters can be calculated by

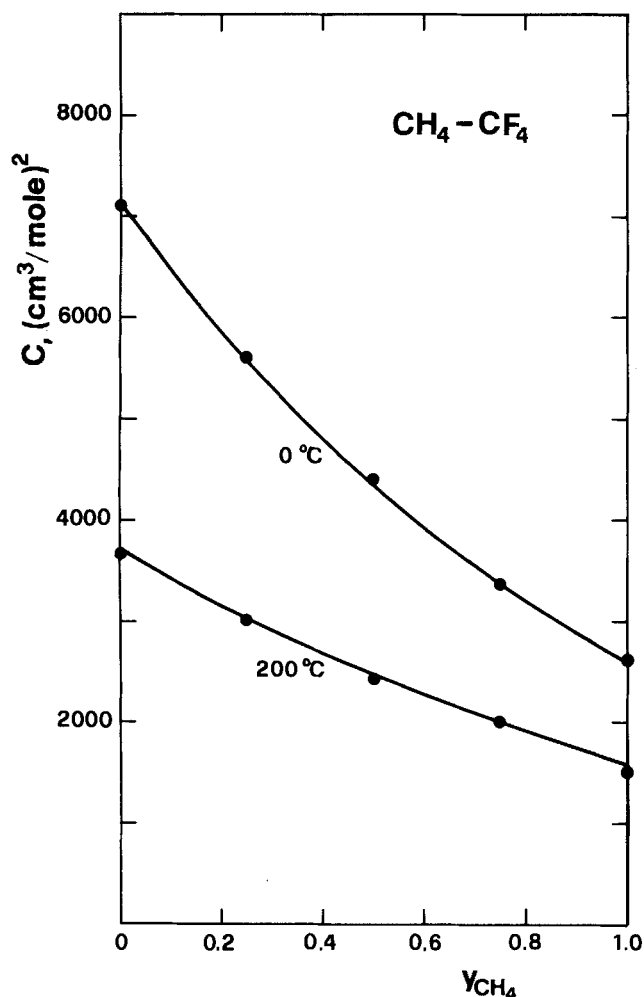


Figure 4. Third virial coefficients for the methane-tetrafluoromethane system.

$$v_{cij} = \frac{1}{8} (v_{ci}^{1/3} + v_{cj}^{1/3})^3 \quad (16)$$

$$T_{cij} = (1 - K_{ij}) (T_{ci} T_{cj})^{1/2} \quad (17)$$

$$d_{ij} = \frac{1}{2} (d_i + d_j) \quad (18)$$

The binary constant K_{ij} can be evaluated from binary data as second virial cross coefficients. Tabulations of K_{ij} for several binaries are reported elsewhere (Prausnitz, 1969).

For mixtures containing quantum fluids, the interaction reducing parameters are given by

$$T_{cij} = \frac{(1 - K_{ij}) (T_{ci}^0 T_{cj}^0)^{1/2}}{1 + \frac{21.8}{2T} \left(\frac{1}{m_i} + \frac{1}{m_j} \right)} \quad (19)$$

$$v_{cij} = \frac{[(v_{ci}^0)^{1/3} + (v_{cj}^0)^{1/3}]^3}{8 \left[1 - \frac{9.91}{2T} \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \right]} \quad (20)$$

Data of the third virial coefficients for mixtures are rare; therefore, only limited checks of this method can be carried out. For the sets of data reported by Chueh and Prausnitz (1967), the predictions are, of course, comparable to those obtained with their correlation. For the case of more recent mixture data, the agreement seems similar to that for pure components, that is, often within the limits of experimental error.

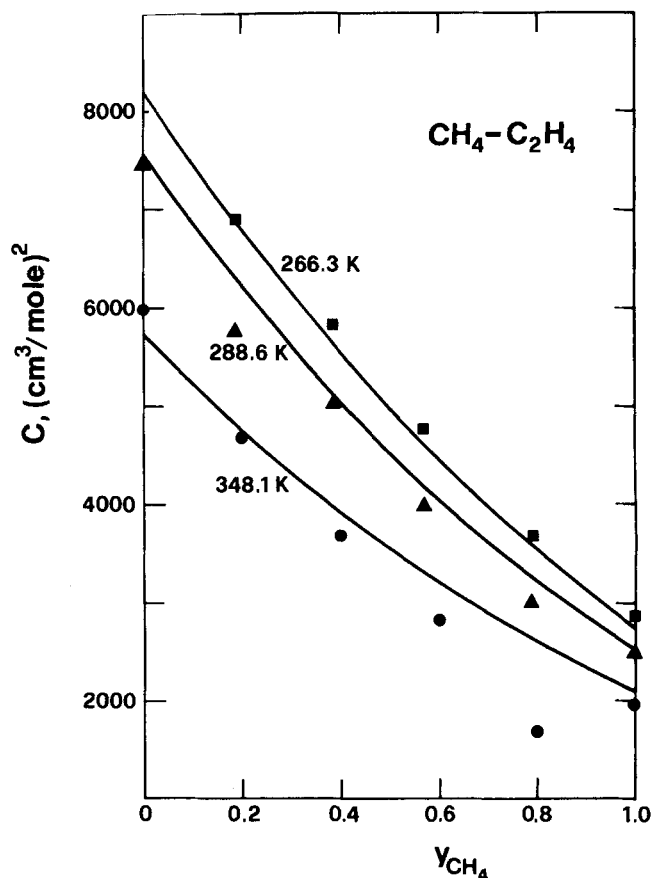


Figure 5. Third virial coefficients for the methane-ethylene system.

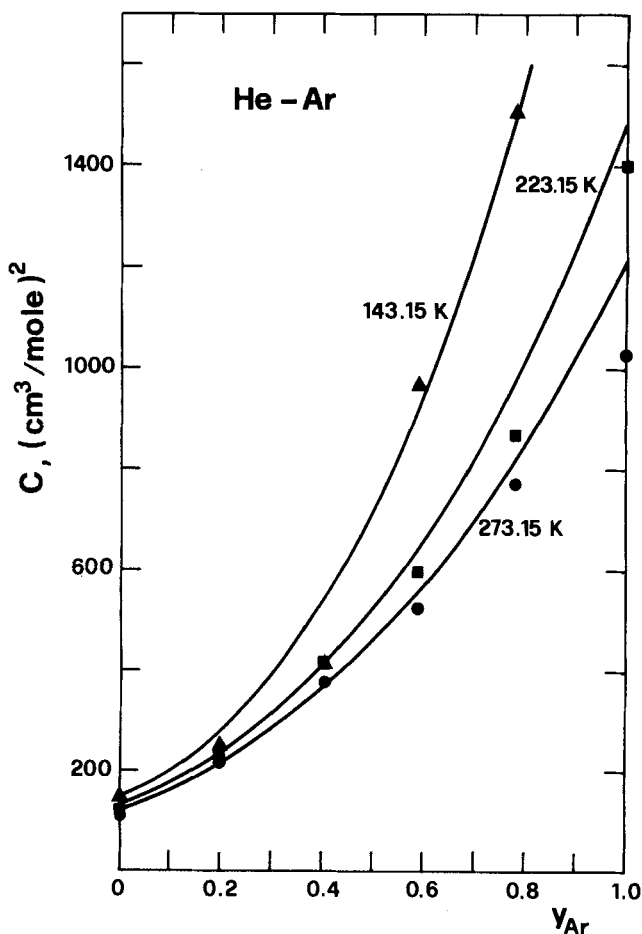


Figure 6. Third virial coefficients for the helium-argon system.

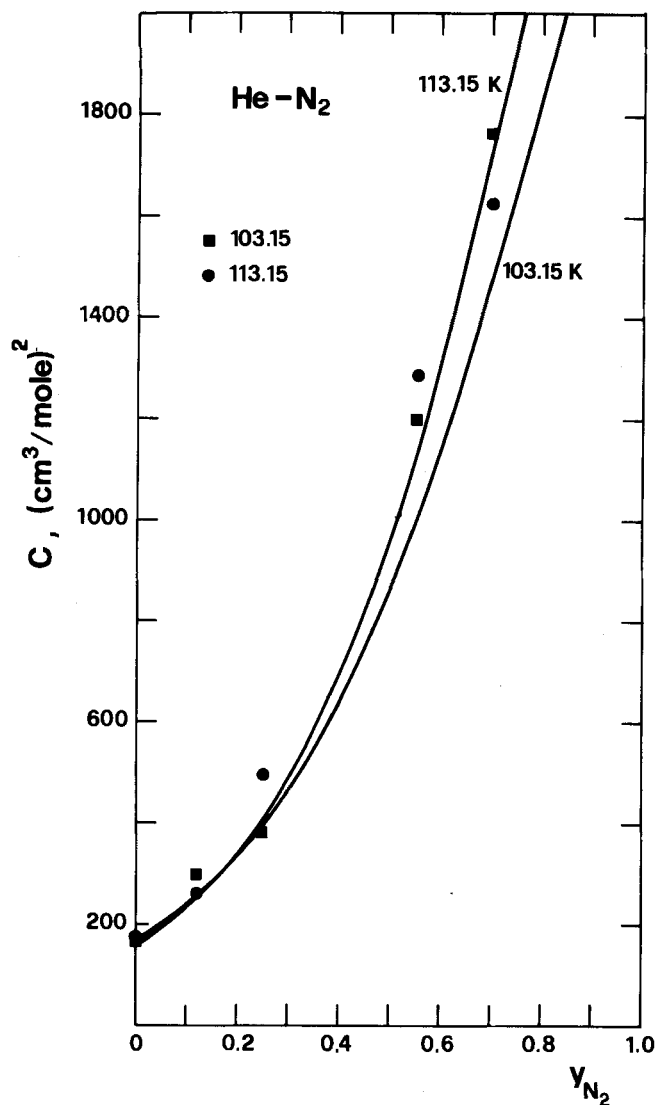


Figure 7. Third virial coefficients for the helium-nitrogen system.

Figures 4 to 7 show the results obtained for the mixtures $\text{CH}_4\text{--CF}_4$ (Douslin et al., 1967), $\text{CH}_4\text{--C}_2\text{H}_4$ (Lee and Edmister, 1970), He--Ar (Blancett et al., 1970; Provine and Canfield, 1971), He--N_2 (Hall and Canfield, 1970). Mixtures C are reported, instead of separate C_{112} and C_{122} , because of the difficulty of obtaining the two coefficients from the cubic function (13). Calculations performed for a few other binary mixtures are not reported because the data for pure components of these sources do not closely follow the proposed equation. Therefore, a check of mixing rules [Equations (14) to (18)] would not be significant.

Even if limited to mixtures of molecules of small acentricity, these results validate the use of the virial equation to calculate fugacity coefficients. In fact, the exact dependence of C on composition eliminates the uncertainties in the derivatives of pressure or volume with respect to the mole number of each component, which is a serious obstacle when using empirical equations of state.

NOTATION

b	= Bondi's molecular volume
B	= second virial coefficient
C	= third virial coefficient
d	= third parameter
D	= fourth virial coefficient

K	= binary interaction constant
m	= molecular weight
n	= number of the components of the mixture
N	= Avogadro number
p	= pressure
R	= gas constant
T	= temperature
v	= molar volume
y	= mole fraction
z	= compressibility factor
α	= dipole polarizability
ω	= acentric factor
ΔC	= three-body contribution to C

Subscripts

add	= contribution of the pairwise additivity of the potential
c	= at critical conditions
d	= instantaneous dipole
i, j, k	= relative to the generic components i, j, k
q	= instantaneous quadrupole
R	= at reduced conditions

LITERATURE CITED

- Barker, J. A., and A. Pompe, "Atomic Interactions in Argon," *Aust. J. Chem.*, **21**, 1683 (1968).
- Barker, J. A., C. H. J. Johnson, and T. H. Spurling, "Third Virial Coefficients of Krypton," *ibid.*, **25**, 1813 (1972).
- Blancett, A. L., K. R. Hall, and F. B. Canfield, "Isotherms for the Helium-Argon System at -50°C , 0°C , 50°C up to 700 Atm," *Physica*, **47**, 75 (1970).
- Bondi, A., *Physical Properties of Molecular Crystals, Liquids and Glasses*, Wiley, New York (1968).
- Caligaris, R. E., "The Intermolecular Pair Potential of Argon and Third Virial Coefficients," *Molec. Phys.*, **25**, 1465 (1973).
- Caligaris, R. E., and D. Henderson, "Third Virial Coefficients of Ar+Kr and Kr+Xe Mixtures," *ibid.*, **30**, 1853 (1975).
- Chueh, P. L., and J. M. Prausnitz, "Third Virial Coefficients of Non-Polar Gases and Their Mixtures," *AIChE J.*, **12**, 896 (1967).
- Connolly, J. F., "Ideality of n -Butane:Isobutane Solutions," *J. Phys. Chem.*, **66**, 1082 (1962).
- Dawson, P. P., Jr., I. H. Silberberg, and J. J. McKetta, "Volumetric Behavior, Vapor Pressures, and Critical Properties of Neopentane," *J. Chem. Eng. Data*, **18**, 7 (1973).
- De Santis, R., and B. Grande, "Non-Pairwise Additivity of Intermolecular Potentials and Third Virial Coefficients," *Quad. Ing. Chim. Ital.*, **15**, 74 (1979).
- Douslin, D. R., R. H. Harrison, and R. T. Moore, "Pressure-Volume-Temperature Relations in the System Methane-Tetrafluoromethane. I. Gas Densities and the Principle of Corresponding States," *J. Phys. Chem.*, **71**, 3477 (1967).
- Douslin, D. R., and R. H. Harrison, "Pressure-Volume-Temperature Relations of Ethane," *J. Chem. Therm.*, **5**, 491 (1973).
- Douslin, D. R., and R. H. Harrison, "Pressure, Volume, Temperature Relations of Ethylene," *ibid.*, **8**, 301 (1976).
- Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Gases*, Clarendon Press, Oxford, England (1969).
- Gibbons, R. M., "The Equation of State of Neon between 27 and 70 K," *Cryogenics*, **8**, 252 (1969).
- Gunn, R. D., P. L. Chueh, and J. M. Prausnitz, "Prediction of Thermodynamic Properties of Dense Gas Mixtures Containing One or More of the Quantum Gases," *AIChE J.*, **12**, 937 (1966).
- Hall, K. R., and F. B. Canfield, "Optimal Recovery of Virial Coefficients from Experimental Compressibility Data," *Physica*, **33**, 481 (1967).
- Hall, K. R., and F. B. Canfield, "Isotherms for the He- N_2 System at -190°C , -170°C , -160°C up to 700 Atm," *ibid.*, **47**, 219 (1970).
- Hayden, J. G., and J. P. O'Connell, "A Generalized Method

- for Predicting Second Virial Coefficients," *Ind. Eng. Chem. Process Design Develop.*, **14**, 209 (1975).
- Johnson, C. H. J., and T. H. Spurling, "Multipolar Third Order Non-Pairwise Additivity of Intermolecular Forces: Effects on Crystal Properties and Third Virial Coefficients," *Aust. J. Chem.*, **24**, 2205 (1971).
- Kalfoglou, N. K., and J. G. Miller, "Compressibility of Gases. V. Mixtures of Spherically Symmetric Molecules at Higher Temperatures. The Helium-Argon and Helium-Tetrafluoromethane Systems," *J. Phys. Chem.*, **71**, 1256 (1967).
- Kerns, W. J., R. G. Anthony, and P. T. Eubank, "Volumetric Properties of Cyclohexane Vapor," *AIChE Symposium Ser.*, **70**, 14 (1974).
- Lange, H. B., Jr., and F. P. Stein, "Volumetric Behaviour of a Polar-Non-Polar Gas Mixture: Trifluoromethane-Tetrafluoromethane System," *J. Chem. Eng. Data*, **15**, 56 (1970).
- Lee, R. C., and W. C. Edmister, "Compressibilities and Virial Coefficients for Methane, Ethylene, and Their Mixtures," *AIChE J.*, **16**, 1047 (1970).
- Lee, S. M., P. T. Eubank, and K. R. Hall, "Truncation Errors Associated with the Virial Equation," *Fluid Phase Equilibria*, **1**, 219 (1978).
- Levelt Sengers, J. M. H., Proc. Symp. Thermophys. Properties 4th, ASME, New York (1968).
- Levelt Sengers, J. M. H., M. Klein, and J. S. Gallagher, "Pressure-Volume-Temperature Relationships of Gases; Virial Coefficients," *A.I.P. Handbook*, McGraw-Hill, New York (1972).
- McMath, H. G., Jr., and W. C. Edmister, "The Experimental Determination of the Volumetric Properties and Virial Coefficients of the Methane-Ethylene System," *AIChE J.*, **15**, 370 (1969).
- Mears, W. H., E. Rosenthal, and J. V. Sinka, "Physical Properties and Virial Coefficients of Sulfur Hexafluoride," *J. Phys. Chem.*, **73**, 2254 (1969).
- Michels, A., J. C. Abels, C. A. Ten Seldam, and W. de Graaff, "Polynomial Representation of Experimental Data Application to Virial Coefficients of Gases," *Physica*, **26**, 381 (1960).
- Mihara, S., H. Sagara, Y. Arai, and S. Saito, "The Compressibility Factors of Hydrogen-Methane, Hydrogen-Ethane, and Hydrogen-Propane Gaseous Mixtures," *J. Chem. Eng. Japan*, **10**, 395 (1977).
- Nothnagel, K. H., D. S. Abrams, and J. M. Prausnitz, "Generalized Correlation for Fugacity Coefficients in Mixtures at Moderate Pressures," *Ind. Eng. Chem. Process Design Develop.*, **12**, 25 (1973).
- Pope, G. A., P. S. Chapplear, and R. Kobayashi, "Virial Coefficients of Argon, Methane and Ethane at Low Reduced Temperatures," *J. Chem. Phys.*, **59**, 423 (1973).
- Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, N.J. (1969).
- Present, R. D., "Nonadditive Triple-Overlap Interactions among Rare-Gas Atoms in the Thomas-Fermi-Dirac Approximation," *J. Chem. Phys.*, **47**, 1793 (1967).
- Provine, J. A., and F. B. Canfield, "Isotherms for the Helium-Argon System at -130, -115, and -90°C up to 700 Atm," *Physica*, **52**, 79 (1971).
- Prydz, R., and G. C. Straty, "PVT Measurements, Virial Coefficients, and Joule-Thomson Inversion Curve of Fluorine," *J. Res. Natl. Bur. Stand.*, **74A**, 747 (1970).
- Righter, W. M., and K. R. Hall, "Optimal Truncation of the Virial Equation," *AIChE J.*, **21**, 406 (1975).
- Sigmund, P. M., I. H. Silberberg, and J. J. McKetta, "Second and Third Virial Coefficients for System Tetrafluoromethane-Sulfur Hexafluoride," *J. Chem. Eng. Data*, **17**, 168 (1972).
- Tarakad, R. R., and R. P. Danner, "An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients," *AIChE J.*, **23**, 685 (1977).
- Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **20**, 263 (1974).
- Warowny, W., P. Wielopolski, and J. Stecki, "Compressibility Factors and Virial Coefficients for Propane, Propene and Their Mixtures by the Burnett Method," *Physica*, **91A**, 73 (1978).
- Weber, L. A., "P-V-T Pressure-Volume-Temperature Thermodynamic and Related Properties of Oxygen from the Triple Point to 300 K at Pressures to 33 MN/m²," *J. Res. Nat. Bur. Stand.*, **74A**, 93 (1970).

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Effects of Acceleration, Deceleration and Particle Shape on Single-Particle Drag Coefficients in Still Air

Measurements were made of the drag coefficients of smooth solid particles moving singly through still air at Reynolds numbers in the range of 10^3 to 10^4 . Spheres were observed during acceleration, deceleration and at terminal velocity. Discs were tested during acceleration and at steady velocity. Other particles in the shapes of discs, circular cylinders and rectangular parallelepipeds were tested at steady velocity in their preferred and, in some cases, non-preferred orientations. The effects of non-steady velocity and of particle form were determined. An unexpected influence of particle density was observed for some of the particles.

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SCOPE

The interaction between particles and a moving fluid forms the basis of an ever-increasing variety of operations

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in chemical and metallurgical processing. Processing operations may be purely physical (pneumatic conveying, settling, cyclone separation). They may involve superimposed mass transfer (spray drying, flash drying, cyclone evaporation). More recent and more exciting developments involve chemical reactions (transport reactors, rocket propulsion, combustion, reactions in plasma flames or electric