matrix as by oxidation of pyrite. It should be noted further that stirring a coal slurry for several hours causes appreciable attrition of particles, especially of larger particles, and that this process contributes to the pyrite removal process. When a treated coal in the 14 to 18 mesh size range was examined after a reaction time of 4 hr, approximately 74% of the particles remained in the 14 to 18 mesh size range, but 21% dropped to the next smaller size range of 18 to 30 mesh. Some of the very fine particles agglomerated into +14 mesh particles during the filtration and drying processes.

ACKNOWLEDGMENT

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NOTATION

a, b, c, d, e, f = stoichiometric coefficients
a_s = pyrite reaction surface area, cm^2
a_{so} = initial pyrite reaction surface area, cm^2
A, B = calibration constants
C_A = concentration of liquid reactant A (ferric iron) in batch liquid, moles/l
C_B = concentration of solid reactant B (pyrite), moles/l
C_{Bo} = value of C_B initially, moles/l
C_C = concentration of liquid product C (ferrous iron) in batch liquid, moles/l
E = electrode potential, mv
$F(\alpha)$ = weighted sum of squares defined by Equation (12)
k = reaction velocity constant
K = adsorption equilibrium parameter
n = reaction order for a given component
R = ratio of ferric iron concentration to ferrous iron concentration, Fe^{III}/Fe^{II}
r = reaction rate of liquid reactant A (ferric iron)
t = time, min
T = temperature, °C
X_I, X_{II} = reaction weights defined by Equations (4) to (6)
σ_i = standard deviation, moles/l

LITERATURE CITED

Chandler, J. P., D. E. Hill, and H. O. Spivey, "A Program for Efficient Integration of Rate Equations and Least-Squares Fitting of Chemical Reaction Data," *Computers Biomed. Res.*, 5, 515 (1972).

Furusawa, T., and J. M. Smith, "Fluid-Particle and Intraparticle Mass Transport Rates in Slurries," *Ind. Eng. Chem. Fundamentals*, **12**, 197 (1973).

Garrels, R. M., and M. E. Thompson, "Oxidation of Pyrite by Iron Sulfate Solutions," *Am. J. Sci.*, **258-A**, 57 (1960).

Hamersma, J., E. Koutsoukos, M. Kraft, R. Meyers, G. Ogle, and L. Van Nice, "Chemical Desulfurization of Coal: Report of Bench Scale Development," Vol. 1, EPA Report No. EPA-R2-73-173a (1973).

King, W. E., "Pyrite Oxidation in Aqueous Ferric Chloride: Rate Studies and Reactor Design," Ph.D. thesis, Univ Pa., Philadelphia (1976).

Mathews, C. T., and R. G. Robins, "The Oxidation of Iron Disulfide by Ferric Sulfate," *Australian Chem. Eng.*, 21 (Aug., 1972).

McKay, D. R., and J. Halpern, "A Kinetic Study of the Oxidation of Pyrite in Aqueous Suspension," *Trans. Met. Soc. AIME*, 301 (June, 1958).

Meyers, R. A., "Desulfurize Coal Chemically," *Hydrocarbon Processing*, 93 (June, 1975).

Mott, R. A., "Determination of Pyritic and Sulfate Sulfur in Coal,'" *Fuel*, **29**, 53 (1950).

Rabinowitch, E., and W. H. Stoukmayer, "Association of Ferric Ions with Chloride, Bromide, and Hydroxyl Ions (A Spectroscopic Study)," *J. Am. Chem. Soc.*, **64**, 335 (1942).

Sasmojo, S., "Oxidation Kinetics of Pyritic Materials in Aqueous Media," Ph.D. thesis, Ohio State Univ. (1969).

Volk, W., *Applied Statistics for Engineers*, pp. 278ff McGraw-Hill, New York (1969).

Walker F. E., and F. E. Hartner, "Forms of Sulfur in U.S. Coals," Pittsburgh Coal Research Center, Technical Report (Oct., 1965).

Warren, I. H., "The Generation of Sulfuric Acid from Pyrite by Pressure Leaching," *Australian J. Appl. Sci.*, 7, 346 (1956).

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An Improved Corresponding States Method for Polar Fluids: Correlation of Second Virial Coefficients

An improved four-parameter corresponding states method that includes polar fluids has been developed. The four parameters are the critical temperature, the critical pressure, the radius of gyration, and a newly developed polarity factor based on the second virial coefficient. These parameters have been used to empirically correlate pure and interaction second virial coefficients of a variety of fluids.

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SCOPE

Reliable physical and thermodynamic data on chemical compounds and their mixtures are needed for efficient design and operation of chemical processing plants. Because experimental determination of all required data is a formidable proposition, it is usual practice to predict these data by the use of suitable correlations. Of the many correlational approaches that have been proposed, the corresponding states principle (CSP) has proved to be the most powerful framework.

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The CSP, in its original form, involves only two independent parameters, and its usefulness is limited to simple monoatomic molecules. The addition of a third parameter extends the practical applicability of the principle to nonpolar nonspherical fluids. A variety of third parameters have been suggested and used in the past (Riedel, 1954; Pitzer et al., 1955; Lydersen et al., 1955), and each has its merits and demerits.

Attempts have also been made to extend the scope of the CSP to include polar fluids. Usually, this involves the addition of a fourth parameter to account for polarity effects. Again, a number of fourth parameters have been proposed (Eubank and Smith, 1962; Thompson, 1966; Halm and Stiel, 1967; Passut, 1973). None of these attempts to introduce a fourth parameter into the CSP have been fully successful. In this work, a new fourth parameter has been defined by studying the effects of polarity on the second virial coefficient behavior.

The second virial coefficient accounts for nonideality in the vapor phase up to moderate densities only. However, since the new fourth parameter is to be used only as a macroscopic indicator of the gross effects of polarity, it is hoped that the parameter will also find use in correlating configurational properties of dense gas and condensed phases.

CONCLUSIONS AND SIGNIFICANCE

The principles underlying the simple theorem of corresponding states have been extended to include complex molecules into the CSP framework. The critical temperature and the critical pressure have been retained as the primary parameters characterizing physical behavior. For molecules whose force fields deviate from spherical symmetry, the radius of gyration defined by Thompson (1966) has been used to describe nonsphericity effects. For molecules whose properties are also significantly affected by the presence of electrostatic charge centers, in the form of dipoles and higher multipoles, an empirical polarity parameter has been obtained to correct for these effects.

The radius of gyration is defined strictly in terms of molecular structure. It is unaffected by the effects of polarity or association. In this respect, the radius of gyration is superior to other conventional third parameters. Fluids whose second virial coefficient behavior could be adequately characterized by the critical temperature, the critical pressure, and the radius of gyration were termed *standard fluids.*

The fourth parameter has been defined in terms of the second virial coefficient behavior. Because the second virial coefficient is an extensively studied and well-understood quantity, direct physical significance could be attached to the new fourth parameter. This parameter accounts for the gross effects of polarity on the physical properties of a fluid. The nature of the third and fourth parameters made it possible to separate the effects of molecular structure from the effects of polarity. It has been shown that though such a separation is artificial, it affords a convenient means to account for the complex behavior of polar fluids.

As a first step in testing the validity of the proposed parameters, the second virial coefficients of nonpolar and polar fluids have been correlated. The proposed correlation was compared with other available generalized equations and was found to be superior. By defining suitable mixing rules for the four parameters, interaction second virial coefficients have also been successfully correlated. Again, a detailed comparison was made with other correlations, and the proposed method was found to be equivalent in accuracy to the best of the available methods.

BACKGROUND

The corresponding states principle (CSP) forms the most powerful framework for predicting configurational properties of fluids. Leland and Chappelear (1968) have given an excellent review of the underlying theory and practical applications of the CSP. In its simplest form, the CSP involves only two independent parameters. A two-parameter CSP accurately characterizes the behavior of simple monoatomic molecules, that is, molecules with spherically symmetric force fields. The addition of a third parameter, usually referred to as the size-shape parameter, enhances the scope of the CSP to include fluids whose force fields deviate from spherical symmetry. Of the many third parameters that have been proposed, the Pitzer acentric factor (Pitzer et al., 1955) is probably the most widely used. The Pitzer three-parameter CSP excludes systems containing highly polar* species and species exhibiting specific interactions like hydrogen bonding.

Several attempts have been made to formulate a four-parameter CSP applicable to polar fluids. Notable among these are the works of Eubank and Smith (1962), Thompson (1966), Halm and Stiel (1967) and Passut (1973). These four-parameter methods suffer from one or more of the following drawbacks: inability to separate size-shape effects from polarity effects, lack of physical significance for the fourth parameter, and the fourth parameter assuming both positive and negative values. These led to complicated correlations, inconsistent results, and difficulties in extending correlations to mixtures.

DEVELOPMENT OF NEW PARAMETERS

The interactions involved in polar systems are complex, and an empirical development cannot be completely free from shortcomings. Yet, the well-identified drawbacks of the previous formulations suggest definite possibilities for improvement. The success of any such attempt hinges heavily on the suitable choice of parameters.

The critical temperature and the critical pressure are the most satisfactory principal parameters for CSP correlations. For polar molecules, the critical constants are certainly influenced by the dipole and quadrupole moments. Though it would be desirable to correct for these effects, undue complications are avoided if true critical properties are used even for polar molecules. The next

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* The term polar is usually reserved for those species having a nonzero dipole moment. However, inasmuch as the contribution to the intermolecular potential energy arising from quadrupole (or higher multipole) moments can be high, the term polar will be used, rather loosely, to represent all species for which electrostatic interactions arising from unsymmetrical charge distributions are important. On the other hand, several molecules that have nonzero dipole moments may be regarded as nonpolar if the influence of the dipole on observed thermophysical properties is small.

step is to obtain suitable parameters for the size-shape and polarity effects.

In this work, an attempt has been made to separate size-shape effects from polarity effects. Commonly used third parameters, because of the way they are defined, are significantly influenced by polarity. This renders it impossible to obtain a true measure of the size-shape effects for polar systems. Thompson (1966) attempted to overcome this problem by defining a size-shape parameter, the radius of gyration $\bar{R}$, strictly in terms of molecular structure. He defined the radius of gyration in terms of the product of the principal moments of inertia A, B, and C, and the molecular mass m:

for three-dimensional molecules

$$\bar{R} = \sqrt{2\pi \frac{(ABC)^{1/3}}{m}} \tag{1}$$

for planar molecules

$$\bar{R} = \sqrt{\frac{(AB)^{1/2}}{m}} \tag{2}$$

In this study, $\bar{R}$ is expressed in units of Angstroms.

Thompson noted that different classes of hydrocarbons exhibited a smooth behavior on a plot of the acentric factor vs. the radius of gyration. However, Figure 1 shows that lines representing different homologous series of nonpolar fluids are all really quite close to each other. The points for the monoatomic gases, the nonpolar diatomics, the normal paraffins, the branched paraffins, the olefins, the naphthenes, and the aromatics all fall on a reasonably smooth curve. Consequently, for nonpolar materials, correlations based on $\bar{R}$ as the third parameter should, on an overall basis, be at least as successful as those based on ω. We are not attempting here to obtain a parameter for normal fluids that is superior to the acentric factor. Rather, we are seeking a parameter that can characterize size-shape effects and allow separation of these effects from polarity effects.

The Thompson radius of gyration $\bar{R}$ thus appears to be an appropriate parameter to account for size-shape effects. There are several advantages in using the radius of gyration as the third parameter. Firstly, $\bar{R}$ is defined from considerations of molecular structure alone and is unaffected by polarity. Secondly, it is a fundamental parameter; whereas other common third parameters require direct experimental information and values of the critical constants for their definition, $\bar{R}$ can be calculated from a knowledge of bond angles and bond lengths. Finally, the moments of inertia, in terms of which the radius of gyration is defined, have long been used in classical physics to characterize the distribution of mass about the center of gravity of a system.

Definitions of the fourth parameter have usually been based on some sort of a deviation in terms of the vapor pressure behavior. This is not surprising, since the vapor pressure is sensitive to the forces acting both in the liquid and vapor phases. In this study, however, deviations from some well-understood quantity other than the vapor pressure were sought. The second virial coefficient, which is directly related to the intermolecular pair potential, afforded such a quantity.

The second virial coefficient provides a measure of the departure from ideal gas behavior arising from two-body interactions and is highly sensitive to both size-shape effects and polarity effects. Also, there is a vast amount of experimental and theoretical information on second virial coefficients that can be put to good use in defining a fourth parameter.

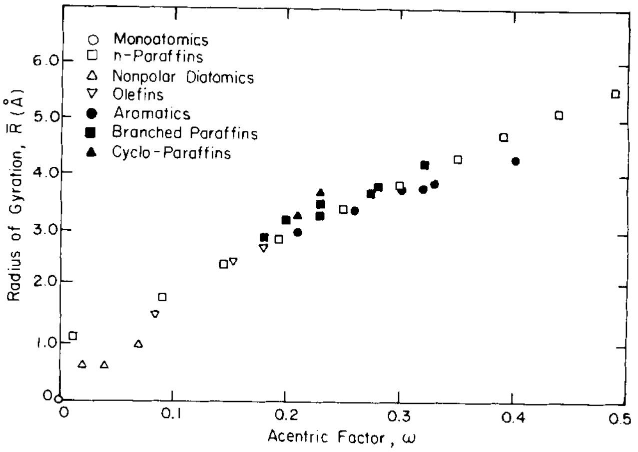

Fig. 1. Relationship between the radius of gyration and the acentric factor for normal fluids.

An obvious approach for defining a macroscopic fourth parameter is to study the difference between the actual behavior of a polar fluid and that of a nonpolar fluid having the same size and shape. The Pitzer-Tsonopoulos equation (Tsonopoulos, 1974) gives an accurate representation of the second virial coefficients of simple fluids:

$$B^*_{\substack{\text{simple}\\\text{fluid}}} = \left(\frac{BP_c}{RT_c}\right)_{\substack{\text{simple}\\\text{fluid}}} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \tag{3}$$

An equation for the size-shape contribution to the second virial coefficient was obtained by fitting the difference between the experimental reduced second virial coefficient (for thirty hydrocarbons) and that predicted by Equation (3). After various functional forms involving $\bar{R}$ and T_r were tried, the following equation was chosen:

$$B^*_{\substack{\text{size-shape}\\\text{correction}}} = \left(\frac{BP_c}{RT_c}\right)_{\substack{\text{size-shape}\\\text{correction}}} = \left(-0.00787 + \frac{0.0812}{T_r^2} - \frac{0.0646}{T_r^3}\right)\bar{R} - \left(\frac{0.00347}{T_r^2} - \frac{0.000149}{T_r^7}\right)\bar{R}^2 \tag{4}$$

The familiar Pitzer correlations using the acentric factor ω as the third parameter are linear in ω. On the other hand, Equation (4) contains terms in both $\bar{R}$ and $\bar{R}^2$. This is to be expected, since Figure 1 shows that the radius of gyration is not a linear function of the acentric factor.

The reduced second virial coefficients of nonpolar fluids may then be represented by the sum of $B^*_{\substack{\text{simple}\\\text{fluid}}}$ and $B^*_{\substack{\text{size-shape}\\\text{correction}}}$ given by Equations (3) and (4), respectively. Table 1 compares the proposed equation with the Pitzer-Tsonopoulos equation (Tsonopoulos, 1974) for accuracy in predicting second virial coefficients of hydrocarbons. The proposed equation, with the radius of gyration $\bar{R}$ used as the third parameter, is equivalent to the Pitzer-Tsonopoulos equation using the acentric factor ω. Hayden and O'Connell (1975) have also used the radius of gyration as a size-shape indicator in their correlation for second virial coefficients. The success of $\bar{R}$ in these correlations confirms that $\bar{R}$ is a viable size-shape parameter.

TABLE 1. COMPARISON OF THE PROPOSED EQUATION WITH THE PITZER-TSONOPOULOS EQUATION FOR PREDICTING SECOND VIRIAL COEFFICIENTS OF HYDROCARBONS*

	Deviations,† (cm^3 $mole^{-1}$) Avg	Bias	RMS
Proposed equation	26.1	−0.2	43.0
Pitzer-Tsonopoulos equation	28.7	−11.0	46.5

* The test data set comprised 512 experimental points representing 30 hydrocarbons.

† Avg = $\Sigma|B_{calc} - B_{expt}|/n$, Bias = $\Sigma(B_{calc} - B_{expt})/n$, RMS = $\sqrt{\Sigma(B_{calc} - B_{expt})^2/n}$ n is the number of points.

The term normal fluid was defined by Pitzer in terms of the acentric factor. This definition is no longer appropriate when the radius of gyration is the third parameter. A new classification will therefore be introduced. Hereafter, all compounds whose second virial coefficient behavior can be represented correctly by the sum of Equations (3) and (4) will be called standard fluids. Thus

$$B^*_{\text{standard}} = \underset{\substack{\text{fluid} \\ \text{[from Equation (3)]}}}{B^*_{\text{simple}}} + \underset{\substack{\text{correction} \\ \text{[from Equation (4)]}}}{B^*_{\text{size-shape}}} \qquad (5)$$

Typically, standard fluid would include all monoatomic fluids (except the quantum fluids), nonpolar diatomics, nonpolar and slightly polar hydrocarbons, and several slightly polar organic compounds. In general, a comparison of Equation (5) against experimental data will be required to classify a fluid. The reliability of experimental virial coefficient data varies quite widely. As a general rule, if Equation (5) reproduces all experimental data at reduced temperatures lower than 0.75 with less than 5% deviation, the fluid may be regarded as standard. The 5% value is somewhat arbitrary and will have to be increased with increasing uncertainty in the experimental data. The restriction of $T_r < 0.75$ is necessary because polarity effects are often quite small at higher temperatures.

At low temperatures, the second virial coefficients of polar compounds are more negative than predicted by Equation (5). Also, the difference between the observed second virial coefficient and that predicted by the standard fluid equation attains large values at low temperatures.

Close examination of second virial coefficient behavior of several compounds indicated that the quantity

$$[-\Delta B^* = -(B^*_{\text{total}} - B^*_{\text{standard}})]_{T_r} \qquad (6)$$

would be a good indication of the effects of polarity on the second virial coefficient. Since the second virial coefficient is closely related to the intermolecular potential function, $\Delta B^*|_{T_r}$ can also be expected to be an effective macroscopic indicator of the gross effects of polar forces on other physical properties of the fluid.

At high temperatures $-\Delta B^*$ is small, while at very low temperatures reliable experimental data are scarce. A reduced temperature of 0.6 appears to be a good compromise for the defining point. The fourth parameter, denoted by Φ, is then formally defined as

$$\Phi = -[\Delta B^*]_{T_r=0.6} = -[B^*_{\text{total}} - B^*_{\text{standard}}]_{T_r=0.6} \qquad (7)$$

By definition, Φ is zero for fluids exhibiting standard behavior. B^*_{total} would typically be an experimental value, and B^*_{standard} can be calculated from Equation (5).

TABLE 2. VALUES OF $\bar{R}$ AND Φ

Compound name	$\bar{R}$(Å)	Φ
Acetylenes		
Ethyne	1.094	0.439(a)
Propyne	1.886	0.133(a)
1-butyne	2.713	0
Aromatics		
Benzene	3.004	0
Methylbenzene	3.443	0.105
Ethylbenzene	3.821	0.101
1,2-dimethylbenzene	3.789	0.229
1,3-dimethylbenzene	3.897	0.329
1,4-dimethylbenzene	3.796	0.308
Isopropylbenzene	4.187	0.199
1-methyl-2-ethylbenzene	4.130	0.049(a)
1-methyl-3-ethylbenzene	4.285	0(a)
1-methyl-4-ethylbenzene	4.166	0.066(a)
1,2,3-trimethylbenzene	4.100	0.179(a)
1,2,4-trimethylbenzene	4.168	0.152(a)
1,3,5-trimethylbenzene	4.341	0.127(a)
Halogenated compounds		
Fluoromethane	1.419	0.867(a)
Trifluoromethane	2.319	0.250
Tetrafluoromethane	2.635	0
Fluoroethane	2.176	0.359(b)
1,1-difluoroethane	2.498	0.425(a)
1,1,1-trifluoroethane	2.672	0(a)
Perfluoroethane	3.380	0
Perfluoro-*n*-butane	4.443	0
Perfluoro-*n*-hexane	5.521	0
Perfluoro-*n*-heptane	6.022	0
Perfluorocyclohexane	4.683	0
Perfluoroethene	3.150	0
Fluorobenzene	3.345	0.040
Perfluorobenzene	4.658	0.323(a)
Fluorodichloromethane	2.880	0
Difluorochloromethane	2.569	0.119
Difluorodichloromethane	3.026	0
Trifluorochloromethane	2.810	0
Fluorotrichloromethane	3.304	0
Chloromethane	1.450	0.436(a)
Dichloromethane	2.342	0.050
Trichloromethane	3.178	0
Tetrachloromethane	3.458	0
Chloroethane	2.281	0.396
1,1-dichloroethane	2.995	0.151
1,2-dichloroethane	2.851	0.071
1,1,1-trichloroethane	3.357	0.229
Chloroethene	2.122	0(b)
cis-1,2-dichloroethene	3.013	0.195
trans-1,2-dichloroethene	3.013	0.041
Trichloroethene	3.759	0.061
Bromomethane	1.180	0.348
Bromoethane	1.988	0
Iodomethane	1.046	0.118
Ethers		
Dimethyl ether	2.127	0.460
Methyl ethyl ether	2.641	0.255(c)
Diethyl ether	3.139	0.157(c)
Ethyl propyl ether	3.547	0.129(c)
Diisopropyl ether	3.681	0.154(c)
Vinyl ethyl ether	2.990	0.200(c)
Ethylene oxide	1.901	0.422

TABLE 2. (cont'd.)

Compound name	$\overline{R}$(Å)	Φ
Alcohols, phenol, and water		
Methanol	1.536	2.146
Ethanol	2.250	2.226
1-propanol	2.736	1.431
Water	0.615	1.220
2-propanol	2.726	1.696
2-Methyl-1-propanol	3.182	1.530(c)
2-Methyl-2-propanol	3.019	1.749(c)
1-butanol	3.225	0.611(a)
2-butanol	3.151	1.349
Phenol	3.550	0.634
Ketones		
Acetone	2.740	0.966
Methyl ethyl ketone	3.139	0.557
Methyl-n-propyl ketone	3.627	0.797
Methyl isopropyl ketone	3.415	0.421
Diethyl ketone	3.482	0.558
Methyl isobutyl ketone	3.572	0.925
Esters		
Methyl formate	2.360	0.683
Ethyl formate	2.870	0.335
Propyl formate	3.419	0.260
Methyl acetate	2.862	0.630
Ethyl acetate	3.348	0.454
Propyl acetate	3.778	0.425
Methyl propionate	3.304	0.454
Ethyl propionate	3.712	0.386
Sulfides and thiols		
Dimethyl sulfide	2.372	0.077
Methyl ethyl sulfide	2.809	0.559
Diethyl sulfide	3.207	0.139
Methyl propyl sulfide	3.317	0.113(d)
Methyl isopropyl sulfide	3.236	0(d)
Methanethiol	1.611	0.197(a)
Ethanethiol	2.341	0.094
2-methyl-2-propanethiol	3.110	0
1-pentanethiol	3.791	0.097
Amines and other nitrogen compounds		
Hydrogen cyanide	0.650	2.065(a)
Acetonitrile	1.821	3.008
Monomethylamine	1.662	0.903
Dimethylamine	2.264	0.552
Trimethylamine	2.736	0.153
Ethylamine	2.309	0.660
Diethylamine	3.161	0.197
Propylamine	2.789	0.452
Nitromethane	2.306	1.398
Inorganic compounds		
Nitric oxide	0.530	0.454
Nitrous oxide	1.191	0.231(a)
Carbon monoxide	0.558	0
Carbon dioxide	0.992	0.152(a)
Sulfur dioxide	1.674	0.512
Hydrogen sulfide	0.638	0.301(b)
Carbon disulfide	1.424	0.074
Ammonia	0.853	0.917
Boron trifluoride	2.356	0(a)
Boron trichloride	3.279	0
Cyanogen	1.423	0

TABLE 2. (cont'd.)

Note: Φ = 0 for all hydrocarbons (except acetylenes and alkylated aromatics) and for monatomic and diatomic molecules. The $\overline{R}$ values for these compounds are listed in Reid et al. (1977), except that in the present work $\overline{R}$ was set equal to zero for the monatomic molecules.

(a) Calculated on basis of Thermodynamic Research Center Tables (1974).

(b) Calculated on basis of correlation of Hayden and O'Connell (1975).

(c) Calculated on basis of correlation of Tsonopoulos (1974).

(d) Calculated on basis of correlation of Nothnagel et al. (1973).

To obtain Φ, the second virial coefficient must be known at the exact reduced temperature of 0.6. When the available data spanned this temperature, a simple graphical interpolation to $T_r = 0.6$ was usually sufficient. The correlation of Nothnagel et al. (1973) also provided an excellent method to interpolate existing data. When data had to be extrapolated, the Hayden-O'Connell (1975) correlation, or the Pitzer-Tsonopoulos (Tsonopoulos, 1974) correlation, was used. In some instances, these two correlations were also used to predict Φ for compounds with no available experimental data. Values of Φ for a number of nonstandard fluids were thus obtained or estimated. Literature values of second virial coefficients of polar fluids often vary by as much as ±100 cm^3 mole^{-1}. In such cases, the value of Φ could change significantly, depending on which value one decides to accept. Table 2 is a list of recommended values of Φ.

Of course, this list can be extended and improved as more and better second virial coefficient data become available. Among the compounds studied, Φ ranges from zero for nonpolar compounds and compounds little influenced by polarity to 3.0 for acetonitrile where polar forces are dominant.

For reasons already indicated, the new parameter should be free from several of the drawbacks suffered by the previous fourth parameters. The main advantages of the parameter Φ are: it has a simple and clear definition that can be directly related to the physical nature of the molecule; unlike several of the existing parameters, Φ does not assume positive and negative values (all Φ's are positive); the Φ's have realistic magnitudes which generally can be explained through intuitive, physical arguments; and the manner in which the fourth parameter is defined permits one to build up a correlation in successive steps, that is, the simple fluid term, the size-shape correction, and the polarity correction.

The main drawback of the parameter is its dependence on experimental second virial coefficients. When such data are not readily available, one has to rely on available correlations which predict the necessary second virial coefficients from other parameters.

GENERALIZED CORRELATION FOR SECOND VIRIAL COEFFICIENTS

The ability of the newly defined parameter to correlate second virial coefficients over the complete temperature range was used as an initial test of its effectiveness. Equation (5) was therefore extended to also include polar fluids.

For nonstandard fluids, there will be, in addition to Equations (3) and (4), a further contribution to the second virial coefficient arising from polar effects. This quantity, represented by $B^*_{\substack{\text{polar}\\ \text{correction}}}$, has to be correlated in terms of the reduced temperature and the fourth parameter. To obtain such a correlation, data were collected from the compilation of Dymond and Smith (1969)

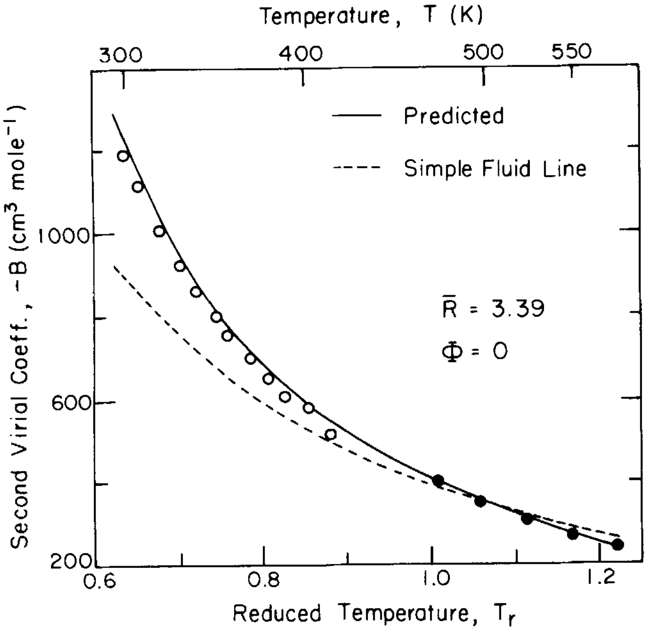

Fig. 2. The second virial coefficients of *n*-pentane. Experimental points: ● Beattie et al. (1952), ○ McGlashan and Potter (1962).

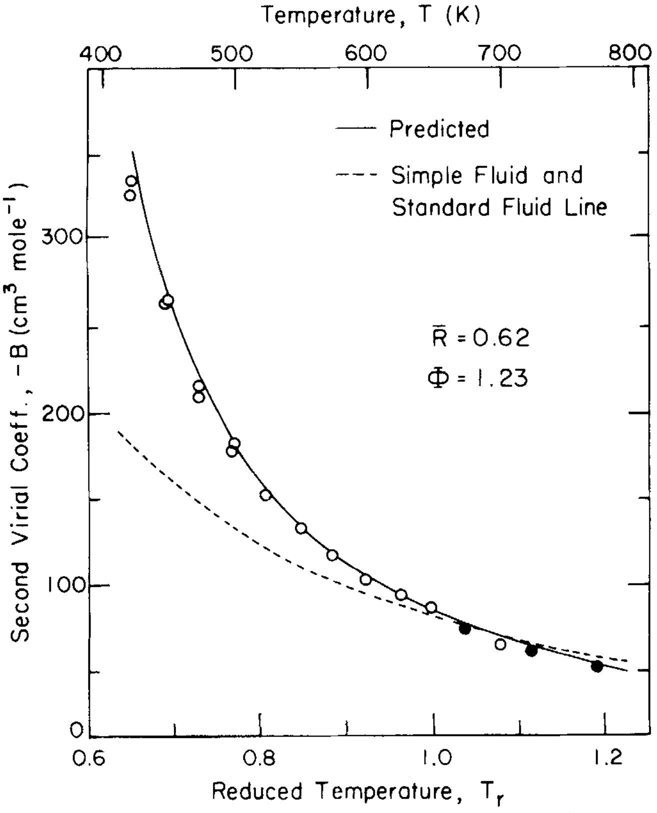

Fig. 4. The second virial coefficients of water. Experimental points: ○ Kell et al. (1968), ● Vukalovich et al. (1967).

for the pre 1968 period and from the literature for the subsequent period. Points that seemed to be inconsistent with the rest of the data, or points whose accuracy was doubtful, were eliminated. Finally, 760 experimental points representing 65 nonstandard fluids were selected.

The final generalized correlation will have the form

$$B^* = \frac{BP_c}{RT_c} = \left[B^*_{\substack{\text{simple}\\ \text{fluid}}} + B^*_{\substack{\text{size-shape}\\ \text{correction}}}\right] + \Delta B^*$$
$$= [B^*_{\text{standard}}] + \left[B^*_{\substack{\text{polar}\\ \text{correction}}}\right] \tag{8}$$

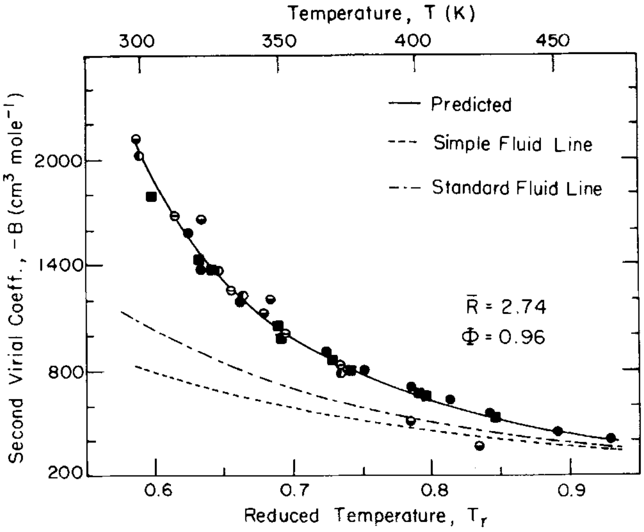

Fig. 3. The second virial coefficients of acetone. Experimental points: ○ Anderson et al. (1968), ■ Bottomley and Spurling (1967), ● Hajjar et al. (1969), ⊖ Knoebel and Edmister (1968). ○ Pennington and Kobe (1957).

Before we attempted a correlation for $B^*_{\substack{\text{polar}\\ \text{correction}}}$, its magnitude and the nature of its variation with temperature were studied. Details of this may be found elsewhere (see Tarakad, 1976).

An effective separation of size-shape effects from polarity effects would require that $B^*_{\substack{\text{polar}\\ \text{correction}}}$ is independent of $\bar{R}$. If this is true, compounds having identical Φ's will exhibit identical values of $B^*_{\substack{\text{polar}\\ \text{correction}}}$ at the same reduced temperature, regardless of their size and shape. A thorough study indicated that this is indeed the case (Tarakad, 1976). Further, plots of $B^*_{\substack{\text{polar}\\ \text{correction}}}$ as a function of T_r for several polar fluids indicated that an equation of the form

$$B^*_{\substack{\text{polar}\\ \text{correction}}} = \Delta B^* = \Phi \Sigma \left(\frac{l_i}{T_r{}^i}\right) \tag{9}$$

would be satisfactory. A statistical analysis showed that a single term

$$B^*_{\substack{\text{polar}\\ \text{correction}}} = \Delta B^* = \frac{\Phi l}{T_r{}^7} \tag{10}$$

could adequately fit the data. Here, l is the regression coefficient, yet to be determined.

To satisfy the definition of Φ in Equation (7), at a reduced temperature of 0.6, $-\Delta B^*$ should be equal to Φ. (Note that $\Delta B^* = B^*_{\text{total}} - B^*_{\text{standard}}$.) Also, from Equation (10), $\Delta B^* = \Phi l / T_r{}^7$. Hence, at $T_r = 0.6$, $l = -(0.6)^7 = -0.028$. Thus, without a formal curve fitting procedure, the equation for $B^*_{\substack{\text{polar}\\ \text{correction}}}$ is

$$B^*_{\substack{\text{polar}\\ \text{correction}}} = -(0.028/T_r{}^7)\Phi \tag{11}$$

An actual least-square regression gave the value of l in Equation (10) as −0.027, which is remarkably close to −0.028 calculated above.

The generalized equation for the second virial coefficient of any fluid, standard or nonstandard, now has the form

$$B^* = \frac{BP_c}{RT_c} = B^*_{\substack{\text{simple}\\ \text{fluid}}} \qquad + B^*_{\substack{\text{size-shape}\\ \text{correction}}}$$

$$\underset{\text{[From Equation (3)]}}{} \quad \underset{\text{[From Equation (4)]}}{} + \underset{\text{[From Equation (11)]}}{B^{*}_{\text{polar correction}}} \qquad (12)$$

Each of the contributions to the second virial coefficient can thus be calculated separately. Since the critical properties have not been corrected for polariy, the separation of the different effects is somewhat artificial. However, the procedure does provide a convenient means for visualizing the various contributions to the configurational properties. Figures 2 through 4 illustrate this for the second virial coefficients of three real fluids.

Figure 2 for *n*-pentane represents a standard fluid with significant size-shape effects. However, the polar contribution is zero. Figure 3 for acetone illustrates a case where the simple fluid term, the size-shape correction, and the polar correction are all significant. Figure 4 is for water. The highly polar nature of the water molecule causes it to behave quite contrary to what one might expect, considering its small size. Owing to the small value of $\overline{R}$ for water, the size-shape correction in the temperature range of the plot is too small to be distinguished. The entire contribution to the second virial coefficient results from the simple fluid term and the polar term. In all the above figures, the experimental points have also been indicated. Agreement between the predicted curves and the experimental values is excellent.

COMPARISON OF CORRELATIONS FOR SECOND VIRIAL COEFFICIENTS OF PURE COMPOUNDS

Four methods were evaluated in detail to study their relative merits in predicting second virial coefficients: the Pitzer-Tsonopoulos [Tsonopoulos (1974)] correlation, which corrects Equation (3) by adding a polarity term and an association term in addition to the acentricity term; the correlation of Nothanagel et al. (1973), which uses the chemical theory to explain imperfections of the vapor phase; the Hayden-O Connell (1975) method, which is a semitheoretical correlation in terms of T_c, P_c, $\overline{R}$, the dipole moment, and an association factor; and the proposed correlation developed in this work. The correlations of O'Connell and Prausnitz (1967), and Halm and Stiel (1971) are also applicable for predicting second virial coefficients of polar fluids. These have not been included in the present evaluation because the more recent correlations have been shown to be superior.

The four correlations evaluated here were tested against a common data set comprising of 1 550 experimental points for 122 compounds. Represented in this set were simple monoatomic and diatomic molecules, hydrocarbons, polar compounds, compounds exhibiting hydrogen bonding, and inorganic compounds. Details regarding the number of points, the temperature ranges, and literature sources for the data can be found elsewhere (Tarakad, 1976).

The results of the evaluation study are summarized in Table 3. For convenience in assessing the merits of each correlation for different groups of compounds, the results have been broken down into various classes. The average, bias, and root-mean-square deviations for each of the methods are given. Detailed results for each compound may be found in the supplementary material for this paper. To give the reader an idea of the magnitude of the second virial coefficient for each group of compounds in the data sets, the average absolute values of *B* are also given. The absolute deviation in the predicted value of the second virial coefficient is likely to be larger when the average value of *B* in the data set is large. The average *B* helps in estimating some sort of an average per-

TABLE 3. DEVIATIONS FROM EXPERIMENTAL DATA FOR SECOND VIRIAL COEFFICIENTS OF PURE COMPOUNDS: COMPARISON OF CORRELATIONS BASED ON CLASSES OF COMPOUNDS

Class of compounds	No. sys	No. pts	Avg* B	Pitzer-Tsonopoulos Avg	Pitzer-Tsonopoulos Bias	Pitzer-Tsonopoulos RMS	Nothnagel et al. Avg	Nothnagel et al. Bias	Nothnagel et al. RMS	Hayden-O'Connell Avg	Hayden-O'Connell Bias	Hayden-O'Connell RMS	Proposed method Avg	Proposed method Bias	Proposed method RMS
Monoatomics and nonpolar diatomics	9	97	93	8	4	20	10	—7	13	10	6	25	8	5	23
Hydrocarbons	34	548	723	26	0	48	26	6	40	27	12	51	25	—5	41
Halogen compounds	28	310	530	35	1	56	39	19	81	39	—10	63	35	—12	57
Ethers and ketones	11	93	1 118	46	1	73	81	—15	176	75	48	126	41	—7	63
Alcohols, phenol, and water	8	118	517	25	13	48	84	37	152	49	0	78	48	—37	70
Esters (acetates, formates and propionates)	7	108	1 056	—	—	—	28	10	37	42	23	56	26	6	35
Sulfides and thiols	7	27	1 275	—	—	—	54	28	79	121	82	185	55	—34	94
Amines	5	52	572	—	—	—	29	19	33	31	—10	39	24	17	28
Acetonitrile, nitromethane, hydrogen cyanide	3	33	2 423	151	—45	196	263	80	326	128	—10	176	128	—28	170
Inorganics	10	164	188	17	2	26	15	—1	24	28	—20	37	12	1	20
Overall	122	1 550	660	29	1	54	40	11	89	38	6	70	30	—7	53

Notes:
The number of systems, the number of points, and the average *B* given here are for the complete data set. For a specific correlation these numbers differ if that correlation can not predict all the compounds in a group. Overall, the Pitzer-Tsonopoulos method could predict 1 349 points representing 100 systems and the Nothnagel et al. method 1 498 points representing 111 systems. The other three correlations could predict all the points in the data set.

All deviations are in cm³ mole⁻¹.

* Avg *B* is defined as $\Sigma|B_{\text{expt}}|/n$.

cent deviation for each class of compounds.

The results in Table 3 show that the proposed method gives the lowest overall average deviation. The Pitzer-Tsonopoulos method is applicable to only 100 of the 122 compounds in the data sets, since the polarity and association constants are not available for the esters, the sulfur compounds, and some of the nitrogen compounds. Since application to polar materials was the major aspect of this study, the overall results from the Pitzer-Tsonopoulos correlation cannot be directly compared with the other results. By and large, the Nothnagel et al. correlation does not appear to be reliable when extrapolated far beyond the temperature range of the data used to obtain the parameter d of that correlation. However, for the applicable temperature range, the results are good.

The method of Hayden and O'Connell is fully generalized. In this evaluation, generalized group values rather than individual values were used for the Hayden-O'Connell association parameter. Significant improvement is obtained in some cases by using individual parameters, for example, for thiols. Even with the generalized parameters, however, the results are very good, though the overall deviations are somewhat larger than those for the proposed method.

These results indicate that the proposed generalized equation for second virial coefficients, besides being a test of the validity of the parameters, is a simple yet accurate method to predict imperfections in the gas phase.

MIXTURE VIRIAL COEFEICIENTS

One aim of the present work was to formulate an approach that could potentially be used to correlate properties of mixtures containing polar materials. The nature of forces involved in such mixtures is extremely complex, and it is usually necessary to rely on empirical or semiempirical methods to predict their behavior. The possibility of extending the present four-parameter CSP approach to mixtures was therefore explored. Correlation of the interaction cross virial coefficient offered an opportunity to do this. If the equations developed for the second virial coefficient of pure compounds could also be successfully used to predict the cross second virial coefficient, it would confirm the validity of these equations. In addition, it also provides a further test of the new parameter Φ and of the ability of the proposed approach to isolate size-shape effects from polarity effects.

The second virial coefficient of an n-component mixture is given exactly by

$$B_{\text{mixture}} = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \tag{13}$$

For a binary i-j mixture, Equation (13) reduces to

$$B_{\substack{\text{binary}\\ \text{mixture}}} = x_i^2 B_{ii} + 2x_i x_j B_{ij} + x_j^2 B_{jj} \tag{14}$$

B_{ii} and B_{jj} are the second virial coefficients of the pure compounds, and B_{ij} is the interaction cross virial coefficient. B_{ii} and B_{jj} may be calculated from Equation (12). The cross virial coefficient B_{ij} may also be obtained from Equation (12) by using appropriate mixing rules for the parameters $T_{c_{ij}}$, $P_{c_{ij}}$, $\overline{R}_{ij}$, and Φ_{ij}. A summary of the rules recommended to calculate these binary parameters is given below. [Equations (15), (16), and (19) are either taken or adapted from those given by Prausnitz (1969).]

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}}\,(1 - k_{ij}) \tag{15}$$

$$P_{c_{ij}} = \frac{4\,T_{c_{ij}}\left(\dfrac{P_{c_i} V_{c_i}}{T_{c_i}} + \dfrac{P_{c_j} V_{c_j}}{T_{c_j}}\right)}{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^3} \tag{16}$$

$$\overline{R}_{ij} = \left(\frac{\overline{R}_i + \overline{R}_j}{2}\right) \tag{17}$$

TABLE 4. DEVIATIONS FROM EXPERIMENTAL DATA FOR INTERACTION SECOND VIRIAL COEFFICIENTS OF MIXTURES: COMPARISON

Class of systems	No. sys	No. pts	Avg* B_{ij}	Tsonopoulos			Nothnagel et al.		
				Avg	Bias	RMS	Avg	Bias	RMS
Systems containing monoatomics and nonpolar diatomics only	15	128	21	3	−1	4	9	4	14
Binaries of hydrocarbons, perhalocarbons, with monoatomics and nonpolar diatomics	86	235	69	13	5	17	19	9	27
Binaries of hydrocarbons with hydrocarbons	35	199	373	20	−7	34	22	−13	34
Binaries of hydrocarbons with perhalocarbons	18	49	303	17	4	32	44	−31	62
Binaries of perhalocarbons with perhalocarbons	6	10	306	16	−3	22	24	16	31
Binaries of monoatomics and nonpolar diatomics with polar compounds	31	100	43	14	−8	21	26	18	39
Binaries of hydrocarbons, perhalocarbons, with polar compounds	67	197	407	54	14	101	85	−10	126
Polar-polar binaries (Association effects either absent or minimal)	16	47	381	32	−17	46	60	−48	83
Polar-polar binaries (Association effects are large)	17	68	896	80	64	134	57	3	92
Overall	291	1 033	265	25	3	56	37	−4	68

Notes:

The number of systems, the number of points, and the average B_{ij} given here are for the complete data set. For a specific correlation, these group. Overall, the Tsonopoulos method could predict 997 points representing 281 systems and the Nothnagel et al. and the Hayden-O'Connell were predicted by the proposed method.

All deviations are in cm³ mole⁻¹.

* Avg B_{ij} is defined as $\Sigma|B_{ij_{\text{expt}}}|/n$.

TABLE 5. POLAR-POLAR BINARY SYSTEMS WITH NEGLIGIBLE ASSOCIATION EFFECTS

System name	No. pts	Φ_{ij}*	Avg B_{ij}	Avg dev
Methylbenzene-carbon dioxide	2	0.128	235	25
Fluoromethane-carbon-dioxide	1	0.509	149	21
Chloromethane-bromomethane	3	0.392	432	4
Dichloromethane-chloroethane	3	0.223	542	173
Chloromethane-carbon disulfide	6	0.255	280	15
Trichloromethane-carbon dioxide	1	0.076	169	14
Chloroethane-bromomethane	2	0.372	417	111
Iodomethane-diethyl ether	4	0.137	604	80
Diethyl ether-ethylene oxide	4	0.289	541	50
Diethyl ether-acetone	4	0.561	680	35
Methanol-nitrous oxide	5	1.188	203	6
Acetone-carbon dioxide	1	0.559	129	64
Acetone-carbon disulfide	6	0.520	466	37
Methyl ethyl ketone-carbon dioxide	1	0.354	184	23
Nitromethane-carbon dioxide	1	0.775	188	39
Carbon monoxide-carbon dioxide	3	0.076	32	2
Overall for 16 systems	47		381	42

* Φ_{ij} calculated from Equation (18*a*).

TABLE 6. POLAR-POLAR BINARIES WITH LARGE ASSOCIATION EFFECTS

System name	No. pts	Φ_{ij}**	Avg B_{ij}	Avg dev
Acetone-benzene	8	1.40	844	84
Chloromethane-acetone	6	3.40	490	41
Dichloromethane-acetone	7	3.35	1 039	57
Trichloromethane-diethyl ether	6	3.10	1 076	52
Trichloromethane-methyl formate	3	1.50	1 033	102
Trichloromethane-propyl formate	4	0.86	1 503	10
Trichloromethane-methyl acetate	4	1.40	1 415	143
Trichloromethane-ethyl acetate	4	1.30	1 686	71
Trichloromethane-diethylamine	2	1.60	1 925	56
Dimethyl ether-sulfur dioxide	4	3.70	594	91
Methyl ethyl ether-sulfur dioxide	4	4.70	921	61
* Diethyl ether-carbon dioxide	1	2.64	491	—
Methanol-carbon dioxide	5	1.65	276	2
* Butanol-carbon dioxide	1	1.81	414	—
* Acetone nitromethane	1	1.87	2 679	—
† Water-nitrous oxide	4	(0)	138	34
† Water-carbon dioxide	4	(0)	147	38
Overall for 17 systems	68		896	57

Note: k_{ij}'s for all systems were calculated from Equation (19).

* These systems have only one experimental data point each. Since Φ_{ij} contains experimental information, the average deviation does not have much meaning for these systems.

† These binary pairs are known to form associated complexes in the vapor phase. A Φ_{ij} value of zero, however, seems to best fit the data for these systems. This discrepancy can be explained by the fact that the large quadrupole moments of CO_2 and N_2O significantly affect the critical properties of these compounds. This has been studied in detail by Hemmaplardh and King (1972).

** Φ_{ij} values calculated from experimental information.

$$\Phi_{ij} = \left(\frac{\Phi_i + \Phi_j}{2}\right) \quad \text{for polar-polar interactions} \qquad (18a)$$

$$= 0 \quad \text{for nonpolar-nonpolar and polar-nonpolar interactions.} \qquad (18b)$$

Where the *i-j* pair exhibits strong association effects, experimental information on the mixture virial coefficient is needed to get a satisfactory value of Φ_{ij}.

The interaction constant k_{ij} is calculated from the following guidelines:

1. For all mixtures where both the components fall into one of these categories (hydrocarbons, rare gases, permanent gases, carbon monoxide, perhalocarbons), the equation to be used is

$$k_{ij} = 1 - \frac{8\sqrt{V_{ci}V_{cj}}}{(V_{ci}^{1/3} + V_{cj}^{1/3})^3} \qquad (19)$$

2. For perhalocarbon-nonaromatic hydrocarbon mixtures, $k_{ij} = 0.1$, rather than as calculated above.
3. For binaries containing ethers, $k_{ij} = 0.1$.
4. For binaries containing ketones, $k_{ij} = 0.12$.
5. For binaries containing alcohols, $k_{ij} = 0.14$.
6. For binaries containing water, $k_{ij} = 0.35$.

In cases where the groups overlap (for example, ether-ketone), use the higher of the two possible values.

7. For all binaries containing carbon dioxide, $k_{ij} = 0.05\,(V_{ci}/V_{cCO_2})$

Where the system does not fall into any definite category given above, Equation (19) may be used to get an estimate for k_{ij}.

OF CORRELATIONS FOR DIFFERENT CLASSES OF MIXTURES

Hayden-O'Connell			Proposed method		
Avg	Bias	RMS	Avg	Bias	RMS
3	−2	5	3	−2	5
10	−1	14	15	−12	20
21	1	32	23	−5	36
26	6	49	16	5	29
14	−11	21	37	−37	48
16	−7	20	19	−13	25
45	9	67	42	7	65
40	−19	61	42	−15	63
68	−4	106	57	−9	80
24	0	46	25	−5	43

numbers differ if that correlation can not predict all the systems in a
methods 1 025 points representing 289 systems each. All the points

COMPARISON OF CORRELATIONS FOR INTERACTION SECOND VIRIAL COEFFICIENTS

The four methods evaluated for the second virial coefficients of pure compounds were also evaluated for the cross second virial coefficients. The test data set consisted of 1 033 experimental points representing 291 binary systems. Details regarding the temperature range, number of points, and literature sources are given elsewhere (Tarakad, 1976).

The results of the evaluation are summarized in Table 4. Again, to aid the reader in making rational generalizations, the error analysis has been broken down into various groupings. Similar results for each of the 291 systems are given in the supplement.

Table 5 lists results from the proposed correlation for polar-polar binaries with negligible association. For these systems, the interaction polarity parameter Φ_{ij} was calculated from Equation (18*a*). The results in this table indicate that when association effects are small, the arithmetic averaging of Φ_i and Φ_j does give an adequate representation of Φ_{ij}.

Table 6 lists result for systems with large association effects. Here, owing to the specific nature of the *i-j* interaction, a knowledge of Φ_i and Φ_j alone cannot accurately characterize the polarity effect on the interaction second virial coefficient. For these systems, Φ_{ij}'s were adjusted so as to best fit the available experimental data.

In evaluating the Tsonopoulos correlation, values of the binary interaction constant k_{ij} for most systems were taken from Chueh and Prausnitz (1967), and from Tsonopoulos (1974, 1975). These interaction coefficients were derived from experimental data, usually on the cross virial coefficient. When such experimental data were not available, Equation (19) was used. All the k_{ij} values required in evaluating the proposed method were obtained from the generalized rules given earlier. In most cases, this involved use of Equation (19) to estimate k_{ij}. The Nothnagel et al. correlation and the Hayden-O'Connell correlation also employ generalized rules for calculating the cross virial coefficients. In the Tsonopoulos correlation, if predicted values of k_{ij}'s had been used even when experimental ones were available, the deviations would have increased to some extent. Furthermore, the Tsonopoulos polarity and association parameters are not available for a number of polar substances. It is, therefore, not possible to make a fair comparison of the other correlations with the Tsonopoulos correlation for cross virial coefficients.

Of the remaining methods, that of Nothnagel et al. gave the maximum deviation from experimental data. The Hayden-O'Connell correlation and the proposed correlation appear to be equivalent, both in overall terms and on a group by group comparison. The proposed method, however, is easier to use than the Hayden-O'Connell method.

The results in Table 4 show that the proposed mixing rules are quite satisfactory for a very wide variety of mixtures. The mixture data sets contain a number of unlike binary pairs of widely different molecular shapes and complexities. That all these mixtures could be correlated with excellent results emphasizes again the usefulness of separating the size-shape and polarity effects.

The fourth parameter developed here is defined from a single piece of experimental information, namely, the second virial coefficient at $T_r = 0.6$. As such, caution is warranted when extending the use of the parameter to other properties, particularly the condensed phase properties. In a subsequent paper the applicability of the new set of parameters to correlate dense phase properties will be shown by the successful correlation of the configurational heat capacity of liquids.

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NOTATION

A, B, C = principal moments of inertia of a molecule
B = second virial coefficient
B^* = reduced second virial coefficient, $(= BP_c/RT_c)$
ΔB^* = $B^*_{\text{total}} - B^*_{\text{standard}}$
i, j = species i and j
k_{ij} = interaction constant
m = molecular mass
P_c = critical pressure
R = gas constant
$\overline{R}$ = radius of gyration, Å
T = absolute temperature
T_c = critical temperature
T_r = reduced temperature, $(= T/T_c)$
V_c = critical molar volume
x = mole fraction
Φ = fourth parameter developed in this work
ω = acentric factor

LITERATURE CITED

Anderson, L. N., A. P. Kudchadker, and P. T. Eubank, "Volumetric Properties of Gaseous Acetone," *J. Chem. Eng. Data*, **13**, 321 (1968).

Beattie, J. A., S. W. Levine, and D. R. Douslin, "The Compressibility of and an Equation of State for Gaseous Normal Pentane," *J. Am. Chem. Soc.*, **74**, 4778 (1952).

Bottomley, G. A., and T. H. Spurling, "Measurement of the Temperature Variation of Virial Coefficients," *Aust. J. Chem.*, **20**, 1789 (1967).

Chueh, P. L., and J. M. Prausnitz, "Vapor-Liquid Equilibrium At High Pressures. Vapor-Phase Fugacity Coefficients in Nonpolar and Quantum-Gas Mixtures," *Ind. Eng. Chem. Fundamentals*, **6**, 492 (1967).

Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Gases: A Critical Compilation*, Oxford University Press, London, England (1969).

Eubank, P. T., and J. M. Smith, "Thermodynamic Properties of Polar Gases in the Dilute Phase," *AIChE J.*, **8**, 117 (1962).

Hajjar, R. F., W. B. Kay, and G. F. Leverett, "Second Virial Coefficients of Eight Compounds in the Range 40° to 200°C," *J. Chem. Eng. Data*, **14**, 377, (1969).

Halm, R. L., and L. I. Stiel, "A Fourth Parameter for the Vapor Pressure and Entropy of Vaporization of Polar Fluids," *AIChE J.*, **13**, 351 (1967).

————, "Second Virial Coefficients of Polar Fluids and Mixtures," *ibid.*, **2**, 259 (1971).

Hayden, J. G., and J. P. O'Connell, "A Generalized Method for Predicting Second Virial Coefficients," *Ind. Eng. Chem. Process Design Develop.*, **14**, 209 (1975).

Hemmaplardh, B., and A. D. King, Jr., "Solubility of Methanol in Compressed Nitrogen, Argon, Methane, Ethylene, Ethane, Carbon Dioxide and Nitrous Oxide," *J. Phys. Chem.*, **76**, 2170 (1972).

Kell, G. S., G. E. McLaurin, and E. Whaley, "PVT Properties of Water. II. Virial Coefficients in the Range 150°-450°C without Independent Measurement of Vapor Volumes," *J. Chem. Phys.*, **48**, 3805 (1968).

Knoebel, D. H., and W. C. Edmister, "Second Virial Coefficients of Binary Mixtures of Benzene with Methanol, Ethanol, Acetone, and Diethyl Ether," *J. Chem. Eng. Data*, **13**, 312 (1968).

Leland, T. W., Jr., and P. S. Chappelear, "Corresponding States Principle: A Review of Current Theory and Practice," *Ind. Eng. Chem.*, **60**, No. 7, 15 (1968).

Lydersen, A. L., R. A. Greenkorn, and O. A. Hougen, "Generalized Thermodynamic Properties of Pure Fluids,"College of Engineering, University of Wisconsin Eng. Sta., Report. No. 4 (Oct., 1955).

McGlashan, M. L., and D. J. B. Potter, "An Apparatus for the Measurement of the Second Virial Coefficients of Vapours; the Second Virial Coefficients of Some n-alkanes and of Some Mixtures of n-alkanes," *Proc. Roy. Soc.*, **A267**, 478 (1962).

Nothnagel, K. H., D. S. Abrams, and J. M. Prausnitz, "Generalized Correlation for Fugacity Coefficients in Mixtures at Moderate Pressures," *Ind. Eng. Chem. Process Design Develop.*, **12**, 25 (1973).

O'Connell, J. P., and J. M. Prausnitz, "Empirical Correlation of Second Virial Coefficients for Vapor-Liquid Equilibrium Calculations," *ibid.*, **6**, 245 (1967).

Passut, C. A., "Development of a Four-Parameter Corresponding States Method for Polar Fluids," Ph.D. thesis, The Pennsylvania State Univ., University Park, Pa. (1973).

Pennington, R. E., and K. A. Kobe, "The Thermodynamic Properties of Acetone," *J. Am. Chem. Soc.*, 79, 300 (1957).

Pitzer, K. S., D. Z. Lippmann, R. F. Curl, Jr., G. M. Huggins, and D. E. Petersen, "The Volumetric and Thermodynamic Properties of Fluids-II; Compressibility Factor, Vapor Pressure and Entropy of Vaporization," *ibid.*, 77, 3433 (1955).

Prausnitz, J. M., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall, Englewood Cliffs, N.J. (1969).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Liquids and Gases*, McGraw-Hill, New York (1977).

Riedel, L., "Eine Nue Universelle Dampfruckformel," *Chemie. Ing. Tech.*, 26, 83 (1954).

Tarakad, R. R., "An Improved Corresponding States Method for Polar Fluids," Ph.D. thesis, The Pennsylvania State Univ., University Park, Pa. (1976).

Thermodynamics Research Center, "Selected Values of Properties of Chemical Compounds," Thermodynamics Research Center, College Station, Tex. (loose-leaf sheets, extant 1974).

Thompson, W. H., "A Molecular Association Factor for use in the Extended Theorem of Corresponding States," Ph.D. Thesis, The Pennsylvania State Univer., University Park, Pa. (1966).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, 20, 263 (1974).

———, "Second Virial Coefficients of Polar Haloalkanes," *ibid.*, 21, 827 (1975).

Vukalovich, M. P., M. S. Trakhtengerts, and G. A. Spiridonov, "An Equation of State for Steam at Temperatures above 500°C," *Thermal Eng.*, 14, No. 7, 86 (1967).

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Separation of Proteins Via Semicontinuous *p*H Parametric Pumping

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A semicontinuous *p*H parametric pump for separating proteins was experimentally investigated using the model system haemoglobin and albumin on a Sephadex ion exchanger. The pump considered had a center feed between an enriching column and a stripping column and was operated batchwise during upflow and continuously during downflow. Various factors affecting separations were examined. It was shown that parametric pumping is capable of separating proteins with high separation factors.

SCOPE

Parametric pumping is a cyclic separation process which involves reciprocating flow of a fluid phase over a solid phase in a packed bed and at the same time synchronous periodic variation of an intensive variable, such as temperature, pressure, or *p*H. The fluid phase contains the mixture to be separated, components of which distribute between the two phases. Change of the intensive variable displaces the equilibrium distribution of these components between phases and, in combination with the reciprocating flow, causes preferential movement of the distributing components toward one end of the bed, leading, under certain conditions, to complete removal of these components from the other end of the apparatus.

The name parametric pumping was applied to the separation process in 1966 by the inventor of the batch pump, the late R. H. Wilhelm of Princeton University. Since the time of that invention, much experimental and theoretical work has been done on thermal and heatless (or pressure cycling) parametric pumps. Included are the studies of Wilhelm et al. (1966, 1968), Jenczewski and Meyers (1968, 1970), Wilhelm and Sweed (1968), Pigford et al. (1969), Rolke and Wilhelm (1969), Aris (1969), Horn and Lin (1969), Gregory and Sweed (1970, 1971, 1972), Turnock and Kadlec (1971), Butts et al. (1972, 1973), Kowler and Kadlec (1972), Shendalman and Mitchell (1972), Weaver and Hamrin (1974), Sweed and Rigaudeau (1975), Camero and Sweed (1976), Grevillot and Tondeur (1976), and Chen et al. (1971, 1972, 1973, 1974*a*, 1974*b*, 1974*c*, 1975, 1976*a*, 1976*b*). By contrast, very little work has been done on *p*H parametric pumping. Sabadell and Sweed (1970) used *p*H changes to concentrate aqueous solutions of K^+ and Na^+ using ion exchange resins. Shaffer and Hamrin (1975) studied trypsin concentration by affinity chromatography and parametric pumping.

In the present work, it was desired to determine the feasibility of *p*H driven parametric pumping separation of a two-component protein mixture. The solid phase was an ion exchange medium, and *p*H levels were to be selected so that one protein was selectively removed from the mixture while not affecting the other.

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