Third Virial Coefficients of Nonpolar Gases and Their Mixtures

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While much attention has been given to second virial coefficients of nonpolar gases, experimental and theoretical studies on third virial coefficients are scarce. This work presents a correlation of third virial coefficients within the framework of the corresponding states principle. The correlation is useful for estimating third virial coefficients of pure and mixed nonpolar gases, including the quantum gases helium, hydrogen, and neon. The importance of third virial cross coefficients in phase equilibrium predictions is illustrated with calculations for the solid-gas, methane-hydrogen system at 76°K.

Brief attention is given to the pressure series form of the virial equation. Because of fortuitous cancellations, it is shown that for reduced temperatures above 1.4, the pressure series, truncated after the second term, is applicable to a wider range of density than the density series truncated after the second term. However, when both series are truncated after the third term, the density series appears to be superior regardless of reduced temperature.

To describe the volumetric properties of gases, many equations of state have been proposed, but of all those in common usage today, only the virial equation rests upon a firm theoretical foundation. The virial equation is

$$z = \frac{Pv}{RT} = 1 + B/v + C/v^2 + \ldots \qquad (1)$$

where B, C, ... are virial coefficients which, at constant composition, depend only on the temperature.

For practical work, the advantages and disadvantages of the virial equation have often been discussed (*16*, *46*, *47*, *48*); briefly, the advantages follow from the direct relationship between virial coefficients and intermolecular forces and the disadvantages follow from our inadequate quantitative knowledge of virial coefficients higher than the second. As a result, the virial equation is most useful at moderate densities, below the critical, but has little practical utility at high densities beyond the critical.

The technical literature abounds with studies of the second virial coefficient and, as a result of much theoretical and experimental work, it is now possible to make good estimates of the second virial coefficient of a large number of gases from a minimum of experimental data (*29*, *30*, *58*). For typical applied calculations, the correlation of Pitzer and Curl (*27*, *45*) is probably the most useful. However, much less attention has been given to the third virial coefficient, primarily for two reasons: first, because of experimental difficulties, good data for the third virial coefficient are scarce, and second, theoretical calculations with potential energy functions used are tedious and, for accurate results, require corrections to the assumption of pairwise additivity which are at best known only approximately (*55* to *57*). In this work we have collected and examined the limited amount of experimental third virial coefficients now available and we have correlated them as best as we can. Our correlation is limited to nonpolar gases but holds also for the quantum fluids helium, hydrogen, and neon. Since the purpose of our correlation is application oriented, we have given brief attention to the third virial coefficient of the pressure series virial equation which, while theoretically less significant, is sometimes more convenient. More important, we have considered how our correlation may be used to estimate third virial coefficients of gas mixtures for which experimental data are extremely scarce. In particular, we discuss the role of third virial cross coefficients as required in typical phase equilibrium calculations.

DATA REDUCTION AND CORRELATION

Sources of experimental third virial coefficients C are given in Table 1; many of these are taken from the compilation of Dymond (*10*). The third virial coefficients are reduced by v_c^2, and are plotted against the reduced temperature T_R as shown in Figure 1. For reduced temperatures greater than 1.75, the reduced third virial coefficients fall on a single curve within the limits of experimental uncertainty. For reduced temperatures below 1.75, however, the reduced third virial coefficients of different gases diverge from each other reaching a maximum near $T_R = 0.9$, with the larger molecules having larger reduced third virial coefficients. This divergence probably follows first, from the need for a three-parameter, rather than a two-parameter, theorem of corresponding states, and second, from contributions of three-body (nonadditive) intermolecular forces as discussed by Sherwood (*55*, *57*). These contributions depend on the polarizability and size of the molecule and become important only at temperatures close to and below the critical. Since experimental data for C tend to be least accurate at lower temperatures, it is extremely difficult to assign precise physical significance to the divergence shown in Figure 1.

CLASSICAL GASES

The data for argon and nitrogen cover the widest range in temperature and appear to be most reliable; therefore these data were first fitted with an analytic expression. The reduced third virial coefficients for argon and nitrogen are

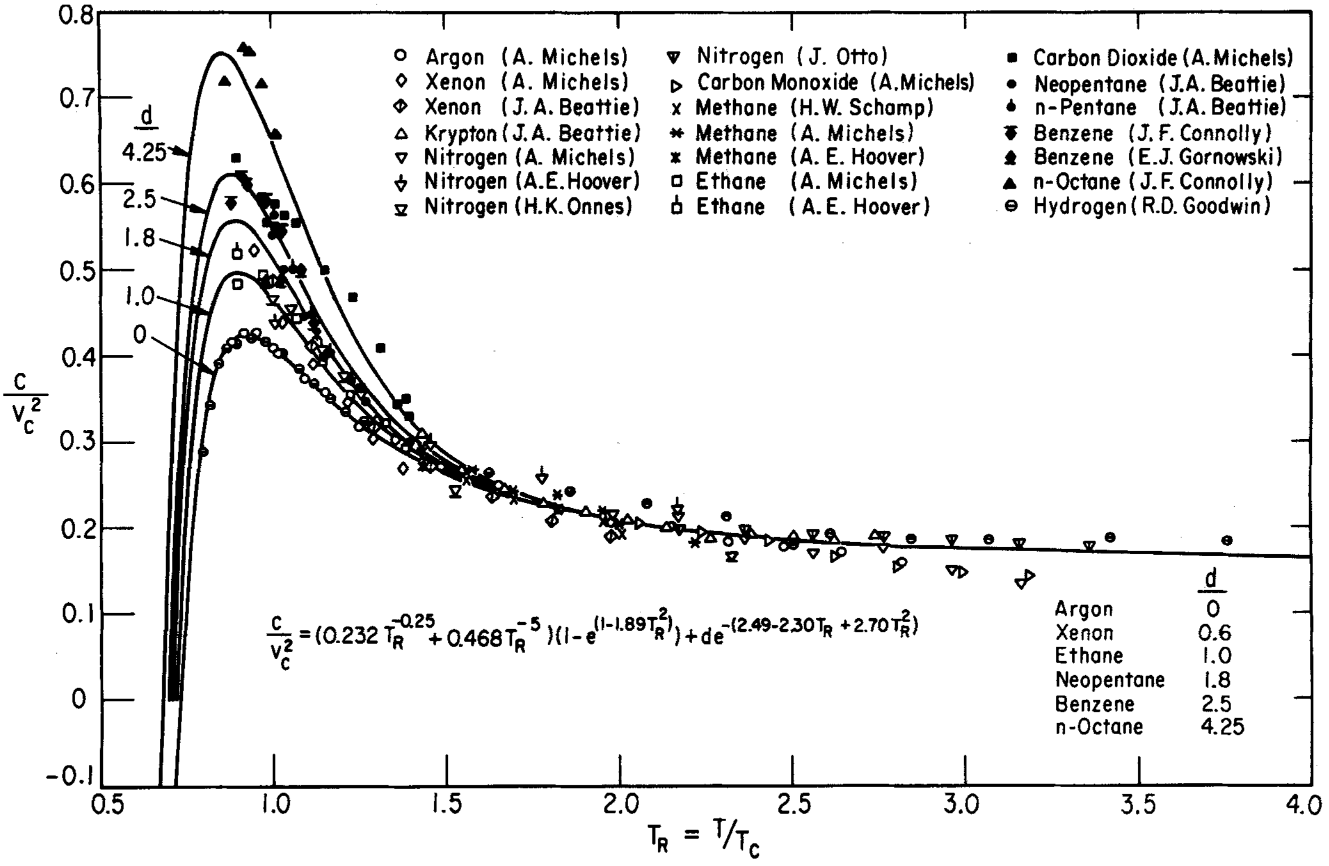

Fig. 1. Corresponding states correlation for third virial coefficients of nonpolar gases.

Table 1. Data Sources for Third Virial Coefficients

Substance	Temperature range, °K.	Source
Argon	133 to 248	*31*
	273 to 423	*38*
Xenon	273 to 423	*36*
	290 to 573	*2*
Krypton	273 to 573	*3*
Nitrogen	273 to 423	*39*
	273 to 423	*44*
	127 to 293	*42*
	133 to 273	*24*
Methane	273 to 423	*54*
	392 to 608	*34*
	215 to 273	*25*
Ethane	273 to 423	*35*
	215 to 273	*25*
Carbon monoxide	273 to 423	*32*
Carbon dioxide	273 to 423	*33*
Neopentane	434 to 548	*4, 56*
n-Pentane	473 to 573	*5, 56*
Benzene	493 to 573	*7*
	553 to 628	*15, 56*
n-Octane	493 to 573	*7*
Hydrogen	24 to 423	*14*
Helium	10 to 573	*26*
Neon	60 to 273	*23*
	273 to 423	*37*

given by

$$\left(\frac{C}{v_c^2}\right)_{\substack{\text{argon}\\ \text{and nitrogen}}} = (0.232\,T_R^{-0.25} + 0.468\,T_R^{-5}) \times (1 - e^{(1-1.89\,T_R^2)}) \quad (2)$$

Equation (2) appears to provide a good correlation for third virial coefficients of small, nearly spherical, nonpolar molecules. Although there are only few data which show that the reduced third virial coefficient goes through a maximum at low temperature, theoretical calculations (*55, 57*) indicate that such a maximum is to be expected. The negative fifth power and the exponential factor in Equation (2) were chosen to conform with this theoretical indication. Equation (2), however, is not intended to describe quantitatively the region with negative third virial coefficients and should not be used at reduced temperatures below 0.8. The negative one-fourth power was chosen to fit data at high reduced temperature and to conform with the theoretical indication that at high temperature the third virial coefficient decreases very slowly with rising temperature.

For reduced temperatures below 1.75, the reduced third virial coefficients of larger or less symmetric molecules begin to deviate from those of argon. We have set this deviation proportional to a parameter d which is some measure of the polarizability, size, and shape of the molecule. The deviation function is given by

$$\frac{\Delta C}{v_c^2} = d\, e^{-(2.49\,-\,2.30\,T_R\,+\,2.70\,T_R^2)} \quad (3)$$

The quantity $\Delta C/v_c^2$ approaches zero for $T_R > 1.75$.

The general expression for the reduced third virial coefficient is then given by the sum of Equations (2) and (3):

$$\frac{C}{v_c^2} = (0.232\ T_R^{-0.25} + 0.468\ T_R^{-5})(1 - e^{(1-1.89\ T_R^2)}) + d\ e^{-(2.49\ -\ 2.30\ T_R\ +\ 2.70\ T_R^2)} \qquad (4)$$

Equation (4) provides a useful correlation for nonpolar gases at reduced temperatures above 0.8. The solid lines in Figure 1 reproduce Equation (4) with several values of the parameter d whose numerical value is given for several representative gases. Attempts to relate d to other fundamental parameters were not successful, partly because of the paucity of reliable data at low temperatures and partly because of our inadequate understanding of three-body intermolecular forces. However, the few values of d shown in Figure 1 are sufficient to suggest good estimates for other nonpolar gases. For example, by judicious interpolation, we suggest $d = 2.0$ for *n*-butane. For carbon dioxide, perhaps because of its large quadrupole moment, d is probably close to 3.

QUANTUM GASES

The configurational properties of low molecular-weight gases (hydrogen, helium, and neon) must be described by quantum, rather than classical, statistical mechanics. As a result, the properties of these gases do not follow the same corresponding states behavior as that for other gases when the true critical constants are used as the reducing parameters. It is possible, however, to define effective critical constants (*17*) with which the quantum gases can be made to follow the same classical corresponding states correlation. These effective critical constants were found to depend on the molecular mass m and temperature in a simple manner. For the effective critical temperature we use the same expression reported previously (*17*)

$$T_c = \frac{T_c^o}{1 + \dfrac{c_1}{mT}} \qquad (5)$$

where

$$c_1 = 21.8°\text{K.} \qquad (6)$$

and where T_c^o is the classical critical temperature, that is, the effective critical temperature in the limit of high temperature. The effective critical volume was found from second virial coefficient data of hydrogen (*1, 14, 19, 40, 41*) and from the generalized equation of Pitzer and Curl (*27, 45*) with $\omega = 0$. The effective critical volume is given by

$$v_c = \frac{v_c^o}{1 + \dfrac{c_2}{mT}} \qquad (7)$$

where

$$c_2 = -9.91°\text{K.} \qquad (8)$$

and where v_c^o is the classical, high-temperature critical volume. Table 2 gives T_c^o and v_c^o for nine quantum gases. For each quantum gas the parameter d is set equal to zero.

TABLE 2. CLASSICAL CRITICAL CONSTANTS FOR QUANTUM GASES

	T_c^o, °K.	v_c^o, cc./g.-mole
Ne	45.5	40.3
He^4	10.47	37.5
He^3	10.55	42.6
H_2	43.6	51.5
HD	42.9	52.3
HT	42.3	52.9
D_2	43.6	51.8
DT	43.5	51.2
T_2	43.8	51.0

With the effective critical temperature and volume defined by Equations (5) and (7), the third virial coefficients of quantum gases can be calculated from Equation (4) in exactly the same manner as that used for classical gases.

The third virial coefficients of hydrogen were calculated over a temperature range of 24° to 423°K. which correspond to effective reduced temperatures of 0.799 to 9.95 The calculated results were compared with the unsmoothed data reported by Goodwin (*14*). The average deviation* was 35 (cc./g.-mole)^2, well within the estimated experimental uncertainty of about 15% or 150 (cc./g.-mole)^2 at the lower temperatures and 50 (cc./g.-mole)^2 at the higher temperatures (*14*). A maximum deviation of +105 (cc./g.-mole)^2 occurred at 24°K. for which the experimental value was 1,207 (cc./g.-mole)^2. For helium, the calculations were made over a temperature range of 10° to 573°K. which correspond to effective reduced temperatures of 0.950 to 55.3. Comparison with the experimental data of Keesom (*26*) showed the average deviation to be 70 (cc./g.-mole)^2; estimated experimental uncertainty is 200 (cc./g.-mole)^2 at the lower temperatures and 50 (cc./g.-mole)^2 at the higher temperatures. A maximum deviation of + 141 (cc./g.-mole)^2 occurred at 10°K. for which the experimental value was 518 (cc./g.-mole)^2. Calculations for neon extended over the temperature ranges 60° to 273°K. ($T_R = 1.34$ to 6.03) and 273° to 423°K. ($T_R = 6.03$ to 9.32), corresponding, respectively, to the data of Holborn (*23*) and of Michels (*37*). The average deviations were 45 and 10 (cc./g.-mole)^2, respectively, well within the experimental uncertainty.

MIXTURES

An important advantage of a corresponding states treatment such as the one presented here follows from its rational extension to mixtures. Our aim is to use the correlation provided by Figure 1 for predicting third virial coefficients of mixtures where experimental data are very rare.

As shown by Mayer (28), the third virial coefficient of a mixture of N components is exactly related to the mole fractions $y_i, y_j, \ldots$ etc., by

$$C = \sum_i^N \sum_j^N \sum_k^N y_i y_j y_k\ C_{ijk} \qquad (9)$$

For the cross coefficients in Equation (9), we propose the following approximation which is essentially the same as that of Orentlicher (*43*):

$$C_{ijk} = (C_{ij}\ C_{jk}\ C_{ik})^{1/3} \qquad (10)$$

where

$$C_{ij} = v_{cij}^2\ f_c(T/T_{cij},\ d_{ij}) \qquad (11)$$

and where T_{cij} and v_{cij} are the energy and size parameters characteristic of the *i-j* interaction:

$$T_{cij} = \sqrt{T_{ci}\ T_{cj}}\ (1 - k_{ij}) \qquad (12)$$

$$v_{cij}^{1/3} = \frac{1}{2}\,(v_{ci}^{1/3} + v_{cj}^{1/3}) \qquad (13)$$

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* Deviation = $C^{calc} - C^{exp}$; average deviation = $\dfrac{\Sigma|C^{calc} - C^{exp}|}{\text{No. of data points}}$.

TABLE 3. EXPERIMENTAL AND CALCULATED THIRD VIRIAL COEFFICIENTS FOR SOME BINARY SYSTEMS

System (1)	System (2)	k_{12}*	Temp., °K.	C_{112}, (cc./g.-mole)^2 Calc'd.	C_{112}, (cc./g.-mole)^2 Expt'l.	Reference
Hydrogen	Methane	0.03	65.0	1,350	1,450	*22*
			70.0	1,530	1,430	
			76.0	1,560	1,600	
			80.0	1,520	1,400	
Neon	Methane	0.28	60.0	1,180	1,000	*21*
			65.0	1,130	950	
			70.0	1,060	650	
Argon	Nitrogen	0.005	273	1,370	1,349	*8*
			203	1,750	1,706	
			163	2,260	2,295	
			143	2,600	2,927	
Nitrogen	Argon	0.005	273	1,490	1,399	*8*
			203	1,860	1,780	
			163	2,370	2,397	
			143	2,770	2,890	
Tetrafluoromethane	Methane	0.07	273	4,790	4,900	9
			373	3,470	3,400	
			473	3,040	2,600	
			573	2,830	2,400	
Nitrogen	Ethylene	0.01	323	2,180	2,300	*18*
Nitrogen	*n*-Butane	0.12	461	3,230	3,230	*12, 59*
n-Butane	Nitrogen	0.12	461	9,050	9,050	*12, 59*

* Obtained from second virial coefficient (B_{12}) data.

The function f_c is that given by Equation (4), and d_{ij} is approximated by the linear average of d_i and d_j. The constant k_{ij} represents the deviation from the geometric mean for $T_{c_{ij}}$; usually k_{ij} must be evaluated from information on the *i-j* interaction such as that given by second virial cross coefficients. Values of k_{ij} for several systems are given in Table 3; others may be found elsewhere (*6, 49*). Equation (10) is useful only for those temperatures where for each *i-j* pair $T/T_{c_{ij}} > 0.8$.

For a binary mixture, Equation (9) reduces to

$$C = y_1^3\ C_{111} + 3y_1^2\ y_2\ C_{112} + 3y_1\ y_2^2\ C_{122} + y_2^3\ C_{222} \tag{14}$$

where C_{111} and C_{222} are the third virial coefficients for pure components 1 and 2, and the cross coefficients C_{112} and C_{122} are, from Equation (10)

$$C_{112} = (C_{11}\ C_{12}^2)^{1/3} \text{ and } C_{122} = (C_{22}\ C_{12}^2)^{1/3} \tag{15}$$

In the notation used here, C_{11} is the same as C_{111} and C_{22} is the same as C_{222}. The coefficient C_{12} is found from Equations (11), (12), and (13).

For mixtures containing one or more of the quantum gases, the effective critical constants are given by

$$T_{c_{ij}} = \frac{\sqrt{T^o_{c_i}\ T^o_{c_j}}\ (1 - k_{ij})}{1 + \dfrac{c_1}{m_{ij}\,T}} \tag{16}$$

$$v_{c_{ij}} = \frac{\left(v^{o\,1/3}_{c_i} + v^{o\,1/3}_{c_j}\right)^3}{8\left(1 + \dfrac{c_2}{m_{ij}T}\right)} \tag{17}$$

with

$$\frac{1}{m_{ij}} = \frac{1}{2}\left(\frac{1}{m_i} + \frac{1}{m_j}\right) \tag{18}$$

Table 3 presents a comparison between calculated and experimental values of the third virial cross coefficient for eight systems, including several mixtures containing quantum gases. The agreement for these cross coefficients is about as good as that for the pure components.

Figure 2 shows calculated and experimental third virial coefficients for mixtures of nitrogen–*n*-butane at several compositions at 370°F. The experimental third virial coefficients were evaluated by Van Ness (*59*) from the volumetric mixture data of Evans and Watson (*12*), from the pure-component data given by the National Bureau of Standards for nitrogen (*20*), and from Sage and Lacey's data (53) for pure *n*-butane. Agreement between calculated and experimental results is excellent over the entire composition range. However, whereas the calculated third virial coefficients for pure nitrogen and for pure *n*-butane agree well with the experimental values, the calculated values of the cross coefficients [3,230 (cc./g.-mole)^2 for $C_{N_2-N_2-C_4}$ and 9,050 (cc./g.-mole)^2 for $C_{N_2-C_4-C_4}$] differ considerably from those obtained by Van Ness [4,950 and 7,270 (cc./g.-mole)^2, respectively] from fitting third virial coefficients of mixtures to Equation (14). This disagreement indicates the difficulty which is frequently encountered in extracting simultaneously two parameters by fitting experimental data to a function which is only slightly nonlinear. It frequently happens that there are several sets of parameters which fit the experimental data at hand equally well.

THIRD VIRIAL COEFFICIENT FOR PRESSURE-SERIES VIRIAL EQUATION

The virial equation is sometimes written as a pressure

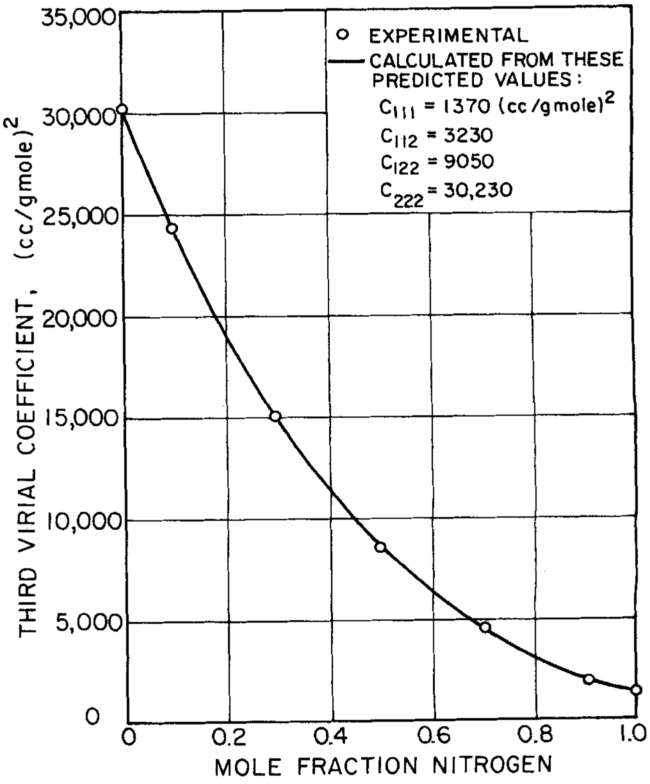

Fig. 2. Third virial coefficients for the nitrogen (1)-*n*-butane (2) system at 370°F.

series. Although this series is less fundamental than the density series, it has computational advantages, since, in most applied problems, the pressure rather than the density is the independent variable. The pressure series form of the virial equation is

$$z = 1 + B'P + C'P^2 + \ldots . \tag{19}$$

where B', C', ... are coefficients which, at constant composition, depend only on temperature.

The coefficients in the pressure series are related to those in the density series (*11*) by

$$B' = B/RT \tag{20}$$

$$C' = (C - B^2)/(RT)^2 \tag{21}$$

From Equation (21), C' can readily be calculated by using Equation (4) for C and Pitzer and Curl's equation (*27, 45*) for B. These calculations were performed for two dissimilar gases: argon ($\omega = 0$ and $d = 0$) and benzene ($\omega = 0.211$ and $d = 2.5$). The results are shown in Figure 3 on reduced coordinates; the two curves do not differ much from one another. For reduced temperatures higher than 1.4, the reduced third virial coefficients in the pressure series are essentially zero for both gases. As a result, we may conclude that for $T_R > 1.4$, neglect of the third virial coefficient in the pressure series introduces less error than it does in the density series; in other words, the pressure series truncated after the second term is essentially applicable over as wide a range of pressure as that truncated after the third term. On the other hand, neglect of the third virial coefficient in the density series significantly restricts the range of applicability.

To illustrate this conclusion, Figure 4 presents compressibility factors of an equimolar mixture of argon and nitrogen for two temperatures, calculated with the density series and with the pressure series, first truncated after the third term and then truncated after the second term. The calculated compressibility factors are compared with the experimental results of Crain and Sonntag (*8*). For both isotherms the density series truncated after the third term gives the best results; it reproduces the observed compressibility factors up to a moderately high pressure corresponding to a density close to the critical. The pressure series truncated after the third term, however, is good only up to a pressure about half that for the density series. On the other hand, for the —70°C. isotherm, the pressure series is much better than the density series when both equations are truncated after the second term. For this system, —70°C. corresponds to a reduced temperature of 1.47 at which the reduced third virial coefficient in the pressure series is essentially zero as shown in Figure 3. However, for the —130°C. isotherm, which corresponds to a reduced temperature of 1.03, the reduced third virial coefficient in the pressure series is not negligible (see Figure 3) and the pressure series truncated after the second term is only as good as the density series truncated after the same number of terms.

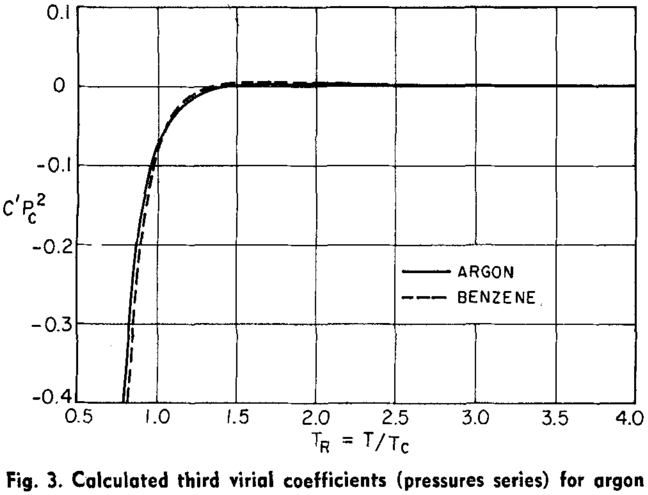

Fig. 3. Calculated third virial coefficients (pressures series) for argon and benzene on reduced coordinates.

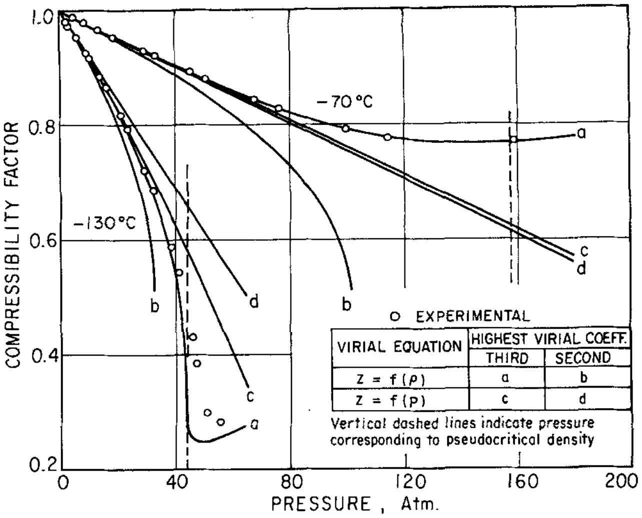

Fig. 4. Compressibility factors from two forms of the virial equation: density series and pressure series (equimolar mixture of argon-nitrogen).

The example illustrated in Figure 4 suggests that the density-series virial equation with the third term included offers a reliable method of describing volumetric behavior up to a pressure corresponding to a density near the critical; but, if for some reason the virial equation must be truncated after the second term, then it is probably better to use the pressure series, especially at reduced temperature higher than 1.4.

APPLICATION TO PHASE EQUILIBRIA

One important application for an equation of state is for calculating fugacity coefficients in phase equilibria with strong vapor-phase nonideality; the virial equation is particularly useful for such equilibria (*13, 46, 50* to *52*). Inclusion of the third virial coefficient extends the range of applicability and improves the accuracy of predicting high-pressure phase behavior. Vapor-solid equilibria provide an instructive example of such application, because in such equilibria the only nonideality is that in the vapor phase. More important, calculations for the solubility of a condensed component in a gas at high pressure offer a most sensitive test for the adequacy of Equations (10) and (11) for predicting third virial cross coefficients.

For a solid component 2 in equilibrium with a high-pressure gas 1, the equation of equilibrium is given by

$$f_2^{\text{solid}} = \phi_2 y_2 P \tag{22}$$

The fugacity of pure solid component 2 is given by

$$f_2^{\text{solid}} = \phi_2^s P_2^s \exp \frac{v_2^s(P - P_2^s)}{RT} \tag{23}$$

where $\phi_2{}^s$ is the fugacity coefficient for the saturated vapor of pure component 2. Since $P_2{}^s$ is generally very small, $\phi_2{}^s$ is essentially unity. The fugacity coefficient ϕ_2 is obtained from the virial equation (density series) truncated after the third term:

$$\ln \phi_2 = 2\rho \sum_{j=1}^{N} y_j B_{2j} + \frac{3}{2}\rho^2 \sum_{j=1}^{N} \sum_{k=1}^{N} y_j y_k C_{2jk} - \ln z_m \tag{24}$$

Substituting Equations (23) and (24) into Equation (22) and simplifying with the condition that $y_1 \simeq 1$ and $\phi_2{}^s \simeq 1$, we obtain for the solubility y_2

$$\ln y_2 = \ln \frac{P_2{}^s}{P} + \frac{v_2{}^s(P - P_2{}^s)}{RT} + \ln z_1 - 2\,\rho_1 B_{12} - \frac{3}{2}\rho_1{}^2\, C_{112} \tag{25}$$

The solubility of component 2 in the gas phase can be found from Equation (25) once B_{12} and C_{112} are determined. To do so accurately, however, requires information on the 1 — 2 interaction, that is, the value of k_{12} which must be found from some binary experimental data such as the second virial cross coefficient, B_{12}, at any temperature, not necessarily the one of interest. From experimental data (22) for the methane-hydrogen system we determine that $k_{12} = 0.03$. With k_{12} known, C_{112} can be calculated from Equations (4) and (15) together with Equations (16) to (18). The predicted C_{112} of 1,560 (cc./g.-mole)^2 and the experimental B_{12} of —102 cc./g.-mole are then used in Equation (24) to calculate y_2, the solubility of methane in hydrogen, shown in Figure 5.

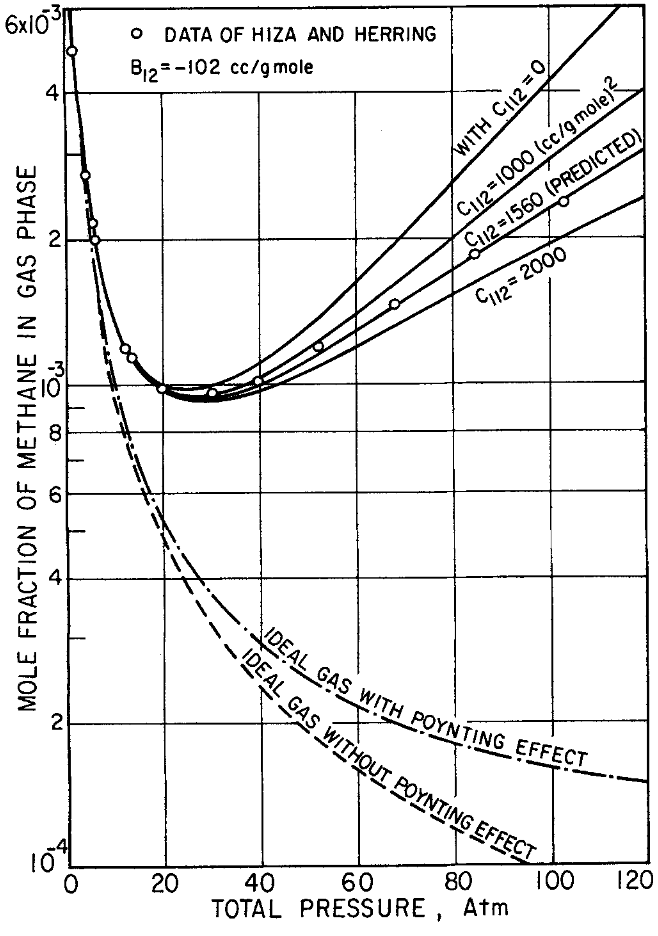

Fig. 5. Effect of third virial coefficient on vapor-solid equilibria of hydrogen (1)-methane (2) system at 76°K.

Using the calculated C_{112}, we can correctly predict the solubilities of methane up to a pressure of 110 atm., which corresponds to a density near the critical. On the other hand, the predictions begin to fail at 30 atm. if only the second virial coefficient is used ($C_{112} = 0$). Inclusion of the third virial coefficient has significantly extended the region of applicability of the virial equation. Calculations with two other values of C_{112} are also shown to give some idea of the accuracy with which the third virial coefficient needs to be known. Also plotted are calculations based on ideal gas behavior, with and without Poynting effect; these calculations show the serious error incurred when gas phase nonideality is neglected entirely.

CONCLUSION

A corresponding-states correlation for third virial coefficients of nonpolar gases has been presented. An analytical expression for the reduced third virial coefficient is given to facilitate implementation in an electronic computer. The correlation can be used to predict third virial coefficients of quantum gases as well as classical gases; furthermore, subject to certain assumptions, it can be applied to mixtures of nonpolar gases.

It has been shown that the reduced third virial coefficient for the pressure-series virial equation is close to zero for reduced temperatures greater than 1.4. As a result, for reduced temperatures greater than 1.4, the pressure series is more accurate than the density series when both series are truncated after the second term. However, when third virial coefficients are not neglected, the density series appears to be superior regardless of reduced temperature; the density series provides a good approximation to a moderately high pressure, roughly corresponding to that of the critical density.

The importance of third virial coefficients in high-pressure equilibria is illustrated with calculations for the methane-hydrogen, solid-gas equilibrium at a low temperature. The calculations show that inclusion of the third virial coefficient in the virial equation significantly extends the region of applicability of that equation.

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NOTATION

B = second virial coefficient in the density series virial equation
B_{ij} = second virial cross coefficient for the $i - j$ interaction
B' = second virial coefficient in the pressure series virial equation
C = third virial coefficient in the density series virial equation
C_{ijk} = third virial cross coefficient for the $i - j - k$ interaction
C_{ii} = C_{iii}, the third virial coefficient for pure component i
C_{ij} = third virial coefficient corresponding to an interaction with $i - j$ pair potential
$\Delta C/v_c{}^2$ = deviation of reduced third virial coefficient from that of argon and nitrogen
C' = third virial coefficient in the pressure series virial equation
c_1, c_2 = constants given by Equations (6) and (8), respectively
d = empirical parameter characterizing polarizability,

size and shape of a molecule

d_{ij} = parameter d for the $i - j$ interaction

f = fugacity

f_c = function given by Equation (4)

k_{ij} = constant representing deviation from geometric mean for $T_{c_{ij}}$

m = molecular weight

m_{ij} = molecular weight characteristic of the $i - j$ interaction; the reduced mass

P = pressure

$P_2{}^s$ = saturated vapor pressure of component 2

R = gas constant

T = temperature

T_c = critical temperature

$T_c{}^o$ = classical critical temperature (high-temperature limit of the effective critical temperature)

$T_{c_{ij}}$ = critical temperature characteristic of the $i - j$ interaction

T_R = reduced temperature

v = molar volume

v_c = critical volume

$v_c{}^o$ = classical critical volume (high-temperature limit of the effective critical volume)

$v_{c_{ij}}$ = critical volume characteristic of the $i - j$ interaction

y = mole fraction

z = compressibility factor

z_m = compressibility factor for mixture

ρ = molar density

ω = acentric factor

ϕ_2 = fugacity coefficient of component 2 in a gas mixture

$\phi_2{}^s$ = fugacity coefficient for a saturated vapor of pure component 2

LITERATURE CITED

1. van Agt, F. P. G. A. J., and H. Kamerlingh Onnes, *Commun. Lab Leiden,* **176b** (1925).
2. Beattie, J. A., R. J. Barriault, and J. S. Brierley, *J. Chem. Phys.,* **19,** 1222 (1951).
3. Beattie, J. A., J. S. Brierley, and R. J. Barriault, *ibid.,* **20,** 1615 (1952).
4. Beattie, J. A., D. R. Douslin, and S. W. Levine, *ibid.,* 1619.
5. Beattie, J. A., S. W. Levine, and D. R. Douslin, *J. Am. Chem. Soc.,* **74,** 4778 (1952).
6. Chueh, P. L., and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals,* in press.
7. Connolly, J. F., and G. A. Kandalic, *Phys. Fluids,* **3,** 463 (1960).
8. Crain, R. W., Jr., and R. E. Sonntag, "Advances in Cryogenic Engineering," K. D. Timmerhaus, ed., Vol. 11, p. 379 Plenum Press, New York (1966).
9. Douslin, D. R., private communication (1963).
10. Dymond, J. H., "A Compilation of Second and Third Virial Coefficients," Univ. Oxford (1964).
11. Epstein, Leo, *J. Chem. Phys.,* **20,** 1981 (1952).
12. Evans, R. B., and G. M. Watson, *Chem. Eng. Data Ser.,* **1,** 67 (1956).
13. Ewald, A. H., W. B. Jepson, and J. S. Rowlinson, *Discussion Faraday Soc.,* **15,** 238 (1953).
14. Goodwin, R. D., D. E. Diller, H. M. Roder, and L. A. Weber, *J. Res. Natl. Bur. Std.* A, **68A,** 121 (1964).
15. Gornowski, E. J., E. H. Amick, Jr., and A. N. Hixson, *Ind. Eng. Chem.,* **39,** 1458 (1947).
16. Guggenheim, E. A., *Rev. Pure Appl. Chem.,* **3,** 1 (1953).
17. Gunn, R. D., P. L. Chueh, and J. M. Prausnitz, *A.I.Ch.E J.,* **12,** 937 (1966).
18. Hagenbach W. P., and E. W. Comings, *Ind. Eng. Chem.,* **45,** 609 (1953).
19. de Haas, W. J., *Commun. Lab. Leiden,* **127a,c** (1912).
20. Hilsenrath et al., "Tables of Thermal Properties of Gases," Natl. Bur. Std. Circ. 564, Washington, (1955); Pergamon Press (1960).
21. Hiza, M. J., and A. J. Kidnay, *Cryogenics,* **6,** 348 (1966).
22. Hiza M. J., and R. N. Herring, "International Advances in Cryogenic Engineering," K. D. Timmerhaus, ed., Vol. 10, Sect. M-U, p. 182, Plenum Press, New York (1965).
23. Holborn L., and J. Otto, *Z. Phys.,* **33,** 1 (1925); **38,** 359 (1926).
24. Hoover, Alan E., Frank B. Canfield, Riki Kobayashi, and Thomas W. Leland, Jr., *J. Chem. Eng. Data,* **9,** 568 (1964).
25. Hoover, Alan E., dissertation, Rice Univ., Houston, Tex. (1965).
26. Keesom, W. H., "Helium," p. 49, Elsevier, Amsterdam (1942).
27. Lewis, G. N., M. Randall, K. S. Pitzer, and L. Brewer, "Thermodynamic," 2 ed., p. 608, McGraw-Hill, New York (1961).
28. Mayer, J. E., *J. Phys. Chem.,* **43,** 71 (1939).
29. McGlashan, M. L., and D. J. B. Potter, *Proc. Roy. Soc. (London),* **A267** 478 (1962).
30. McGlashan, M. L., and C. J. Wormald, *Trans. Faraday Soc.,* **60,** 646 (1964).
31. Michels, A., J. M. Levelt, and W. de Graaff, *Physica,* **24,** 659 (1958).
32. Michels, A., J. M. Lupton, T. Wassenaar, and W. de Graaff, *ibid.,* **18,** 121 (1952).
33. Michels, A., and C. Michels, *Proc. Roy. Soc. (London),* **A153,** 201 (1935).
34. Michels, A., and C. W. Nederbragt, *Physica,* **3,** 569 (1936).
35. Michels, A., W. van Straaten, and J. Dawson, *ibid.,* **20,** 17 (1954).
36. Michels, A., T. Wassenaar, and P. Louwerse, *ibid.,* **20,** 99 (1954).
37. *Ibid.,* **26,** 539 (1960).
38. Michels, A., Hk. Wijker, and Hub Wijker, *ibid.,* **15,** 627 (1949).
39. Michels, A., H. Wouters, and J. de Boer, *ibid.,* **1,** 587 (1934).
40. Nighoff, G. P., and W. H. Keesom, *Commun. Lab. Leiden,* **188d,e** (1928).
41. Onnes, H. Kamerlingh, and C. Braak, *ibid.,* **100b** (1907).
42. Onnes, H. Kamerlingh, and A. T. van Urk, *ibid.,* **169d,e** (1924).
43. Orentlicher, M., and J. M. Prausnitz, *Can. J. Chem.,* **45,** 373 (1967).
44. Otto, J., A. Michels, and H. Wouters, *Phys. Z.,* **35,** 97 (1934).
45. Pitzer, K. S., and R. F. Curl, Jr., *J. Am. Chem. Soc.,* **79,** 1269 (1957).
46. Prausnitz, J. M., *A.I.Ch.E. J.,* **5,** 3 (1959).
47. ———, and A. L. Myers, *ibid.,* **9,** 5 (1963).
48. Prausnitz, J. M., and R. N. Keeler, *ibid.,* **7,** 399 (1961).
49. Renon, H., C. A. Eckert, and J. M. Prausnitz, *Ind. Eng. Chem. Fundamentals,* **6,** 52, 58 (1967).
50. Reuss, J., and J. J. M. Beenakker, *Physica,* **22,** 869 (1956).
51. Robin, S., and B. Vodar, *Discussions Faraday Soc.,* No. 15, 233 (1953).
52. Rowlinson, J. S., and M. J. Richardson, "Advances in Chemical Physics," I. Prigogine, ed., Vol. II, p. 85, Interscience, New York (1959).
53. Sage, B. H., and W. N. Lacey, "Thermodynamic Properties of the Lighter Hydrocarbons and Nitrogen," Am. Petrol. Inst., New York (1950).
54. Schamp, H. W., E. A. Mason, A. C. B. Richardson, and A. Altman, *Phys. Fluids,* **1,** 329 (1958).
55. Sherwood A. E., and J. M. Prausnitz, *J. Chem. Phys.,* **41,** 413 (1964).
56. *Ibid.,* 429.
57. Sherwood, A. E., A. G. De Rocco and E. A. Mason, *ibid.,* **44,** 2984 (1966).
58. Tee, L. S., Sukehiro Gotoh, and W. E. Stewart, *Ind. Eng. Chem. Fundamentals,* **5,** 356, 363 (1966).
59. Van Ness, H. C., "Classical Thermodynamics of Nonelectrolyte Solutions," Macmillan, New York (1964).

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