

Estimating the Virial Coefficients of Small Polar Molecules

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We adapt existing models for estimating the second and third virial coefficients of small molecules to the halogenated methanes and ethanes. We compare the results with the abundant new, high-quality PVT data resulting from the search for alternative refrigerants. The present model provides an accurate method for calculating densities, and therefore it should provide reliable thermodynamic properties and fugacity coefficients. We give equations and parameters useful for estimating the properties of pure refrigerants and their mixtures when no PVT data are available.

KEY WORDS: density; PVT ; polar molecules; refrigerants; virial coefficients.

1. INTRODUCTION

A virial equation of state provides the most satisfactory way to represent accurate gas-phase density data over a wide range of temperatures. The virial representation is especially well suited for expressing the nonideal behavior of mixtures because the mixing rules are simple and they have a theoretical foundation. In addition, the virial coefficients allow the convenient calculation of component fugacities for the analysis and correlation of vapor-liquid equilibrium data in binary and multicomponent mixtures. When virial coefficients are combined with the ideal-gas heat capacity, all of the equilibrium gas-phase thermodynamic properties can be calculated. With a reliable vapor-pressure curve, virial coefficients can also be used to calculate several of the thermodynamic functions of the saturated liquid. At

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low reduced temperatures they can be very useful when included in multi-property fits of complex, wide-range equations of state. In such fits, they constrain the equations at low temperatures in the gas phase.

Measurement of the virial coefficients at low reduced temperatures presents a number of experimental difficulties, particularly for those molecules of industrial interest which are often polar or associating. Thus an attractive alternative has been the development of wide-range correlations or models for the extrapolation or prediction of virial coefficients where data are sparse or nonexistent. Such models can also point out cases where the data may be of questionable quality. These models have been used extensively for the second virial coefficient; much less work has been done with the third and higher virial coefficients.

The second virial coefficient can be calculated directly from a model for the intermolecular potential, and vice versa. This technique has been used many times with impressive results; two references of special interest here are Saxena and Joshi [1] and Schramm and Weber [2]. The drawback for the present purpose is that some data are needed for each molecule to determine the intermolecular potential parameters. Here, we have chosen to develop further one of the empirical wide-range correlations available in the literature, exploiting its reliability, predictive power, and ease of implementation. Any such model should contain, in addition to a basic corresponding-states function, terms which account for molecular size, deviation from spherical shape, dipole moments, chemical association, and quantum effects. In this work we neglect the last two effects because we concentrate on molecules and conditions for which they are unimportant.

The present correlation for the second virial coefficient is based on the work of Pitzer and Curl [3] for nonpolar molecules. Their correlation was updated and applied to polar molecules by Tsonopoulos [4]. Here we take advantage of the plethora of new data on the haloalkanes, chlorofluorocarbons, hydrochlorofluorocarbons, and hydrofluorocarbons (CFCs, HCFCs, and HFCs) to make further improvements to the correlation and to apply it to this class of molecules. These data are some of the best and most comprehensive in the literature. We show that, contrary to previous published results, the virial coefficients have a form that is compatible with the Stockmayer potential. For the third virial coefficient, our correlation is an adaptation of the model of Van Nhu et al. [5]. It agrees very well with the best third virial coefficient data and it has very good predictive power. We apply these models to both pure fluids and binary mixtures. The refrigerants, CFCs, HCFCs, and HFCs, form an ideal subject group for this study since they span a wide range of polarities but they do not associate chemically. We also make a limited number of comparisons for other classes of fluids.

2. SECOND VIRIAL COEFFICIENT

2.1. Pure Fluids

The correlation of Pitzer and Curl [3] for the second virial coefficient, published in 1957, has been used extensively with great success, and it is the basis for several later correlations. It gives an expression for B ,

$$BP_c/RT_c = f_{PC}^{(0)}(T_r) + \omega f_{PC}^{(1)}(T_r) \quad (1)$$

where P_c and T_c are the critical pressure and temperature, R is the universal gas constant, and ω is the Pitzer acentric factor. The f 's are polynomials in inverse powers of $T_r = T/T_c$. They were claimed to be universal functions, applicable to all molecules, and that claim has generally been substantiated. The first term, $f_{PC}^{(0)}$, was found by fitting data for small spherical molecules such as the noble gases. Then the second term was found from data for larger, nonspherical molecules, i.e., molecules with large acentric factors. Pitzer and Curl made no explicit provision for polar molecules.

In 1974, Tsonopoulos [4], using newer and more extensive data, improved the polynomials of Pitzer and Curl. His functions were

$$f_T^{(0)} = 0.1445 - 0.330/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 \quad (2a)$$

$$f_T^{(1)} = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8 \quad (2b)$$

These functions improved the agreement with data for B , especially at reduced temperatures, below 0.75. This correlation has been used with considerable success. For example, Bich et al. found that for benzene ($\omega = 0.211$) [6] and for *n*-hexane ($\omega = 0.299$) [7], the calculated values of B agreed with the best experimental results to within about 1% for temperatures almost down to the normal boiling point.

Tsonopoulos also added a third term to Eq. (1) to account for the behavior of polar molecules. This term has the form

$$f^{(2)}(T_r) = a/T_r^6 \quad (3)$$

and it is most important at reduced temperatures less than unity. The parameter a is written as a function of the reduced dipole moment, μ_R , and it is expected always to be negative to account for the fact that B for polar molecules is more negative than B for corresponding nonpolar molecules. The reduced dipole moment can be defined in several different ways. We follow Tsonopoulos in using the definition

$$\mu_R = 10^5 \mu^2 P_c / T_c^2 \quad (4)$$

where μ is the dipole moment in Debye, T_c is in kelvins, and P_c , by convention, is in atmospheres (1 atm = 101,325 Pa). For the small polar molecules of interest here, $0 < \mu_R < 250$. Tsounopoulos used a relation of the form

$$a = a_1 \mu_R + a_2 \mu_R^8 \quad (5)$$

to fit the second virial coefficient data for several ketones, ethers, acetaldehyde, and acetonitrile. However, he emphasized that a is not expected to be a universal function, capable of fitting all classes of molecules, because the intermolecular potential is affected by the dipole's direction and location within the molecule, in addition to its magnitude.

In a later publication, Tsounopoulos [8] applied the above relations to the data available at that time for the haloalkanes. For this he used a function of the form, $a = a_1 \mu_R^4$. Surprisingly, for some of the less polar fluids, with $\mu_R < 75$, the data were better fit with a equal to zero, or even slightly positive. This situation is considered to be unacceptable. O'Connell and Prausnitz [9] found a similar effect when fitting a wide variety of organic molecules.

It is generally agreed that the spurious behavior (positive value of a) arises from the fact that the measured acentric factor is also affected by the presence of the dipole moment, causing an overcorrection when calculating B . One remedy which has been tried is the substitution of ω_H , the acentric factor of the homomorph, for ω . A homomorph is a nonpolar molecule with the same size and shape as the molecule of interest; e.g., the homomorph of fluoromethane would be ethane. This scheme has been used with mixed results. It has the disadvantage of requiring the parameters for more molecules, the homomorphs. An example of interest here is the homomorph of 1,1-dichloro-2,2,2-trifluoroethane (R123), which would be 2,2,3-trimethylbutane. One could carry this line of reasoning further and argue in favor of using the critical parameters of the homomorphs as well. The difficulties become obvious. For these reasons we have decided against using homomorphs and seek another solution to this problem.

One result of the search for substitutes for the ozone-destroying CFC refrigerants has been the production of new sets of high-quality PVT data for the halogen-substituted methanes and ethanes. The sources of some of these new data are given in Table I. The molecules range in polarity from R14 ($\mu_R = 0$) to R41 ($\mu_R = 186$). We also include in Table I references to some older published data which are summarized by Dymond and Smith [10]. When these data were compared with Eqs. (1)–(3) we found almost exactly the same curve for a that was found by Tsounopoulos (Fig. 3 of Ref. 8), namely, $a = a_1 \mu_R^4$. Data for some of the less polar fluids were best fit by a small positive value for a , as found earlier.

Table I. Pure Fluid Parameters and References for the Virial Coefficients of Some Refrigerants (Most Dipole Moments Were Taken from Refs. 37 and 38)

Fluid	T_c (K)	P_c (bar) ^a	μ_R	ω	b (10 ³ L · mol ⁻¹)	t_c (10 ³ L · mol ⁻¹)	Ref. No.(s)
R12	384.95	41.25	8.5	0.186	76.6	217	27, 28
R134a	374.25	40.55	122	0.323	72.1	201	13, 22
R13	301.9	38.85	10	0.263	71.3	198	10
R22	369.3	50.54	78	0.218	58.6	169	27, 28
R23	299.0	48.16	142	0.264	48.1	133	10, 29
R32	351.36	57.93	182	0.277	45.4	123	23, 29
R115	353.1	31.53	6.7	0.256	92.1	252	10
R123	456.9	36.62	32	0.282	98.3	278	32, 33
R124	395.4	36.18	49.5	0.289	86.4	246	24
R125	339.4	36.29	75.7	0.304	73.7	210	30, 31
R141b	477.3	42.5	74	0.225	91.1	253	34, 36
R142b	410.3	40.41	109	0.254	83.2	231	2, 10
R143a	346.3	37.87	171	0.260	69.8	194	31
R152a	386.4	45.17	152	0.275	65.8	181	13, 31
R14	227.5	37.45	0	0.180	48.7	141	10, 29
R114	418.9	32.48	8.6	0.254	106	294	2, 10
R41	317.42	58.75	186	0.197	39.2	109	29, 35
R11	471.2	44.67	4.0	0.185	88.9	247	10

^a 1 bar = 100 kPa.

The Stockmayer potential,

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] - \frac{\mu^2}{r^3} g(\theta_1, \theta_2, \varphi) \quad (6)$$

was designed to represent the intermolecular potential for polar fluids. Here σ is the value of r at which the potential energy is zero, and ϵ is the well depth. This potential leads to a second virial coefficient of the form [1, 11]

$$B(T) = b \{ \mathcal{B}_1(T) + \mathcal{B}_2(T) \mu_R^2 + \mathcal{B}_3(T) \mu_R^4 + \dots \} \quad (7)$$

where b is the hard sphere volume. Guided by Eq. (7), we looked for a representation for $B(T)$ containing a term proportional to μ_R^2 . Because the second term in Eq. (1), containing ω , is assumed to cause the problem, we sought a solution by modifying $f^{(1)}$ in Eq. (2b). We found that deleting the last term in Eq. (2b) produced a function for $B(T)$ with the proper behavior.

The result is shown in Fig. 1, where we see that the best available data can be represented with the function

$$a = -9 \times 10^{-7} \mu_R^2 \quad (8)$$

All of the new data on the more polar molecules are well represented by this modified function for B . For R12, data extend down to a reduced temperature of 0.6, but even at that low temperature the polar term amounts to only $1 \text{ cm}^3 \cdot \text{mol}^{-1}$, which is less than the experimental uncertainty. Therefore the agreement for R12 shown in Fig. 1 is somewhat fortuitous. Nevertheless, the data support a polar term which is proportional to μ_R^2 .

Figure 2 shows the data for R152a (1,1-difluoroethane). Here we can see the effect of the changes made. The two curves labeled "nonpolar" show the effect of eliminating the last term in Eq. (2b). Tsionopoulos [8] stated that the second virial coefficient of R152a could be represented with the nonpolar terms only, Eqs. (2), even though $\mu_R = 152$. That conclusion was based on the older data of Mears et al. [12]. Figure 2 shows that the new, very high-quality data of Baehr and Tillner-Roth [13] justify the inclusion of the polar term, and they are well represented by the present formulation.

Figures 3a-c illustrate how the present model represents recent second virial coefficient data for 15 halogen-substituted methanes and ethanes. Table I gives the values of the parameters used in the calculations. In the

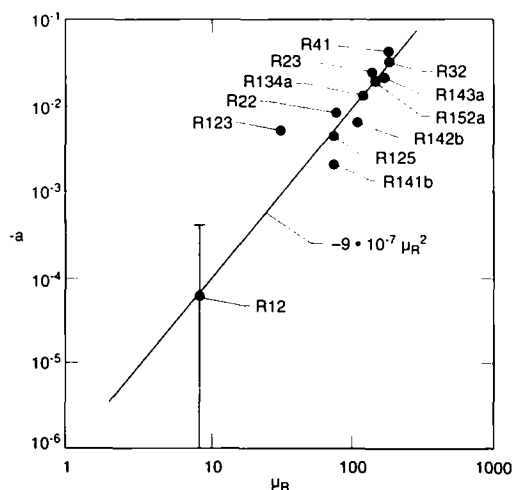


Fig. 1. The variation of a in Eq. (3) with μ_R for several refrigerants of interest. The line corresponds to $a = -9 \times 10^{-7} \mu_R^2$.

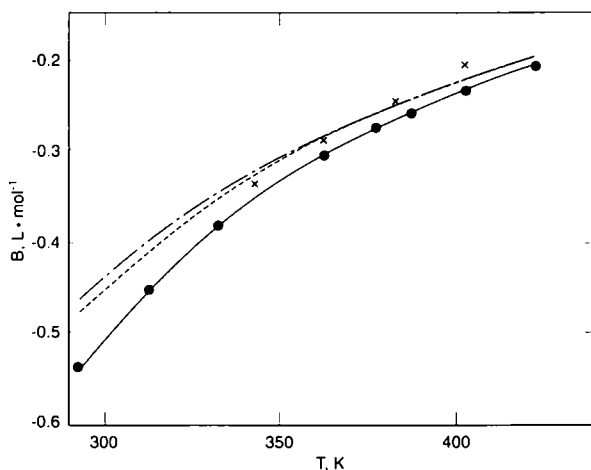


Fig. 2. The second virial coefficient for R152a (1,1-difluoroethane): (x) Mears et al. [12]; (●) Tillner-Roth and Baehr [13]; (----) Tsionopoulos, nonpolar [8]; (— · — · —) this work, nonpolar; (—) this work with polar term.

figures, only one symbol is used for all of the data for each fluid, for clarity. The sources of the data are given in Table I. The agreement between the model and the data is generally comparable to the agreement between the different sets of data. The notable exceptions are R123 and R141b. In the case of R141b, the calculated values of $B(T)$ are more negative by approximately 5%. A possible explanation is the fact that R141b has a tendency to decompose in the presence of metals, and this created some experimental difficulties for both the PVT and the acoustic measurements shown. Because of this problem we neglected the third virial coefficient, C , in the analysis of the data, and as a result, the experimental values of the second virial coefficient would tend to be a little too positive. For R123 the agreement is good at reduced temperatures above 0.9; with decreasing temperature the calculated values become less negative than the data, and the difference increases to 7% at a T_r of 0.57. We have no explanation for this difference. The agreement between the model and the data for the other fluids is of the order of 1% of $B(T)$.

2.2. Binary Mixtures

The model can be readily extended to binary mixtures with the assumption that the interaction virial coefficient, B_{12} , has the same corresponding-states temperature dependence as the pure-component coefficients,

i.e., Eqs. (1)–(3). Mixing rules are necessary for the substance-specific parameters, and we employ the commonly used formulations,

$$T_{c12} = (T_{c1} T_{c2})^{1/2} (1 - k_{12}) \tag{9a}$$

$$\omega_{12} = \frac{1}{2}(\omega_1 + \omega_2) \tag{9b}$$

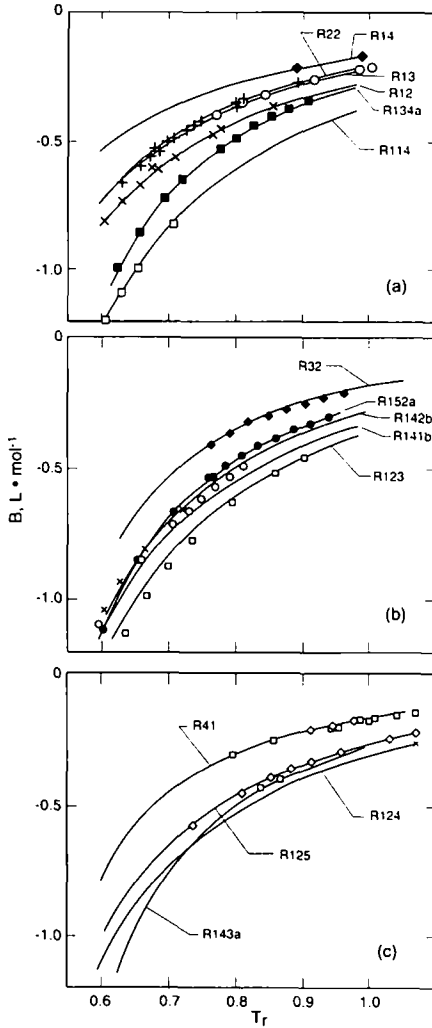


Fig. 3. Comparison of second virial data for the refrigerants with values calculated from Eqs. (1)–(3) and (8). See Table I for data references.

$$P_{c12} = \frac{4T_{c12}(P_{c1}v_{c1}/T_{c1} + P_{c2}v_{c2}/T_{c2})}{(v_{c1}^{1/3} + v_{c2}^{1/3})^3} \tag{9c}$$

$$\mu_{R12} = \frac{10^5 \mu_1 \mu_2 P_{c12}}{T_{c12}^2} \tag{9d}$$

Equation (9d) has the property that mixtures of polar and nonpolar gases are treated as nonpolar, in keeping with the idea that induced dipole moments have only a relatively small effect.

Only one additional parameter is needed, the binary interaction parameter k_{ij} . This parameter is usually determined by one of four methods: (i) from mixture virial coefficient data with Eqs. (9a)–(9d) above, (ii) from the analysis of vapor–liquid equilibrium data with a simple equation

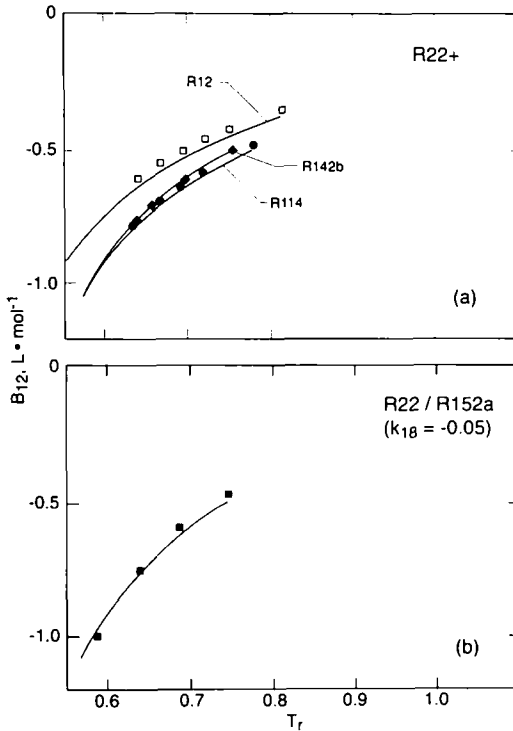


Fig. 4. Comparison of the model with data for the cross second virial coefficients for four binary mixtures containing R22. The binary interaction parameter, k_{12} , was taken from other sources; (a) using bubble curve pressures and orthobaric liquid densities; (b) using the fit of a cubic equation of state to VLE data.

of state (such as Peng–Robinson, Carnahan–Starling–De Santis, etc.), (iii) from an analysis of bubble-pressure curves and liquid-phase compositions, or (iv) from an empirical correlation such as that given by Morrison and McLinden [14]. For the molecules of interest here, these methods are reasonably consistent and give approximately the same values for k_{ij} for many systems. As an example, we show in Figs. 4a and b comparisons of the model with some recent data from Schramm and Weber [2] for B_{12} for the binary systems R22 plus R12, R142b, R114, and R152a. The curves were calculated with Eqs. (2a) and (2b) (without the term in T_r^{-8}), Eq. (3), and Eq. (8). In Fig. 4a the interaction parameters were derived from bubble-pressure curve–composition data, while in Fig. 4b k_{12} came from an analysis of vapor–liquid equilibrium (VLE) data. The agreement is reasonably good, although it can be seen that in two of the four cases it could be improved somewhat by optimizing the interaction parameter to fit the virial coefficient data. In Fig. 4b the average absolute deviation is $22 \text{ cm}^3 \cdot \text{mol}^{-1}$ (3%), whereas the experimental uncertainty estimates given by the authors vary from 5 to $15 \text{ cm}^3 \cdot \text{mol}^{-1}$. Figure 5 shows a comparison of the present model with the Burnett data of Lange and Stein [15] for the system R14 + R23, a polar–nonpolar system. Here the interaction parameter has been fitted to the B_{12} data, and the resulting value, 0.11, is very close to that found from VLE data, 0.117. This single value for k_{12} suffices quite well over a wide temperature range. The average absolute deviation for B_{12} is $1.2 \text{ cm}^3 \cdot \text{mol}^{-1}$, compared with an experimental uncertainty of 1.0 – $1.8 \text{ cm}^3 \cdot \text{mol}^{-1}$.

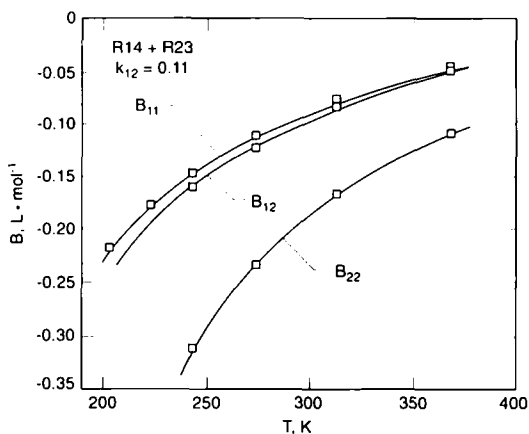


Fig. 5. Comparison of the model with virial coefficient data from Ref. 15 for R14 + R23, with k_{12} found from B_{12} .

For some other systems, however, values of k_{12} found from mixture virial coefficients do not agree with those found from VLE data. Morrison and McLinden [14] give a more complete discussion of this parameter in systems of mixed refrigerants. Perhaps the greatest advantage of the present correlation for mixtures is the fact that one reliable datum at a convenient temperature will suffice to determine k_{12} . We may then extrapolate the calculated B_{12} to lower, more inaccessible temperatures, with confidence. Calculations for multicomponent mixtures follow in a straightforward way.

3. THIRD VIRIAL COEFFICIENT

3.1. Pure Fluids

In contrast to the situation with light gases such as argon and nitrogen, the third virial coefficients of the polar refrigerants make significant contributions to the density, and they must be taken into account even at moderate pressures. For example, R134a at $T_r = 0.9$ (336 K) and at a density of $1 \text{ mol} \cdot \text{L}^{-1}$ ($0.2\rho_c$), has a pressure of 19 bar, and the third virial coefficient makes a 4.7% contribution to the density. As the pressure is reduced to 4.7 bar this contribution decreases to 0.1%, the approximate level of accuracy of modern PVT data. At the density of the saturated vapor, C should be included down to a reduced temperature of about 0.75.

Rowlinson [16] calculated the third virial coefficient of polar molecules from the Stockmayer potential, assuming pairwise additivity. Whereas the second virial coefficient is larger and more negative than that of a corresponding nonpolar molecule, the third virial coefficient is larger and more positive. Hirschfelder et al. [11] showed that the third virial coefficient is a strong function of the reduced dipole moment. Others have calculated the third virial coefficient using various intermolecular potentials, and attempts have been made to include the effects of nonadditivity. These efforts have had some success for simple molecules such as argon. However, the calculations are quite complicated, and the intermolecular potentials are not sufficiently well-known for more complex molecules.

For this reason the alternative of a corresponding-states correlation is attractive. In the past such efforts have been hampered by a paucity of reliable data for both pure fluids and mixtures. Chueh and Prausnitz [17] presented a correlation of C/r_c^3 for some nonpolar fluids in terms of T_r and a third parameter, d . A simple two-parameter corresponding-states function worked well for $T_r > 1.5$. However, they were unable to predict values for the parameter d , which was necessary to extend their correlation to lower temperatures. De Santis and Grande [18] used a similar approach and defined $d = \omega\alpha N/b$, where α is the molecular polarizability, and N is

Avogadro's constant. They reproduced the experimental third virial coefficients of some nonpolar fluids and their mixtures quite successfully. Orbey and Vera [19] correlated the function $C(P_c/RT_c)^2$, analogous to the representation of Pitzer and Curl for B , as a function of T_r and ω for nonpolar fluids. Their results were comparable with those of De Santis and Grande, and their function was somewhat simpler and did not require values for α .

Kohler and co-workers [5, 20] have produced models for both the second and the third virial coefficients of polar molecules as functions of reduced temperature and the dipole moment based on descriptions of molecules as hard convex bodies. They offer a semitheoretical argument that the third virial coefficient can be linked to the second virial coefficient via the quantity $(C - C_h)/(B - B_h)^2$, where C_h and B_h are the virial coefficients of the corresponding hard convex body molecule. We adopt Kohler's ideas here, with some simplification and a different functional form.

For hard body molecules we decided for simplicity to ignore nonsphericity parameters and assume that we have simple hard spheres. Then $B_h = b$, the hard sphere volume, and $C_h = 0.625b^2$. For values of b for the refrigerants, we used those resulting from the fit of the CSD hard sphere equation of state of Gallagher et al. [21] to the available data. They treated b as a soft sphere and allowed it to vary as a quadratic function of temperature. We took the values calculated at the critical temperatures for each fluid. Very similar results are obtained by simply letting $b \approx 0.36r_c$.

We used a functional form for C similar to that used by Orbey and Vera [19] and by Van Nhu et al. [5],

$$C = C_h + (B - B_h)^2 \tilde{\mathcal{F}}_c \mathcal{F}(T_r) \quad (10)$$

where $\tilde{\mathcal{F}}_c$ is a scaling factor at the critical temperature (near the maximum in C) and $\mathcal{F}(T_r)$ is a simple temperature function which is equal to unity at T_c . In accordance with the calculations of Rowlinson and others, we let

$$\tilde{\mathcal{F}}_c = c_1 + c_2 \mu_R^3 \quad (11)$$

to incorporate the dependence on the dipole moment. The parameters, $c_1 = 0.17$ and $c_2 = 1.85 \times 10^{-8}$ were determined from the data for several refrigerants, with heavy weight given to the data for R134a [13, 22], R32 [23], and R124 [24]. With these parameters, for R32 ($\mu_R = 182$), $C(T_c)$ is a factor of 1.66 greater than that for the corresponding nonpolar molecule. For the temperature dependence we used

$$\mathcal{F}(T_r) = \mathcal{C} + (1 - \mathcal{C})/T_r^4 \quad (12)$$

and we found that the data are better represented if we let \mathcal{C} be a weak function of μ_R , $\mathcal{C} = c_3 + c_4\mu_R^3$, with $c_3 = 1.584$ and $c_4 = -4.9 \times 10^{-8}$. This extra degree of freedom allows the location of the maximum in C to be a function of μ_R .

Equation (10) contains an implicit dependence on ω through the second virial coefficient, B . In fact, for nonpolar fluids at the critical temperature, Eq. (10) has essentially the same dependence on ω that was shown by Orbey and Vera [19]. There is no explicit dependence on the polarizability, α .

For our purposes, Eq. (10) has another very important property. When a low-order virial-type function is fit to PVT data the uncertainty in the individual coefficients, B and C , is offset to a large extent by the fact that they are correlated, and if the fit has been done properly, the combination will reproduce the original PVT surface within the experimental error. When B and C are estimated independently, this correlation is lost, and the combination may not reproduce the PVT surface with the desired accuracy. Equation (10) preserves some of this correlation, and a shortcoming in our estimate for B will be partially compensated by a corresponding offset with the opposite sign for C . This effect is illustrated below.

Figure 6 shows $\mathcal{F}(T_r)$ for several fluids of interest. The weak dependence on μ_R can be seen there. The lower precision at higher temperatures has a

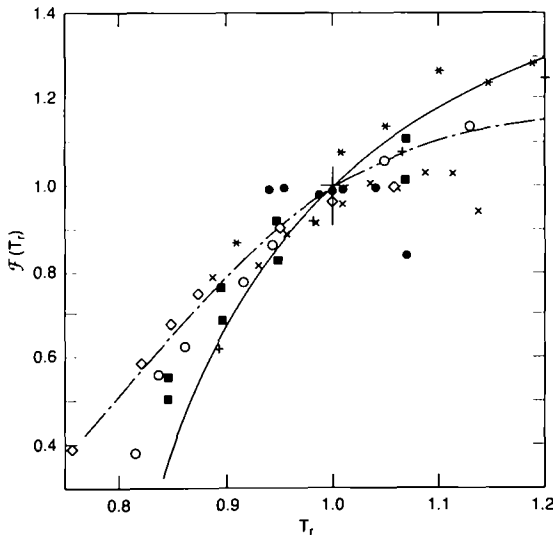


Fig. 6. The function $\mathcal{F}(T_r)$ in Eq. (12) for several refrigerants, showing its variation with μ_R : (■) R123; (○) R134a; (*) R22; (+) R14; (◇) R32; (●) R41; (×) R152a; (—) $\mu_R = 0$; (---) $\mu_R = 182$.

minimal effect on the calculated values of C . Figures 7a and b compare the model with the third virial coefficient data for a variety of refrigerants. For T greater than the temperature of the maximum in C the agreement is very good; around the maximum there is some disagreement, but also some imprecision in the data. At lower temperatures, both the curves and the data are somewhat uncertain. The maximum moves to lower reduced temperatures with increasing reduced dipole moment. The magnitude of the reduced maximum, $C(P_c/RT_c)^2$ or C/v_c^3 , for the most polar molecules, R32 and R41, is almost twice that for a corresponding nonpolar molecule.

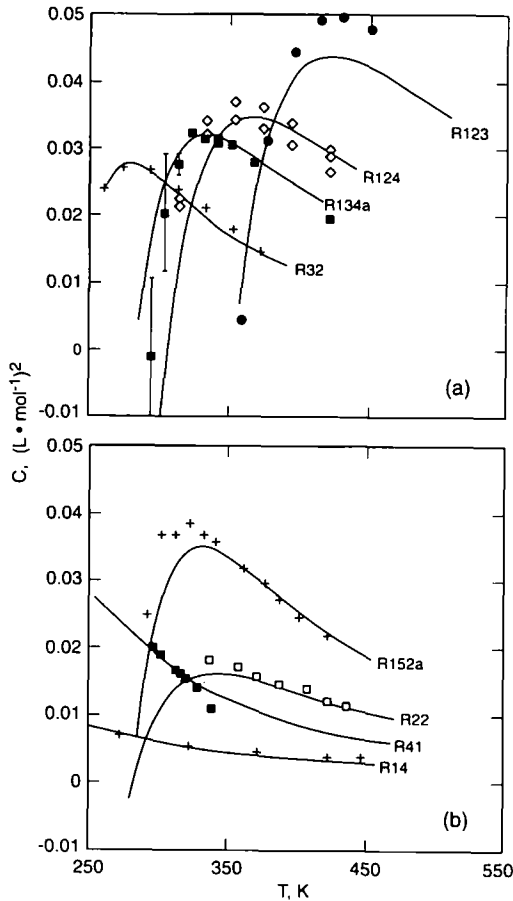


Fig. 7. Comparison of calculated values of third virial coefficients, using Eqs. (10)–(12) with data for several refrigerants.

Again, the only noteworthy discrepancy occurs for R123, where the deviations in C are opposite in sign from those for B . This leads to some cancellation of errors when calculating densities. Table I provides the necessary parameters for calculating a predicted curve when no reliable data are available.

3.2. Binary Mixtures

For treating mixtures, no parameters are required beyond those already available. We merely need to devise a mixing rule for μ_R and decide on a formalism for handling C_h and the B 's in Eq. (10). We define

$$\mu_{R,112} = (\mu_{R,1} \mu_{R,12}^2)^{1/3} \quad (13a)$$

$$\mu_{R,122} = (\mu_{R,2} \mu_{R,12}^2)^{1/3} \quad (13b)$$

$$B_{h,12} = (B_{h,1} + B_{h,2})/2 \quad (13c)$$

$$C_{h,112} = 0.625(B_{h,1}^2 + 2B_{h,12}^2)/3 \quad (13d)$$

$$C_{h,122} = 0.625(B_{h,2}^2 + 2B_{h,12}^2)/3 \quad (13e)$$

and in Eq. (10) we make the substitution,

$$(B_{ii} - B_{h,ii})^2 \rightarrow [(B_{ii} - B_{h,ii})(B_{ij} - B_{h,ij})^2]^{2/3} \quad (13f)$$

where all of the terms on the right side have been defined.

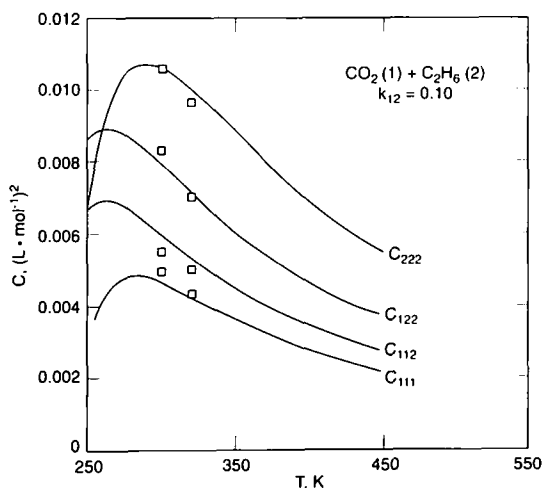


Fig. 8. Comparison of the calculated pure and cross third virial coefficients for the system $\text{CO}_2 + \text{C}_2\text{H}_6$ with data from Refs. 39 and 40.

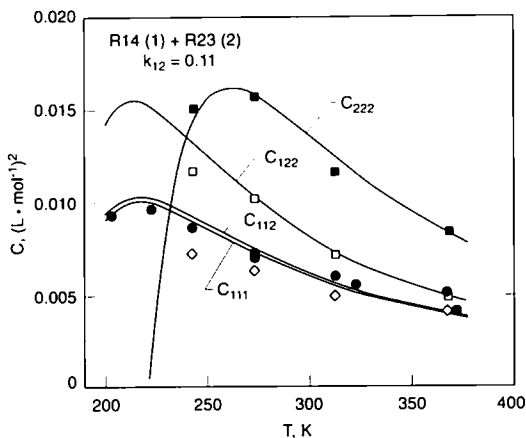


Fig. 9. Comparison of the calculated pure and cross-third virial coefficients for the system R14 + R23 with data from Ref. 15; filled symbols, pure fluid virials; open symbols, cross virials.

Third virial coefficient data and cross third virial coefficient data for mixtures are extremely scarce in the literature. Among the best data reported are those for the nonpolar system $\text{CO}_2 + \text{C}_2\text{H}_6$ [39, 40]. Figure 8 compares the present correlation with the data at two temperatures. The agreement is excellent, considering the difficulty of the measurements; thus, we have confidence in the extrapolation of the curves. Figure 9 compares the results for the system R14 + R23 [15], a polar–nonpolar system, with the model. Here again the agreement is also very good, except for some disagreement for C_{112} . For another system, R14 + SF_6 [25], not shown here, the agreement is also reasonably good, although the data have a lower accuracy. The model treats all these three cases as nonpolar systems since $\mu_{R112} = \mu_{R122} = 0$ [see Eqs. (13a) and (13b)]; thus these examples do not test the mixing rule for $\mu_{R_{i\mu}}$. This test must await new experimental results.

4. DISCUSSION

In the foregoing sections we have modified previous correlations for the second and third virial coefficients of polar molecules, and we have made specific applications to the halogen-substituted methanes and ethanes. The simple mathematical forms, Eq. (12) in particular, are very successful in

reproducing the best available data without overfitting experimental imprecision. Extension to mixtures requires only one additional parameter, the binary interaction parameter. We have found that interaction parameters derived from other types of measurements work reasonably well for calculating B_{12} in many cases, but not in general. Where these binary interaction parameters are not known, they can be obtained from one data point, or from one Burnett isotherm, or possibly from a prediction scheme. Then, using the parameters in Table I, one can calculate the properties for any mixture at any temperature with acceptable accuracy. The built-in correlation between B and C tends to compensate for small inaccuracies in the estimations. The overall success indicates that we have incorporated into our functions the most important properties affecting the behavior of the virial coefficients. Small discrepancies seen near the maxima in C for some molecules indicate that some improvement might be obtained by using a more complex function instead of Eq. (12).

It is interesting to compare the model with data for other classes of fluids. The second virial coefficient data for argon are of course reproduced very well, because these data were important in the original determination of $f^{(0)}$. The third virial coefficient for argon is also reproduced well, with maximum deviations being $2.5 \times 10^{-4} (\text{L} \cdot \text{mol}^{-1})^2$ near the critical temperature. This would lead to a density error of 0.1% at a pressure of 25 bar. The second virial coefficient of helium is not fit particularly well at room temperature ($T_r = 57$), even if we use the pseudo-critical parameters; $\Delta B = 0.003 \text{ L} \cdot \text{mol}^{-1}$ (30%). Helium data were not used in the original determination of Eq. (2), and small adjustments probably could be made without upsetting the fits for other fluids. The third virial coefficient for helium is reproduced very well. For SF_6 , B and C are calculated to within $0.002 \text{ L} \cdot \text{mol}^{-1}$ and $(7-15) \times 10^{-4} (\text{L} \cdot \text{mol}^{-1})^2$, respectively. The virial coefficients of the light hydrocarbons, methane, ethane, and propane, are reproduced very well, as are those of carbon dioxide.

We could not expect the model to predict the behavior of water very well because it does not incorporate the effect of association in the vapor phase. This effect manifests itself primarily in the behavior of the third virial coefficient, which takes on very small positive values for $T_r > 0.9$ but becomes very negative at lower temperatures. The maximum positive value is $C(\text{max})/v_c^2 = 0.3$, which may be contrasted with values for (nonpolar) nitrogen and for (polar) R32 of 0.45 and 1.8, respectively. Our model does not follow this behavior quantitatively. The results are better than expected, however. Over the range 400–723 K the predicted B is more negative than the best experimental data by about $0.01 \text{ L} \cdot \text{mol}^{-1}$, increasing to about $0.02 \text{ L} \cdot \text{mol}^{-1}$ near 400 K. The effect of this offset is partially compensated for by a calculated C which is more positive than the experimental values.

The result is that the densities of saturated water vapor at 423 and at 498 K are predicted with an accuracy of 0.35 and 0.02 %, respectively; this is about as good as the agreement among the best data sets.

Methanol is less polar than water, but it forms hydrogen bonds to a much greater extent in the vapor phase. Our model for B agrees with the recommended data to within 0.015–0.025 L · mol⁻¹ at temperatures above 400 K, where the experimental uncertainty is ± 0.015 L · mol⁻¹, but it does not reproduce its steep descent below that temperature. Tsionopoulos used an additional term, of the form λ/T_r^8 , in Eq. (3), which successfully accounted for association. With our representation we would need a term of the order of T_r^{-12} , or an exponential, to reproduce the data. Others have used a chemical model to describe this behavior.

Ammonia associates to a lesser extent than water. Our calculated second virial coefficient is slightly less negative than the experimental values. Haar and Gallagher [26] found similar deviations from their thermodynamic surface, which they ascribed to possible adsorption effects in the measurements. As a result we estimate errors no larger than 0.01 L · mol⁻¹ in B . We found no data for the third virial coefficient of ammonia, but the shape of our calculated curve looks similar to that for water. This fact plus the expectation of some association leads us to assume that the calculated curve is somewhat too positive. The model should be relatively accurate for calculations at pressures less than about 15 bar.

The most polar small molecule is acetonitrile ($\mu_R = 245$), and it forms a good test of the model because it does not associate. It has very large virial coefficients: $B(T_r = 0.6)/v_c = -23$, compared to a value of -7.3 for R32. At $T_r = 0.9$, $C/v_c^2 = 8.3$, compared to 1.8 for R32. As T_r decreases to 0.78, the calculated C is still increasing to a value of $C/v_c^2 = 33$, whereas most third virial coefficients become negative at about this temperature. There are several sets of second virial coefficient data for acetonitrile, all of which agree reasonably well. Our model does not follow the strong negative behavior of the data. Differences range from 20% at 450 K to almost a factor of two at 300 K. A possible explanation and a remedy may be found in Eq. (7), where we have used only the first two terms of an expansion. In the case of acetonitrile the polarity effects may be so strong at these relatively low reduced temperatures that we should include the next term, proportional to μ_R^4 . We have made some preliminary efforts in that direction, and a two-term function for a can be found which fits the data for both acetonitrile and the refrigerants reasonably well. It is interesting to note that if we use the correct values of B for acetonitrile, Eq. (10) predicts C within the experimental uncertainty of recent data sets. At this polarity, however, Eq. (10) does not exhibit a maximum but increases indefinitely at lower temperatures. This behavior may, or may

not, be physically correct, but the consequences are negligible. At the normal boiling point, 354 K, the predicted C contributes only 0.2% to the vapor density.

5. CONCLUDING REMARKS

We have presented a physically based, semiempirical scheme for estimating the second and third virial coefficients, which is consistent with

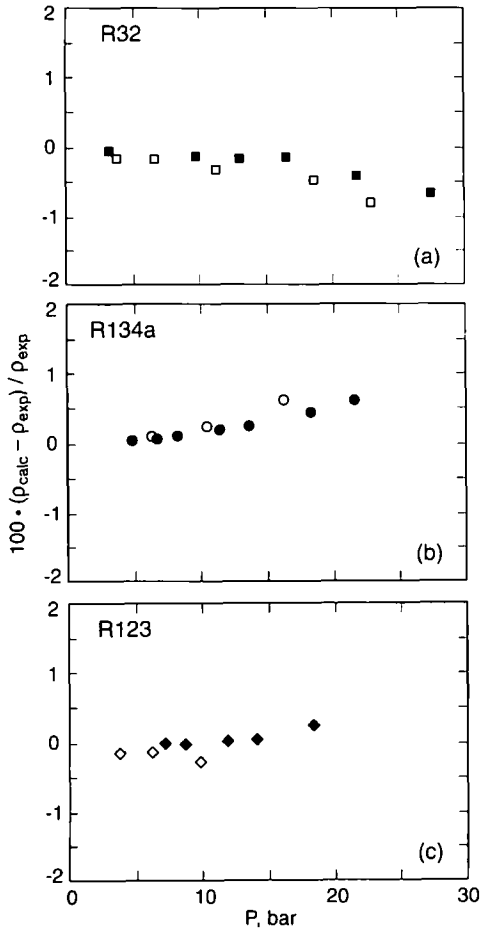


Fig. 10. Comparison of densities calculated from the estimated virial coefficients with experimental gas-phase data for three fluids. R32: (\square) 333 K; (\blacksquare) 373 K. R134a: (\circ) 340 K; (\bullet) 368 K. R123: (\diamond) 383 K; (\blacklozenge) 433 K.

the polarity dependence specified by the Stockmayer potential. This scheme provides reliable results for the halogenated hydrocarbons and it can be extended to some other classes of molecules.

Good-quality PVT measurements in the gas phase have an experimental accuracy of about 0.1%, or a little better, in density. Corresponding states-type correlations, including the present one, do not normally achieve this accuracy. However, we can make some generalized estimates concerning accuracy, and we can give some examples to support these estimates.

We have seen that polar fluids have much larger second and third virial coefficients than corresponding nonpolar fluids. We assume that this situation is also true for the higher-order virials, which we have neglected. Therefore, we should be somewhat cautious about the maximum density at which we use this representation. Experience has shown us that for light, nonpolar gases, such as oxygen and nitrogen, B and C provide a very good fit to precise PVT data for densities up to about $0.5\rho_c$. For the polar molecules of interest here, this maximum density decreases to about $0.25\rho_c$. To be a little more conservative, we limit our comparisons to densities $\leq 1 \text{ mol} \cdot \text{L}^{-1}$ [equivalent to $(0.12\text{--}0.25)\rho_c$ for most refrigerants], which includes most of the pressure range of interest to the refrigeration industry.

For the refrigerants and nonpolar fluids the present model calculates the gas-phase nonideality with an uncertainty of about 2%. Therefore, at the critical temperature and a density of $1 \text{ mol} \cdot \text{L}^{-1}$ (≈ 21 bar) we can expect an accuracy in density of about 0.50%. At a lower temperature, for example, $T_r = 0.78$, the vapor pressure may be only about 5 bar, and the maximum density is about $0.25 \text{ mol} \cdot \text{L}^{-1}$. Under these conditions the accuracy of the computed density should be approximately 0.1%. We test these estimates with three examples taken from our own data, in Figs. 10a–c. We see that for R32, R134a, and R123 the comparisons are consistent with our estimates. In the case of R123, the estimated densities are quite good, even though the individual estimated virial coefficients did not agree well with the ones resulting from the fit to the data.

NOMENCLATURE

B	Second virial coefficient
B_{12}	Mixture cross second virial
B_h	Second virial of a hard sphere fluid
$\mathcal{B}_i(T)$	Temperature function, second virial, Eq. (7)
C	Third virial coefficient
C_{112}, C_{122}	Mixture cross third virials
C_h	Third virial of a hard sphere fluid
N	Avogadro's number

P_c	Critical pressure
P_{c12}	Characteristic critical pressure of a binary mixture
T_c	Critical temperature
T_{c12}	Characteristic critical temperature of a binary mixture
T_r	Reduced temperature, T/T_c
a	Parameter measuring polar contribution to B , Eq. (3)
b	Volume of a hard sphere molecule
$f^{(i)}$	Polynomials determining temperature dependence of the nonpolar part of B
k_{12}	Binary interaction parameter for mixtures, Eq. (9a)
v_c	Critical volume
α	Molecular polarizability
μ	Dipole moment
μ_R	Reduced dipole moment, Eq. (4)
μ_{R12}	Mixture reduced dipole moment, second virial
μ_{R112}, μ_{R122}	Mixture reduced dipole moment, third virial
ω	Pitzer acentric factor
ω_{12}	Mixture acentric factor
$\phi(r)$	Intermolecular potential
ρ_c	Critical density ($1/v_c$)

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