Correlation of Second Virial Coefficients Through Potential Function Parameters

ROBERT G. KUNZ and ROBERT S. KAPNER

Rensselaer Polytechnic Institute, Troy, New York

An analytical technique based on the method of least squares has been developed to fit experimental second virial coefficients to the functional form derived from the Lennard-Jones (6-12) potential. Both the functional form and the normal equations of the least squares fit are rigorously derived. Because of the implicit, nonlinear dependence upon one of the adjustable parameters, a computer solution of the normal equations is required. Second virial coefficient data for a large number (60) of materials, including hydrocarbons, halides, alcohols, and cyclic compounds, have been extracted from published sources, carefully evaluated for consistency, and fitted to the Lennard-Jones potential function.

Force constants for these materials as determined from fitting the data in this uniform manner have been found to be related to structural parameters. The final correlation, with the potential well-depth related to critical temperature and the collision diameter calculated from a set of group contributions with appropriate corrections for polarity and/or association, produces average deviations between computed and experimental second virial coefficients of 10 to 15% or 100 cc./g.-mole, whichever is greater. In many cases the agreement is much better.

A LEAST SQUARES METHOD OF CALCULATING LENNARD-JONES FORCE CONSTANTS

When the integral characterizing the second virial coefficient for molecules whose intermolecular attractions and repulsions can be approximated by the Lennard-Jones (6-12) potential

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{1}$$

the expression

$$B(T) = b_0 B^*(T^*) = - b_0 \sum_{j=0}^{\infty} \frac{2^{j+1/2}}{4j!} \Gamma\left(\frac{2j-1}{4}\right) \left(\frac{1}{T^*}\right)^{\frac{2j+1}{4}} \tag{2}$$

where

$$T^* = kT/\epsilon \quad \text{and} \quad b_0 = \frac{2}{3} \pi \tilde{N} \sigma^3$$

results from the expansion of the exponential in the defining function

$$B(T) = 2\pi \tilde{N} \int_0^{\infty} \left[1 - \exp\left(- \frac{\phi(r)}{kT} \right) \right] r^2 \, dr \tag{3}$$

followed by term-by-term integration using the properties of the gamma function. B^* and the related function

$$B_1^* = T^* \frac{dB^*}{dT^*} = \sum_{j=0}^{\infty} \frac{2^{j+1/2}}{4j!} \frac{2j+1}{4} \Gamma\left(\frac{2j-1}{4}\right) \left(\frac{1}{T^*}\right)^{\frac{2j+1}{4}} \tag{4}$$

have been newly evaluated on an IBM 360/50 computer for use in the subsequent analysis. Both series, summed in double precision to the point where additional terms contribute a remainder less than 10^{-16}, are in excellent agreement with the earlier tabulations of Hirschfelder, Curtiss, and Bird (*16*).

To overcome the drawbacks of other techniques (*2, 16, 24, 25*), an analytical method for fitting second virial coefficients versus temperature to the functional form derived from the Lennard-Jones (6-12) potential has been developed using the method of least squares to minimize the residual function Q with respect to ϵ/k and b_0

$$Q = \sum_{i=1}^{n} (B_{i_{obs}} - B_{i_{calc}})^2 \tag{5}$$

where B_{obs} is an experimental observation and B_{calc} is given by Equation (2) abbreviated below:

$$B_{calc} = b_0 \, B^*(T^* \, (\epsilon/k, T)). \tag{2}$$

The condition that $(\partial Q/\partial b_0)_{\epsilon/\kappa} = 0$ leads to normal Equation (1).

$$\sum_{i=1}^{n} B_{i_{obs}} B_i^* = b_0 \sum_{i=1}^{n} (B_i^*)^2 \tag{6}$$

The condition that $(\partial Q/\partial \epsilon/k)_{b_0} = 0$ leads to normal Equation (2).

$$\sum_{i=1}^{n} B_{i_{obs}} T_i^* \frac{dB^*}{dT_i^*} = b_0 \sum_{i=1}^{n} B_i^* \, T_i^* \frac{dB_i^*}{dT_i^*} \tag{7}$$

The dependence on ϵ/k hidden in T^* is nonlinear, and explicit relationships for b_0 and ϵ/k cannot be obtained. However b_0 can be eliminated between Equations (6) and (7) to give Equation (8).

$$b_0 = \frac{\sum_{i=1}^{n} B_{i_{obs}} B_i^*}{\sum_{i=1}^{n} (B_i^*)^2} = \frac{\sum_{i=1}^{n} B_{i_{obs}} T_i^* \frac{dB_i^*}{dT_i^*}}{\sum_{i=1}^{n} B_i^* \, T_i^* \frac{dB_i^*}{dT_i^*}} \tag{8a, b}$$

Robert G. Kunz is with Esso Research and Engineering, Florham Park, New Jersey, Robert S. Kapner is with The Cooper Union, New York, New York.

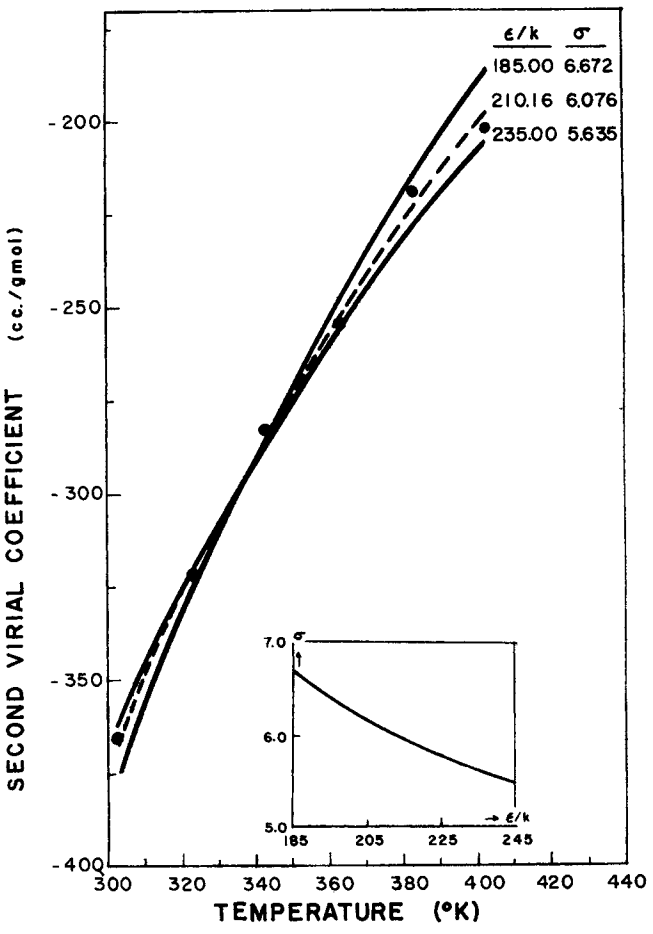

Fig. 1. Comparison of calculated second virial coefficients for cyclopropane using conjugate pairs of Lennard-Jones (6-12) force constants. ● Data from references 4 and 12. —— Best fit parameters (this work).

The solution is carried out by defining a function

$$f(\epsilon/k) = \frac{\sum_{i=1}^{n} B_{i_{obs}} B_i^*}{\sum_{i=1}^{n} (B_i^*)^2} - \frac{\sum_{i=1}^{n} B_{i_{obs}} T_i^* \frac{dB_i^*}{dT_i^*}}{\sum_{i=1}^{n} B_i^* T_i^* \frac{dB_i^*}{dT_i^*}} \quad (9)$$

formed by subtracting b_0 given by Equation (8*b*) from b_0 given by Equation (8*a*). When the correct choice of ϵ/k makes the two expressions for b_0 identical, $f(\epsilon/k)$ will equal zero. The problem reduces to finding a root by the standard interval-halving technique. Because this one-parameter search technique displays the functional form of the relationship among all of the variables, it is superior to what may be termed the brute force attack of direct numerical minimization of the sums of the squares of the deviations by a two-parameter search. Although proper application of both methods will produce equivalent results, more information is gained from this new approach. One very important piece of additional information is elucidated below.

It is probably better not to speak of the Lennard-Jones parameters of a substance, but rather of a spectrum of matched pairs, one of which is the absolute best based upon the single data set treated. Within limits, it is even possible to fit the same set of data with more than one set of parameters without sacrificing by too much the quality of the fit.

An example of such an adjustment is shown in Figure 1. As ϵ/k is arbitrarily increased or decreased from its optimal value for the example material, cyclopropane, the deviation of calculated second virial coefficients from observed values is kept small, provided a conjugate σ is used for each assumed ϵ/k (inset of Figure 1). Considering the change imposed on ϵ/k, about $\pm 12\%$, the errors produced in calculated virial coefficients are reasonably small.

Although this lack of uniqueness has been known for some time and the mathematical limitations imposed upon the mathematical form of the intermolecular potential function have been discussed (*7, 17*), up to the present a simple mathematical expression relating ϵ/k and σ has not been clear. However, it now follows directly from Equation (8*a*) which prescribes the method of calculating the best b_0, and from it the best σ, at a given, fixed ϵ/k. Besides showing simply how the force constants are interrelated, this functional form also predicts by how much σ will react to a change in ϵ/k.

THE DATA

Following the development of an analytical technique for determining rational force constants from second virial coefficient data, the method was applied to as many literature data as could be found. Second virial coefficients for over 60 materials were extracted from the literature and carefully checked for consistency on their own merit prior to evaluation with the Lennard-Jones potential. Force constants were then estimated for each of these materials. The second virial coefficients used for fitting are essentially the same as those contained in Dymond and Smith's compilation (*6*) published after the cut-off date of the work reported here. We did not have access to earlier privately circulated limited editions of this review. In the case of four compounds—$B(OCH_3)_3$, $CClF_3$, CCl_2F_2, CCl_3F—PVT data found in the literature were first reduced to second virial coefficient form (*22*) and then treated as described above. Force constants for the inert gases were not calculated for this study but used directly as reported (*9, 16, 34*).

A tabulation of the computed results would be too extensive to report here. Complete documentation of all original data treated, criteria used for selecting the best data from multiple sources, and the best fit force constants can be found elsewhere (*21*). Instead, only a sample is offered for ten representative materials to illustrate the results of the fitting process and subsequent improvement of the first estimates of ϵ/k and σ. Columns 1 and 2 of

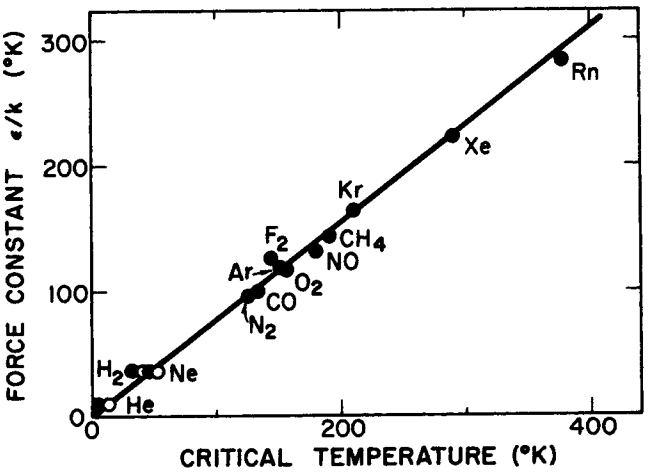

Fig. 2. ϵ/k versus T_c for inert gases and small nearly spherical molecules, type I molecules. ● Using unadjusted critical temperature. ○ Critical temperature for H_2, He, Ne, adjusted by Newton's method (28). $T_c = T_c + 8$.

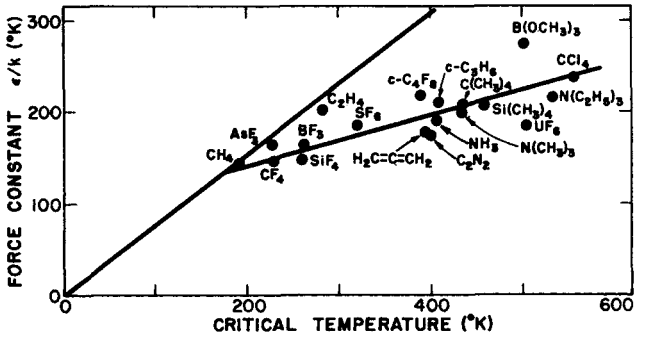

Fig. 3. ϵ/k versus T_c for symmetrical molecules, type II molecules.

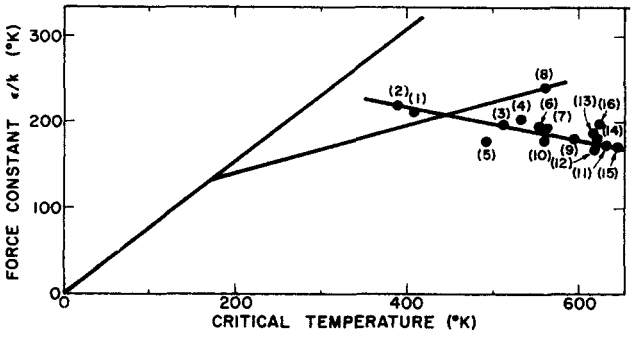

Fig. 4. ϵ/k versus T_c for cyclic molecules, type III molecules. *1*, Cyclopropane. *2*, Perfluorocyclobutane. *3*, Cyclopentane. *4*, Methylcyclopentane. *5*, 1, cis-3-Dimethylcyclopentane. *6*, Cyclohexane. *7*, Benzene. *8*, Fluorobenzene. *9*, Toluene. *10*, Benzo trifluoride. *11*, o-Xylene. *12*, *m*-Xylene. *p*-Xylene (two points). *13*. Pyridine. *14*, α-Picoline. *15*, β-Picoline. γ-Picoline (two points). *16*, 2,6-Lutidine.

Table 1, labeled ϵ/k_{raw} and σ_{raw}, are these first estimates. The next six columns are concerned with subsequent treatment of these first estimates to be described below. Although agreement is better in some cases and worse in others, in general root-mean-square deviations in Table 1 are of the same order of magnitude as those for each class of compounds shown in reference *29*.

CORRELATION OF LENNARD-JONES PARAMETERS BASED UPON STRUCTURAL CONSIDERATIONS

Several empirical relationships between ϵ/k and the critical temperatures of these materials were obtained, depending upon structural considerations, as depicted in Figures 2, 3, and 4. (In each of these figures, the ordinate is the best fit ϵ/k, that is, ϵ/k_{raw}.) However, the only usable relationship between b_0 and the analogous property of critical volume occurs for the inert gases.

TYPE I: INERTS AND RELATED MATERIALS

The inert gases and other small molecules approximating spherical shape and central force fields comprise type I. The relationships between their force constants and critical properties are particularly simple ones, discussed previously by Hirschfelder (*16*) and shown in Figure 2 ($\epsilon/k = 0.77T_c$) and Figure 5 ($b_0 = 0.75V_c$).

TYPE II: SYMMETRICAL MOLECULES

The structure of type II materials is more involved, and correspondingly the relationship of ϵ/k to T_c is more complex. Figure 3 depicts this relationship along with the line for the inert gases, shown again but without data points. This line and the one for the inert gases cross at methane, which is a member of both groups.

In the absence of a critical property correlation, an empirical approach to calculate σ from structure was adopted. A complete listing of group contribution values can be found in Table 2.

OTHER COMPACT MOLECULES: TYPE II NONPOLAR

The direct fits of other small organic molecules show deviations in various degrees from the type II line in Figure 3. However, when ϵ/k was adjusted to the T_c line

Table 1. Sample Results for Ten Materials. Lennard-Jones Force Constants Calculated from Virial Data and Subsequent Adjustment

Material	ϵ/k_{raw}	σ_{raw}	ϵ/k_{adj}	σ_{adj}	ϵ/k‡	σ_{adj}‡	σ_{calc}	σ_{final}	RMS deviation, cc./g.-mole	% RMS deviation (range)
Small, nearly spherical, nonpolar molecules										
CH_4	142.87	4.010	——	——	——	——	4.010	4.010	——	——
$C(CH_3)_4$	207.88	8.071	——	——	——	——	8.071	8.071	13	1 to 3
Unsymmetrical, nonpolar molecules										
C_3H_8	195.05	6.444	187.22	6.648	——	——	6.648	6.648	4	1 to 2
2-Methylbutane	197.40	9.123	212.91	8.642	——	——	8.546*	8.546	50	4 to 13
Polar materials										
CH_3Cl	211.41	6.177	200.29	6.416	——	——	5.835	6.355	13	3 to 28
$N(C_2H_5)_3$	214.70	10.116	233.77	9.599	——	——	9.278	9.319	95	6 to 10
Polar, associated (alcohols)										
iso-C_3H_7OH	154.93	12.786	226.40	8.932	231.28	7.681	7.541	7.760	36	3 to 9
iso-C_4H_9OH	159.85	13.556	237.38	9.182	242.56	8.636	8.582	8.720	75	5 to 12
Cyclic										
Cyclohexane	195.40	10.306	189.39	10.571	——	——	10.740	10.740	68	4 to 11
2,6-Lutidine	199.58	12.729	177.01	14.281	——	——	15.750	15.750	172	9 to 14

* Average of two methods of assembling molecule *i*) $(-CH_2-) + (-CH_3) + (-C_3H_7\text{–iso}) = 8.582$

ii) $(-\underset{|}{CH}) + 2(-CH_3) + (-C_2H_5) = 8.510$

† All critical properties used in calculations are from reference *19*; except isobutyl alcohol which is from reference *1*.
** All dipole moments used are from reference *35*.
‡ Obtained from a fit of Berthelot equation data.

and the matching σ was determined from the data, second virial coefficients fit nearly as well as they did previously. Moreover the adjusted σ's are more internally consistent. (This adjustment is depicted for selected type II molecules in columns 3 and 4 of Table 1, labeled ϵ/k_{adj} and σ_{adj}.) Additional group contributions were then added; the entries in the column labeled σ_{calc} in Table 1 are formed by summing these fragmentary group contributions.

OTHER COMPACT MOLECULES: TYPE II POLAR

The same procedure was followed for small polar molecules, the results for which are displayed for two sample polar materials in Table 1. For polar materials the calculated σ put together from elements of the set of group contribution values already evaluated from the nonpolar compounds is not large enough to agree with the σ calculated from the data, even after adjustment of ϵ/k.

A rational procedure was sought therefore to augment σ to account for polarity. A plot of σ^3 (adjusted) $- \sigma^3$ (group contribution calculated) against $\mu P_c^{1/2}/T_c$ turns out to be linear within the error of the data, passing through the origin as might be expected, and provides a means of correcting σ (Figure 6). The abscissa is the Stockmayer potential's third parameter in terms of macroscopic quantities. For all of these polar materials the deviation function was used to correct σ for polarity. These values are tabulated in column 8 of Table 1.

Although the reduced dipole moment is a theoretically sound correlating variable, increasing the collision diameters of polar molecules for this purpose is legitimate only below the Boyle temperature. Above that temperature, the present method would correct in the wrong direction. However, except for very high temperature work, this is of no substantial consequence.

COMPACT ALCOHOLS: POLAR, ASSOCIATED

Small aliphatic alcohols, C_1–C_4, present another degree of complexity. They are asymmetric, polar, and associated.

TABLE 2. CORRELATION SUMMARY

A. Calculation of Force Constants

$\epsilon/k = a + b\,T_c$, $b_o = cV_c$

Type of Material	a	b	c
I. Inert gases and small nearly spherical molecules	0	0.77	0.75
II. Symmetrical molecules	82.789	0.282	——
III. Cyclic molecules	286.06	−0.175	——

B. Collision Diameter Correction To Account for Polarity

where $\sigma_{corr} = (\sigma^3 + \Delta\sigma)^{1/3}$ $\Delta\sigma = 1.591 \times 10^3\ \mu P_c^{1/2}/T_c$

C. Correction to the Second Virial Coefficient Due to Vapor-Phase Association of Alcohols

$\Delta B = AT \exp(b/T)$

Alcohol	A, cc./(g.-mole)(°K.)	b, °K.
Methyl	2.729 (10^{-3})	2.210 (10^{+3})
Ethyl	6.649 (10^{-4})	2.753 (10^{+3})
Propyls and butyls	5.586 (10^{-5})	3.571 (10^{+3})

D. Set of Group Contribution Values

Structural element	Contribution	Structural element	Contribution	Structural element	Contribution
—B—	2.210	=C— (aromatic)	2.173	$-CH_3$	1.614
—C—	1.614	=CH (aromatic)	1.695	$-C_2H_5$	2.583
—C—H	2.699	—CH (cycloparaffin)	1.449	$-C_3H_7$ (normal)	3.624
H—C—H	3.420	$-CH_2$ (cycloparaffin)	1.790	$-C_3H_7$ (iso)	3.548
H—C—H (H above)	3.993	—N= (pyridine structure)	3.091	—Cl	1.842
H—C—H (H above and below)	4.010			—F	0.826
—N—	1.529			—OH	1.614
—Si—	2.345				

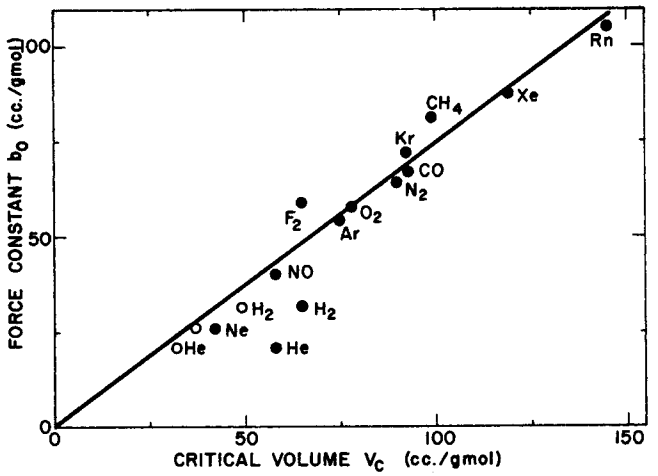

Fig. 5. b_o versus V_c for inert gases and small nearly spherical molecules, type I molecules. ● Using unadjusted critical volume. ○ Critical volumes calculated from gas law with critical temperatures and pressures adjusted by Newton's method (28). $T_c = T_c + 8$, $P_c = P_c + 8$.

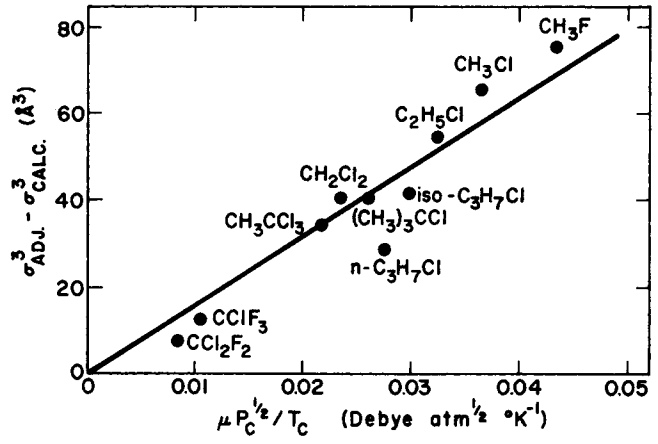

Fig. 6. Sigma deviation function versus reduced dipole moment.

An attempt to fit their second virial coefficients directly was unsatisfactory. The homomorph concept (29) was tried by evaluating ϵ/k from the T_c line using the critical temperature of those hydrocarbons of similar size, but the fits are equally poor.

However, by assuming that the nonpolar, nonassociated part of the second virial coefficient can be estimated by the Berthelot equation, a set of such values could be generated at the temperatures of the experimental data points and then fitted to the Lennard-Jones function. The values of ϵ/k for these direct fits (column 5, Table 1) are very close to those originally determined from the type II T_c relationship. And the σ's (column 6, Table 1) also agree well with group contribution calculations, using for the hydroxyl group the contribution previously obtained for a methyl group; in this case the idea of a homomorph works very well. The Berthelot equation, although a useful intermediate in the calculation, has now been completely discarded and has no effect upon the final nonpolar, nonassociated contribution to the second virial coefficient.

Polarity was accounted for using Figure 6, and association was considered through a relationship between the observed second virial coefficient for a gas containing dimers, the true monomer second virial coefficient, and the equilibrium constant of the dimerization (15, 23). From this, it can be shown that the residual ln $(\Delta B/T)$ plotted versus $1/T$ yields a straight line.

The difference $B_{L\text{-}J} - B_{exp} = \Delta B$ was evaluated and related to temperature (Figure 7). Discounting the presumably incorrect *n*-propyl alcohol data of Foz et al. (8), there are effectively three lines, of increasing steepness, but all values of the slope are in the neighborhood of the hydrogen bond energy in alcohols (~5 kcal./g.-mole) calculated by Pauling (30).

TYPE III: CYCLIC COMPOUNDS

Cyclic compounds lie on still a third line, as pictured in Figure 4 along with the lines for types I and II shown for comparison. Cyclopropane and perfluorocyclobutane lie close to the intersection of this line and the one through the second structural type in a manner similar to methane, previously discussed.

Following previous experience, each ϵ/k was adjusted to this line and a σ calculated. These calculated collision diameters are also amenable to the group contribution approach. However, the polar contribution where applicable is of minor importance, and no correction for polarity has been made.

SUMMARY OF ESTIMATING TECHNIQUE

A summary of the relationships developed for the estimation of Lennard-Jones (6-12) force constants is found in Table 2. For ϵ/k, the relationships are simple linear

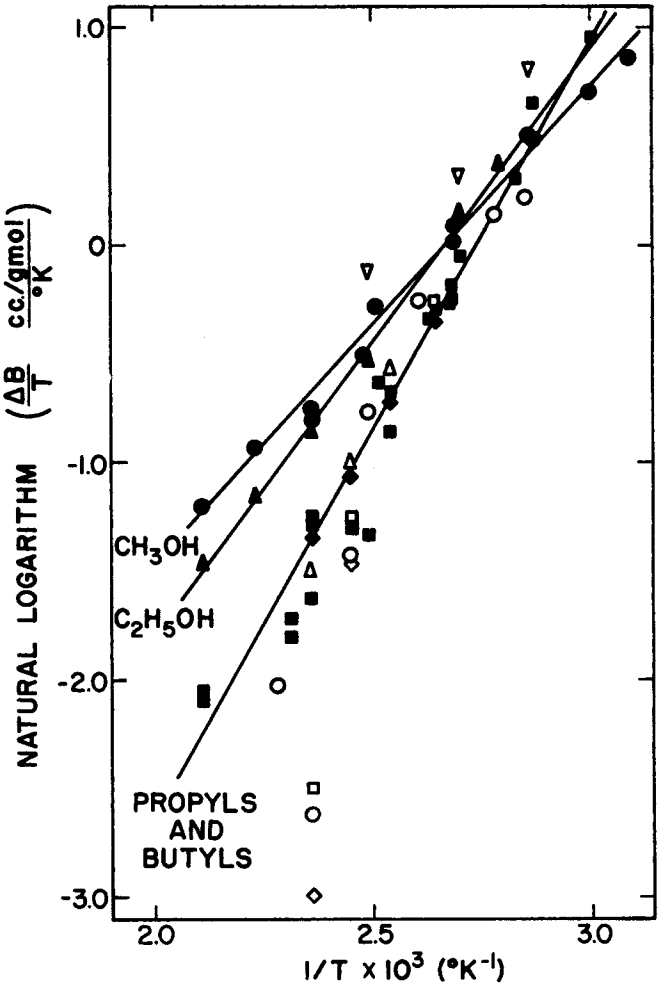

Fig. 7. ln $\left(\frac{\Delta B}{T}\right)$ versus $1/T$. ● CH_3OH. ■ iso-C_3H_7OH. □ sec-C_4H_9OH. ▲ C_2H_5OH. ○ *n*-C_4H_9OH. ◇ tert-C_4H_9OH. ◆ *n*-C_3H_7OH. △ iso-C_4H_9OH. ▽ *n*-C_3H_7OH data from reference (8).

TABLE 3. EXAMPLE OF SECOND VIRIAL COEFFICIENT ESTIMATION METHOD

Material: Isopropanol, $CH_3CH(OH)CH_3$ $T_c = 508.8°K.$, $P_c = 53.$ atm., $\mu = 1.69$ Debye

Calculation of ϵ/k

For type II molecules $\epsilon/k = 82.789 + 0.282\,T_c$
$= 226.40°K.$

Calculation of σ

$\sigma_{corr} = (\sigma^3 + \Delta\sigma)^{1/3}$

where σ = Σ (group contributions)
= (structural element) + (substituents)

$$= (-\overset{|}{\underset{|}{C}}H) + 2(-CH_3) + (-OH)$$

$= 2.699 + 2(1.614) + 1.614$
$= 7.541$ Å.

and $\Delta\sigma$ = polarity correction $= 1.591\,(10^3)\,\mu P_c^{1/2}/T_c$
$= 1.591\,(10^3)\,(1.69)\,(53.)^{1/2}/(508.8)$
$= 38.472$ Å.^{3}

then $\sigma_{corrected} = [(7.541)^3 + 38.472]^{1/3}$
$= 7.760$ Å.

With $\epsilon/k = 226.40°K.$ and $\sigma = 7.760$ Å., $B(T)$ is calculated using Equation (1). From each $B(T)$ so calculated a correction term ΔB, accounting for vapor-phase association, is subtracted, where $\Delta B = 5.586\ (10^{-5})T \exp(3571/T)$ for isopropanol. The resulting second virial coefficients, when plotted, produce the solid line in Figure 8.

functions of critical temperature with equation constants depending upon which of the three types of materials are involved.

For σ the relationships take the form of group contributions depending upon molecular structure. In assembling a molecule from its fragments, one starts with a central atom (or atoms for ring type structures) and then adds appropriate substituents as listed in Table 2. The numerical value of the estimated collision diameter is then the simple sum of the contributions to σ of all constituent fragments. To this must be added the correction for polarity calculated from the functional form shown in Table 2.

Where applicable, a final correction for association, to be made directly to the calculated second virial coefficient, is found from the exponential function shown in Table 2. An example of the full calculational procedure is displayed in Table 3 for a single specimen material, isopropyl alcohol. Figure 8 is the end product of this calculation, and is typical of the results.

EXTENSION OF THE TECHNIQUE

Encouraged by agreement of calculation and experiment where such a comparison is possible, it is logical to consider materials for which data are limited and the results highly speculative. However, because of a special type of structural similarity, one might reasonably expect a relationship to exist among the properties of compounds containing tetravalent silicon, germanium, tin, and lead, known collectively as organometallics, and the corresponding organic, called the analog of the metallic compounds.

In the table below are the force constants from the direct fit of data for two analog pairs.

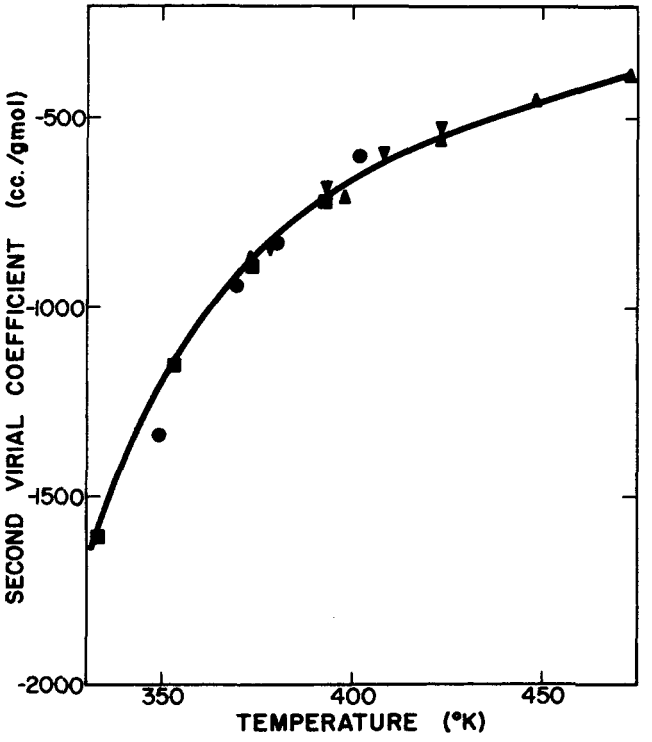

Fig. 8. iso-C_3H_7OH second virial coefficient versus temperature. ▼ Cox (3). ● Foz et al. (8). ■ Kretschmer and Wiebe (20). ▲ Moreland et al. (27). — Calculated (this work).

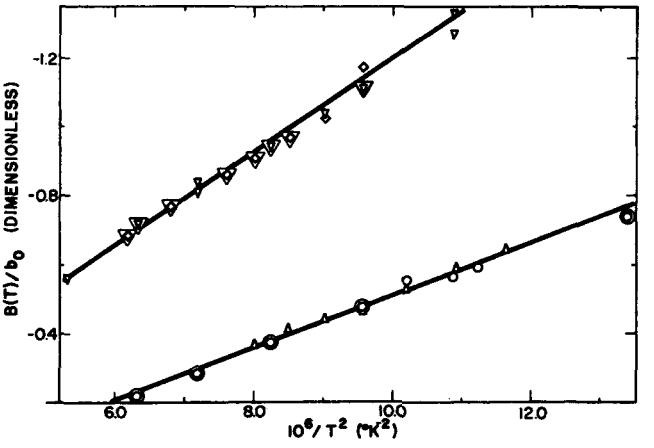

Fig. 9. Lennard-Jones reduced second virial coefficients versus square of reciprocal absolute temperature. ○ CF_4, $b_0 = 149.87$ cc./g.-mole. △ SiF_4, $b_0 = 227.16$ cc.g.-mole. ▽ $C(CH_3)_4$, $b_0 = 663.24$ cc./g.-mole. ◇ $Si(CH_3)_4$, $b_0 = 855.58$ cc./g.-mole.

Force Constants of Analog Pairs†

	ϵ/k, °K.	σ, Å.
CF_4	146.14	4.196
SiF_4	147.88	5.647
$C(CH_3)_4$	207.88	8.071
$Si(CH_3)_4$	207.10	8.786

† Force constants calculated with methods of this paper using data from references *5, 10* to *12, 25, 26.*

As expected, differing molecular sizes are reflected in the regular variation of the collision diameters. In addition, the potential well depth is essentially equal for each of the two pairs. These data therefore can be made to coincide at equal temperatures by dividing the virial coefficients of each set by the proper b_0, as shown in Figure 9.

For want of additional information, it is proposed that ϵ/k of a metallic compound be taken as equal to ϵ/k of the analog. For σ, additional group contribution values will be needed. The contribution for Si is available, but for other metal atoms, the complete lack of data makes the approach even more speculative. However, a preliminary attempt to derive group contribution values from a relationship to the covalent radius appears promising at this time.

DISCUSSION

There are two distinct problems concerning the relationship between second virial coefficients and the intermolecular potential. The first involves the use of a macroscopic property as a probe of the correct form of the potential (*14, 18, 31*). For this purpose, the second virial coefficient is perhaps the worse property to use, for measurements over an extremely wide temperature range are needed to differentiate among several likely candidates, even with perfect data (*18*). That is not our purpose here.

Rather we address the second problem, how a somehow suitably chosen form can be made to fit experimental data. Since second virial coefficients are relatively insensitive to the mathematical form of the potential, provided the proper adjustable parameters are employed, any reasonable potential can be made to fit data, at least over short temperature ranges. Therefore the popular and familiar Lennard-Jones (6-12) potential with force constants varying consistently from one material to another has been used as a correlation tool. The subsequent discussion centers on this potential and its force constants.

Since the Lennard-Jones potential is inadequate as a completely theoretical description of the forces between complex molecules, a word of warning is in order. Although the σ's summed by group contribution in conjunction with the ϵ/k's from T_c represent the values of the second virial coefficient within reasonable limits of accuracy, they should not be used to calculate other properties. For example, one should not expect to obtain reliable viscosity values for the complex molecules using the Lennard-Jones collision integrals and the values of ϵ/k and σ determined from second virial coefficient data. In addition, a comparison between the values of σ calculated here and the intermolecular separations in the low temperature liquid state reveals σ to be too large for the complex molecules.

Indeed, there is considerable evidence summarized by Rowlinson (*32, 33*) to indicate that the Lennard-Jones model does not correctly represent the true pair potential of even the inert gases in the dilute gas region for which it was developed. It is, however, quite adequate as an effective intermolecular potential in predicting physical properties, and a certain amount of consistency is encountered when the data for molecules similar in structure are compared on the basis of a common potential.

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NOTATION

a = arbitrary constant
B, $B(T)$ = second virial coefficient
B^* = reduced second virial coefficient = B/b_0
B_1^* = derivative function = $T^* \dfrac{dB^*}{dT^*}$
b = arbitrary constant
b_0 = collision volume = $\dfrac{2}{3}\pi\tilde{N}\sigma^3$
c = arbitrary constant
f = functional operator
$\tilde{N}$ = Avogadro's number
n = number of data points
P_c = critical pressure
T = absolute temperature
T_c = critical temperature
T^* = reduced temperature = kT/ϵ
V_c = critical molar volume

Greek Letters

Δ = denotes difference
ϵ/k = depth of potential well
μ = dipole moment
μ^* = reduced dipole moment = $\mu/(\epsilon\sigma^3)^{1/2}$
π = numerical constant
σ = collision diameter

Subscripts

adj = adjusted
calc = calculated
i = denotes the i^{th} data point
obs = observed
raw = as derived from experimental data, unadjusted

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Heat and Mass Transfer in the Vicinity of the Triple Interline of a Meniscus

P. C. WAYNER, JR. and C. L. COCCIO

Rensselaer Polytechnic Institute, Troy, New York

Effective experimental and theoretical techniques for studying the heat transfer characteristics of a stationary evaporating meniscus formed on a flat plate immersed in a pool of liquid were developed. Integral heat transfer data were obtained for the four systems: 304 stainless steel-water, 6061 aluminum-water, 304 stainless steel-methanol, and 6061 aluminum-methanol. High rates of heat transfer were obtained in the triple interline region with a stable meniscus. Detailed descriptions of the heat flux and temperature field were obtained for the stainless steel-water and stainless steel-methanol systems. The effect of the evaporation coefficient on the heat flux distribution was evaluated. The heat transfer process in the interline region proved to be more efficient than a simple conduction process in an evaporating liquid meniscus.

In engineering processes it is desirable to find ways of improving performance by increasing the effectiveness of the underlying phenomena. In some cases a large increase in performance can be achieved by utilizing previously neglected factors. In this vein, it is believed that the rates of heat and mass transfer in some applications can be greatly increased by the proper utilization of surface phenomena. In porous medium heat exchangers (for example, sweat cooled walls, vapor chamber fins, and suction nucleate boiling devices), a large area is covered by a thin evaporating liquid film which can be in the form of many menisci located at the exit of the capillaries, where the effects of surface phenomena are sig-

C. L. Coccio is with the General Electric Company, Schenectady, New York.