x_j = mole fraction of ion j in the membrane based on the molar concentration c_m^o
y_j = mole fraction of ion j in the solution based on the molar concentration c_s^o
z = distance parallel to the membrane surface, cm.
α = separation factor
θ = thickness of the stagnant diffusion layer, cm.
μ = total ionic concentration, moles/liter
ν = kinematic viscosity of the solution, sq. cm./sec.

Dimensionless Groups

N_{Re} = Reynolds number = $d_e U/\nu$
N_{Sc_i} = Schmidt number for ion i = ν/D_i

Superscripts

o = bulk of the solution
I = interface between the membrane and the solution
$-$ = an anion
$+$ = a cation
$\bar{I}$ = bar over symbol represents an average value

Subscripts

$\pm$ = mean value
A or $-$ = an anion
c or $+$ = a cation
i, j = ion i and ion j respectively
1, 2 = ion 1 and ion 2 respectively
L = limiting condition
m = membrane phase
s = solution phase
T = total

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Volumetric Properties of Gas Mixtures Containing One or More Polar Components

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A study has been made of the second virial coefficients of binary gas mixtures containing one or two polar components. Methods for calculating these coefficients are presented. The interaction coefficient B_{ij} for a polar-polar interaction cannot be calculated with the Stockmayer potential with pure component parameters only; such calculations tend to underestimate the strong forces of attraction between dissimilar polar molecules. It is shown that the characteristic distance for the reduced dipole moment for two dissimilar polar molecules is less than the arithmetic average of the distance parameter of the similar molecules by an amount which can be related to the enthalpy of complex formation. When this corrected collision diameter is used in the Stockmayer potential, good results can be obtained for interaction coefficient B_{ij}. In the case of a polar-nonpolar mixture the coefficient B_{ij} depends on dispersion and on induction forces. Techniques are proposed for estimating these forces from pure component parameters, and it is shown that for accurate calculation of B_{ij} it is necessary to correct for the displacement of the dipole from the center of the polar molecule. The paper concludes with some illustrations of how these ideas may be applied to typical chemical engineering problems.

The aim of this work is to present techniques for estimating volumetric properties in the moderate density region for gas mixtures containing one or more polar components. Previous studies on the volumetric properties of gas mixtures are almost entirely concerned with nonpolar mixtures, but this work considers the available experimental data and theory for gas mixtures which contain one or more polar components. This study is confined to intermediate densities, for it is only under such conditions that the results of statistical thermodynamics can be conveniently utilized in applying the theory of intermolecular forces to the prediction of macroscopic properties.

For densities up to approximately one-half of the critical, the pressure of either a pure or mixed gas is adequately represented by the virial equation terminated after the second virial coefficient:

$$P = \frac{RT}{v}\left[1 + \frac{B}{v}\right] \qquad (1)$$

For a pure gas, B is a function of temperature only. For a mixture, B is also a function of composition, and it has been shown theoretically (*6, 13*) that the composition dependence for a mixture containing n components is given by

$$B = \sum_i^n \sum_j^n y_i y_j B_{ij} \qquad (2)$$

Prediction of the volumetric properties of gaseous mixtures in the moderate density region therefore reduces to the prediction of the various coefficients B_{ij} which depend on the temperature and on the physical properties of the components i and j. For mixtures containing one or more polar components three types of second virial coefficients are needed. First there is the case where $i = j$, and in this case the virial coefficient B_{ii} (or B_{jj}) refers to interactions between two molecules of the same species; this coefficient can be evaluated from the properties of the pure component, and various methods have been proposed for its prediction both for nonpolar and polar substances (*7, 9, 16, 17, 18, 20, 24*). Second there is the case where $i \neq j$ and where i and j are dissimilar polar species. In this case the coefficient B_{ij} reflects interaction between two different polar molecules; the prediction of this coefficient comprises the first topic discussed below. Finally there is the case where $i \neq j$, where j is a polar and i is a nonpolar component; the prediction of B_{ij} for this case constitutes the second topic considered.

BINARY MIXTURES CONTAINING ONLY POLAR COMPONENTS

The second virial coefficients of pure polar substances have been adequately represented by calculations based on the Stockmayer potential which assumes that the potential energy between two polar molecules is given by the sum of three terms: a repulsion term which is dominant at very short intermolecular separations, an attraction (dispersion) term which varies as the inverse of the sixth power of the distance between molecular centers, and an electrostatic dipole term which varies as the reciprocal of the third power of the intermolecular separation and which depends on the mutual orientation of the two molecules such that it gives rise to an attraction for some orientations and a repulsion for others. For the case of zero dipole moment this potential reduces to the well-known Lennard-Jones function.

On the basis of Stockmayer's potential the second virial coefficient can be represented by

$$\frac{B_{ii}}{\frac{2}{3}\pi N \sigma^3_{ii}} = F\left(\frac{kT}{\epsilon_{ii}}, t^*_{ii}\right) \qquad (3)$$

where

$$t^*_{ii} = \frac{\mu_i^2}{\sqrt{8}\,\epsilon_{ii}\,\sigma^3_{ii}}$$

The universal function F has been tabulated, and values have been given for the collision diameter and characteristic energy for many common polar gases (*7*). It has been suggested (*7*) that for the cross-coefficient B_{ij} the same function F can be used with the following semiempirical mixing rules:

$$\sigma_{ij} = \frac{1}{2}\cdot(\sigma_{ii} + \sigma_{jj}) \qquad (4)$$

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\ \epsilon_{jj}} \qquad (5)$$

$$t^*_{ij} = \frac{\mu_i \mu_j}{\sqrt{8}\,\epsilon_{ij}\,\sigma^3_{ij}} \qquad (6)$$

However virial coefficients for mixtures as calculated from Equations (3) to (6) tend frequently to underestimate greatly the attractive forces between dissimilar molecules. For mixtures of two polar gases the calculated absolute values of B_{ij} are frequently much less than those found experimentally. The difference between the experimental and the calculated values is often very large. One of the most striking examples of this difference is that for the acetonitrile-acetaldehyde system, where at 313°K. B_{ij} calculated is −2,040 cc./g.-mole while B_{ij} experimental is −8,710 cc./g.-mole (*18*). It appears that the mixing rules given in Equations (4), (5), and (6) do not adequately reflect the nature of the intermolecular forces between two dissimilar polar molecules.

Rowlinson (*21*) has shown that in principle the dipole-quadrupole interaction cannot always be neglected in calculations for the second virial coefficient for complex polar molecules. However if this interaction is included in the Stockmayer potential for calculations of the second virial coefficient for water vapor the calculated results do not differ from those obtained with the uncorrected Stockmayer potential by more than 10 cc./mole. Furthermore the quadrupole moments for most molecules are not known, and therefore inclusion of the quadrupole effect is not practical at this time.

Equations (4) and (5) have been used quite successfully in predicting virial cross coefficients of nonpolar gas mixtures; Equation (4) is based on the hard-sphere model, and Equation (5) follows approximately from the London theory of dispersion forces. While these two equations do not give perfect results for nonpolar mixtures, they provide very good approximations for mixtures of components whose sizes are not too greatly different. In nonpolar systems they do not give rise to any systematic deviations, that is the predicted B_{ij}'s are sometimes larger and sometimes smaller than those observed. To bring calculated and experimental results for polar gas mixtures into better agreement it appeared desirable therefore to modify Equation (6), and indeed there is good reason to believe that such modification can be supported on theoretical grounds. The parameter t^* is a measure of the strength of the dipole-dipole attraction relative to that of dispersion. The strength of the dipole-dipole attraction is very sensitive to the distance parameter characterizing the collision between molecules i and j, and if the dipole-dipole force between i and j is in some qualitative sense different from those operating between two molecules i or two molecules j, then one would expect that the arithmetic mean for σ is improper in Equation (6).

A qualitative difference in dipole-dipole forces does, in fact, exist between those for pure and those for mixed gases whenever chemical bonding may be expected to play an important role in the mixture but is not present in the pure components. For example in the chloroform-diethyl ether system hydrogen bonding undoubtedly occurs in the gas mixture but not in the pure gases; in the acetonitrile-acetaldehyde system hydrogen bonding occurs slightly in pure acetaldehyde, not at all in pure acetonitrile, and very strongly in the mixture. The presence of hydrogen bonding would tend to shorten the characteristic distance between two polar molecules in the same way that an increased bond strength shortens the internuclear distance between two atoms in a molecule.

It therefore appeared reasonable to fit experimental B_{ij} data for polar gas mixtures to the generalized Stockmayer potential function by means of Equations (4) and (5) and a modification of Equation (6):

$$t^* = \frac{\mu_i \mu_j}{\sqrt{8}\,\epsilon_{ij}(\sigma_{ij} - \Delta_{ij})^3} \qquad (7)$$

In this modification the new parameter is characteristic of the nature of the i-j interaction and is independent of temperature. In systems where hydrogen bonding is negligible in both pure gases and in the mixed gas, Δ_{ij} must be zero. In systems where hydrogen bonding in the mixture is strong, but weak (or absent) in the pure gases, Δ_{ij} is positive and should increase with rising i-j hydrogen bond strength. Finally, in systems where hydrogen bonding is of about equal strength in both pure gases and in the mixture, the arithmetic mean distance parameter σ_{ij} would be expected to be quite suitable for the determination of t^*; in this case Δ_{ij} is small compared with σ_{ij} and Equation (6) should be satisfactory.

Equations (3), (4), (5), and (7) have been applied to the few polar gas mixtures for which reliable volumetric data are available. Table 1 lists the pure component parameters. Some of these were obtained from Rowlinson (*20*), while others were based on data published since Rowlinson's work. For the mixtures considered it was possible to obtain a good fit for all experimental B_{ij} values over the entire temperature range for which data were available. The parameters Δ_{ij} obtained for eight of these systems are shown in Figure 1 which relates them to the strength of the hydrogen-bond characteristic of each mixture. The values of ΔH shown on the abscissa were obtained from various physicochemical measurements as reported by Pimentel and McClellan *(14)*. Unfortunately these values are not known with high accuracy, and the horizontal lines are a rough measure of their probable uncertainty.

Figure 1 shows that the proposed physical interpretation of Δ_{ij} is in accord with the experimental facts. For the eight systems shown in Figure 1 the relative shortening of the characteristic distance between two molecules i and j is, within experimental error, proportional to the enthalpy of hydrogen bond formation. For the ninth system (diethylamine-butanol) the experimental data showed that $\Delta_{ij} = 0$. This is to be expected, since in this mixture hydrogen bonding in both pure gases is approximately of the same strength as hydrogen bonding in the mixture. No new parameter is needed in this case, since the intermolecular forces operating in the mixture can be satisfactorily estimated with only those intermolecular forces which operate in the pure components. On the other hand in the first eight cases something new occurs in the mixture which cannot be predicted solely from the properties of the pure gases which comprise the mixture.

A proper evaluation of the intermolecular forces which may be expected in a mixture of polar gases, coupled with the judicious use of the correlation shown in Figure 1, now makes it possible to predict second virial coefficients for many polar gas mixtures with considerably more accuracy than was previously possible.

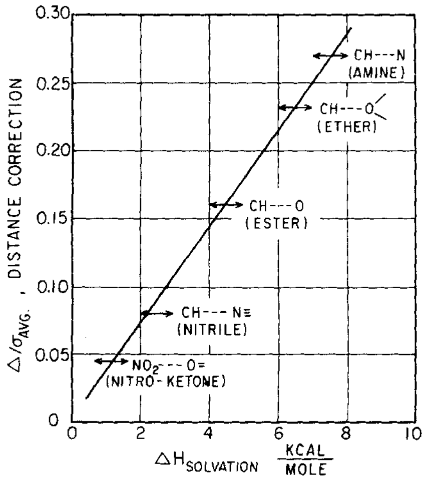

Fig. 1. Correction to Stockmayer dipole-dipole interaction distance for solvating molecules.

BINARY MIXTURES CONTAINING ONE POLAR AND ONE NONPOLAR COMPONENT

The potential function which describes the intermolecular forces between one polar molecule and one nonpolar but polarizable molecule is commonly written as the sum of three parts: the first considers forces of repulsion which vary as the inverse twelfth power of the distance between molecular centers, the second considers attraction (dispersion) forces due to the polarizability of both molecules, and the third considers the forces of attraction which result from the dipole which is induced in the nonpolar molecule by the polar molecule. These last two parts of the potential function vary as the inverse sixth power of the intermolecular distance. It is therefore possible to write the potential between a polar molecule j and a nonpolar molecule i in the Lennard-Jones form

$$\Gamma_{ij} = 4\,\epsilon'_{ij}\left[\left(\frac{\sigma'_{ij}}{r}\right)^{12} - \left(\frac{\sigma'_{ij}}{r}\right)^{6}\right] \tag{8}$$

where

$$\sigma'_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}[1 + \xi_{ij}]^{-1/6} \tag{9}$$

$$\epsilon'_{ij} = (\epsilon_{ii}\,\epsilon_{jj})^{\frac{1}{2}}[1 + \xi_{ij}]^{2} \tag{10}$$

with

$$\xi_{ij} = \frac{\alpha_i \mu_j^{\,2}}{4\left(\dfrac{\sigma_{ii} + \sigma_{jj}}{2}\right)^{6} (\epsilon_{ii}\,\epsilon_{jj})^{\frac{1}{2}}} \tag{11}$$

[In the limiting case where the dipole moment of molecule j vanishes $\xi_{ij} = 0$, and Equations (8), (9), and (10) reduce to the Lennard-Jones formula for mixtures of nonpolar molecules.]

With the use of the parameters σ'_{ij} and ϵ'_{ij} it is possible to calculate B_{ij} for nonpolar-polar mixtures from published tables of second virial coefficients (7) based on the Lennard-Jones potential.

As in the case of polar-polar gas mixtures the absolute values of B_{ij} calculated with Equations (8) to (11) are often significantly less than experimental B_{ij} values. For four systems at several different temperatures the average difference $|B_{ij}|_{\text{expt}} - |B_{ij}|_{\text{calc}}$ was 200 cc./g.-mole, the maximum difference being 279 cc./g.-mole. This indicates that the computations tend to underestimate the attractive forces between the polar and nonpolar molecules. A likely explanation for this disagreement may be based on the fact that the physical significance of ϵ_{jj} and σ_{jj} as used in Equations (8) to (11) is not quite the same as that in the Stockmayer potential. Equation (8) as well as the Stockmayer potential assume that all molecules are spherical and that the polar molecules have point dipoles at the molecular centers. If this assumption were in fact strictly true, then ϵ_{jj} and σ_{jj} would have the same significance in the Stockmayer potential and in Equation (8); for two molecules of species j, ϵ_{jj} would be the depth of the energy well due to nonpolar forces alone and σ_{jj} would be the intermolecular distance at which the potential energy due to nonpolar forces is zero. In fact however very few polar molecules correspond to the ideal model which is implied by the Stockmayer potential, and thus, while it is possible successfully to fit volumetric data for polar molecules to the Stockmayer potential, the parameters obtained do not have the same physical significance as that assigned to them by the model; rather, when obtained in this way, ϵ_{jj} is an effective energy parameter and σ_{jj} an effective collision diameter which when applied to mixtures of j with nonpolar i have lost their empirical value. This is especially true in cases where the dipole in molecule j is exposed near the surface of the molecule rather than buried at its center.

In Equations (8) to (11) ϵ_{jj} and σ_{jj} are parameters characteristic of the nonpolar intermolecular forces of species j and should properly be labeled $\epsilon_{jj(np)}$ and $\sigma_{ii(np)}$. These are not in general given by fitting B_{jj} data to the Stockmayer potential, and it appeared worth while therefore to consider alter-

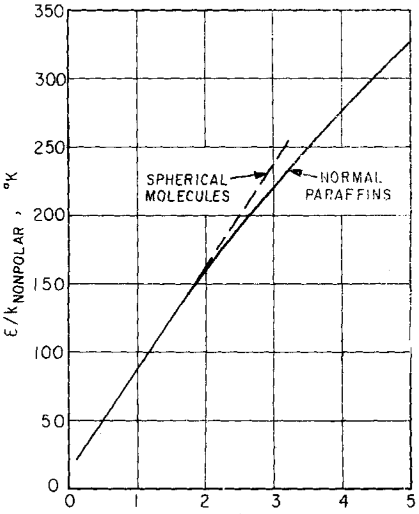

Fig. 2. Lennard-Jones energy parameter for nonpolar molecules.

nate methods for estimating their values.

METHODS FOR ESTIMATING THE NONPOLAR INTERMOLECULAR FORCES IN POLAR MOLECULES

For nonpolar molecules the collision diameter is determined by the size of the molecule, and hence there is a correlation between the collision diameter and the cube root of the critical volume. Empirically it is found that

$$\sigma_{ii} = 0.84\, v_{c_{ii}}^{\frac{1}{3}} \qquad (12)$$

when the collision diameter is expressed in Angstrom units and the critical volume in cubic centimeters per gram mole. Since polar forces do not seriously affect the molar volume at the critical point, an approximate method for estimating the collision diameter due to nonpolar forces only is to write

$$\sigma_{jj(np)} = 0.84\, v_{c_{jj}}^{\frac{1}{3}} \qquad (13)$$

The London theory of dispersion forces for spherical molecules provides a useful method for estimating the depth of the energy well due to nonpolar forces. In accordance with London's theory the depth of the well is proportional to the ionization potential and to the square of the polarizability and inversely proportional to the sixth power of the collision diameter.

For small or approximately spherical polar molecules it is therefore reasonable to write

$$\frac{\epsilon_{jj(np)}}{k} = \beta\, \frac{\alpha_j^2 I_j}{\sigma_{jj}{}^6{}_{(np)}} \qquad (14)$$

The proportionality constant β can be determined from data on small nonpolar molecules and is found to be 4.82×10^8 °K./ev.

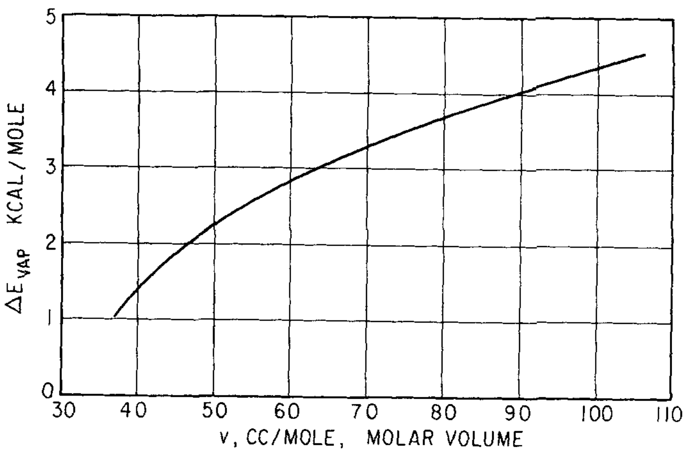

Fig. 3. Energy of vaporization of straight-chain hydrocarbons at $T_R = 0.7$.

For larger polar molecules, and especially for those which deviate significantly from spherical shape, Equation (14) is not satisfactory. For such cases it is useful to utilize the homomorph concept of Brown (*3*) as used by Bondi and Simkin (*2*) in their study of energies of vaporization of polar species. The homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape as those of the polar molecule. For a nonpolar molecule *i* the parameter ϵ_{ii} is intimately related to the energy of vaporization of *i*, as shown in Figure 2. The parameter $\epsilon_{jj(np)}$ can then be estimated from Figure 2, provided the energy of vaporization of the homomorph of *j* is used as the independent variable. In those cases where the polar molecule has a straight-chain structure a normal paraffin may be used as a homomorph. In that case the energy of vaporization of the homomorph (to be used in Figure 2) may be estimated from the plot shown in Figure 3. The homomorph may be considered as a continuous rather than a discontinuous variable, and where a normal paraffin may, because of its shape, be considered a suitable homomorph for a polar molecule, it is most convenient to use the molar volume of the polar component as the independent variable in Figure 3; this step follows from the basic idea that the molar volume of the polar component is equal to that of its homomorph. A plot similar to that shown for normal paraffins may be prepared for nonpolar molecules having some other shape. Nonpolar force constants for several polar components are given in the application section.

EFFECT OF A NONCENTRAL DIPOLE ON INDUCTION FORCES

The considerable disagreement between the force constants for polar species as obtained from the Stockmayer potential and those obtained by the estimation procedures described above shows the large effect of a noncentral dipole moment; if the dipole were ideal and in the center of the (spherical) polar molecule, there should be essentially complete agreement between the two methods of calculation.

The fact that a dipole is not located at the center of a polar molecule *j* affects not only B_{jj} but also B_{ij}, since an exposed dipole will always have associated with it a larger induction energy than a central dipole, provided all other variables are held constant:

$$\Gamma(r)_{\text{induction}} = -\left[\frac{\alpha\mu^2}{r^6} + \frac{6\alpha\mu^2}{r^6}\left(\frac{s}{r}\right)^2 + \dots\right] \qquad (15)$$

Equation (15) shows that the potential energy of interaction between a dipole and an induced dipole is larger if the dipole is not at the center of the molecule. The distance *s* is from the center of a spherical polar mole-

Table 1. Stockmayer Parameters

Molecule	μ, Debye	σ, A	ϵ/k, °K.	t^*	Reference for $B(T)$ data
Acetonitrile	3.94	4.38	219	2.2	18
Nitromethane	3.54	4.16	290	1.6	4
Acetaldehyde	2.7	3.68	270	1.4	20*
Acetone	2.88	3.67	479	0.8	4
Ethanol	1.70	2.45	620	0.8	8
Chloroform	1.05	2.98	1,060	0.6	20*
n-Butanol	1.66	2.47	1,125	0.42	5
n-Butyl amine	0.85	1.58	1,020	0.45	5
Methyl formate	1.77	2.90	684	0.46	11
n-Propyl formate	1.92	3.06	877	0.37	11
Methyl acetate	1.67	2.83	895	0.34	11
Ethyl acetate	1.76	2.99	956	0.33	11
Diethyl ether	1.16	3.10	935	0.13	10
Diethyl amine	1.01	2.99	1,180	0.09	10

* From table in Rowlinson (*20*).

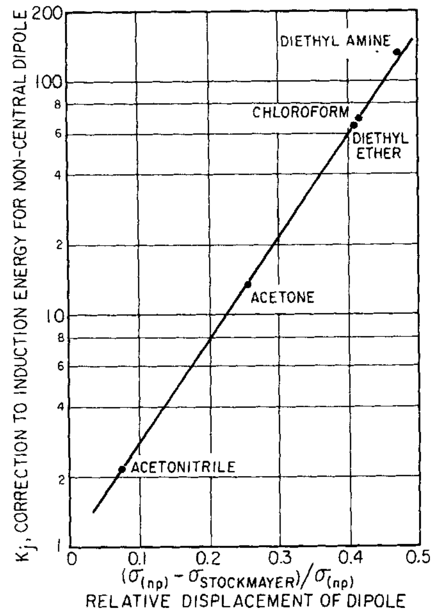

Fig. 4. Correction for induction energy for noncentral dipoles (from mixture data containing hexane or cyclohexane as nonpolar component).

cule to the ideal dipole. The first term in Equation (15) is the result obtained for a spherical molecule with an ideal dipole at its center. In addition it can be shown that if the dipole is not ideal the induced energy is increased further (*1*). An important feature of the derivation of Equation (15) is the fact that to a very good first approximation the increase in induction energy is a function only of the dipole displacement from the molecular center and not of the temperature. Hence it appears justified to utilize Equations (8) to (10) with force constants as determined by methods discussed in the last section plus an empirical, temperature-independent, correction factor K_j to be used as follows:

$$\xi_{ij} = \frac{K_j\, \alpha_i\, \mu_j^2}{4\left(\dfrac{\sigma_{ii} + \sigma_{jj(np)}}{2}\right)^6 (\epsilon_{ii}\, \epsilon_{jj(np)})^2} \tag{16}$$

This factor must never be less than unity. It will be equal to unity in those cases where the (ideal) dipole of molecule *j* is located at the intermolecular center; for all other cases it will be larger than unity, but it will always depend only on the properties of *j* and not on those of *i*.

Reliable second virial coefficient data for polar-nonpolar mixtures are not plentiful. Data for a few systems have been fitted to tables for B_{ij} based on the Lennard-Jones potential with Equations (8), (9), (10), and (16) used. The parameters σ_{ii} and ϵ_{ii} were obtained from data on B_{ii}; parameters $\sigma_{jj(np)}$ and $\epsilon_{jj(np)}$ were calculated as described above. A good fit of the experimental data could be obtained over the entire available temperature range by choosing a temperature-independent constant K_j. Since this constant depends primarily on the displacement of the dipole from the molecular center, it was plotted as shown in Figure 4. (See Appendix.) For the five systems studied the constant K_j is surprisingly large, especially for diethylamine. In view of the very limited data available not too much confidence can as yet be placed on the general applicability of Figure 4. Nevertheless *K* increases, as expected, with the displacement of the dipole from the molecular center, and Figure 4 shows very clearly the important effect which a noncentral dipole has on the induction energy between a polar and a nonpolar molecule.

Utilization of the techniques discussed in this and the two preceding sections should enable the calculation of second virial coefficients for polar-nonpolar mixtures with more accuracy than has previously been possible.

APPLICATIONS

The analysis presented in this work is no more than an attempt to provide useful, simple, and yet physically sensible methods for predicting the volumetric properties of mixtures containing at least one polar component. Hopefully, as understanding of intermolecular forces increases and as new data become available, these empirical methods will be replaced by more rigorous techniques.

Whereas the discussion of actual systems has here been limited to binaries, it is clear from Equation (2) that the methods recommended in this work are applicable to mixtures containing any desired number of components and are subject only to the restriction that Equation (1) applies, that is that virial coefficients beyond the second may be neglected.

To illustrate the prediction methods developed in this work a few examples are given below.

1. The compressibility factor of a mixture of steam and oxygen was calculated from the relations

$$z_{mix} = \frac{Pv_{mix}}{RT} = 1 + B_{mix}\frac{P}{RT} \tag{17}$$

$$B_{mix} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_j^2 B_{jj} \tag{18}$$

The values B_{ii} (pure oxygen) and B_{jj} (pure steam) were obtained from the pure component data, with the Lennard-Jones potential and the Stockmayer potential, respectively, used. The value for B_{ij} was found by means of Equations (9), (10), and (16), together with Figure 4 and Table 1B in reference 7. Figure 5 shows that the results of this calculation are in good agreement with the experimental points of Luker et al. (*12*).

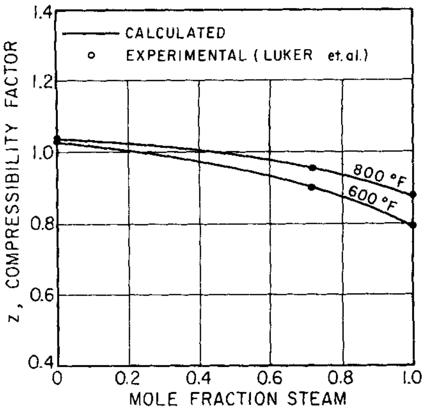

Fig. 5. Compressibility factors for steam-oxygen mixtures at 100-atm. pressure.

2. For intermediate pressure ranges the effect of pressure on the isothermal change in enthalpy for a gas mixture relative to zero pressure is given by

$$\Delta H_{(P)} = \left(B_{mix} - T\frac{dB_{mix}}{dT}\right) P \tag{19}$$

Equations (18) and (19) were used to calculate the enthalpy-pressure behavior of ethanol-pentane and ethanol-benzene vapors. The values B_{ii} (pure nonpolar component) and B_{jj} (pure ethanol) are obtained for each temperature from the pure component data, with the Lennard-Jones potential for the nonpolar gases and the Stockmayer potential for ethanol. The value for B_{ij} at each temperature is found from Equations (9), (10), and (16), with Figure 4 and Table 1B in reference 7.

The Stockmayer distance parameter for pure ethanol $\sigma_{Stockmayer}$ is determined in part by chemical forces which are present in the associated ethanol vapor. These forces act to shorten the distance parameter. To remove the effect of association forces in calculating polar-nonpolar forces the empirical constant K_j from Figure 4 was found by means of the relation

$$\sigma_{(np)} - (\sigma_{Stockmayer} + \Delta_{jj})$$

as the abscissa. The quantity Δ_{jj}, from Figure 1, effectively lengthens the distance parameter $\sigma_{Stockmayer}$ to use in calculating the interaction B_{ij}. Thus the distance parameter for the

TABLE 2. IMPORTANT PARAMETERS IN SAMPLE CALCULATIONS
(All distance parameters in Å., energy parameters in °K.)

	$\sigma_{(np)}$	$\sigma_{\text{Stockmayer}}$	$\Delta H_{\text{assoc.}}$, kcal./g.-mole	K_j	$(\epsilon/k)_{\text{Stockmayer}}$	$(\epsilon/k)_{(np)}$
Example 1						
Water	3.20	2.65	4.8	2.1†	380	100*
Oxygen	3.58	—	—	—	—	118
Example 2						
Ethanol	5.20	2.45	4.8	21	620	220
Pentane	5.77	—	—	—	—	345
Benzene	5.37	—	—	—	—	406
Example 3						
Acetaldehyde	5.21	3.70	4.5	6	270	225
Hydrogen	2.87	—	—	—	—	29
Krypton	3.60	—	—	—	—	171
Methane	3.82	—	—	—	—	148
Nitrogen	3.70	—	—	—	—	95

* (ϵ/k) from Figure 2 and estimated $(\Delta E_{\text{vap}})_{np}$.
† $[\sigma_{np} - (\sigma_{\text{Stockmayer}} + \Delta_{ij})]/\sigma_{np}$.

polar component, to be used in Equation (16), does not reflect the association present in the pure vapor. The results of this calculation are in very good agreement with the experimental data of Storvick and Smith (25). Table 2 summarizes the parameters used in the calculation.

3. It has been shown previously (*16*) how the second virial coefficient may be used to calculate thermodynamic equilibrium properties. The solubility of a polar liquid j in a compressed nonpolar gas i may be calculated from the relation

$$y_j = \frac{\gamma_j^L x_j P_j^\circ \phi_j^\circ}{\phi_j P} \exp\left[v_j^{oL} \frac{(P - P_j^\circ)}{RT} \right] \tag{20}$$

The fugacity coefficient of component j in the binary vapor is related to the virial coefficients by

$$\ln(\phi_j \, z_{\text{mix}}) = \frac{2}{v_{\text{mix}}} [y_i B_{ij} + y_j B_{jj}] \tag{21}$$

and by Equation (17). The second virial coefficients for the pure components and the cross coefficients for the mixture are obtained with the procedure shown in examples 1 and 2.

The solubility of acetaldehyde in compressed hydrogen and in compressed krypton was computed at 274°K. The results are shown in Figure 6. The solubility of the acetaldehyde in krypton is higher than the solubility of acetaldehyde in hydrogen owing to the stronger forces of attraction between krypton and acetaldehyde. The ideal gas law, if used, would predict equal solubilities for acetaldehyde in krypton and in hydrogen and would not predict the minimum solubility as found for krypton at this temperature. The important parameters for these calculations are summarized in Table 2.

CONCLUSIONS

Previously proposed methods for calculating the second virial cross coefficient B_{ij} for polar gas mixtures often predict values of B_{ij} which do not agree with experimental results. For polar-polar binary gas mixtures it is necessary to estimate the effect of the strong chemical forces of interaction present in the mixture. The characteristic reduced dipole moment to be used in the Stockmayer potential for two dissimilar polar molecules is sometimes greater than the geometric mean of the reduced dipole moment of the similar molecules by an amount which can be related to the enthalpy of complex formation.

In the case of a polar-nonpolar gas mixture the coefficient B_{ij} depends on dispersion and induction forces. To compute the contributions of these forces it is necessary to estimate the magnitude of the dispersion forces associated with a polar molecule. For accurate calculations of B_{ij} a correction must be made for the displacement of the dipole from the center of the polar molecule.

Data for second virial coefficients of polar-polar and polar-nonpolar gas mixtures are very scarce. It is not possible rigorously to allow for the effects mentioned above on the basis of presently available data. The methods of calculating B_{ij} proposed in this paper are based on limited experimental data and are only temporary methods of calculation to be used until further data become available and until current theories of intermolecular forces more nearly reflect actual physical situations. However better values for B_{ij} may be calculated from the ideas presented here than could previously be obtained.

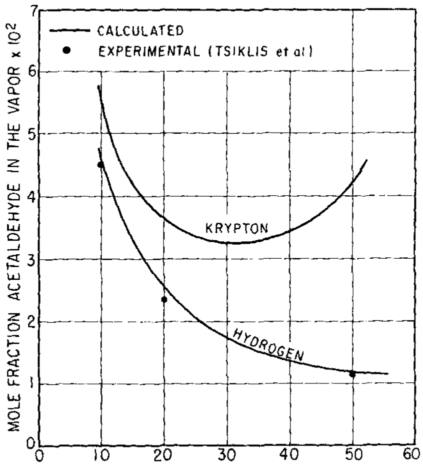

Fig. 6. Solubility of acetaldehyde in compressed hydrogen and krypton at 274°K.

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NOTATION

B = second virial coefficient
$\vec{E}$ = vector field
ΔE = energy of vaporization
e = charge of dipole
f = fugacity of a component in a mixture
ΔH = enthalpy of complex formation
I = ionization potential
K = correction factor for noncentral dipoles
k = Boltzmann constant
n = number of components
P = pressure
R = gas constant
r = intermolecular separation
s = displacement of an ideal dipole from the center of a spherical polar molecule
t^* = reduced dipole moment, Stockmayer potential
T = absolute temperature
T_R = reduced temperature, T/T_c
T^* = reduced temperature, Lennard-Jones or Stockmayer potential
v = molar volume
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
z = compressibility factor

Greek Letters

Γ = potential energy
ϵ = energy parameter
σ = characteristic distance
μ = dipole moment
Δ = correction to intermolecular distance parameter for solvating molecules
ϕ = fugacity coefficient in the vapor phase
γ = activity coefficient
α = polarizability
ξ = induction parameter

Subscripts

np = nonpolar
c = critical
i = nonpolar component
j = polar component
avg = arithmetic average

Superscripts

o = pure material
L = liquid
V = vapor

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TABLE 3. ENERGIES OF VAPORIZATION FOR POLAR MOLECULES, KCAL./G.-MOLE
(At normal boiling point)

Molecule	ΔE_{vap}	ΔE_{vap} disp.	$\Delta E_{central}$ dipole	$\Delta E_{noncentral}$ dipole	ΔE chemical	$\sigma_{(np)} - \sigma_{Stock.}$ Å
Diethyl amine	6.32	4.95	0.112	1.26	—	2.6
Diethyl ether	5.59	4.90	0.179	0.509	—	2.1
Ethanol	8.73	3.05	0.945	0.237	4.5	1.73
Acetone	6.22	3.95	2.200	0.070	—	1.3

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APPENDIX: RELATIVE DIPOLE DISPLACEMENT

An estimate of the relative displacement of a point dipole from the center of a spherical molecule is developed.

Rowlinson has shown for the Stockmayer potential that by placing

$$\frac{d\,\Gamma(r, \theta, \Phi)}{dr} = 0$$

one obtains a cubic equation for $\left(\frac{\sigma}{r_o}\right)^3$ where r_o is the equilibrium separation of the molecules. When the interaction energy between the molecules is largely due to dipole-dipole attraction, r_o will not be determined so much by the size of the molecules as by the equilibrium separation of the dipoles. The distance r_o is related to $\sigma_{Stockmayer}$ by an equation containing the reduced dipole moment t^*.

For $t^* = 0$ the Stockmayer potential energy equation reduces to the Lennard-Jones potential. Then setting $d\,\Gamma/dr = 0$ will give r^*_{LJ}, the equilibrium separation between the centers of the molecules. Figure A shows two spherical polar molecules at a separation where $d\,\Gamma/dr = 0$. The dipole of the molecule is displaced from the center of the molecule by a distance s. From Figure A,

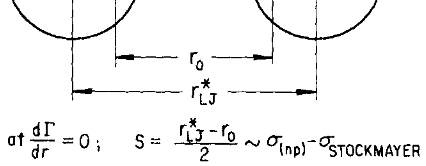

Fig. A. Equilibrium position of two polar molecules having noncentral point dipoles.

$$r^*_{LJ} = r_o + 2s \qquad (1A)$$

which can be rewritten

$$s = \frac{r^*_{LJ} - r_o}{2} \qquad (2A)$$

Now since

$$r^*_{LJ} = 2^{1/6}\,\sigma \qquad (3A)$$

using Equation (13) one obtains

$$r^*_{LJ} = 2^{1/6}\,\sigma_{(np)} \qquad (4A)$$

Equation (13) is the defining equation for the distance parameter of the homomorph of the polar molecule. In order to obtain r_o it would be necessary to solve a cubic equation for each molecule in question, after having obtained $\sigma_{Stockmayer}$ from experimental data. In order to facilitate calculation, one replaces r_o by $\sigma_{Stockmayer}$ as a first approximation. Then $\sigma_{(np)} - \sigma_{Stockmayer}$ is an estimate of the displacement of the dipole from the center of the molecule, which may be used to find the correction factor Kj from Figure 5.

By an alternate procedure one might estimate the distance s in the following manner. Suppose that the total energy of vaporization of the polar molecule were divided into parts as shown in Equation (5):

$$\underset{\text{total}}{\Delta E_{vap}} = \underset{\substack{\text{non-}\\ \text{polar}\\ \text{forces}}}{\Delta E_{vap}} + \underset{\substack{\text{polar}\\ \text{forces}}}{\Delta E_{vap}} \qquad (5A)$$

$$\underset{\substack{\text{polar}\\ \text{forces}}}{\Delta E_{vap}} = \underset{\substack{\text{central}\\ \text{dipole}}}{\Delta E_{vap}} + \underset{\substack{\text{non-}\\ \text{central}\\ \text{dipole}}}{\Delta E_{vap}} + \underset{\substack{\text{chemical}\\ \text{forces}}}{\Delta E_{vap}} \qquad (6A)$$

The energy of vaporization due to the nonpolar (dispersion) forces may be estimated by means of the homomorph of the polar molecule. The energy of vaporization due to a central dipole may be calculated from equations of Böttcher (page 154). If no chemical bonding is present the residual ΔE_{vap} may be found from experimental values of E_{vap}, and s may then be related to $\Delta E_{vap\ noncentral\ dipole}$. If chemical forces (such as hydrogen bonding) are present, a separate estimate must be made of the heat of formation of the chemical bond considered. Unfortunately there are not enough accurate experimental data available to make this method of estimating s practical. Table 3 compares the various energies of vaporization for a few molecules. There evidently is a correlation between the fourth and sixth columns as expected.