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An Empirical Correlation of Second Virial Coefficients

A new correlation of second virial coefficients of both polar and nonpolar systems is presented. It uses the Pitzer-Curl correlation for nonpolar compounds, but in a modified form. The second virial coefficient of nonhydrogen bonding compounds (ketones, acetaldehyde, acetonitrile, ethers) and weakly hydrogen bonding compounds (phenol) is fitted satisfactorily with only one additional parameter per compound, which is shown to be a strong function of the reduced dipole moment. Two parameters are needed for hydrogen bonding compounds (alcohols, water), but for alcohols, one parameter has been kept constant and the other expressed as a function of the reduced dipole moment. The extension of the correlation to mixtures is satisfactory, direct, and involves only one coefficient per binary.

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SCOPE

Vapor-phase nonideality should properly be taken into account in the analysis and correlation of vapor-liquid equilibria, especially at superatmospheric pressures. For reduced densities up to $1/4$ (roughly speaking, up to pressures of 15 atmospheres), the effect of vapor-phase imperfection can be reliably calculated using only the second virial coefficient B of the pure components and cross-coefficients for each binary (for example, see Prausnitz, 1969).

A very successful correlation of the B of nonpolar gases has been proposed by Pitzer and Curl (1957); see Equation (6). The soundness and reliability of the Pitzer-Curl correlation make its use as the basis of a correlation of the B of polar systems highly desirable. The objective of this study was to extend the Pitzer-Curl correlation to the following polar compounds of interest: ketones, aldehydes, acetonitrile, ethers, alcohols, phenol, and water.

A similar approach has been taken by O'Connell and Prausnitz (1967) and by Halm and Stiel (1971), but both of these correlations are lacking in several respects, including reliability; they are fully discussed in the Appendix.[*] The O'Connell-Prausnitz correlation has been used widely (for example, in two important monographs on computer calculations for vapor-liquid equilibria; Prausnitz et al., 1967; Renon et al., 1971); it is therefore used as the basis of comparison with the new correlation.

Another correlation of the B of polar system which, while not using the Pitzer-Curl correlation, is based on a similar idea to ours is that proposed by Black (1958); it is discussed in the Appendix. Other correlations that are not based on the Pitzer-Curl correlation and are not considered here are those of Kreglewski (1969), Nothnagel et al. (1973), O'Connell (1971), and of Polak and Lu (1972).

CONCLUSIONS AND SIGNIFICANCE

A modified form of the Pitzer-Curl correlation is used for nonpolar compounds. The modification mainly improves the fit at low reduced temperatures ($T_R < 0.75$) but is also shown to have some advantage at high reduced temperatures.

The actual acentric factor is used for all polar compounds, thus obviating the need of determining and using homomorphs (for example, ethane is methanol's homomorph). The second virial coefficient of the nonhydrogen bonding compounds investigated (ketones, acetaldehyde, acetonitrile, ethers), and even of the weakly hydrogen bonding phenol, is satisfactorily fitted with only one additional parameter per compound. A strong correlation is shown to exist between this parameter and the compound's reduced dipole moment μ_R.

Hydrogen bonding compounds (alcohols, water) require two parameters for the polar term, but all alcohol data are fitted with one parameter fixed; the other has a weak dependence on μ_R.

The polar contribution to B can be readily modified when new or better data become available—without invalidating the model. The form of the polar term is such that its value drops to zero at high reduced temperatures in accordance with theoretical and experimental evidence.

The new correlation is especially superior to the other correlations in its extension to mixtures. A characteristic binary constant is introduced, as it has already been done for nonpolar/nonpolar mixtures (Chueh and Prausnitz, 1967; Hiza and Duncan, 1970), to account for the deviation of the characteristic critical temperature T_{cij} from the geometric mean; see Equation (18).

The principal significance of this work is that the new B correlation makes possible the reliable calculation of fugacity coefficients and therefore improves the fit and extends the useful pressure range of vapor-liquid equilibrium data obtained at pressures of, roughly, 15 atmospheres or below. This application is the most sensitive as far as the second virial cross-coefficients are concerned.

THE VIRIAL EQUATION OF STATE

The virial equation is a power series in the reciprocal molar volume, $1/v$

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \ldots \tag{1}$$

where z is the compressibility factor. B is the second virial coefficient, and C is the third virial coefficient. For pure components, these coefficients are functions only of temperature. Equation (1) predicts z accurately up to one half the critical density. The third virial coefficient of polar gases, however, is rarely known. When the equation is truncated after the second virial coefficient term, it is reliable up to one fourth of the critical density, or roughly up to 15 atm. For most chemicals applications, the pressure is under 15 atm., and hence the second virial coefficient alone can account for vapor phase nonidealities.

Thus, the equation of state that will be used is

$$z = 1 + \frac{B}{v} \tag{2}*$$

For the evaluation of B from low-density P-v-T data, however, Equation (1) should be used, that is,

$$B \equiv \lim_{1/v \to 0} [v(z - 1)] \tag{3}$$

(If the limit to zero density is not taken, then the apparent B calculated will have a density dependence, as it will incorporate the contribution of C, etc.)

A great advantage of the virial equation is that it can be extended to mixtures without arbitrary assumptions. For a mixture of n components, the mixture second virial

coefficient B_M is given exactly by

$$B_M = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j B_{ij} \tag{4}$$

B_{ij} ($i \neq j$) is the second virial cross-coefficient; it is a function only of temperature like the pure-component coefficients (B_{ii} and B_{jj}).

Equations (2) and (4) can be used to calculate vapor-phase densities, fugacities, etc. if we know (1) the temperature dependence of the second virial coefficients and (2) how B_{ij} is related to B_{ii} and B_{jj}.

NONPOLAR GASES

Nonpolar gases, for example, inert gases and hydrocarbons, are characterized by a zero dipole moment. In addition to critical temperature T_c and critical pressure P_c, Pitzer and Curl (1957) had to use a third parameter for the correlation of B for nonpolar gases. This parameter is the acentric factor ω defined as (Pitzer et al., 1955)

$$\omega = -\log_{10}\left(\frac{P^\circ}{P_c}\right)_{T_R = 0.7} - 1.000 \tag{5}$$

Fluids with spherical molecules, for example, Ar, Kr, have a zero acentric factor; the quantum gases, for example, He, H_2, have negative ω's; and everything else has a positive ω.

The Pitzer-Curl correlation is the best available for second virial coefficients of nonpolar gases. In reduced form, it is (Pitzer and Curl, 1957)

$$\frac{BP_c}{RT_c} = f_{PC}^{(0)}(T_R) + \omega f_{PC}^{(1)}(T_R) \tag{6}$$

where

$$f_{PC}^{(0)}(T_R) = 0.1445 - 0.330/T_R$$
$$- 0.1385/T_R^2 - 0.0121/T_R^3 \tag{7}$$

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* This form is superior to the pressure-explicit form

$$z = 1 + BP/RT \tag{2a}$$

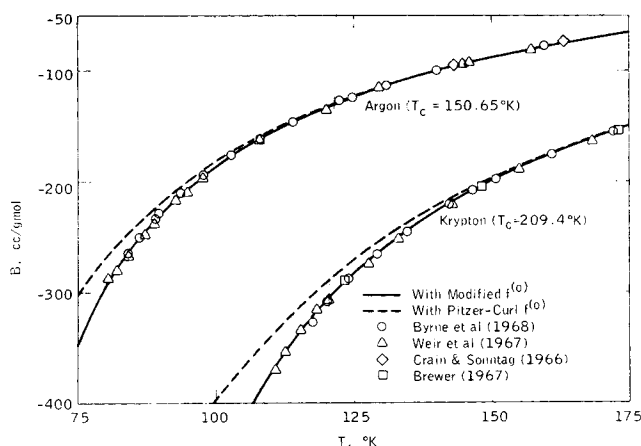for subcritical temperatures, but the reverse is true at $T_R > 1$.

Fig. 1. Second virial coefficient of gases with zero acentric factor.

$$f_{PC}^{(1)} (T_R) = 0.073 + 0.46/T_R$$
$$- 0.50/T_R^2 - 0.097/T_R^3 - 0.0073/T_R^8 \quad (8)$$

Pitzer and Curl determined the coefficients of $f_{PC}^{(0)}$ by fitting the B data for Ar, Kr, and Xe, which have zero acentric factor. The temperature range of the data used, however, was limited. Recent measurements on Ar and Kr (Brewer, 1967; Byrne et al., 1968; Crain and Sonntag, 1966; Weir et al., 1967) down to $T_R = 0.53$ have shown that $f_{PC}^{(0)}$ is unsatisfactory for $T_R < 0.75$; at $T_R = 0.53$, the error is $+ 10$ percent.

A slight modification to $f_{PC}^{(0)}$ makes it possible to fit all these data to within 1%; the modified $f^{(0)}$ is

$$f^{(0)}(T_R) = f_{PC}^{(0)} (T_R) - 0.000607/T_R^{8} \quad (9)$$

The improvement in the fit is clearly shown in Figure 1, where the most recent B data for Ar and Kr have been plotted along with the calculated values. $f^{(0)}$ and $f_{PC}^{(0)}$ are virtually identical for $T_R > 0.8$ (120°K for Ar; 168°K for Kr).

$f_{PC}^{(1)}$ can be checked against reliable B data for compounds with large acentric factors. Two such compounds are n-butane ($\omega = 0.200$) and n-octane ($\omega = 0.398$). Dymond and Smith (1969) have smoothed the data for n-butane, while for n-octane we used the data of Mc-Glashan and Potter (1962) and Connolly and Kandalic (1960). The comparison showed that $f_{PC}^{(1)}$ predicted results that were too positive at low temperatures (6% error at $T_R = 0.55$), and too negative at $0.8 \leqq T_R \leqq 1.0$ (2 to 4% errors). These errors are rather small, but they indicate the need for some adjustment. The modified $f^{(1)}$ has one term less than $f_{PC}^{(1)}$:

$$f^{(1)} (T_R) = 0.0637 + 0.331/T_R^2$$
$$- 0.423/T_R^3 - 0.008/T_R^8 \quad (10)$$

The differences between the Pitzer-Curl correlation and our modification are illustrated in Figure 2 for benzene ($\omega = 0.211$). The spread in the experimental data (Baxendale and Enüstün, 1951; Bottomley and Spurling, 1966; Connolly and Kandalic, 1960; Hajjar et al., 1969; Knoebel and Edmister, 1968; Zaalishvili and Belousova, 1964) is larger than the difference between the two correlations. [More negative and more positive data than those plotted

in Figure 2 have also been reported; see Dymond and Smith (1969).]

At high reduced temperature ($T_R > 1.5$), $f^{(1)}$ becomes progressively more negative than $f_{PC}^{(1)}$. Data are available for ethane ($\omega = 0.105$) up to $T_R = 1.67$ (Reamer et al., 1944). The results from the two correlations, which differ by 3 cc/gmol, bracket the experimental value. A better example is offered by carbon dioxide ($\omega = 0.225$), whose quadrupole moment has an entirely negligible effect at supercritical temperatures. B data are available up to $T_R = 2.87$ (MacCormack and Schneider, 1950; Vukalovich and Masalov, 1966) and the modified correlation is clearly superior to the Pitzer-Curl correlation, as shown in Figure 3.

POLAR GASES

Polar compounds are characterized by a nonzero dipole moment μ which expresses the effect of electrostatic forces between molecules. Polar compounds considered in this study are alcohols, phenols, water, ketones, aldehydes, ethers, and alkyl nitriles. The first three are hydrogen bonding compounds (a bond forms between the hydrogen atom attached to oxygen in one molecule with the oxygen atom of another molecule); this makes their behavior in the vapor different and more complex than that of non-hydrogen bonding compounds (ketones, etc.). These two broad classes of compounds will be treated separately.
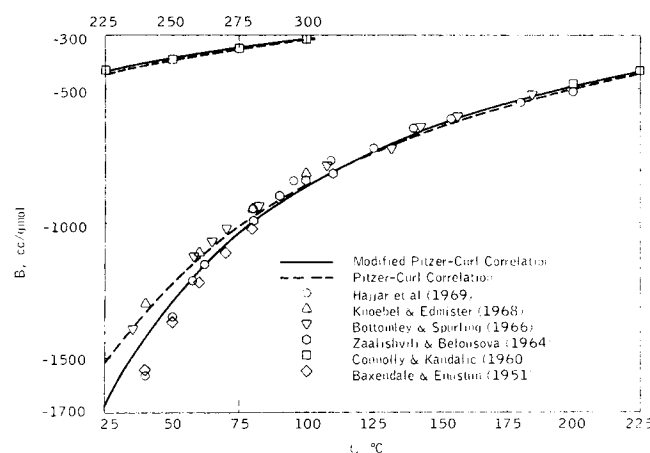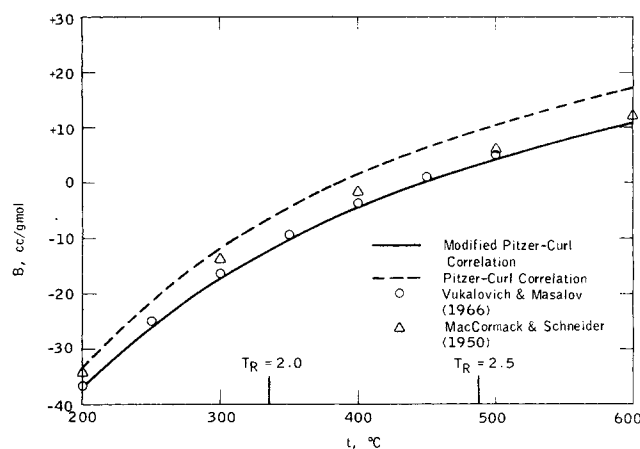

Fig. 2. Second virial coefficient of benzene.

Fig. 3. Second virial coefficient of carbon dioxide at high temperatures.

Nonhydrogen Bonding Compounds

The second virial coefficients of ketones, acetaldehyde, acetonitrile, and ethers were fitted very satisfactorily by adding a one-parameter term to the modified Pitzer-Curl correlation:

$$\frac{BP_c}{RT_c} = f^{(0)}(T_R) + \omega f^{(1)}(T_R) + f^{(2)}(T_R) \quad (11)$$

where the polar term is given by

$$f^{(2)}(T_R) = \frac{a}{T_R^6} \quad (12)$$

The second virial coefficient of polar compounds is more negative than that of nonpolar compounds (for the same T_R, ω); hence, $f^{(2)} < 0$, or $a < 0$. The contribution of $f^{(2)}$ to B diminishes rapidly with increasing temperature, in agreement with observed behavior. For $a = -0.01$, $f^{(2)} = -0.64$ at $T_R = 0.50$, but at $T_R = 1.5$ it is only $f^{(2)} = -0.0009$.

The results of fitting Equations (11) to (12) to B data for five ketones, acetaldehyde, acetonitrile, and three ethers are given in Table 1. The root mean square deviations of B are small, but the accuracy can be clearly illustrated only when B data for a given compound are available over a wide temperature range.

A sensitive check of the new correlation is provided by the extensive data for acetone reported since 1960, which

are plotted in Figure 4. [The data of Anderson et al. (1968), Kappallo et al. (1963), and Zaalishvili et al. (1960; 1964) differ from the other data in their temperature dependence and were not used in determining the value of a.] The new correlation gives a good fit. For comparison, we have also plotted the results from the O'Connell-Prausnitz correlation (1967), which is clearly poor at low and high temperatures. The discontinuity at 210°C ($T_R = 0.95$) is inherent in the correlation: at T_R
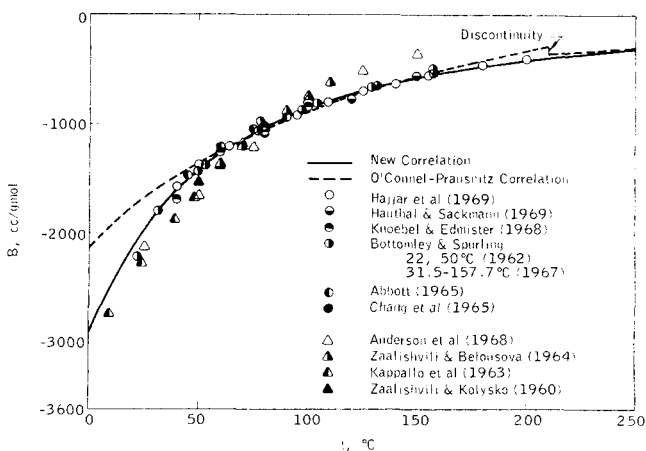

Fig. 4. Second virial coefficient of acetone.

TABLE 1. NONHYDROGEN BONDING POLAR COMPOUNDS

Compound	ω	$\mu_R{}^a$	a	Root mean square deviation of B, cc/gmol (no. points)	References[b]
Acetone	0.31	147.0	−0.03090	32.3 (36)	Abbott (1965); Bottomley and Spurling (1962; 1967); Chang et al. (1965); Hajjar et al. (1969); Hauthal and Sackmann (1969); Knoebel and Edmister (1968).
Methyl ethyl ketone	0.33	112.0	−0.02224	70.4[c] (19)	Chang et al. (1965); Hauthal and Sackmann (1969); Hofmann and Pfestorf (1968); Nickerson et al. (1961).
Methyl n-propyl ketone	0.34	90.0	−0.02277	8.4[d] (4)	Nickerson et al. (1961).
Diethyl ketone	0.35	87.4	−0.01686	66.3[e] (11)	Chang et al (1965); Hales et al. (1967); Hauthal and Sackmann (1969).
Methyl tert-butyl ketone	0.29	81.4	−0.01065	25.5 (10)	Hauthal and Sackmann (1969); Hofmann and Pfestorf (1968).
Acetaldehyde	0.314	188	−0.05081	33.8 (16)	Alexander and Lambert (1941); Prausnitz and Carter (1960).
Acetonitrile	0.323	250.4	−0.1198[f]	151[f] (23)	Lambert et al (1949); Prausnitz and Carter (1960).
Methyl ether	0.21	56.0	−0.01513	19.2 (14)	Cawood and Patterson (1933); Haworth and Sutton (1971); Kennedy et al. (1941); Osipiuk and Stryjek (1970); Tripp and Dunlap (1962).
Ethyl ether	0.282	22.6	−0.00202	50.3[g] (37)	Bottomley and Reeves (1958); Chevalier (1969); Knoebel and Edmister (1968); Lambert et al. (1949); Rätzsch and Bittrich (1965); Russell and Maass (1931); Stryjek and Kreglewski (1965); Zaalishvili and Kolysko (1960; 1962).
Isopropyl ether	0.34	14.5	−0.00089	31.8[h] (4)	Chevalier (1969).

[a] $\mu_R = 10^5\mu^2 P_c/T_c{}^2$; the units are Debyes^2-atm-°K^{-2}. Dipole moment data taken from McClellan (1963).

[b] Only those used in the regression analysis are listed.

[c] Most of the deviation is due to three widely scattered points at 41.5 to 60°C.

[d] The 61.7°C point was discarded because it is about 300 cc/gmol too negative. With it, the average deviation increases from 7.4 to 64.4 cc/gmol.

[e] Three of Chang's (1965) data are clearly inconsistent with all the rest; without them, the root mean square deviation drops to 29.7 cc/gmol for $a = -0.01873$.

[f] Including the 4 data points of Zaalishvili et al. (1971) makes $a = -0.1211$ and the root mean square deviation of B 156 cc/gmol.

[g] Removing the questionable references identified in the text drops the root mean square deviation to 23.4 cc/gmol for $a = -0.00246$.

[h] Root mean square deviation = 36.8 cc/gmol for $a = 0.0$ (i.e., no polar correction).

= 0.95 the polar corrections (analogous to $f^{(2)}$) are set equal to zero. More about this correlation can be found in the Appendix.

Figure 5 is a plot of experimental and calculated B values for acetaldehyde and acetonitrile. The new correlation is again shown to be most satisfactory, while the O'Connell-Prausnitz correlation leads to serious errors.

The new correlation is very satisfactory for methyl ether (maximum deviation is 42 cc/g-mol), but less so for ethyl ether. All available B data were used in determining the value of a; however, the results of Knoebel and Edmister (1968) and Rätzsch and Bittrich (1965) have too steep a temperature dependence, while those of Russell and Maass (1931) and Lambert et al. (1949) are consistently too positive. There is good agreement (less than 30 cc/g-mol difference) between the new correlation and that of O'Connell and Prausnitz.

Listed in Table 1 are values for the reduced dipole moment μ_R defined by

$$\mu_R = \frac{10^5 \mu^2 P_c}{T_c^2} \qquad (13)$$

O'Connell and Prausnitz (1967) introduced the factor 10^5 to make the μ_R values greater than unity (when μ is given in Debyes*, P_c in atmospheres, and T_c in degrees Kelvin). Eubank and Smith (1962) have shown that μ_R by itself is inadequate as a correlating parameter since the location and direction of the dipole moment are also important. It follows, therefore, that the polar contribution to B cannot be given for all polar compounds by a unique function of μ_R.

Figure 6 clearly demonstrates the diminishing importance of a, and hence of $f^{(2)}$, with decreasing μ_R. However, the reduced dipole moment is a satisfactory correlating parameter only when each family of compounds is considered separately.

In the case of ketones, a is best expressed as a linear function of μ_R:

$$a = -0.00020483 \ (\mu_R); \text{ketones} \qquad (14)$$

The predicted value of a for methyl isobutyl ketone is -0.016, with which B at $120°C$ is calculated to be -1590 cc/g-mol; the experimental value is -1580 cc/g-mol (Hauthal and Sackmann, 1969). With a values from Equation (14), it was possible to predict satisfactorily the B data of Hales et al. (1967) for methyl isopropyl ketone (average error of 122 cc/g-mol or 6.6%) and ethyl n-propyl ketone (average error of 19 cc/g-mol or 1.1%). Rough but useful values for the a of $C_3{}^+$ aldehydes and alkyl nitriles can be estimated from Figure 6.

There is an excellent linear relationship between ln $(-a)$ and ln (μ_R) for ethers:

$$\ln (-a) = -12.63147 + 2.09681 \ln (\mu_R); \text{ethers}$$
$$(15)$$

The value of $-a$ drops very rapidly with decreasing μ_R; the fit of the B data for isopropyl ether is nearly equally good when $a = 0.0$ (see Table 1). The predicted a values for methyl ethyl ether ($\mu_R = 33.7$) and ethyl n-propyl ether ($\mu_R = 17.2$) are, respectively, -0.0052 and -0.0013, but the limited available data (Osipiuk and Stryjek, 1970; Chevalier, 1969) lead to small positive values for a.

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* 1 Debye = 10^{-18} esu-cm. An extensive compilation of dipole moments is given by McClellan (1963).

Hydrogen Bonding Compounds

Molecules containing hydrogen linked to an electronegative atom (for example, O, N) tend to associate with each other by forming hydrogen bonds, that is, they dimerize. This is especially true of alcohols. Phenols associate in the liquid phase (Prausnitz, 1969), but their dimerization in the vapor (up to moderate densities) is much weaker than that of alcohols. Similarly, dimerization in water is limited (Tsonopoulos and Prausnitz, 1970; this reference treats the very strong dimerization of carboxylic acids).

The effect of dimerization is to make more complex the temperature dependence of the polar contribution to the second virial coefficient of dimerizing compounds: it is steeper at very low T_R ($\to 0.5$), but flatter at $T_R > 0.8$. The polar term of Equation (11) must now have two parameters:

$$f^{(2)} (T_R) = \frac{a}{T_R^6} - \frac{b}{T_R^8} \qquad (16)$$

Both a and b assume positive values. At low temperatures the last term predominates, while at high temperatures both terms become negligible.

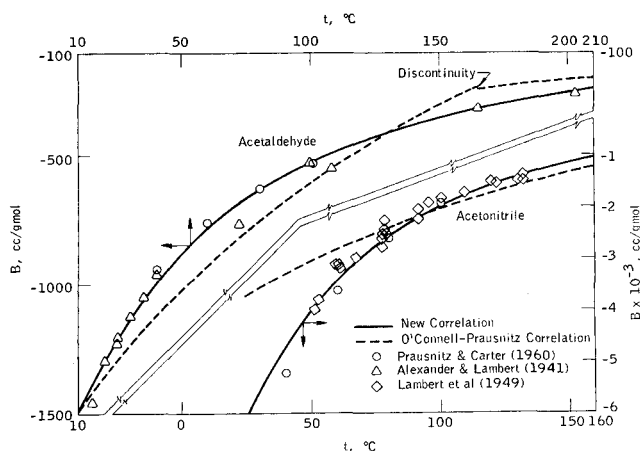The B data for eight alcohols, phenol, and water were

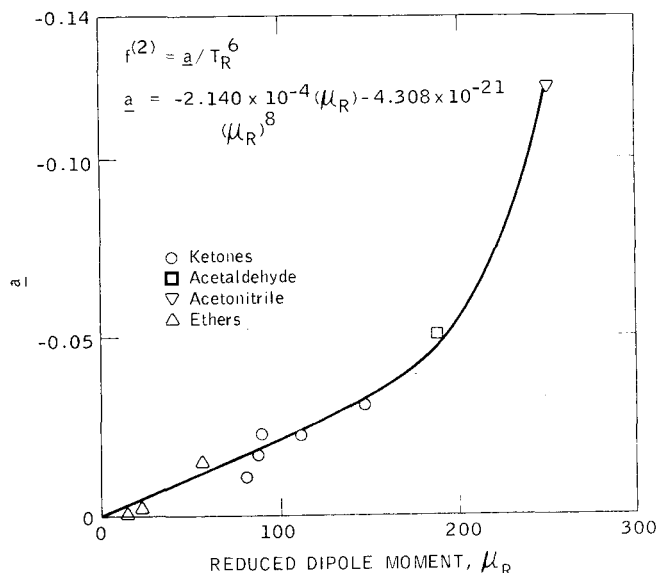Fig. 5. Second virial coefficient of acetaldehyde and acetonitrile.

Fig. 6. Dependence of a on reduced dipole moment for nonhydrogen bonding compounds.

TABLE 2. HYDROGEN BONDING POLAR COMPOUNDS

Compound	ω	$\mu_R{}^a$	a	b	Root mean square deviation of B, cc/gmol (no. points)		References[b]
Methanol	0.572	87.9	0.0878	0.0560	28.2	(22)	Kell and McLaurin (1969); Knoebel and Edmister (1968); Kretschmer and Wiebe (1954); Kudchadker and Eubank (1970).
Ethanol	0.635	68.3	0.0878	0.0572	71.3[c]	(8)	Knoebel and Edmister (1968); Kretschmer and Wiebe (1954).
1-Propanol	0.625	51.2	0.0878	0.0447	15.1	(4)	Cox (1961).
2-Propanol (isopropanol)	0.666	52.6	0.0878	0.0537	19.2	(13)	Cox (1961); Kretschmer and Wiebe (1954); Moreland et al. (1967).
1-Butanol	0.590	39.7	0.0878	0.0367	61.2	(6)	Cox (1961); Foz et al. (1954)[d].
2-Butanol (sec-Butanol)	0.578	41.6	0.0878	0.0487	14.6	(4)	Cox (1961).
2-Methyl-1-Propanol (isobutanol)	0.586	40.8	0.0878	0.0481	23.2	(4)	Cox (1961).
2-Methyl-2-Propanol (tert-Butanol)	0.614	44.2	0.0878	0.0508	33.1	(4)	Cox (1961).
Phenol	0.443	24.6	—0.0136	—	16.2	(8)	Opel (1969).
Water	0.344	172.6	0.0279	0.0229	1.74	(22)	Kell et al (1968); Vukalovich et al (1967).

[a] See Table 1. All alcohols have $\mu = 1.70 \pm 0.03$ Debyes (McClellan, 1963).

[b] Only those used in the regression analysis are listed.

[c] This large deviation is misleading; the experimental values at 60°C are $+109$ and -126.5 cc/gmol off the calculated value. If the too negative value is removed, $b = 0.056$.

[d] The 98°C point is inconsistent with the rest and has been discarded.
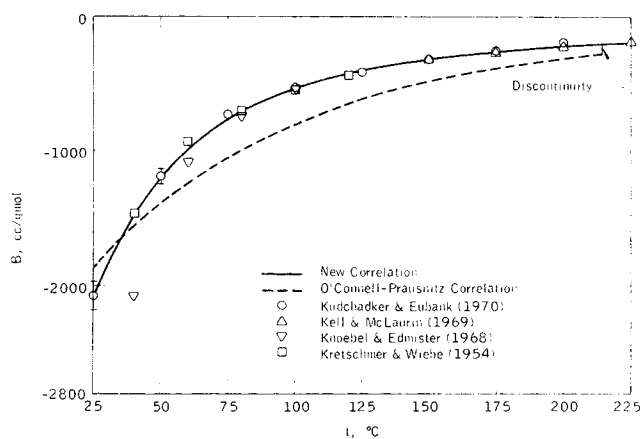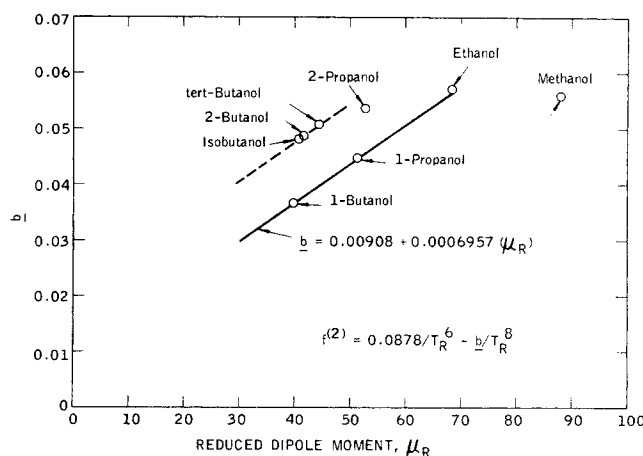

Fig. 7. Second virial coefficient of methanol.

Fig. 8. Dependence of b on reduced dipole moment for alcohols.

analyzed with Equations (11) and (16). The results are given in Table 2.

The same value of a was used for all eight alcohols. A good example of the fit is illustrated in Figure 7 for methanol—for which we have the most extensive information. Only the most recent data (Kell and McLaurin, 1969; Knoebel and Edmister, 1968; Kudchadker and Eubank, 1970) have been plotted, together with the results of an earlier careful investigation (Kretschmer and Wiebe, 1954)*. The new correlation provides an excellent fit of the data over the whole temperature range. The O'Connell-Prausnitz correlation (1967) only fits the less precise data of Lambert et al. (1949)*. The discontinuity in the correlation at $T_R = 0.95$ is 80 cc/g-mol, or 40% of the B value.

The B data for ethanol and 2-propanol are adequate,

but those for 1-propanol and all C_4 alcohols are limited in number and temperature range. In every case the new correlation has provided a satisfactory fit (superior to that obtained with the O'Connell-Prausnitz correlation).

Figure 8 shows that the alcohols' b has a weak dependence on reduced dipole moment. Reliable B data for $C_4{}^+$ alcohols are needed to clarify this, but it appears that the b of $C_2{}^+$ straight-chain 1-alkanols is given by

$$b = 0.00908 + 0.0006957 \ (\mu_R);$$
$$\text{straight-chain 1-alkanols } (a = 0.0878) \quad (17)$$

The branching in all other alcohols should make their B less negative, and hence their b less positive, but the reverse is shown in Figure 8.

Opel's (1969) data for phenol were adequately fitted with only one parameter. The data of Andon et al. (1960) were inconsistent with Opel's and were discarded. (If they had also been considered, the value for a would have been -0.0101.) A two-parameter $f^{(2)}$ may be needed to fit low-temperature ($T_R < 0.6$) data.

The data for water are plotted in Figure 9. The results

* The data of Bottomley and Spurling (1967) have been discarded. Their values at 125° and 150°C are 150 and 100 cc/g-mol, respectively, more negative than those plotted in Figure 7.

* Other alcohol data discarded were those of Hanks and Lambert (1951) for ethanol, and of Foz et al. (1954) for C_1-C_3 alcohols.

of Keyes et al. (1936, 1938) are in serious disagreement with the recent measurements of Kell et al. (1968), especially for $t < 250°C$. Only Kell's data (150 to 450°C) were used in the regression analysis. At higher temperatures (500° to 900°C) we used the values of Vukalovich et al. (1967). As shown in Figure 9, the fit of Kell's data with the new correlation is excellent. (An almost equally good fit can be obtained using only one parameter.) The maximum deviation in B, up to 900°C ($T_R = 1.81$) is less than 4 cc/g-mol.

CROSS-COEFFICIENTS FOR MIXTURES

The second virial cross-coefficient B_{ij} has the same temperature dependence that B_{ii} and B_{jj} have, but the parameters to be used with Equations (11), (12), and (16) are P_{cij}, T_{cij}, ω_{ij}, a_{ij}, and b_{ij}. The mixing rules given below make it possible to relate these characteristic constants to pure-component parameters:

$$T_{cij} = (T_{ci}T_{cj})^{1/2} (1 - k_{ij}) \quad (18)$$

$$P_{cij} = \frac{4T_{cij}(P_{ci}v_{ci}/T_{ci} + P_{cj}v_{cj}/T_{cj})}{(v_{ci}^{1/3} + v_{cj}^{1/3})^3} \quad (19)$$

$$\omega_{ij} = 0.5 (\omega_i + \omega_j) \quad (20)$$

where k_{ij} is a characteristic constant for each binary.

Equations (18) to (20) suffice for nonpolar/nonpolar binaries. An extensive tabulation of characteristic binary constants for nonpolar systems is given by Chueh and Prausnitz (1967). Hiza and Duncan (1970) have presented both data and a correlation for the k_{ij} of nonpolar binaries of He, H₂, Ne, etc.

For polar/nonpolar binaries, B_{ij} is assumed to have no polar term:

$$a_{ij} = 0 \quad (21)$$

$$b_{ij} = 0 \quad (22)$$

For polar/polar binaries, the polar contribution to B_{ij} is calculated by assuming that

$$a_{ij} = 0.5 (a_i + a_j) \quad (23)$$

$$b_{ij} = 0.5 (b_i + b_j) \quad (24)$$

The suitability of the mixing rules, Equations (18) to (24), will be indicated by the degree of success in fitting B_{ij}, or B_M data. [The relationship between B_{ii}, B_{jj}, B_{ij}, and B_M is given by Equation (4).] The most sensitive
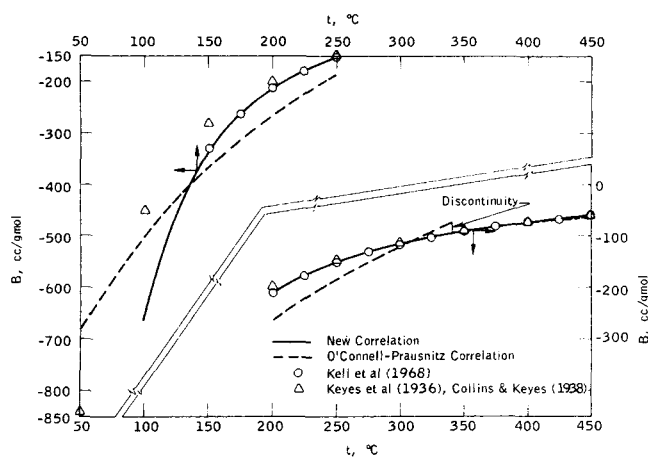

Fig. 9. Second virial coefficient of water.

mixing rule is Equation (18). T_{cij} can be assumed to be the geometric mean of T_{ci} and T_{cj} ($k_{ij} = 0$) only when i and j are very similar in size and chemical nature. For methane/n-heptane, $k_{ij} = 0.10$ (Chueh and Prausnitz, 1967). For systems with polar components, k_{ij} can be even larger. If there is strong solvation (hydrogen bonding between molecules of different species), k_{ij} can assume a negative value.

There are relatively few mixture data for polar/nonpolar or polar/polar systems. The property usually measured is B_M, but it is also possible to determine B_{ij} directly by measuring the solubility of liquid i in gas j at elevated pressures.

The average deviation of the calculated B_{ij} values for methanol/nonpolar and water/nonpolar binaries is given in Table 3. The cross-coefficients have been directly determined from measurements of the solubility of liquid methanol or water in the compressed gas. The new correlation, with a temperature-independent k_{ij} for each binary, provides an excellent fit of the data, even over a range of 213°C (for H₂O/CH₄). The O'Connell-Prausnitz correlation gives B_{ij}'s that are always much too negative (except for the CH₃OH/CO₂ binary). This correlation uses Equation (18) with $k_{ij} = 0$ (see the Appendix), which is clearly unsatisfactory.

Most of the B_M data are of unsatisfactory quality. The uncertainty in B_{ij} reflects the uncertainty in both the mixture and the pure-component data (which can be sub-

TABLE 3. SECOND VIRIAL CROSS-COEFFICIENTS

i/j	Average deviation of B_{ij}, cc/gmol		O'Connell-Prausnitz	t range, °C (no. points)		References
	New	(k_{ij})				
Methanol/nitrogen	1.9	(0.05)	15	15-60	(5)	Hemmaplardh and King (1972).
Methanol/argon	3.2	(0.07)	19	15-60	(5)	Hemmaplardh and King (1972).
Methanol/methane	3.4	(0.13)	40	15-60	(5)	Hemmaplardh and King (1972).
Methanol/ethylene	7.6	(0.10)	39	15-60	(5)	Hemmaplardh and King (1972).
Methanol/ethane	6.4	(0.12)	54	15-60	(5)	Hemmaplardh and King (1972).
Methanol/carbon dioxide	9.5	(0.01)	22	15-60	(5)	Hemmaplardh and King (1972).
Methanol/nitrous oxide	7.5	(0.13)	55	15-60	(5)	Hemmaplardh and King (1972).
Water/nitrogen	1.7	(0.30)	41	25-100	(4)	Rigby and Prausnitz (1968).
Water/argon	1.7	(0.35)	49	25-100	(4)	Rigby and Prausnitz (1968).
Water/methane	2.9	(0.34)	52	25-237.8	(9)	Olds et al. (1942); Rigby and Prausnitz (1968).
Water/ethane	6.4	(0.37)	117	25-171.1	(7)	Coan and King (1971); Reamer et al. (1943).
Water/carbon dioxide	16.8	(0.14)	41	25-100	(4)	Coan and King (1971).
Water/nitrous oxide	7.6	(0.16)	45	25-100	(4)	Coan and King (1971).

stantial, as already shown). It is therefore preferable to compare B_M at $y = 0.5$, rather than B_{ij}.

The average deviation of the calculated B_M $(y = 0.5)$ values for eleven polar/nonpolar and two polar/polar binaries is listed in Table 4. The new correlation is again satisfactory and superior to the O'Connell-Prausnitz correlation. The recent phenol/water data (Opel et al., 1969) have been fitted extremely well, but the fit for acetone/ethyl ether (Zaalishvili and Kolysko, 1960) is less satisfactory.

A temperature-dependent k_{ij} is needed to fit the B_M $(y = 0.5)$ data for acetone/benzene and acetaldehyde/acetonitrile, as shown in Table 5. In the case of acetone/benzene, experimental error cannot be excluded [the data of Zaalishvili and Belousova (1964) should certainly be discarded; see Table 5], but the steep temperature dependence of B_M has a physicochemical explanation: there is spectroscopic evidence (Weimer and Prausnitz, 1966) that benzene (electron donor) forms a complex with acetone (electron acceptor). As temperature is raised,

the complex becomes weaker, and k_{ij} approaches its temperature-independent value of 0.12 (which it assumes when there is no significant complex formation).

The negative k_{ij}'s for acetaldehyde/acetonitrile are a clear indication of the existence of a strong complex, probably formed by hydrogen bonding between nitrogen and the hydrogen attached to the carbonyl group. The existence of this complex has been recognized by Prausnitz and Carter (1960). Because of the strong chemical interaction between acetaldehyde and acetonitrile, which weakens as the temperature is raised, k_{ij} should be more negative at 40°C than it is at a higher temperature (compare acetone/benzene). This is supported by the data: at 40°C, the optimum k_{ij} is -0.32; at 100°C, it is -0.23. (When there is complex formation, O'Connell and Prausnitz add a specific association constant for the dimer. With such a constant, the O'Connell-Prausnitz correlation should provide a much better fit than that indicated in Table 5.)

The paucity of experimental B_M data will make it necessary to predict rough k_{ij} values in most cases. The avail-

TABLE 4. MIXTURE SECOND VIRIAL COEFFICIENTS AT $y = 0.5$

Average deviation of B_M $(y = 0.5)$, cc/gmol

i/j	New	(k_{ij})	O'Connell-Prausnitz	t range, °C (no. points)	References
Acetone/n-butane	11	(0.07)	47	9.15-47.85 (4)	Kappallo et al. (1963).
Acetone/n-hexane	19	(0.13)	143	45-90 (4)	Abbott (1965).
Acetone/cyclohexane	23	(0.20)	178	75,90 (2)	Abbott (1965).
	118	(0.20)	61	53,76 (2)	Lambert et al. (1954).[a]
Acetone/carbon disulfide	5.6	(0.10)	42	51.7-158.9 (5)	Bottomley and Spurling (1967).
Acetone/ethyl ether	29	(0.10)	58	50-80 (4)	Zaalishvili and Kolysko (1960).
Methyl ethyl ketone/benzene	19	(0.12)[b]	122	80 (1)	Chang et al. (1965): -950 ± 100.
Diethyl ketone/benzene	18	(0.12)[b]	263	80 (1)	Chang et al. (1965): -1120 ± 100.
Acetonitrile/cyclohexane	25	(0.40)	216	53,76 (2)	Lambert et al. (1954).
Ethyl ether/n-hexane	22	(0.08)	88	53.2,78 (2)	Fox and Lambert (1952).
Ethyl ether/benzene	20	(0.10)	82	60-100 (3)	Knoebel and Edmister (1968).
Methanol/benzene	46	(0.20)[c]	160	40-100[c] (4)	Knoebel and Edmister (1968).
Ethanol/benzene	27	(0.20)	158	60-100 (3)	Knoebel and Edmister (1968).
Phenol/water	2.8	(0.15)	164	175-250 (6)	Opel et al. (1969).

[a] Their data are inconsistent with the more reliable results of Abbott (1965).
[b] 0.12 is the limiting k_{ij} value for acetone/benzene (see Table 5); the agreement is even better with $k_{ij} = 0.14$.
[c] The 40°C is most probably too negative (B of methanol is 500 cc/gmol too negative!); without this point, the optimum k_{ij} value is 0.25.

TABLE 5. B_M $(y = 0.5)$ OF CROSS-DIMERIZING BINARIES

B_M $(y = 0.5)$, cc/gmol

i/j	t, °C	Experimental[a]	Calculated New (k_{ij})	O'Connell-Prausnitz
Acetone/benzene	40	-1450[b]	-1384 (0.00)	-1258
	60	-1060	-1060 (0.05)	-1069
	75	-860 ± 100	-858 (0.12)	-955
	80	-855	-824 (0.12)	-920
	80	(-960)[c]	-824 (0.12)	-920
	90	-750 ± 100	-761 (0.12)	-857
	90	(-850)[c]	-761 (0.12)	-857
	100	-710	-706 (0.12)	-800
	100	(-765)[c]	-706 (0.12)	-800
	110	(-710)[c]	-657 (0.12)	-747
Acetaldehyde/acetonitrile	40	-5900	-5854 (-0.32)	-2081
	60	-4180	-4209 (-0.32)	-1757
	80.1	-2540	-2553 (-0.25)	-1477
	100.4	-1810	-1856 (-0.23)	-1232

[a] Acetone/benzene: Abbott, 1965 (75, 90°C); Chang et al. 1965 (80°C); Knoebel and Edmister, 1968 (40, 60, 80, 100°C); Zaalishvili and Belousova, 1964 (80, 90, 100, 110°C). Chang et al. are in agreement with Knoebel and Edmister at 80°C.
Acetaldehyde/acetonitrile: Prausnitz and Carter (1960).
[b] Too negative, like the other measurements by Knoebel and Edmister (1968) at 40°C.
[c] The B_M data of Zaalishvili and Belousova (1964) have the wrong composition dependence.

$$(k_{ji} = k_{ij})$$

Type	$i \backslash j$	1	2	3	4	5
Hydrocarbons	1	1	—	0.13	0.10	0.15	0.40
Ketones	2	2		—	0.13	0.05	0.15
Ethers	3	3			—	0.13	0.35
Alcohols	4	4				—	0.10*
Water	5	5					—

* $k_{ij} = 0.15$ for phenol/water.

able information can be used as the basis for all such predictions. Consideration of relative size and chemical nature should facilitate the prediction of the binary constants. As a rough guide, average values for k_{ij} are given in Table 6.

ACKNOWLEDGMENT

NOTATION

a, b = parameters of polar contribution term to B, $f^{(2)}$; see Equations (12) and (16)
B = second virial coefficient
C = third virial coefficient
$f^{(0)}, f^{(1)}, f^{(2)}$ = dimensionless terms of Equation (11), the new correlation of second virial coefficients
k_{ij} = characteristic binary constant; see Equation (18)
P = pressure
$P°$ = vapor pressure of pure component
R = gas constant
T = absolute temperature
v = molar volume
y_i = vapor mole fraction of component i
z = compressibility factor

Greek Letters

μ = dipole moment
ω = acentric factor

Subscripts

c = critical property
i, j = property of component i, j
ij = characteristic property used in the calculation of the second virial cross-coefficient
M = mixture property
PC = terms in Pitzer-Curl correlation
R = reduced property

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