Second Virial Coefficients of Polar Fluids and Mixtures

ROLAND L. HALM and LEONARD I. STIEL

Syracuse University, Syracuse, New York

Relationships have been developed for the calculation of second virial coefficients of polar fluids from the critical constants, acentric factor ω, and fourth parameter x of the substance. Coefficients for the expansion of the reduced second virial coefficient in ω and x are presented for $0.64 \leq T_R \leq 0.94$. Comparisons with available experimental data indicate that good results are obtained by the method of this study for most polar fluids. The second virial coefficient for water is found to exhibit anomalous behavior. Procedures have also been established for extending the relationships for pure fluids to the second virial coefficient of mixtures containing nonpolar or polar components.

Accurate procedures are required for the calculation of the thermodynamic properties of polar fluids. One approach is to use theoretical relationships and to determine the necessary parameters through experimental data for a particular property. An alternate procedure is to correlate the experimental data directly to macroscopic parameters defined through other properties of the fluid.

The microscopic approach has the advantage that it provides the dependence of the property on temperature and pressure directly. If the theoretical model is realistic and accurate experimental data are available, the parameters determined will have physical significance. The macroscopic approach has the major advantage that it can be used when accurate theoretical relationships for the desired property are difficult to formulate, and it enables inaccurate data for a particular substance to be detected. However, both approaches ultimately lead to identical relationships and both can provide insight into the actual physical behavior of the system.

SECOND VIRIAL COEFFICIENTS OF POLAR FLUIDS

The second virial coefficient for dilute gases is one of the few properties of polar fluids for which theoretical relationships have been developed. Rowlinson (*41*) has established an expression for the second virial coefficient of polar fluids for the Stockmayer potential, a superposition of the Lennard-Jones potential for nonpolar fluids with a term accounting for dipole-dipole interactions. Values of the parameters ϵ/κ and σ for this potential were established from experimental dipole moments and second virial coefficient data for polar substances of small molecular size.

Suh and Storvick (*44*) have extended the Kihara core potential to nonspherical polar molecules by a perturbation solution for the polar contribution. Although this model was found to be more accurate for polar fluids than the Stockmayer potential, an improved version of the final expression for the second virial coefficient has been presented (*43*).

O'Connell and Prausnitz (*31*) derived relationships for the second virial coefficient of polar fluids for a potential consisting of the Kihara spherical core potential extended to polar fluids. The functional form of the second virial coefficient is

$$\frac{B}{2/3\pi N\sigma^3} = f\left(T\kappa/\epsilon,\ \frac{2a}{\sigma},\ \frac{\mu^2}{\sqrt{8}\,\epsilon\,(\sigma-2a)^3}\right) \qquad (1)$$

Tables of the reduced second virial coefficient $\overline{B} = B/(2/3)\pi N\sigma^3$ were established for values of $\overline{T} = T\kappa/\epsilon$ from 0.4 to 5.0, of $\overline{t} = \mu^2/[\sqrt{8}\,\epsilon(\sigma-2a)^3]$ from 0.0 to 1.5, and of $\delta = 2a/\sigma$ from 0 to 0.2. Values of the parameters obtained from experimental PVT data for water were found to yield calculated second virial coefficients at low temperatures which were not sufficiently negative (*31*).

The parameters of Equation (1) can be related to empirical macroscopic variables ω and x which represent the effects of shape and polarity (*42*). For nonpolar fluids, Pitzer and Curl (*36*) obtained the following relationship for the reduced second virial coefficient:

$$B^* = \frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega\frac{B^{(1)}P_c}{RT_c} \qquad (2)$$

Where ω, the acentric factor, is defined as

$$\omega = -\log P_R|_{T_R=0.7} - 1.000 \qquad (3)$$

The reduced virial coefficient functions were expressed as follows:

$$\frac{B^{(0)}P_c}{RT_c} = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} \qquad (4)$$

and

$$\frac{B^{(1)}P_c}{RT_c} = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8} \qquad (5)$$

Equations (2), (4), and (5) have proved to yield good results.

Roland L. Halm is with Dow-Corning, Midland, Michigan. Leonard I. Stiel is at the University of Missouri, Columbia, Missouri.

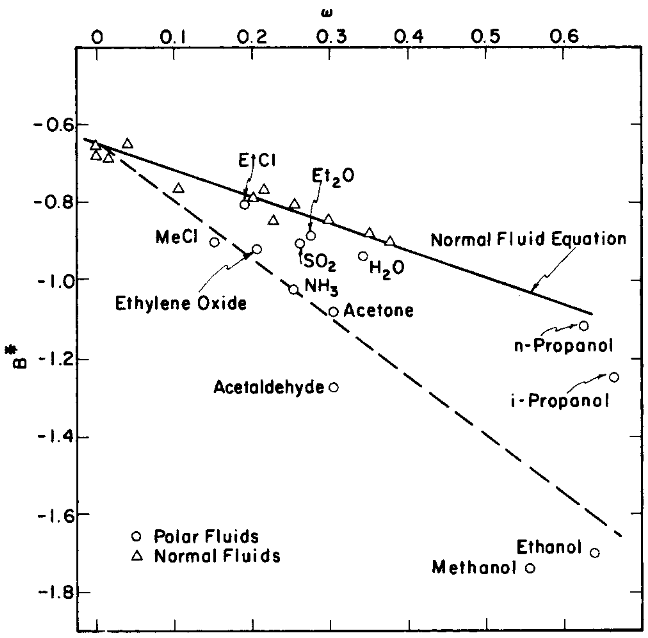

Fig. 1. B^* versus ω for normal and polar fluids at $T_R = 0.70$.

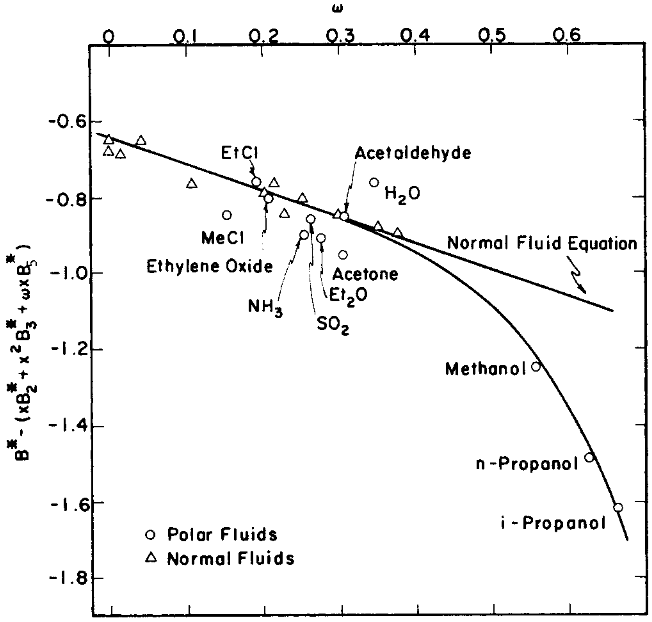

Fig. 2. Relationship between $B^* - B_p^*$ and ω for normal and polar fluids at $T_R = 0.70$.

O'Connell and Prausnitz (*32*) have extended Equation (2) to polar fluids as follows:

$$B^* = \frac{BP_c}{RT_c} = \frac{B^{(0)}P_c}{RT_c} + \omega_h \frac{B^{(1)}P_c}{RT_c} + B_\mu^* (\mu_R, T_R) - \eta B_a^* (T_R) \quad (6)^\dagger$$

where ω_h is the acentric factor of a homomorph compound (a nonpolar substance having the same size and shape), μ_R is defined as the reduced dipole group $\mu^2 P_c / T_c^2 \cdot 10^5$, η is an empirical parameter, and analytical expressions have been established for B_a^* and B_μ^* as functions of reduced temperature. While η was defined to represent the effects of association, it was found that this parameter was zero for certain fluids which might be expected to exhibit this effect.

For polar fluids, Halm and Stiel (*13*) have defined a fourth parameter x as

$$x = \log P_R|_{T_R = 0.6} - \log P_{Rn}|_{T_R = 0.6} = \log P_R|_{T_R = 0.6} + 1.552 + 1.7\omega \quad (7)$$

where ω is defined as previously by Equation (3). Polar fluid correction terms were obtained for the vapor pressure and entropy of vaporization (*13*) and for the critical compressibility factor, density of saturated liquids, and compressibility factor of saturated vapors (*14*).

For nonpolar fluids, ω defined in Equation (3) represents the dimensionless shape group a/σ. For polar fluids, the effects of shape and polarity are not segregated in Equations (3) and (7), so that the parameters ω and x do not represent, respectively, the groups δ and $\bar{t}$ in Equation (1). However, because two vapor pressure values are used in the definitions of ω and x, these parameters are related to, and can be used in place of, the physically significant parameters (ω' which represents exclusively shape effects and x' which characterizes polarity).

RELATIONSHIP OF THE SECOND VIRIAL COEFFICIENT OF POLAR FLUIDS TO ω AND x

In Figure 1 values of B^* for both normal and polar fluids are plotted versus ω at a reduced temperature of 0.7. It can be seen that the reduced second virial coefficients for polar fluids deviate considerably from the normal fluid relationship, Equation (2). For most of the polar fluids of small molecular size, the reduced second virial coefficients fall on a single line, corresponding to the use of a three-parameter intermolecular potential function, such as the Stockmayer potential.

For polar fluids, the following series expansion in ω and x was utilized:

$$B^* = B_0^* + \omega B_1^* + x B_2^* + x^2 B_3^* + \omega^6 B_4^* + \omega x B_5^* \quad (8)$$

where the coefficients B_0^*, B_1^*, B_2^*, B_3^*, B_4^*, and B_5^* were determined as functions of reduced temperature by a multidimensional least squares analysis. Experimental second virial coefficient data were employed for normal fluids and for ammonia (*4, 41*), acetone (*18, 23, 32, 34, 41, 48*), methyl ether (*3, 46*), ethyl ether (*1, 48*), methyl chloride (*2, 15, 41*), ethyl chloride (*32*), sulfur dioxide (*17*), acetaldehyde (*32, 39, 41*), methanol (*2, 23, 32, 41*), *n*-propanol (*5, 28*), *i*-propanol (*5, 11, 21, 30*), and water (*25, 32, 33*). In addition, experimental PVT data for ethylene oxide (*47*) were used to establish second virial coefficients for this substance for $T_R = 0.63$ to $T_R = 1.02$ (*12*). An analysis of the data indicated that a higher order term in ω in Equation (8) was required. The exponent of six enabled B_0^* and B_1^* to be obtained from the normal fluid relationships, Equations (4) and (5).

The data for water exhibit anomalous behavior as indicated by Figure 1, in which the reduced second virial coefficient for this substance essentially follows normal fluid behavior. These deviations may be due to the effects of adsorption on the walls of the experimental apparatus (*20*) or the neglect of higher virial coefficients. Second virial coefficients for water determined from the experimental heat capacity data of McCullough, Pennington, and Waddington (*27*) for low reduced temperatures are more consistent with the behavior of other polar fluids. It

---

† Professor Prausnitz has pointed out that the last term in Equation (6) should be negative instead of positive as presented in reference 32.

TABLE 1. VALUES OF POLAR FLUID FUNCTIONS FOR EQUATION (8)

T_R	B_2^*	B_3^*	B_4^*	B_5^*
0.64	−26.4	+50.8	−18.7	+16.7
0.66	−16.9	−6.2	−14.0	+3.80
0.68	−9.88	−55.2	−9.55	−4.67
0.70	−6.77	−77.5	−6.29	−6.57
0.72	−5.64	−85.0	−3.48	−4.53
0.74	−5.54	−79.4	−2.09	−1.97
0.76	−5.33	−70.1	−1.15	+0.13
0.78	−5.51	−58.0	−0.34	+2.82
0.80	−5.09	−50.1	+0.24	+3.82
0.82	−4.72	−43.9	+0.79	+4.77
0.84	−4.45	−34.7	+1.09	+5.60
0.86	−3.94	−27.9	+1.27	+5.65
0.88	−3.63	−19.9	+1.36	+5.96
0.90	−3.56	−12.1	+1.40	+6.52
0.92	−3.12	−8.85	+1.50	+6.29
0.94	−3.12	−3.5	+1.55	+6.88

TABLE 2. COMPARISON BETWEEN CALCULATED AND EXPERIMENTAL SECOND VIRIAL COEFFICIENTS FOR WATER

T_R	$-B$, Equation (8)	$-B$, from viscosity data	$-B$, experimental
0.654	356	323	284
0.731	243	230	197
0.885	130	137	112

is difficult to obtain second virial coefficients of high accuracy; an error of 1% in the compressibility factor can result in a 10 to 20% error in the second virial coefficient.*

In Table 1 the values of B_2^*, B_3^*, B_4^*, and B_5^* are tabulated for reduced temperatures from 0.64 to 0.94. The maximum root mean square error for interpolated values of B^* for the polar fluids considered was 8.5% at $T_R = 0.64$. The maximum percent error for an individual substance was 18.6% for water at the same reduced temperature. The polar corrections for reduced temperatures below $T_R = 0.64$ are large, while for $T_R > 0.94$ the deviation from normal fluid behavior is small but not necessarily negligible. Additional data for the second virial coefficient of polar substances are required to establish the polar fluid correction terms beyond the range of this investigation. In Figure 2 values of $B^* - xB_2^* - x^2B_3^* - \omega x B_5^*$ are plotted against ω for both normal and polar fluids at $T_R = 0.70$. It can be seen that polar molecules with large values of ω are treated satisfactorily.

Monchick and Mason (29) have determined collision integrals for the calculation of the transport properties of polar gases for the Stockmayer potential. The use of this potential should be a good approximation for water since the molecule is small in size. Monchick and Mason (29) calculated second virial coefficients for water from the potential parameters determined from experimental viscosity data for this substance. The second virial coefficients for water calculated from Equation (8) are in better agreement with the values calculated by Monchick and Mason (*29*) than with the corresponding experimental values (*41*), as shown in Table 2.

Values of the second virial coefficient for ethanol (*22*) and methyl fluoride (*26*), which were not employed in the establishment of the polar fluid correction terms of Equation (11), and for ethyl chloride (*32*), were compared with the values calculated with the normal fluid relationship [Equation (2)], Equation (6) of O'Connell and Prausnitz (*32*), and Equation (8). The method of this study to characterize the effects of shape and polarity on the second virial coefficient yields results that are comparable to those obtained with Equation (6), without the necessity of a fifth parameter (*12*).

RELATIONSHIP OF ω AND x TO MOLECULAR PARAMETERS

For normal fluids, the following relationships have been developed for the parameters of the Kihara potential by the use of potential parameters reported in the literature for realistic cores for each substance:

$$\rho^* = \rho_0 \, (P_c/T_c)^{1/3} = 2.17 - 3.44\omega \tag{9}$$

$$U_n^*(\omega) = \epsilon/\kappa T_c = 1.0 + 2.84\omega \tag{10}$$

$$s^* = 3M_0/2\pi\rho_0 = 0.3 + 11.1\omega \tag{11}$$

Similar relationships for the shape group s^* have been presented by Danon and Pitzer (*6*) and for a spherical core by Tee, Gotoh, and Stewart (*45*). While all the core dimensions are not uniquely determined by Equations (9) to (11), the second virial coefficient can be calculated directly from the Kihara core expression if higher than first-order effects are neglected (*35*).

The potential parameters obtained by Suh and Storvick (*44*) for the Kihara core potential with a superimposed dipole interaction term enabled the relationships for the molecular parameters for normal fluids to be extended to polar fluids as follows:

$$U^*(\omega, x) = (\epsilon/\kappa T_c) = U_n^*(\omega) - 73.7x \tag{12}$$

$$t^* = \mu^2/\sqrt{8} \, \epsilon\sigma_0^3 = 70x \tag{13}$$

where $\sigma_0 = \rho_0 + 2a$ and a is an equivalent radius of a nonspherical core. The available data did not permit any dependence of t^* on ω to be established. Since values of ρ_0 were not determined explicitly by Suh and Storvick (*44*), it was necessary to convert Equation (13) by the use of the following approximation:

$$\sigma_0 = \rho_0 + M_0/2\pi \tag{14}$$

Equation (14) is exact for a spherical core. In this manner the following relationship was obtained for polar fluids:

$$\sigma^* = \sigma_0(P_c/T_c)^{1/3} = 2.39 + 4.25\omega - 12.7\omega^2 - 71.4x \tag{15}$$

The group $3M_0/2\pi\sigma_0$ for polar fluids was found to be a strong function of ω and relatively independent of x. In Figures 3, 4, and 5 values of $U^* - U_n^*$, t^*, and $\sigma^* - \sigma_n^*$ are plotted versus x, and good agreement is seen to result for the equations developed in this study. The deviations of the molecular parameters determined for different cores for the same substance (*44*) indicate that a considerable error in the parameters is tolerable.

The potential parameters for polar fluids of Suh and Storvick (*44*) were determined using a perturbation solution; and while this approach gives an improvement over the Stockmayer potential by including shape effects, it is not strictly applicable for strongly polar molecules. Relationships similar to Equations (12), (13), and (15) ap-

---

[*] The experimental virial coefficients for water, reported by Kell, McLaurin, and Whalley (*J. Chem. Phys.*, **48**, 3805, 1968) after this study was completed, are closer to the values calculated from Equation (8) than the previous experimental values.

plicable for a wider range of polar fluids cannot be established until potential parameters are available for a more realistic model for complex polar molecules. However, these results do indicate that the parameters ω and x defined from the vapor pressure can be related to molecular parameters resulting from a four-parameter intermolecular potential function for polar fluids.

SECOND VIRIAL COEFFICIENTS OF NONPOLAR AND POLAR MIXTURES

The development of functions for the second virial coefficients of polar substances provides a basis for the calculation of the second virial coefficients of mixtures containing nonpolar and/or polar components by the use of suitable combining rules for the parameters of the pure fluids. The composition dependence of the second virial coefficient of a binary mixture can be expressed as follows:

$$B_m = y_1^2\, B_{11}\,(T) + 2\, y_1\, y_2\, B_{12}\,(T) + y_2^2\, B_{22}\,(T) \tag{16}$$

where B_{11} and B_{22} are the second virial coefficients of the pure components and B_{12} is the interaction second virial coefficient for the mixture. Values of the interaction coefficients B_{12} were calculated from Equation (8) by assuming arithmetic average values of ω_{12} and x_{12}, as follows:

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} \tag{17}$$

$$x_{12} = \frac{x_1 + x_2}{2} \tag{18}$$

The potential energy parameter for the mixture $(\epsilon/\kappa)_{12}$ was taken as

$$(\epsilon/\kappa)_{12} = \sqrt{(\epsilon/\kappa)_1\,(\epsilon/\kappa)_2} \tag{19}$$

The critical temperature of the mixture $T_{c_{12}}$ was then obtained by the substitution of Equation (12) into Equation (19) to give

$$T_{c_{12}} = \frac{[T_{c_1}\, T_{c_2}\, U^*(\omega_1, x_1)\, U^*(\omega_2, x_2)]^{1/2}}{U^*(\omega_{12}, x_{12})} \tag{20}$$

For nonpolar mixtures, $\rho_{0_{12}}$ is obtained as

$$\rho_{0_{12}} = \frac{\rho_{0_1} + \rho_{0_2}}{2} \tag{21}$$

By the substitution of Equation (9) into Equation (21), the following relationship resulted for $P_{c_{12}}$:

$$P_{c_{12}} = T_{c_{12}} \left[\frac{2\rho^*(\omega_{12})}{\rho^*(\omega_1)\left(\dfrac{T_{c_1}}{P_{c_1}}\right)^{1/3} + \rho^*(\omega_2)\left(\dfrac{T_{c_2}}{P_{c_2}}\right)^{1/3}} \right]^3 \tag{22}$$

The interaction coefficient B_{12} is then calculated from Equation (8) by the use of Equations (17), (20), and (22).

Values of the second virial coefficient were calculated in this manner for the nonpolar mixtures listed in Table 3 (*16*) for mole fractions of 0.2, 0.4, 0.6, and 0.8 at each reduced temperature. The root mean square deviations in the virial coefficient for each mixture are included in Table 3. Considerably better results are obtained by this method than by the use of previous relationships, particularly for nonpolar mixtures containing dissimilar components. For 128 points the overall root mean square deviation was 6.35%, comparable to the results from Equations (2),

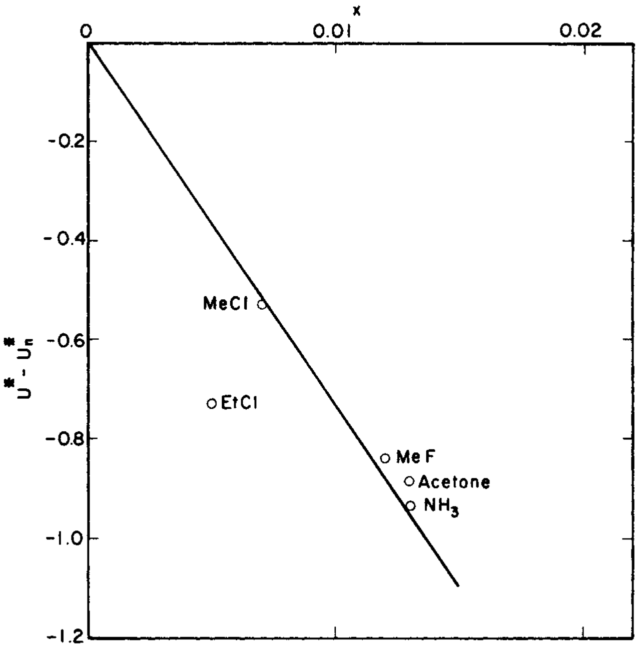

Fig. 3. Relationship between U^* — U_n^* and x for small polar fluids.

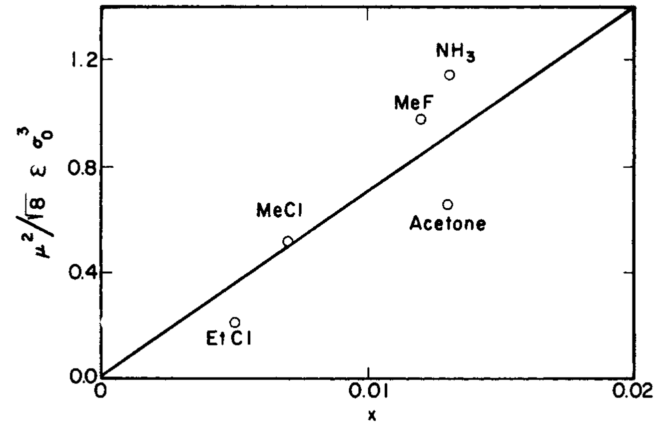

Fig. 4. Reduced dipole moment versus x for small polar fluids.

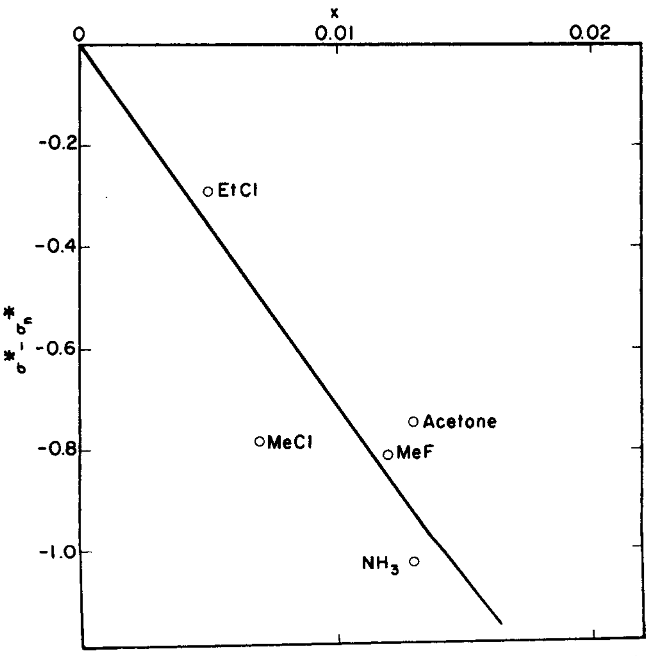

Fig. 5. Relationship between σ^* — σ_n^* and x for small polar fluids.

TABLE 3. DEVIATIONS FOR SECOND VIRIAL COEFFICIENTS OF NONPOLAR MIXTURES

System	No. of points	RMS % deviations Equations (17), (20), (22)
Methane-ethane	8	1.21
Methane-propane	12	3.98
Methane-*n*-butane	12	3.42
Methane-*i*-butane	12	5.57
Methane-*n*-pentane	20	2.44
Benzene-cyclohexane	12	2.39
n-Butane-carbon dioxide	16	14.62
Benzene-chloroform	20	5.26
Carbon tetrachloride-chloroform	16	4.18

(4), and (5) for pure nonpolar fluids, without the requirement of experimental interaction data for the binary components.

For mixtures containing polar components, an arithmetic average for σ_{012} was employed in place of Equation (21), since values of ρ_0 were not available for polar fluids. The following relationship for P_{c12} resulted from the use of Equation (15):

$$P_{c12} = T_{c12}\left[\frac{2\sigma^*(\omega_{12}, x_{12})}{\sigma^*(\omega_1, x_1)\left(\dfrac{T_{c1}}{P_{c1}}\right)^{1/3} + \sigma^*(\omega_2, x_2)\left(\dfrac{T_{c2}}{P_{c2}}\right)^{1/3}}\right]^3 \qquad (23)$$

The interaction virial coefficient B_{12} is calculated from Equation (8) by the use of Equations (17), (18), (20), and (23). In Table 4, the root mean square percent deviations resulting from this method are presented for polar binary mixtures. For 124 points the overall root mean square deviation in the second virial coefficient was 7.0%, similar to the error for normal fluid mixtures.

O'Connell and Prausnitz (*32*) have presented relationships for T_{c12}, P_{c12}, ω_{12}, μ_{R12}, and η_{12} for the calculation of the interaction virial coefficients of mixtures from Equation (7).† O'Connell and Prausnitz (*32*) have also considered the first six binary systems in Table 4. The deviations in the interaction virial coefficients calculated by O'Connell and Prausnitz (*32*) were compared with the results obtained from Equation (8) with the mixing rules developed in this study (*12*). The overall root mean square errors were 20.8 and 24.1%, respectively.

Values of B_m for nonpolar and polar mixtures were also calculated directly from Equation (8) by the use of the Prausnitz and Gunn pseudocritical rules (*40*). For polar mixtures, the fourth parameter of the mixture was obtained as

$$x_m = \sum_i y_i\, x_i \qquad (24)$$

A similar approach has been used for nonpolar mixtures by Pitzer and Hultgren (*37*) by the use of pseudocritical constants obtained from experimental volumetric data, and for the viscosity of nonpolar mixtures by Dean and Stiel (*7*). Somewhat higher errors resulted for this procedure (*12*), and for nonpolar mixtures largest errors were obtained for mixtures containing dissimilar components.

TABLE 4. DEVIATIONS FOR SECOND VIRIAL COEFFICIENTS OF MIXTURES CONTAINING POLAR COMPONENTS

System	References	No. of points	RMS % deviations Equations (17), (18) (20), (23)
Ethyl ether-*n*-hexane	*10*	8	1.6
Acetone-benzene	*32, 49*	24	4.3
Acetone-cyclohexane	*32*	12	11.3
Acetone-*n*-hexane	*32*	8	8.1
Acetone-ethyl ether	*48*	12	6.5
Methyl chloride-propane	*19*	4	3.9
Acetone-carbon-disulfide	*2*	16	3.0
Methyl chloride-acetone	*2*	20	11.0
Methyl chloride-carbon disulfide	*2*	20	5.1

Most of the binary systems considered did not contain highly polar substances with large values of ω and x. Larger errors might be encountered for mixtures of this type, since some of the equations used in the derivation of the mixing rules are not strictly applicable for fluids with strong polarity effects. When molecular parameters for a four-parameter intermolecular potential function are available for a wide range of polar fluids, improved results for polar mixtures can be obtained by the use of the theoretical relationship for the second virial coefficient. This approach has recently been applied successfully for nonpolar mixtures (*9*).

DISCUSSION OF RESULTS

As mentioned by Rowlinson (*41*), two main approaches have been used to analyze the second virial coefficient of polar fluids. The first method is to employ an intermolecular potential function involving the dipole moment to describe the interaction between two molecules. The second procedure is to assume that the behavior of polar fluids can be characterized as chemical association between the molecules. In this latter method equilibrium constants are used to describe the reactions for the formation of dimers or larger molecules. Rowlinson (*41*) concluded that it is not correct to consider the interaction of two polar molecules as a combination of physical and chemical effects, except as a correction for the case in which the Stockmayer potential is used for polar molecules which may have significant shape effects and for which the dipole moment may not be at the center of the molecule.

The success of the approach of the present study in which the parameters ω and x are used to characterize the effects of molecular interaction on the second virial coefficient of polar fluids lends credence to these conclusions. A number of thermodynamic and transport properties of polar fluids have been observed to exhibit similar behavior in terms of the parameters ω and x, indicating that most

---

† Procedures for the calculation of second virial coefficients of mixtures containing polar components have also been presented by Blanks and Prausnitz [*AIChE J.*, **8**, 86 (1962)].

polar fluids can be analyzed effectively by the use of a four-parameter intermolecular potential, including the effects of both dispersion and dipole-dipole interactions.

Nonpolar-polar and polar-polar mixtures represent an extreme test for a molecular model involving only physical interactions. O'Connell and Prausnitz (*32*) found that a specific interaction constant determined from the experimental data was required for several binary polar mixtures. The study of mixtures of this type is complicated by the large errors which can occur in the experimental determination of the interaction virial coefficients. However, the results of this study indicate that the thermodynamic properties of a wide range of polar mixtures can be determined by the use of combining rules for the molecular parameters expressed in terms of ω and x.

Lawley and Smith (*24*) have discussed the limitations of the Stockmayer potential in describing polar molecules for which the dipole moment is displaced from the center of the molecules, and in the representation of the behavior of polar-nonpolar mixtures for which dipole-induced dipole effects may be significant. Lawley and Smith (*24*) and Dymond and Smith (*8*) modified the Stockmayer potential with a model involving a point dipole displaced from the center of the molecule. The effect on the second virial coefficient is the introduction of nonlinear terms in the dimensionless groups characterizing shape and polarity effects. It has been found that there is inherently considerable curvature in the dependence of the reduced thermodynamic properties of polar fluids on ω and x, and terms involving the product ωx are of particular importance.

Additional theoretical studies are required to characterize accurately the combined effects of dispersion and polarity on the second virial coefficient of polar substances of large molecular size. Accurate experimental data for the compressibility factor at low pressures are also required for these substances to obtain the necessary molecular parameters, and to establish improved relationships in terms of the macroscopic variables.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for the support of this work.

NOTATION

a = radius of a spherical core

B = second virial coefficient, cu.cm./g.-mole

$\bar{B}$ = reduced second virial coefficient for Kihara spherical core potential, $B/\frac{2\pi}{3}N\sigma^3$

B^* = reduced second virial coefficient, BP_c/RT_c

B_a^* = function accounting for association effects in Equation (6)

B_μ^* = function accounting for dipole effects in Equation (6)

$g(\theta)$ = angle-dependent term of dipole-dipole interaction

M_0 = mean curvature of molecular core integrated over the core surface

N = Avogadro's number

P_c = critical pressure, atm.

r = distance between molecules

R = gas constant, 1.987 cal./(g.-mole) (°K.)

$\bar{t}$ = reduced dipole group for Kihara spherical core potential, $\mu^2/\sqrt{8}\ \epsilon(\sigma - 2a)^3$

t^* = reduced dipole group, $\mu^2/\sqrt{8}\ \epsilon\sigma_0^3$

T = temperature, °K.

T_c = critical temperature, °K.

T_R = reduced temperature, T/T_c

U^* = $\epsilon/\kappa T_c$

x = fourth parameter for polar molecules

x' = fourth parameter characteristic solely of dipole-dipole interactions

Greek Letters

δ = reduced shape group for Kihara spherical core potential, $2\frac{a}{\sigma}$

ϵ = maximum energy of attraction, erg

η = association parameter in Equation (6)

κ = Boltzmann constant

μ = dipole moment of molecule

μ_R = reduced dipole group, $\mu^2P_c/T_c^2\cdot10^5$

ρ_0 = shortest distance between molecular cores at the potential minimum

ρ^* = $\rho_0(P_c/T_c)^{1/3}$

σ = distance between molecular centers when potential energy is zero

σ_0 = distance between molecular centers at the potential minimum

σ^* = $\sigma_0(P_c/T_c)^{1/3}$

ψ = intermolecular potential function

ω = acentric factor

ω' = third parameter characteristic solely of shape effects

Subscripts

i, 1, 2 = components of a mixture

m = property of a mixture

n = normal fluid

12 = interaction term for binary mixture

p = polar fluid contribution

LITERATURE CITED

1. Bottomley, G. A., and G. G. Reeves, *J. Chem. Soc.*, 3794 (1958).
2. Bottomley, G. A., and T. H. Spurling, *Australian J. Chem.*, **20**, 1789 (1967).
3. Cawood, W., and H. S. Patterson, *J. Chem. Soc.*, 619 (1933).
4. Cheh, H. Y., J. P. O'Connell, and J. M. Prausnitz, *Can. J. Chem.*, **44**, 429 (1966).
5. Cox, J. D., *Trans. Faraday Soc.*, **57**, 1674 (1961).
6. Danon, F., and K. S. Pitzer, *J. Chem. Phys.*, **36**, 425 (1962).
7. Dean, D. E., and L. I. Stiel ,*AIChE J.*, **11**, 526 (1965).
8. Dymond, J. H., and E. B. Smith, *Trans. Faraday Soc.*, **60**, 1378 (1964).
9. Eisenman, L. I., M. S. thesis, Syracuse Univ., N. Y. (1968).
10. Fox, J. H. P., and J. D. Lambert, *Proc. Roy. Soc. (London)*, **A 210**, 557 (1952).
11. Foz, O. R., J. Morcillo, and A. Mendez, *Anal. Real Soc. Espan. Fis. Quim. (Madrid)*, **50 B**, 17 (1954).
12. Halm, R. L., Ph.D. dissertation, Syracuse Univ. N. Y. (1968).
13. ———, and L. I. Stiel *AIChE J.*, **13**, 351 (1967).
14. *Ibid.*, **16**, 3 (1970).
15. Hirschfelder, J. O., F. T. McClure, and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).
16. Huff, J. A., and T. M. Reed, *J. Chem. Eng. Data*, **8**, 306 (1963).
17. Kang, T. L., L. J. Hirth, K. A. Kobe, and J. J. McKetta, *ibid.*, **6**, 220 (1961).
18. Kappallo, W., N. Lund, and K. Schafer, *Z. Phys. Chem.*, **37**, 196 (1963).
19. Kappallo, W., and K. Schafer, *Z. Elektrochem.*, **66**, 508 (1962).
20. Keyes, F. G., *J. Heart Mass Transfer*, **5**, 137 (1962).
21. Kretschmer, C. B., and R. Wiebe, *J. Am. Chem. Soc.*, **76**, 2579 (1954).
22. Lambert, J. D., *Discussions Faraday Soc.*, **15**, 226 (1953).
23. ———, E. N. Staines, and S. D. Woods, *Proc. Roy. Soc. (London)*, **A 200**, 262 (1950).

24. Lawley, K. P., and E. B. Smith, *Trans. Faraday Soc.*, **59**, 301 (1963).
25. Liley, P. E., "Thermodynamic and Transport Properties of Gases, Liquids and Solids," p. 211, Am. Soc. Mech. Engrs, New York (1959).
26. Lunbeck, R. J., and C. A. ten Seldam, *Physica*, **17**, 788 (1951).
27. McCullough, J. P., R. E. Pennington, and G. Waddington, *J. Am. Chem. Soc.*, **74**, 4439 (1959).
28 Martin, J. J., J. A. Campbell, and E. M. Siedel, *J. Chem. Eng. Data,* **8**, 560 (1963).
29. Monchick, L., and E. A. Mason, *J. Chem. Phys.*, **35**, 1676 (1961).
30. Moreland, M. P., Ph.D. dissertation, Univ. Texas, Austin (1966).
31. O'Connell, J. P., and J. M. Prausnitz, "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," p. 19, *Am. Soc. Mech. Engrs.*, New York (1965).
32. ———, *Ind. Eng. Chem. Proc. Design Develop.*, **6**, 245 (1967). Supplementary data deposited as Document No. 9362 with ADI.
33. Osborne, N. S., H. F. Stimson, and D. C. Ginnings, *J. Res. Natl. Bur. Stds.*, **23**, 261 (1939).
34. Pennington, R. E., and K. A. Kobe, *J. Am. Chem. Soc.*, **79**, 300 (1957).
35. Pitzer, K. S., *ibid.*, **77**, 3427 (1955).
36. ———, and R. F. Curl, Jr., *ibid.*, **79**, 2369 (1957).
37. Pitzer, K. S., and G. O. Hultgren, *ibid.*, **80**, 4793 (1958).
38. Pitzer, K. S., D. Z. Lippmann, R. F. Curl, Jr., C. M. Huggins, and D. E. Peterson, *ibid.*, **77**, 3433 (1955).
39. Prausnitz, J. M., and W. B. Carter, *AIChE J.*, **6**, 611 (1960).
40. Prausnitz, J. M., and R. D. Gunn, *ibid.*, **4**, 432 (1955).
41. Rowlinson, J. S., *Trans. Faraday Soc.*, **45**, 975 (1949).
42. Stiel, L. I., *Ind. Eng. Chem.*, **60**, 50 (1968).
43. Storvick, T. S., and T. H. Spurling, *J. Phys. Chem.*, **72**, 1821 (1968).
44. Suh, K. W., and T. S. Storvick, *ibid.*, **71**, 1450 (1967).
45. Tee, L. S., S. Gotoh, and W. E. Stewart, *Ind. Eng. Chem. Fundamentals*, **5**, 356 (1966).
46. Tripp, T. B., and R. D. Dunlap, *J. Phys. Chem.* **66**, 635 (1962).
47. Walters, C. J., and J. M. Smith, *Chem. Eng. Progr.*, **48**, 337 (1952).
48. Zaalishvili, S. D., *Zh. Fiz. Khim.*, **34**, 2596 (1960).
49. ———, and L. E. Kolysko, *ibid.*, **38**, 503 (1964).

Manuscript received Januray 14, 1969; revision received December 15, 1969; paper accepted December 19, 1969. Paper presented at AIChE Washington, D. C., meeting.

Catalytic Reduction of Nitric Oxide with Various Hydrocarbons

J. W. AULT and R. J. AYEN

University of California, Berkeley, California

Conversion data for the reduction of nitric oxide with C_1 to C_8 hydrocarbons over a barium-promoted copper chromite catalyst were obtained in an integral flow reactor operated at atmospheric pressure and temperatures of 225° to 525°C. In general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number the required temperature for a given nitric oxide conversion decreased with degree of saturation. The data were fitted to empirical rate expressions.

Most recent research on prevention of air pollution by oxides of nitrogen has been devoted to the possibility of chemical destruction of air pollutants. Cohn and co-workers (*1*) reported in a U.S. patent the feasibility of a catalytic reactor to reduce nitrogen oxides by a suitable fuel and to oxidize the excess fuel. Baker and Doerr (*2*) demonstrated the application of a catalytic reactor for the reduction of nitrogen oxides by carbon monoxide in an automobile exhaust system.

Catalyst surveys for the oxidation of hydrocarbons have been performed by many authors (*3* to *7*). For the oxidation of methane, Anderson and co-workers (*5*) found that supported Cr_2O_3 was an effective catalyst. In a study of the light hydrocarbons (C_1-C_3), Accomazzo and Nobe (*3*) found that acetylene was more easily oxidized than methane over a copper oxide-alumina catalyst. By assuming first-order kinetics, Innes and Duffy observed that rate constants for carbon monoxide and hydrocarbon oxidation over vanadiaalumina catalysts increased with degree of unsaturation and molecular weight (*6*).

In contrast to the studies on oxidation of hydrocarbons and carbon monoxide, the work done on reduction of nitrogen oxides, particularly nitric oxide, has been mainly in the field of basic kinetics (*8* to *13*). Malling (*12*) found that over a zinc-promoted copper chromite catalyst methane reduced nitric oxide to nitrogen, carbon dioxide, and water. Ayen and Mahendroo (*8*) observed the same products for the reaction of ethane and nitric oxide over a barium-promoted copper chromite catalyst. The reaction of ethylene and nitric oxide has been found to produce essentially the same results (*13*).

The purpose of the work reported here was to study the effect of chain length, degree of saturation, and structure of various hydrocarbons on the rate of catalytic reduction of nitric oxide. The reaction

$$\text{NO} + \text{reducing agent} \rightarrow N_2 + CO_2 + H_2O$$

was studied in an isothermal integral reactor, with methane, ethane, ethylene, acetylene, propane, propylene, *n*-hexane, benzene, and *n*-octane used individually as reducing agents. At temperatures below 300°C. nitrous oxide, N_2O is formed in reactions of nitric oxide (*11*, *14*).

J. W. Ault is at the University of California, Santa Barbara, California. R. J. Ayen is with Stauffer Chemical Company, Richmond, California.