Effective Collision Diameters and Correlation of Some Thermodynamic Properties of Solutions

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Volumetric data on gas mixtures and vapor-phase data for gas-liquid equilibria have been correlated within the framework of the theory of corresponding states. An expression based on the London potential for dispersion forces was used to compute characteristic temperatures for various binary systems, and a correlation was developed relating these temperatures to the polarizabilities, ionization potentials, and critical volumes of the pure components. The correlation shows how the molecular shape of a liquid affects its vapor-phase solubility. With the help of this correlation it is possible to make very good predictions of such gas-liquid equilibria as are required in high-pressure distillation, absorption, and petroleum hydrofining operations.

A study of volumetric data for mixtures of gases at moderate pressures has shown that the properties of gas-phase mixtures can be successfully interpreted within the framework of the theory of corresponding states (*5, 18*). Further it has been shown (*14*) that by extending the theory of corresponding states with techniques based on the theory of intermolecular forces one can make good predictions of fugacities as required in high-pressure phase equilibria and rate processes.

In the work referred to above, a correlation was presented for estimating the parameters required for the calculation of mixture properties. Specifically techniques were given for calculating the second virial coefficient of a mixture, which is given by

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \qquad (1)$$

The second virial coefficient can be calculated from an expression of the form

$$\frac{B_{ij}}{V_{c_{ij}}} = \theta_B\left(\frac{T}{T_{c_{ij}}}, \omega_{ij}\right) \qquad (2)$$

The semiempirical correlations proposed in the earlier work were limited by the scarcity of data for highly asymmetric systems, that is for those systems having one component of low and one of high molecular weight. To overcome this limitation, data were recently obtained on the solubility of several liquids in compressed hydrogen, nitrogen, and carbon dioxide (*16*). These data indicated that the previously proposed correlation could be considerably improved by taking into account the shape as well as the size of the molecules in determining the characteristic temperature of the interaction between dissimilar molecules. The method of correlation described here uses simple mixing rules for the characteristic volume and the characteristic acentric factor. For a binary system containing components 1 and 2

$$V_{c_{12}} = 1/2[V_{c_1} + V_{c_2}] \qquad (3)^*$$

and

$$\omega_{12} = 1/2[\omega_1 + \omega_2] \qquad (4)$$

However the characteristic temperature, which is the most important parameter in the determination of the second virial coefficient, cannot be computed by any simple formula. The temperature characteristic of the interaction between two molecules of different size and/or shape is usually less than the geometric mean of the critical temperatures of the pure components, with the geometric mean as an upper limit. Prausnitz and Gunn (*18*) showed that for some hydrocarbons and related compounds with a common gas the correction which must be applied to the geometric mean is a straight-line function of the critical-volume ratio of the two pure components. However some of the results of recent experimental work (*16*) and of previously published phase-equilibrium data could not be correlated by this method, especially the data for systems containing carbon tetrachloride or *n*-decane. It therefore appeared advisable to consider an alternate method of correlation based on the attraction part of the potential-energy function acting between the dissimilar molecules.

CHARACTERISTIC TEMPERATURES FROM COLLISION DIAMETERS

According to the London theory of dispersion forces (*7*), one can express the potential energy between two molecules 1 and 2 by

$$\Gamma_{12} = -\frac{3\alpha_1\alpha_2 I_1 I_2}{2r^6(I_1 + I_2)} \qquad (5)$$

London's formula can be rewritten in terms of a dimensionless distance:

$$\Gamma_{12} = \epsilon_{12}\left(\frac{\sigma_{12}}{r}\right)^6 \qquad (6)$$

The characteristic energy can be related to the characteristic temperature by

$$\frac{\epsilon_{12}}{k} = \frac{3}{2}\beta T_{c_{12}} \qquad (7)$$

London's formula is strictly valid only for monatomic molecules. However by a suitable choice of parameters the London theory has been applied successfully to the calculation of thermodynamic and transport properties of a variety of polyatomic substances (*7*).

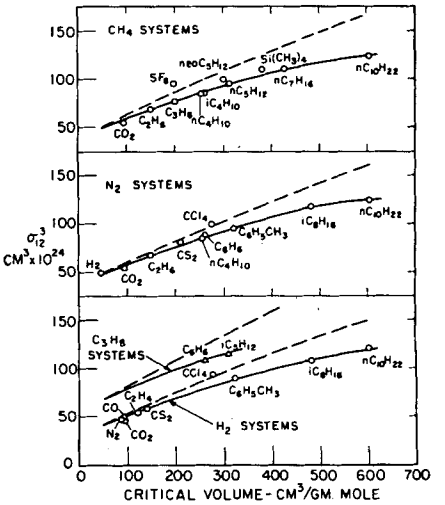

Fig. 1. Collision diameters for binary systems containing methane, nitrogen, hydrogen, and propane.

When one substitutes (6) and (7) into (5),

$$T_{c_{12}} = \frac{\alpha_1\alpha_2 I_1 I_2}{\beta k \sigma_{12}^6 (I_1 + I_2)} \qquad (8)$$

For spherical molecules the characteristic distance of interaction can be related to the characteristic distances for the pure components by

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \qquad (9)$$

In addition for pure components consisting of spherical molecules the characteristic interaction distance σ_{11} can be related to the critical volume by the empirical relation (*7*)

$$0.75 V_{c_1} = \tfrac{2}{3}\pi N \sigma_{11}^3 \qquad (10)$$

Equation (10) becomes increasingly poor as the molecule becomes more asymmetric.

The constant β in Equation (8) was evaluated by the use of published data for the polarizabilities and ionization potentials of the pure components and by use of characteristic temperatures for binary systems whose components consist of small spherical molecules (*18*). In this calculation the collision diameter σ_{12} was computed by Equations (9) and (10), which are appropriate for small, spherical (or nearly spherical) molecules such as nitrogen, methane, hydrogen, and carbon monoxide. The value of β was found to be 0.744; values of β for pure components

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*The somewhat more complicated method of obtaining $V_{c_{12}}$ presented earlier (*18*) has not been used in this work.

TABLE 1. COLLISION DIAMETERS, Å.

Component	Major axis	Minor axis	Equivalent sphere	Observed from binary data
n-Heptane	13.4	4.36	6.33	5.71
n-Decane	18.8	4.36	7.10	6.17
Carbon tetrachloride	5.47	5.47	5.47	5.48

TABLE 2. EFFECTIVE COLLISION DIAMETERS FOR VARIOUS MOLECULES OBTAINED FROM BINARY DATA CONTAINING ONE SMALL COMPONENT

Molecule	σ, Å.	Molecule	σ, Å.
H_2	3.55	iC_4H_{10}	4.91
N_2	3.77	nC_5H_{12}	5.16
H_2S	3.87	iC_5H_{12}	5.25
CO	3.80	$neoC_5H_{12}$	5.37
CO_2	3.68	nC_7H_{16}	5.71
CS_2	4.80	iC_8H_{18}	5.98
CH_4	3.89	$nC_{10}H_{22}$	6.17
C_2H_4	4.10	C_6H_6	5.04
C_2H_6	4.33	$C_6H_5CH_3$	5.38
C_3H_6	4.53	CCl_4	5.48
C_3H_8	4.65	SF_6	5.27
nC_4H_{10}	4.96	$Si(CH_3)_4$	5.67

having small molecules range from 0.70 to 0.79 (*7*). When this value for β was used, binary collision diameters were evaluated for a number of binary systems containing hydrogen, nitrogen, methane, carbon dioxide, hydrogen sulfide, and propane by the use of Equation (8) with values of $T_{c_{12}}$ obtained from previously published volumetric and vapor-liquid equilibria data (*1, 2, 4, 8, 9, 10, 11, 18, 19, 20*). The results of these calculations are shown in Figures 1 and 2, where the cube of the collision diameter is plotted as a function of the critical volume of the second component. The dashed lines are calculated by means of Equation (9) for σ_{12} and Equation (10) for the collision diameter of the second component; thus one assumes the second molecular species to be spherical. To plot the dashed curves for hydrogen, carbon dioxide, and propane, an effective collision diameter σ_{22}* for these molecules was defined by

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{22}^* + \sigma_{11}) \qquad (9a)$$

The effective diameters were calculated from observed collision diameters of these compounds with small, spherical (or nearly spherical) molecules. For carbon dioxide, effective collision diameters with nitrogen, methane, and hydrogen were 3.71, 3.69, and 3.63 Å., respectively.

EFFECT OF MOLECULAR SHAPE

Figures 1 and 2 indicate that the observed collision diameters for binary systems including one small, spherical (or nearly spherical) molecule and one nonspherical molecule are significantly less than those for binary systems containing two spherical molecules. These figures show the interesting result that the points for large molecules having spherical symmetry, such as carbon tetrachloride, sulfur hexafluoride, neopentane, and tetramethyl silane, lie well above the curves for nonspherical molecules.

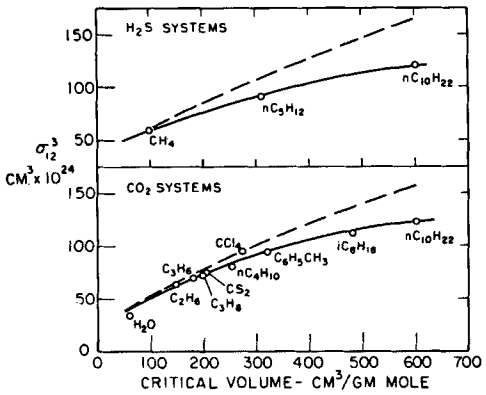

Fig. 2. Collision diameter for binary systems containing hydrogen sulfide and carbon dioxide.

The characteristic temperatures of some of the binary systems containing methane and higher paraffins reported here on the basis of phase-equilibrium data are somewhat larger than those previously reported (*18*) on the basis of vapor-phase compressibility data. The earlier calculations used an indirect method which gives considerably less accurate values for $T_{c_{12}}$ than those which used phase-equilibrium data.

Since only a few substances consist of spherical molecules, Equations (9) and (10) are not generally valid. Most polyatomic molecules could be described more accurately as ellipsoids than as spheres, and it is therefore to be expected that the effective collision diameters of ellipsoidal molecules should lie somewhere between the lengths of their minor and major axes. In a collision between a small spherical molecule and a larger ellipsoidal molecule the spherical molecule would interact mainly with the atoms closest to the point of collision. One might expect therefore that the distance between the colliding spherical molecule and the interacting atoms of the large molecule, that is the collision diameter, should be less than the collision diameter for the same small spherical molecule with a different spherical molecule having the same volume as the ellipsoidal molecule. For example when one considers the collision of a small molecule such as hydrogen with either of two larger molecules of similar size such as *n*-pentane and neopentane, it would appear likely that the collision diameter of hydrogen with *n*-pentane (which is rod-shaped) would be considerably smaller than the collision diameter of hydrogen with neopentane (which is spherical), even though *n*-pentane and neopentane have approximately the same size, as indicated by their critical volumes. It is this effect which is so clearly shown in Figures 1 and 2.

If the assumption is made that a polyatomic molecule is ellipsoidal in shape, the lengths of the two axes can be estimated from the critical volume, bond lengths, and bond angles. To illustrate, measured bond angles and bond lengths reported by Pauling (*13*) were used to calculate the ratio of the length to the width of the molecule for *n*-heptane and *n*-decane. Equating this ratio to the ratio of the lengths of the two axes of an ellipse, and assuming rotation about the major axis, one could calculate the lengths of the axes by means of a modification of Equation (10):

$$0.75v_{c_1} = \tfrac{2}{3}\pi N\sigma_S{}^2\sigma_M \qquad (10a)$$

The results are given in Table 1.

Table 1 shows that for ellipsoidal molecules the collision diameters observed from the data, as expected, lie between the lengths of the minor and the major diameters of the ellipsoids, much closer to the lengths of the minor axes. Also, as indicated in Figures 1 and 2, the observed collision diameters for the ellipsoidal molecules are less than the diameters of spherical molecules having the same size.

Table 2 gives effective collision diameters calculated from published binary data.* These may be used to compute thermodynamic properties of mixtures; for example, to predict the vapor-phase solubility of a liquid in a gas, it is necessary to know only the collision diameter for the pair, the polarizabilities, and the ionization potentials. This information is used to calculate $T_{c_{12}}$, which, together with the generalized function, yields the virial coefficient B_{12}. Once this coefficient is known, the vapor-phase solubility can be found from the thermodynamic equations discussed previously (*16*).

The use of effective collision diameters is not restricted to binary mixtures but, as indicated by Equation (1), may be used for multicomponent mixtures, provided the density is not too high (*14*).

APPLICATIONS

The collision diameters in Table 2 and the correlations shown in Figures 1 and 2 are useful for predicting gas-liquid phase equilibria as may be required in such diffusional operations as high-pressure absorption, distillation, partial condensation, freezing out, etc. The collision diameters are required to determine the characteristic temperature [Equation (8)], which, together with Equations (3) and (4) and the generlized function, determines the cross-virial coefficient B_{12} [Equation (2)], which in turn is required in the phase-equilibrium equations given in reference *16*.

The correlations presented here are useful for the prediction of vapor-phase fugacities

*The effective collision diameters in Table 2 should not be applied to binary mixtures consisting entirely of large molesules, since the values tabulated here were obtained exclusively from binaries containing at least one component which consisted of small spherical molecules.

and hence are of direct applicability in the calculation of the phase-equilibrium behavior of the heavy component in gas-liquid equilibria; however they are not useful for the calculation of the phase-equilibrium behavior of the lighter component whose major correction for nonideality is in the liquid phase. For the light component a different approach must be used (*15, 17*).

One particular application of the ideas developed here is in hydrofining processess in the petroleum industry, where accurate K values for hydrocarbons in the presence of excess hydrogen are needed in process design, for example when one desires to know the equilibrium ratio for n-hexane in hydrogen (a system not used in the correlation presented here) at 340°F. and 100 atm. total pressure.

The collision diameter is obtained by the use of the curve for hydrogen-containing systems. Since the critical volume of n-hexane is 368 cc./g.-mole, $\sigma_{12}^3 = 96 \times 10^{-24}$ cc. The following data are needed for the calculation:

	Hydrogen
(pseudo)V_c	= 47.0 cc./g.-mole
(pseudo)ω	= 0.00
α	= 7.9×10^{-25} cc.
I	= 15.4 e.v.
	n-Hexane
T_c	= 508°K.
ω	= 0.30
α	= 118×10^{-25} cc.
I	= 10.4 e.v.
v^{0L}	= 168 cc./g.-mole
P_1^0	= 10.8 atm.

From Equation (8), $T_{c_{12}} = 98$°K. By using Equations (3) and (4) and tabulated values of θ_B (*14*), one obtains

$v_{c_{12}} = 208$ cc./g.-mole
$\omega_{12} = 0.15$
$B_{12} = (0.322)(208) = 66.9$ cc./g.-mole

The fugacity of pure liquid n-hexane at 100-atm. pressure is 12.9 atm., and a first estimate of y_1 is calculated with an assumption of ideal behavior and the use of an estimate of x_2, the solubility of hydrogen in the liquid phase (*3*). Since x_2 is small compared to unity, the estimated solubility need not be highly accurate. The second virial coefficient for n-hexane, when one uses tabulated values of θ_B, is −688 cc./g.-mole, and the second virial coefficient for hydrogen is 15 cc./g.-mole from published volumetric data (*6*). The molar volume of the vapor mixture is now calculated from the second virial coefficient of the mixture; it is $v = 369$ cc./g.-mole. Using these quantities, one finds that the vapor-phase fugacity coefficient of n-hexane is 0.627 and that the equilibrium ratio $K_1 = y_1/x_1 = 0.206$.* Using this computed value of K, one finds a new value of y_1, and if necessary the calculation is repeated. Convergence in these calculations is very rapid. Similar calculations were also made at 220°F. and at various pressures; the results are compared with observed data (*12*) in Figure 3, where the equilibrium ratio is plotted as a function of pressure for two temperatures.

The correlations presented in this work may be particularly useful for the calculation of gas-liquid equilibria at lower temperatures, where experimental vapor-phase compositions are very difficult to determine accurately.

*See reference *16* for details of this type of calculation.

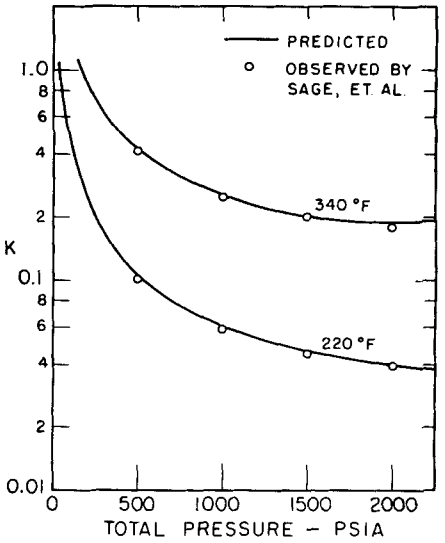

Fig. 3. Equilibrium ratios of hexane in hydrogen at 220 and 340°F.

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NOTATION

B = second virial coefficient
B_{ij} = second virial coefficient characteristic of interaction between one molecule of species i and one molecule of species j
I = first ionization potential
k = Boltzmann constant
N = Avogadro's number
P = pressure
r = distance between molecules
R = gas constant
T = absolute temperature
$T_{c_{ij}}$ = temperature characteristic of i — j interaction
$T_{c_{12}}$ = characteristic temperature of 1-2 interaction
V = volume
$V_{c_{ij}}$ = volume characteristic of i — j interaction
V_{c_1} = critical volume of pure component 1
v = molar volume
x = mole fraction in liquid phase
y = mole fraction in vapor phase

Greek Letters

α = polarizability
β = a dimensionless constant
ϵ = characteristic energy
ϵ_{12} = energy characteristic of 1-2 interaction
Γ = potential energy
σ = collision diameter
σ_{11} = characteristic interaction distance
σ_{12} = collision diameter characteristic of 1-2 interaction
σ_{22}^* = effective collision diameter
σ_M = major diameter
σ_s = minor diameter
ω = acentric factor
ω_{ij} = acentric factor characteristic of i — j interaction
ω_1 = acentric factor of pure component 1
θ_B = generalized function for the second virial coefficient

Subscripts

c = critical or characteristic
1, 2 = components
m = mixture
M = major
S = minor

Superscripts

L = liquid phase
0 = pure component

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