

from "Molecular Thermodynamics of Fluid-Phase Equilibria", J.M. Prausnitz, R.N. Lichtenhaler, + E.G. deAzevedo, 3rd ed, (Prentice-Hall, NJ, 1999).

Prausnitz-5

## 5.2 The Virial Equation of State

As indicated at the beginning of this chapter, the problem of calculating fugacities for components in a gaseous mixture is equivalent to the problem of establishing a reliable equation of state for the mixture; once an equation of state exists, fugacities can be found by straightforward computation. Such computation presents no difficulties in principle although it may be tedious because it may require trial-and-error calculations.

Many equations of state have been proposed and each year additional ones appear in the literature, but most of them are either totally or at least partially empirical. All empirical equations of state are based on more or less arbitrary assumptions that are not generally valid. Because the constants in an empirical equation of state for a pure gas have at best only approximate physical significance, it is difficult (and frequently impossible) to justify mixing rules for expressing the constants of the mixture in terms of the constants of the pure components that comprise the mixture. As a result, because mixing rules introduce further arbitrary assumptions, for typical empirical equations of state, one set of mixing rules may work well for one or several mixtures but poorly for others (Cullen and Kobe, 1955).

To calculate with confidence fugacities in a gas mixture, it is advantageous to use an equation of state where the parameters have physical significance, i.e. where the parameters can be related directly to intermolecular forces. One equation of state that possesses this desirable ability is the *virial equation of state*.

Figure 5-1 shows a plot of the compressibility factor as a function of density for helium, methane, and three binary mixtures containing 10, 25 and 50 mole per cent water in methane. For these systems, the magnitudes of the intermolecular forces differ appreciably and depend strongly on density (or pressure). The compressibility factor for the methane mixture containing 10 mol % water deviates little from unity over a wide range of density, even when compared with the compressibility factors of pure methane or helium. However, as density increases, the compressibility factor plot for the same mixture shows a change in the slope from negative to positive. It is apparent that, to describe systems as those in Fig. 5-1, the parameters that appear in a gas-phase equation of state must account for a large variety of intermolecular forces that are responsible for the nonideality of the gas.

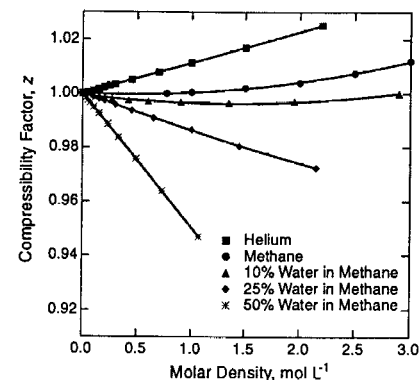


Figure 5-1 Compressibility factors for helium, methane and three water/methane mixtures as a function of density at 498.15 K (Joffron and Eubank, 1988).

The virial equation of state for nonelectrolyte gases has a sound theoretical foundation, free of arbitrary assumptions (Mason and Spurling, 1969). The virial equation gives the compressibility factor as a power series in the reciprocal molar volume  $1/v$ :

<sup>1</sup> Equation (5-9) is frequently written in the equivalent form

$$z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots$$

where  $\rho$ , the molar density, is equal to  $1/v$ . It is most conveniently derived using the grand partition function (see App. B) as, for example, in Hill (1986). The derivation shows that the virial equation is remarkably general, provided that the intermolecular potential obeys certain well-defined restrictions.

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (5-9)$$

In Eq. (5-9),  $B$  is the second virial coefficient,  $C$  is the third virial coefficient,  $D$  is the fourth, and so on. All virial coefficients are independent of pressure or density; for pure components, they are functions only of the temperature. The unique advantage of the virial equation follows, as shown later, because there is a theoretical relation between the virial coefficients and the intermolecular potential. Further, in a gaseous mixture, virial coefficients depend on composition in an exact and simple manner.

The compressibility factor is sometimes written as a power series in the pressure:

$$z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \dots \quad (5-10)$$

where coefficients  $B'$ ,  $C'$ ,  $D'$ , ... depend on temperature but are independent of pressure or density. For mixtures, however, these coefficients depend on composition in a more complicated way than do those appearing in Eq. (5-9). Relations between the coefficients in Eq. (5-9) and those in Eq. (5-10) are derived in App. C with the results

$$B' = \frac{B}{RT} \quad (5-11)$$

$$C' = \frac{C - B^2}{(RT)^2} \quad (5-12)$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \quad (5-13)$$

Equation (5-9) is usually superior to Eq. (5-10) in the sense that when the series is truncated after the third term, the experimental data are reproduced by Eq. (5-9) over a wider range of densities (or pressures) than by Eq. (5-10), provided that the virial coefficients are evaluated as physically significant parameters. In that case, the second virial coefficient  $B$  is properly evaluated from low-pressure  $P$ - $V$ - $T$  data by the definition

$$B = \lim_{\rho \rightarrow 0} \left( \frac{\partial z}{\partial \rho} \right)_T \quad (5-14)$$

Similarly, the third virial coefficient must also be evaluated from  $P$ - $V$ - $T$  data at low pressures; it is defined by

$$C = \lim_{\rho \rightarrow 0} \frac{1}{2!} \left( \frac{\partial^2 z}{\partial \rho^2} \right)_T \quad (5-15)$$

Reduction of  $P$ - $V$ - $T$  data to yield second and third virial coefficients is illustrated in Fig. 5-2, taken from the work of Douslin (1962) on methane. In addition to Douslin's data, Fig. 5-2 also shows experimental results from several other investigators. The coordinates of Fig. 5-2 follow from rewriting the virial equation in the form

$$v \left( \frac{Pv}{RT} - 1 \right) = B + \frac{C}{v} + \dots \quad (5-16)$$

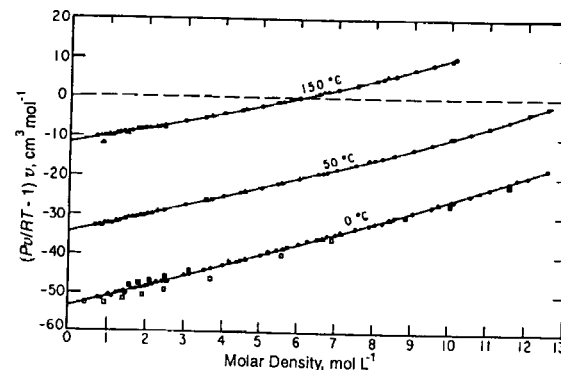


Figure 5-2 Reduction of  $P$ - $V$ - $T$  data for methane to yield second and third virial coefficients (data from various sources).

When isothermal data are plotted as shown, the intercept on the ordinate gives  $B$ , while  $C$  is found from the limiting slope as  $1/v \rightarrow 0$ . For mixtures, the same procedure is used, but in addition to isothermal conditions, each plot must also be at constant composition. An example is given in Fig. 5-3 for the mixture methanol/methyl acetate at several temperatures (Olf *et al.*, 1989).

An illustration of the applicability of Eqs. (5-9) and (5-10) at two different temperatures is given in Figs. 5-4 and 5-5, based on Michels' accurate volumetric data for argon (Michels *et al.*, 1960; Guggenheim and McGlashan, 1960; Munn, 1964; Munn *et al.*, 1965, 1965a). Using only low-pressure data along an isotherm,  $B$  and  $C$  were calculated as indicated by Eq. (5-16). These coefficients were then used to predict the

compressibility factors at higher pressures (or densities). One prediction is based on Eq. (5-9) and the other on Eq. (5-10) together with Eqs. (5-11) and (5-12). Experimentally determined isotherms are also shown. In both cases, Eq. (5-9) is more successful than Eq. (5-10).<sup>2</sup>

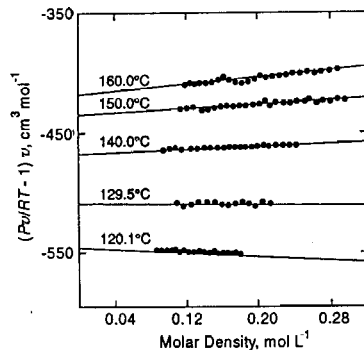


Figure 5-3 Reduction of  $P$ - $V$ - $T$  data for methanol/methyl acetate to yield second and third virial coefficients of approximately equimolar mixtures (Olf *et al.*, 1989).

For many gases, it has been observed that Eq. (5-9), when truncated after the third term (i.e., when  $D$  and all higher virial coefficients are neglected), gives a good representation of the compressibility factor to about one half the critical density and a fair representation to nearly the critical density.

For higher densities, the virial equation is of little practical interest. Experimental as well as theoretical methods are not sufficiently developed to obtain useful quantitative results for fourth and higher virial coefficients. The virial equation is, however, applicable to moderate densities as commonly encountered in many typical vapor-liquid and vapor-solid equilibria.

The significance of the virial coefficients lies in their direct relation to intermolecular forces. In an ideal gas, the molecules exert no forces on one another. In the real world, no ideal gas exists, but when the mean distance between molecules becomes very large (low density), all gases tend to behave as ideal gases. This is not surprising because intermolecular forces diminish rapidly with increasing intermolecular distance and therefore forces between molecules at low density are weak. However, as density rises, molecules come into closer proximity with one another and, as a result, interact more

<sup>2</sup> The comparisons shown in Figs. 5-4 and 5-5 are for the case where Eqs. (5-9) and (5-10) are truncated after the quadratic terms. When similar comparisons are made with these equations truncated after the linear terms, it often happens that, because of compensating errors, Eq. (5-10) provides a better approximation at higher densities than Eq. (5-9). See Chueh and Prausnitz (1967).

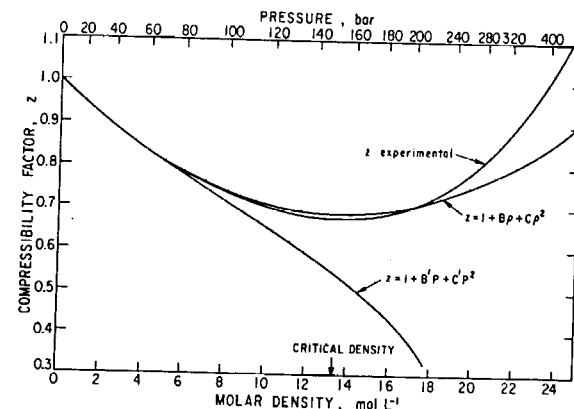


Figure 5-4 Compressibility factor for argon at  $-70^{\circ}\text{C}$ .

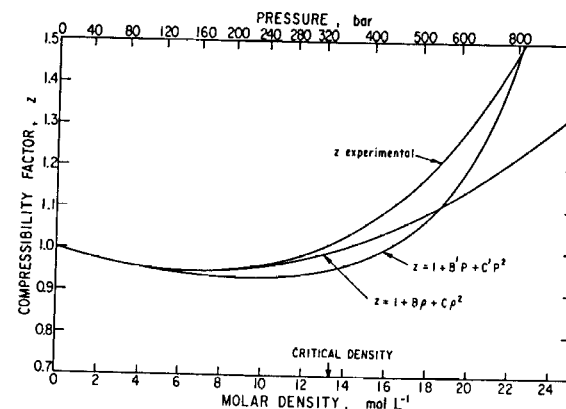


Figure 5-5 Compressibility factor for argon at  $25^{\circ}\text{C}$ .

frequently. The purpose of the virial coefficients is to take these interactions into account. The physical significance of the second virial coefficient is that it takes into account deviations from ideal behavior that result from interactions between two molecules. Similarly, the third virial coefficient takes into account deviations from ideal behavior that result from the interaction of three molecules. The physical significance of each higher virial coefficient follows in an analogous manner.

From statistical mechanics we can derive relations between virial coefficients and intermolecular potential functions (Hill, 1986). For simplicity, consider a gas composed of simple, spherically symmetric molecules such as methane or argon. The potential energy between two such molecules is designated by  $\Gamma(r)$ , where  $r$  is the distance between molecular centers. The second and third virial coefficients are given as functions of  $\Gamma(r)$  and temperature by

$$B = 2\pi N_A \int_0^\infty \left[ 1 - e^{-\Gamma(r)/kT} \right] r^2 dr \quad (5-17)$$

and

$$C = \frac{-8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} f_{12} f_{13} f_{23} r_{12}^2 r_{13}^2 dr_{12} dr_{13} dr_{23} \quad (5-18)$$

where  $f_{ij} \equiv \exp(-\Gamma_{ij}/kT) - 1$ ,  $k$  is Boltzmann's constant and  $N_A$  is Avogadro's constant.

Similar expressions can be written for the fourth and higher virial coefficients. While Eqs. (5-17) and (5-18) refer to simple, spherically symmetric molecules, we do not imply that the virial equation is applicable only to such molecules; rather, it is valid for essentially all stable, uncharged (electrically neutral) molecules, polar or nonpolar, including those with complex molecular structure. However, in a complex molecule the intermolecular potential depends not only on the distance between molecular centers but also on the spatial geometry of the separate molecules and on their relative orientation. In such cases, it is possible to relate the virial coefficients to the intermolecular potential, but the mathematical expressions corresponding to Eqs. (5-17) and (5-18) are necessarily more complicated.

Special care must be taken with "reactive" molecules, for example, molecules like acetic acid that dimerize, as discussed in Sec. 5.9.

<sup>3</sup> Similarly, the McMillan-Mayer solution theory provides the link between the osmotic second virial coefficient ( $B_{22}$ ) of a solute (see Sec. 4.11) dilute in a solvent medium and the potential of mean force,  $w_{22}$ :

$$B_{22}^*(T, \mu_s) = 2\pi N_A \int_0^\infty \left[ 1 - e^{-w_{22}(r, \mu_s, T)/kT} \right] r^2 dr$$

where  $\mu_s$  is the chemical potential of the solvent. Osmotic third virial coefficients can also be calculated from the potential of mean force. While in a gas  $B$  depends only on temperature, in a dilute solution  $B_{22}^*$  depends on temperature and chemical potential of the solvent.

<sup>4</sup> Equation (5-18) assumes, for convenience, that the potential energy of molecules 1, 2, and 3 is given by the sum of the three binary potential energies (additivity assumption):  $\Gamma_{123}(r_{12}, r_{13}, r_{23}) = \Gamma_{12}(r_{12}) + \Gamma_{13}(r_{13}) + \Gamma_{23}(r_{23})$ . This assumption is unfortunately not strictly correct, although in many cases, it provides a good approximation.

## 5.3 Extension to Mixtures

Perhaps the most important advantage of the virial equation of state for application to phase equilibrium problems lies in its direct extension to mixtures. This extension requires no arbitrary assumptions. The composition dependences of all virial coefficients are given by a generalization of the statistical-mechanical derivation used to derive the virial equation for pure gases.

First, consider the second virial coefficient that takes into account interactions between two molecules. In a pure gas, the chemical identity of each of the interacting molecules is always the same; in a mixture, however, there are various types of two-molecule interactions depending on the number of components present. In a binary mixture containing species  $i$  and  $j$ , there are three types of two-molecule interactions, designated  $i$ - $i$ ,  $j$ - $j$ , and  $i$ - $j$ . For each of these interactions there is a corresponding second virial coefficient that depends on the intermolecular potential between the molecules under consideration. Thus  $B_{ii}$  is the second virial coefficient of pure  $i$  that depends on  $\Gamma_{ii}$ ;  $B_{jj}$  is the second virial coefficient of pure  $j$  that depends on  $\Gamma_{jj}$ ; and  $B_{ij}$  is the second virial coefficient corresponding to the  $i$ - $j$  interaction as determined by  $\Gamma_{ij}$ , the potential energy between molecules  $i$  and  $j$ . If  $i$  and  $j$  are spherically symmetric molecules,  $B_{ij}$  is given by the same expression as that in Eq. (5-17):

$$B_{ij} = 2\pi N_A \int_0^\infty \left[ 1 - e^{-\Gamma_{ij}(r)/kT} \right] r^2 dr \quad (5-19)$$

The three second virial coefficients  $B_{ii}$ ,  $B_{jj}$ , and  $B_{ij}$  are functions only of the temperature; they are independent of density (or pressure) and, what is most important, they are independent of composition. Because the second virial coefficient is concerned with interactions between *two* molecules, it can be rigorously shown that the second virial coefficient of a mixture is a *quadratic* function of the mole fractions  $y_i$  and  $y_j$ . For a binary mixture of components  $i$  and  $j$ ,

$$B_{\text{mixt}} = y_i^2 B_{ii} + 2y_i y_j B_{ij} + y_j^2 B_{jj} \quad (5-20)$$

For a mixture of  $m$  components, the second virial coefficient is given by a rigorous generalization of Eq. (5-20):

$$B_{\text{mixt}} = \sum_{i=1}^m \sum_{j=1}^m y_i y_j B_{ij} \quad (5-21)$$

## 5.5 Calculation of Virial Coefficients from Potential Functions

In previous sections we discussed the nature of the virial equation of state and, in Eq. (5-28), we indicated the way it may be used to calculate the fugacity of a component in a gaseous mixture. We must now consider how to calculate the virial coefficients that appear in Eq. (5-28) and, to do so, we make use of our discussion of intermolecular forces in Chap. 4.

First, we must recognize that the first term on the right-hand side of Eq. (5-28) is frequently much more important than the second term; at low or moderate densities, the second term is sufficiently small to allow us to neglect it. This is fortunate because we can estimate  $B$ 's with much more accuracy than we can estimate  $C$ 's.

Equation (5-19) gives the relation between the second virial coefficient  $B_{ij}$  and the intermolecular potential function  $\Gamma_{ij}(r)$  for spherically symmetrical molecules  $i$  and  $j$ , where  $i$  and  $j$  may, or may not, be chemically identical. If the potential function  $\Gamma_{ij}(r)$  is known, then  $B_{ij}$  can be calculated by integration as indicated by Eq. (5-19) and similarly, if the necessary potentials are known,  $C_{ijk}$  can be found from Eq. (5-24). Such integrations have been performed for many types of potential functions corresponding to different molecular models. A few models are illustrated in Figs. 5-8 and 5-9. We now give a brief discussion of each of them with reference to second virial coefficients, followed by a short section on third virial coefficients.

**Ideal-Gas Potential.** The simplest (trivial) case is to assume that  $\Gamma = 0$  for all values of the intermolecular distance  $r$ . In that case, the second, third, and higher virial coefficients are zero for all temperatures and the virial equation reduces to the ideal-gas law.

**Hard-Sphere Potential.** This model takes into account the nonzero size of the molecules but neglects attractive forces. It considers molecules to be like billiard balls; for hard-sphere molecules there are no forces between the molecules when their centers are separated by a distance larger than  $\sigma$ , the hard-sphere diameter, but the force of repulsion becomes infinitely large when they touch, at a separation equal to  $\sigma$ . The potential function  $\Gamma(r)$  is given by

$$\Gamma = \begin{cases} 0 & \text{for } r > \sigma \\ \infty & \text{for } r \leq \sigma \end{cases} \quad (5-34)$$

Substituting into Eqs. (5-19), we obtain for a pure component

$$B = -\frac{2}{3}\pi N_A \sigma^3 \quad (5-35)$$

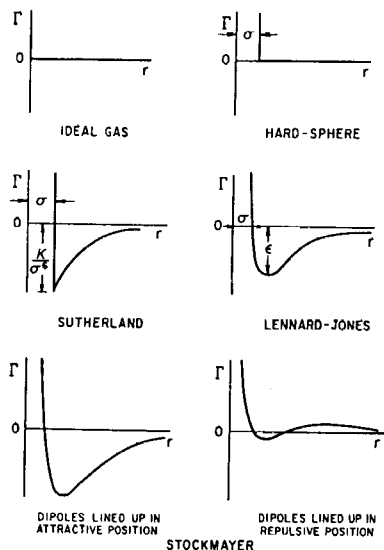


Figure 5-8 Potential functions with zero, one, or two adjustable parameters.

For mixtures, the second virial coefficient  $B_{ij}$  ( $i \neq j$ ) is

$$B_{ij} = \frac{2}{3} \pi N_A \left( \frac{\sigma_i + \sigma_j}{2} \right)^3 \quad (5-36)$$

The hard-sphere model gives a highly oversimplified picture of real molecules because, for a given gas, it predicts second virial coefficients that are independent of temperature. These results are in strong disagreement with experiment but give a rough approximation for the behavior of simple molecules at temperatures far above the critical. For example, helium or hydrogen have very small forces of attraction; near room temperature, where the kinetic energies of these molecules are much larger than their potential energies, the size of the molecules is the most significant factor that contributes to deviation from ideal-gas behavior. Therefore, at high-reduced temperatures, the hard-sphere model provides a reasonable but rough approximation. Because Eq. (5-34) requires only one characteristic constant, the hard-sphere model is a one-parameter model.

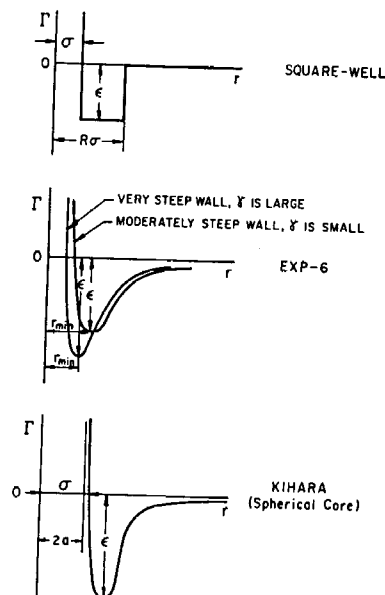


Figure 5-9 Potential functions with three adjustable parameters.

**Sutherland Potential.** According to London's theory of dispersion forces, the potential energy of attraction varies inversely as the sixth power of the distance of separation. When this result is combined with the hard-sphere model, the potential function becomes

$$\Gamma = \begin{cases} \infty & \text{for } r \leq \sigma \\ -\frac{K}{r^6} & \text{for } r > \sigma \end{cases} \quad (5-37)$$

where  $K$  is a constant depending on the nature of the molecule. London's equation [Eq. (4-19)] suggests that  $K$  is proportional to the ionization potential and to the square of the polarizability. The Sutherland model provides a large improvement over the hard-sphere model and it is reasonably successful in fitting experimental second-virial-coefficient data with its two adjustable parameters. Like the hard-sphere model, however, it predicts that at high temperatures the second virial coefficient approaches a constant value, although the best available data show that it goes through a weak

maximum at a temperature very much higher than the critical. This limitation is not serious in typical phase-equilibrium problems where such high-reduced temperatures are almost never encountered except, perhaps, for helium.

**Lennard-Jones' Form of Mie's Potential.** As discussed in Chap. 4, Lennard-Jones' form of Mie's equation is

$$\Gamma = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (5-38)$$

where  $\epsilon$  is the depth of the energy well (minimum potential energy) and  $\sigma$  is the collision diameter, i.e., the separation where  $\Gamma = 0$ . Equation (5-38) gives what is probably the best known two-parameter potential for small, nonpolar molecules. In Lennard-Jones' formula, the repulsive wall is not vertical but has a finite slope; this implies that if two molecules have very high kinetic energy, they may be able to interpenetrate to separations smaller than the collision diameter  $\sigma$ . Potential functions with this property are called *soft-sphere potentials*. The Lennard-Jones potential correctly predicts that, at a temperature very much larger than  $\epsilon/k$  ( $k$  is Boltzmann's constant), the second virial coefficient goes through a maximum. The temperature where  $B = 0$  is called the *Boyle temperature*.

When Lennard-Jones' potential is substituted into the statistical mechanical equation for the second virial coefficient [Eq. (5-17)], the required integration is not simple. However, numerical results have been obtained (Hirschfelder *et al.*, 1954) as shown in Fig. 5-10, where the reduced (dimensionless) virial coefficient is a function of the reduced (dimensionless) temperature. The reducing parameter for the virial coefficient is proportional to collision diameter  $\sigma$  raised to the third power and that for the temperature is proportional to characteristic energy  $\epsilon$ .

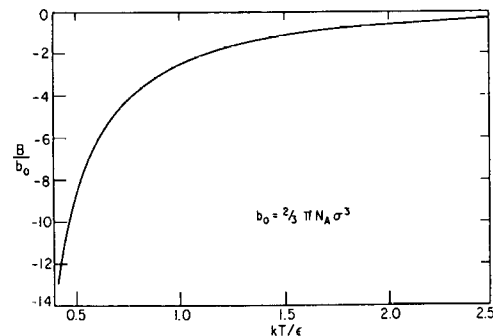


Figure 5-10 Second virial coefficients calculated from Lennard-Jones 6-12 potential.

For many gases, second virial coefficients, as well as other thermodynamic and transport properties, have been interpreted and correlated successfully with the Lennard-Jones potential. Unfortunately, however, it has frequently been observed that for a given gas, one set of parameters ( $\epsilon$  and  $\sigma$ ) is obtained from data reduction of one property (e.g., the second virial coefficient) while another set is obtained from data reduction of a different property (e.g., viscosity). If the Lennard-Jones potential were the *true* potential, then the parameters  $\epsilon$  and  $\sigma$  should be the same for all properties of a given substance.

But even if attention is restricted to the second virial coefficient alone, there is good evidence that the Lennard-Jones potential is only an approximation, albeit a very good one in certain cases. It has been shown by Michels *et al.* (1958) that his highly accurate data for the second virial coefficient of argon over the temperature range -140 to +150°C cannot be fitted with the Lennard-Jones potential within the experimental error using only one set of parameters. This conclusion can be supported through a revealing series of calculations suggested by Michels *et al.* (1960). We take an experimental value of  $B$  corresponding to a certain temperature and then arbitrarily assume a value for  $\epsilon$ . We now calculate the corresponding value of  $b_0 = (2/3)N_A\sigma^3$  that is required to force agreement between the experimental  $B$  and that calculated from the Lennard-Jones function. Next, we repeat the calculation at the same temperature assuming some other value of  $\epsilon$ . In this way we obtain a curve on a plot of  $b_0$  versus  $\epsilon$ . We now perform the same series of calculations for another experimental value of  $B$  at a different temperature and again obtain a curve; where the two curves intersect should be the "true" value of  $\epsilon$  and  $b_0$ . However, we find that when we repeat these calculations for several different temperatures, all the curves do not intersect at one point, as they should if the Lennard-Jones potential were exactly correct.

Such a plot is shown in Fig. 5-11; instead of a point of intersection, the curves define an area that gives a region rather than a unique set of potential parameters. Therefore, we conclude that even for a spherically symmetric, nonpolar molecule such as argon, the Lennard-Jones potential is not completely satisfactory (Guggenheim and McGlashan, 1960; Munn, 1964; Munn *et al.*, 1965, 1965a). Such a conclusion, however, was reached only because Michels' data are of unusually high accuracy and were measured over a large temperature range. For many practical calculations the Lennard-Jones potential is adequate. Lennard-Jones parameters for some fluids are given in Table 5-1.

**The Square-Well Potential.** The Lennard-Jones potential is not a simple mathematical function. To simplify calculations, a crude potential was proposed having the general shape of the Lennard-Jones function. This crude potential is obviously an unrealistic simplification because it has discontinuities, but its mathematical simplicity and flexibility make it useful for practical calculations. The flexibility arises from the square-well potential's three adjustable parameters: the collision diameter,  $\sigma$ ; the well depth (minimum potential energy),  $\epsilon$ ; and the reduced well width,  $R$ . The *square-well potential* function is

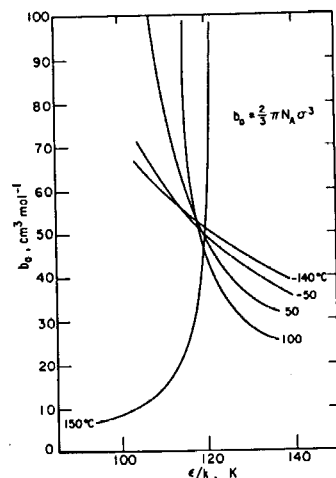


Figure 5-11 Lennard-Jones' parameters calculated from second-virial-coefficient data for argon. If perfect representation were given by Lennard-Jones' potential, all isotherms would intersect at one point.

Table 5-1 Parameters for the Lennard-Jones potential obtained from second-virial coefficient data.<sup>§</sup>

	$\sigma$ (Å)	$\epsilon/k$ (K)
Ar	3.499	118.13
Kr	3.846	162.74
Xe	4.100	222.32
CH <sub>4</sub>	4.010	142.87
N <sub>2</sub>	3.694	96.26
C <sub>2</sub> H <sub>4</sub>	4.433	202.52
C <sub>2</sub> H <sub>6</sub>	5.220	194.14
C <sub>3</sub> H <sub>8</sub>	5.711	233.28
C(CH <sub>3</sub> ) <sub>4</sub>	7.420	233.66
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	7.152	223.74
C <sub>6</sub> H <sub>6</sub>	8.443	247.50
CO <sub>2</sub>	4.416	192.25
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	8.540	217.69

<sup>§</sup> L. S. Tee, S. Gotoh, and W. E. Stewart, 1966, *Ind. Eng. Chem. Fundam.*, 5: 336.

$$\Gamma = \begin{cases} \infty & \text{for } r \leq \sigma \\ -\epsilon & \text{for } \sigma < r \leq R\sigma \\ 0 & \text{for } r > R\sigma \end{cases} \quad (5-39)$$

leading to

$$B = b_0 R^3 \left( 1 - \frac{R^3 - 1}{R^3} \exp \frac{\epsilon}{kT} \right)$$

The square-well model has an infinitely steep repulsive wall and therefore, like the Sutherland model, it does not predict a maximum for the second virial coefficient. With its three adjustable parameters, good agreement can often be obtained between calculated and experimental second virial coefficients (Sherwood and Prausnitz, 1964).

**The Exp-6 Potential.** A potential function for nonpolar molecules should contain an attractive term of the London type in addition to a repulsive term; little is known about that term but it must depend strongly on the intermolecular distance. For the repulsive term Mie, and later Lennard-Jones, used a term inversely proportional to  $r$ , the intermolecular distance, raised to a large power. Theoretical calculations, however, have suggested that the repulsive potential is not an inverse-power function but rather an exponential function of  $r$ . A potential function that uses an exponential form for repulsion and an inverse sixth power for attraction is called an *exp-6 potential*. (It is also sometimes referred to as a *modified Buckingham potential*.) This potential function contains three adjustable parameters and is written<sup>7</sup>

$$\Gamma = \frac{\epsilon}{1 - (6/\gamma)} \left\{ \frac{6}{\gamma} \exp \left[ \gamma \left( 1 - \frac{r}{r_{\min}} \right) \right] - \left( \frac{r_{\min}}{r} \right)^6 \right\} \quad (5-40)$$

where  $-\epsilon$  is the minimum potential energy at intermolecular separation  $r_{\min}$ . The third parameter,  $\gamma$ , determines the steepness of the repulsive wall; in the limit, when  $\gamma = \infty$ , the exp-6 potential becomes the Sutherland potential that has a hard-sphere repulsive term.

The collision diameter  $\sigma$  (i.e., the intermolecular distance where  $\Gamma = 0$ ) is only slightly less than the distance  $r_{\min}$ , but the exact relation depends on the value of  $\gamma$ , as shown in Table 5-2. Numerical results for the second virial coefficient, based on Eq. (5-40), are available (Sherwood and Prausnitz, 1964a). Good agreement can often be obtained between calculated and observed second virial coefficients.

<sup>7</sup> Equation (5-40) is valid only for  $r > s$ , where  $s$  (a very small distance) is that value for  $r$  where  $\Gamma$  goes through a (false) maximum. For completeness, therefore, it should be added that  $\Gamma = \infty$  for  $r < s$ . The quantity  $s$ , however, is not an independent parameter and has no physical significance.



**Table 5-2** Ratio  $a/r_{\min}$  for the exp-6 potential as a function of the repulsive steepness parameter  $\gamma$ .

$\gamma$	$a/r_{\min}$
15	0.894170
18	0.906096
20	0.912249
24	0.921911
30	0.932341
40	0.943914
100	0.970041
300	0.986692
$\infty$	1.000000

**The Kihara Potential.** According to Lennard-Jones' potential, two molecules can interpenetrate completely provided that they have enough energy; according to this model, molecules consist of point centers surrounded by "soft" (i.e., penetrable) electron clouds. An alternative picture of molecules is to think of them as possessing impenetrable (hard) cores surrounded by penetrable (soft) electron clouds. This picture leads to a model proposed by Kihara. In crude mechanical terms, Kihara's model (for spherically symmetric molecules) considers a molecule to be a hard billiard ball with a foam-rubber coat; a Lennard-Jones molecule, by contrast, is a soft ball made exclusively of foam rubber.

Kihara (1953, 1958, 1963) writes a potential function identical to that of Lennard-Jones except that the intermolecular distance is taken not as that between molecular centers but rather as the distance between the surfaces of the molecules' cores.<sup>8</sup> For molecules with spherical cores, the *Kihara potential* is

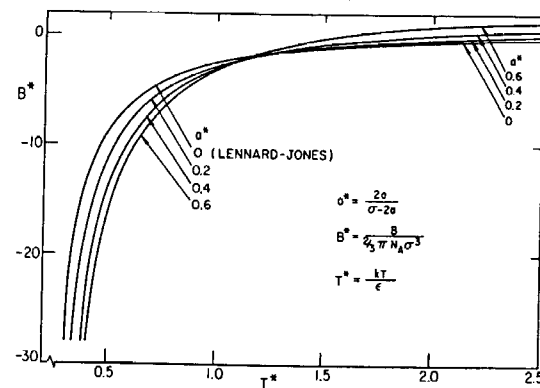
$$\Gamma = \begin{cases} \infty & \text{for } r < 2a \\ 4\epsilon \left[ \left( \frac{\sigma - 2a}{r - 2a} \right)^{12} - \left( \frac{\sigma - 2a}{r - 2a} \right)^6 \right] & \text{for } r \geq 2a \end{cases} \quad (5-41)$$

where  $a$  is the radius of the spherical molecular core,  $\epsilon$  is the depth of the energy well, and  $\sigma$  is the collision diameter, i.e., the distance  $r$  between molecular centers when  $\Gamma = 0$ .

Equation (5-41) is for the special case of a spherical core, but a more general form has been presented by Kihara for cores having other convex shapes such as rods,

<sup>8</sup> When the cores are not spherical, the intermolecular distance is for the orientation that gives a minimum distance of separation.

tetrahedra, triangles, prisms, etc. (Connolly and Kandakic, 1960; Prausnitz and Keeler, 1961; Prausnitz and Myers, 1963). Numerical results, based on Kihara's potential, are available for second virial coefficients for several core geometries and, in particular, for reduced (spherical) core sizes  $a^*$ , where  $a^* \equiv 2a/(\sigma - 2a)$ . When  $a^* = 0$ , the results are identical to those obtained from Lennard-Jones' potential. Because it is a three-parameter function, Kihara's potential is successful in fitting thermodynamic data for a large number of nonpolar fluids, including some complex substances whose properties are represented poorly by the two-parameter Lennard-Jones potential. Figure 5-12 shows reduced second virial coefficients calculated from Kihara's potential.



**Figure 5-12** Second virial coefficients calculated from Kihara's potential with a spherical core of radius  $a$ .

In our discussion of Lennard-Jones' potential we indicated that Michels' highly accurate second-virial-coefficient data for argon could not be represented over a large temperature range by the Lennard-Jones potential using only one set of potential parameters. However, these same data can be represented within the very small experimental error by the Kihara potential using only one set of parameters (Myers and Prausnitz, 1962; Rossi and Danon, 1966; O'Connell and Prausnitz, 1968). The ability of Kihara's potential to do what Lennard-Jones' potential cannot do is hardly surprising because the former potential has three adjustable parameters whereas the latter has only two. In fitting data for argon, the three Kihara parameters were determined by trial and error until the deviation between experimental and theoretical second virial coefficients reached a minimum less than the experimental error. The magnitude of the core diameter obtained by this procedure is physically reasonable when compared to the diameter of the "impenetrable core" of argon as calculated from its electronic structure. Figure 5-13 shows results of a theoretical calculation of the electron density

as a function of distance. While the results shown appear to justify confidence in the Kihara potential, the agreement indicated must not be considered "proof" of its validity. The "true" potential between two argon atoms is undoubtedly quite different from that given by Eq. (5-41) especially at very small separations. However, it appears that for practical calculation of common thermodynamic properties (except those at very high temperatures), Kihara's potential is one of the most useful potential functions now available.

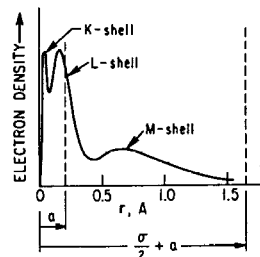


Figure 5-13 Charge distribution in argon (quoted by C. A. Coulson, 1962, *Valence*, 2<sup>nd</sup> Ed. London: Oxford University Press).

One practical application of Kihara's potential is for prediction of second virial coefficients at low temperatures where experimental data are scarce and difficult to obtain. To illustrate, Fig. 5-14 shows predicted and observed second virial coefficients for krypton at low temperatures; two sets of predictions were made, one with the Kihara potential and the other with the Lennard-Jones potential. In both cases potential parameters were obtained from experimental measurements made at room temperature and

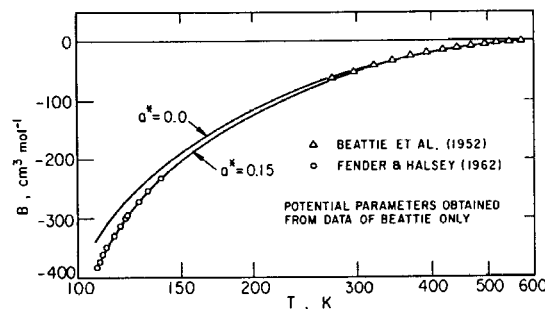


Figure 5-14 Second virial coefficients for krypton. Predictions at low temperatures based on Lennard-Jones potential ( $a^* = 0$ ) and on Kihara potential.

above. It is evident from Fig. 5-14 that even for such a "simple" substance as krypton, the Kihara potential is significantly superior to the Lennard-Jones potential. Kihara parameters for some fluids are given in Table 5-3.

Table 5-3 Parameters for the Kihara potential (spherical core) obtained from second-virial-coefficient data.<sup>§</sup>

	$a^*$	$\sigma$ (Å)	$\epsilon/k$ (K)
Ar	0.121	3.317	146.52
Kr	0.144	3.533	213.73
Xe	0.173	3.880	298.15
CH <sub>4</sub>	0.283	3.565	227.13
N <sub>2</sub>	0.250	3.526	139.2 <sup>†</sup>
O <sub>2</sub>	0.308	3.109	194.3 <sup>‡</sup>
C <sub>2</sub> H <sub>6</sub>	0.359	3.504	496.69
C <sub>3</sub> H <sub>8</sub>	0.470	4.611	501.89
CF <sub>4</sub>	0.500	4.319	289.7 <sup>‡</sup>
C(CH <sub>3</sub> ) <sub>4</sub>	0.551	5.762	557.75
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	0.661	4.717	701.15
C <sub>6</sub> H <sub>6</sub>	0.750	5.335	832.0 <sup>†</sup>
CO <sub>2</sub>	0.615	3.760	424.16
<i>n</i> -C <sub>3</sub> H <sub>12</sub>	0.818	5.029	837.82

<sup>§</sup> L. S. Tee, S. Gotoh, and W. E. Stewart, 1966, *Ind. Eng. Chem. Fundam.*, 5: 363.

<sup>†</sup> A. E. Sherwood and J. M. Prausnitz, 1964, *J. Chem. Phys.*, 41: 429.

<sup>‡</sup> C. E. Hunt, unpublished results.

For mixtures, Kihara's potential gives  $B_{ij}$  ( $i \neq j$ ) when the pure-component core parameters and the unlike-pair potential parameters  $\epsilon_{ij}$  and  $\sigma_{ij}$  are specified. The latter two are frequently related to the pure-component parameters by empirical combining rules. However, the core parameter for the  $i$ - $j$  interaction can be derived exactly from the core parameters for the  $i$ - $i$  and  $j$ - $j$  interactions even for nonspherical cores (Kihara, 1953, 1958, 1963; Myers and Prausnitz, 1962).

The difficulty of determining "true" intermolecular potentials from second virial-coefficient data is illustrated in Figs. 5-15 and 5-16 that show several potential functions for argon and for neopentane. Each of these functions gives a good prediction of the second virial coefficient; the three-parameter potentials give somewhat better predictions than the two-parameter potentials, but all of them are in fairly good agreement with experiment. However, the various potential functions differ very much from one another, especially for neopentane.

Figures 5-15 and 5-16 give striking evidence that agreement between a particular set of experimental results and those calculated from a particular model should not be regarded as proof that the model is correct.<sup>9</sup> Models are useful in molecular thermodynamics but one must not confuse utility with truth. Figures 5-15 and 5-16 provide a powerful illustration of A. N. Whitehead's advice to scientists: "Seek simplicity but distrust it".

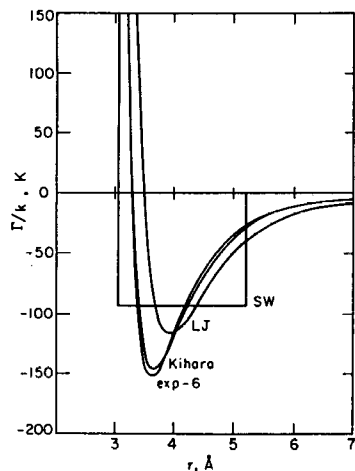


Figure 5-15 Potential functions for argon as determined from second-virial-coefficient data.

**The Stockmayer Potential.** All of the potential functions previously described are applicable only to nonpolar molecules. We now briefly consider molecules that have a permanent dipole moment; for such molecules Stockmayer proposed a potential that adds to the Lennard-Jones formula for nonpolar forces an additional term for the potential energy due to dipole-dipole interactions. Dipole-induced dipole interactions are not considered explicitly although it may be argued that because these forces, like London forces, are proportional to the inverse sixth power of the intermolecular separation, they are, in effect, included in the attractive term of the Lennard-Jones formula. For polar molecules, the potential energy is a function not only of intermolecular separation but also of relative orientation. *Stockmayer's potential is*

<sup>9</sup> A more nearly "true" potential can be obtained by simultaneous analysis of experimental data for a variety of properties: second virial coefficients, gas-phase viscosity, diffusivity, and thermal diffusivity. Such analysis has produced a "best" potential function for argon. See Dymond and Alder (1969) and Barker and Pompe (1968).

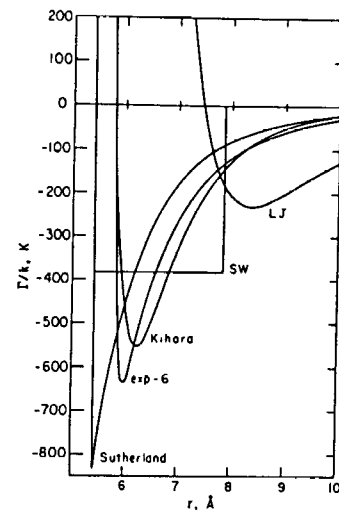


Figure 5-16 Potential functions for neopentane as determined from second-virial-coefficient data.

$$\Gamma = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \frac{\mu^2}{r^3} F_{\theta}(\theta_1, \theta_2, \theta_3) \quad (5-42)$$

where  $F_{\theta}$  is a known function of the angles  $\theta_1$ ,  $\theta_2$ , and  $\theta_3$  that determine the relative orientation of the two dipoles [see Eq. (4-7)]. This potential function contains only two adjustable parameters because the dipole moment  $\mu$  is an independently determined physical constant.

The collision diameter  $\sigma$  in Eq. (5-42) is the intermolecular distance where the potential energy due to forces other than dipole-dipole forces becomes equal to zero.

Numerical results, based on Stockmayer's potential, are available for the second virial coefficient (Rowlinson, 1949). Figure 5-17 shows reduced second virial coefficients calculated from Stockmayer's potential as a function of reduced temperature and reduced dipole moment. The top curve (zero dipole moment) is for nonpolar Lennard-Jones molecules and it is evident that the effect of polarity is to lower (algebraically) the second virial coefficient due to increased forces of attraction, especially at low temperatures, as suggested by Keesom's formula (see Sec. 4.2). Stockmayer's potential has been used successfully to fit experimental second-virial-coefficient data for a variety of polar molecules; Table 5-4 gives parameters for some polar fluids and Table 5-5 shows some illustrative results for trifluoromethane.

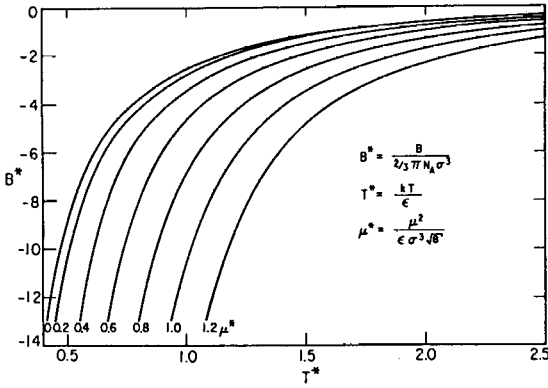


Figure 5-17 Second virial coefficients calculated from Stockmayer’s potential for polar molecules.

Table 5-4 Parameters for Stockmayer’s potential for polar fluids.\*

	μ (debye)	σ (Å)	ε/k (K)
Acetonitrile	3.94	4.38	219
Nitromethane	3.54	4.16	290
Acetaldehyde	2.70	3.68	270
Acetone	2.88	3.67	479
Ethanol	1.70	2.45	620
Chloroform	1.05	2.98	1060
n-Butanol	1.66	2.47	1125
n-Butyl amine	0.85	1.58	1020
Methyl formate	1.77	2.90	684
n-Propyl formate	1.92	3.06	877
Methyl acetate	1.67	2.83	895
Ethyl acetate	1.76	2.99	956
Ethyl ether	1.16	3.10	935
Diethyl amine	1.01	2.99	1180

\* R. F. Blanks and J. M. Prausnitz, 1962, *AIChE J.*, 8: 86.

The various potential models discussed above may be used to calculate  $B_{ij}$  as well as  $B_{ii}$ . The calculations for  $B_{ij}$  are exactly the same as those for  $B_{ii}$  when potential  $\Gamma_{ij}$  is used rather than potential  $\Gamma_{ii}$ . In the Stockmayer potential, when  $i \neq j$ , the reduced dipole moment  $\mu^*$  in Fig. (5-17) becomes  $\mu^* = \mu_i \mu_j (\epsilon_{ij} \sigma_{ij}^3 \sqrt{8})^{-1}$ .

Table 5-5 Second virial coefficients of trifluoromethane. Calculated values from Stockmayer potential with  $\epsilon/k = 188$  K,  $\sigma = 4.83$  Å, and  $\mu = 1.65$  debye.

Temperature (°C)	-B (cm <sup>3</sup> mol <sup>-1</sup> )	
	Experimental*	Calculated
0	233	215
25	187	185
50	154	150
75	127	127
100	107	108
150	76	76
200	53	53

\* J. L. Belzile, S. Kaliaguine, and R. S. Ramalho, 1976, *Can. J. Chem. Eng.*, 54: 446.

5.6 Third Virial Coefficients

In the preceding section, attention was directed to the second virial coefficient. We now consider briefly our limited knowledge concerning third virial coefficients.

Equations (5-18) and (5-24) give expressions for the third virial coefficient in terms of three two-body intermolecular potentials. In the derivation of these equations, an important simplifying assumption was made; i.e., we assumed *pairwise additivity* of potentials. The third virial coefficient takes into account deviations from ideal-gas behavior due to three-molecule interactions; for a collision of three molecules  $i$ ,  $j$ , and  $k$ , we need  $\Gamma_{ijk}$  the potential energy of the three-molecule assembly. However, in the derivation of Eqs. (5-18) and (5-24) it was assumed that

$$\Gamma_{ijk} = \Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk} \tag{5-43}$$

Equation (5-43) says that the potential energy of the three molecules  $i$ ,  $j$ , and  $k$  is equal to the sum of the potential energies of the three pairs  $i$ - $j$ ,  $i$ - $k$ , and  $j$ - $k$ . This assumption of pairwise additivity of intermolecular potentials is a common one in molecular physics because little is known about three-, four- (or higher) body forces. For an  $m$ -body assembly, the additivity assumption takes the form

$$\Gamma_{1,2,3,\dots,m} = \sum_{\text{all possible } ij \text{ pairs}} \Gamma_{ij} \tag{5-44}$$

We also used this assumption in Sec. 4.5, where we briefly considered some properties of the condensed state. While there is no rigorous proof, it may well be that because of

cancellation effects, the assumption of pairwise additivity becomes better as the number of particles increases. However, it is likely that the assumption is somewhat in error for a three-body assembly (Rowlinson, 1965). Therefore, calculations for the third virial coefficient using Eq. (5-18) must be considered as approximations.

For any realistic potential, the calculation of third virial coefficients is complicated and, to obtain numerical results, we require a computer. Numerical computations have been carried out for several potential functions and results for pure nonpolar components are available (Sherwood and Prausnitz, 1964a; Kihara, 1953, 1958, 1963; Graben and Present, 1962; Sherwood *et al.*, 1966). For example, Fig. 5-18 gives reduced third virial coefficients as calculated from Kihara's potential. In these calculations, a spherical core was used and pairwise additivity was assumed. The reduced third virial coefficient, reduced temperature, and reduced core are defined by

$$C^* = \frac{C}{\left(\frac{2}{3}\pi N_A \sigma^3\right)^2} \quad T^* = \frac{kT}{\epsilon} \quad a^* = \frac{2a}{\sigma - 2a}$$

where  $-\epsilon$  is the minimum energy in the potential function,  $\sigma$  is the intermolecular distance when the potential is zero, and  $a$  is the core radius. For  $a^* = 0$ , the results shown are those obtained from Lennard-Jones' potential.

Some efforts have been made to include nonadditivity corrections in the calculation of third virial coefficients (Sherwood and Prausnitz, 1964a; Kihara, 1953, 1958, 1963). These corrections are based on a quantum-mechanical relation derived by Axilrod and Teller (1943) for the potential of three spherical, nonpolar molecules at separations where the London dispersion forces dominate. The *nonadditive correction* is a function of the polarizability and at lower temperatures it is large; its overall effect is that it approximately doubles the calculated third virial coefficient at its maximum, steepens the slope near the peak value and shifts the maximum to a lower reduced temperature.

Calculated and observed third virial coefficients for argon are shown in Fig. 5-19. Calculated results are based on four potential functions; for each of these, the parameters were determined from second-virial-coefficient data. The solid lines include the nonadditivity correction but the dashed lines do not; it is clear that the nonadditivity correction is appreciable.

Barker and Henderson (1976) have presented a definitive study of the third virial coefficient of argon; their results are shown in Fig. 5-20. The lowest line shows calculations based on the assumption of pairwise additivity as given by Eq. (5-43). For the two-body potential for argon, Barker and Henderson used an expression obtained from data reduction using two-body experimental information: second virial coefficients and gas-phase transport properties at low densities. The middle line shows calculations based on a three-body potential ( $\Gamma_{ijk}$ ) that includes first-order corrections to the additivity assumption. (This correction is called the *Axilrod-Teller correction*.) The top line shows calculations that include second- and third-order corrections. These calculations agree with experiment within experimental error.

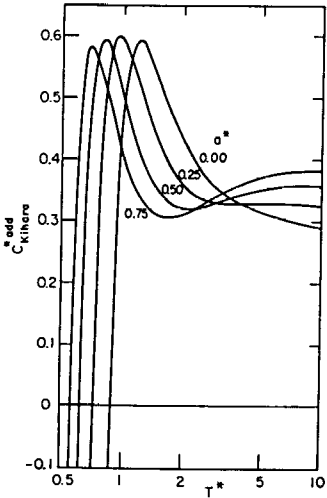


Figure 5-18 Third virial coefficient from Kihara potential assuming pairwise additivity.

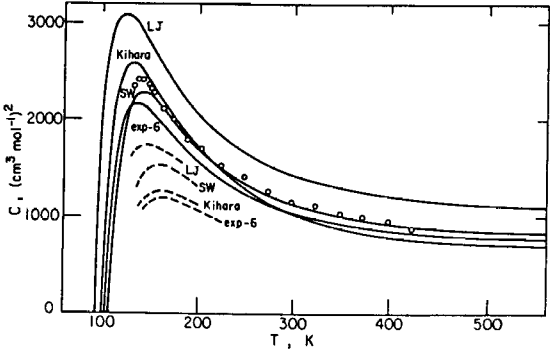


Figure 5-19 Calculated and observed third virial coefficients for argon. Solid lines include Axilrod-Teller nonadditivity corrections. Dashed lines show a portion of calculated results assuming additivity. Circles represent experimental data of Michels (1958).

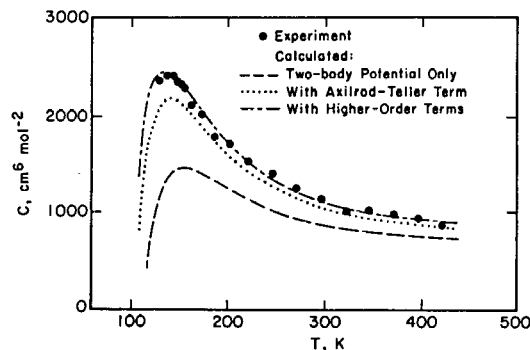


Figure 5-20 Third virial coefficients for argon (Barker and Henderson, 1976).

Without going into details, we can indicate the nature of the three-body corrections. First, we recall that in London's theory of dispersion forces, the potential is approximated by a series; for a two-body potential it has the form

$$\Gamma(r) = -\frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} - \dots \quad (5-45)$$

where  $r$  is the center-to-center distance between two molecules. The leading coefficient is

$$C_6 = \frac{3}{4} \frac{\alpha^2 I}{(4\pi\epsilon_0)^2} \quad (5-46)$$

where  $\alpha$  is the polarizability,  $I$  is the ionization potential, and  $\epsilon_0$  is the vacuum permittivity. Coefficients  $C_8$  and  $C_{10}$  (not reproduced here) give the higher-order terms in London's potential. (In many practical calculations these terms are ignored.)

For a three-body potential, the first-order correction to the additivity assumption is obtained from London's theory, restricting attention to the leading ( $C_6/r^6$ ) term. This first-order (Axilrod-Teller) correction to  $\Gamma_{ijk}$  is

$$\Delta\Gamma_{ijk}(r_{ij}, r_{jk}, r_{ik}) = \frac{9}{16} \frac{I\alpha^3(1 + 3\cos\theta_i \cos\theta_j \cos\theta_k)}{(4\pi\epsilon_0)^2(r_{ij}r_{jk}r_{ik})^3} \quad (5-47)$$

where  $\theta_i$ ,  $\theta_j$ , and  $\theta_k$  are the three angles of a triangle whose sides are  $r_{ij}$ ,  $r_{jk}$ , and  $r_{ik}$ .

Second-order corrections for nonadditivity are based on London's theory, restricting attention to the first two terms in the series; third-order corrections for nonad-

ditivity are based on London's theory, restricting attention to the first three terms in the series. Still higher corrections appear to be negligible.

The important difference between Barker and Henderson's results (Fig. 5-20) and those of earlier workers (Fig. 5-19) lies in the two-body potential. The earlier work is based on a two-body potential that follows only from second virial-coefficient data and, as suggested by Fig. 5-15, these data alone do not yield a unique potential function. However, Barker and Henderson were able to use a *unique* two-body potential obtained from other dilute-gas data in addition to second-virial-coefficient data. The excellent agreement between theory and experiment, shown in Fig. 5-20, follows from an excellent two-body potential.

Due to experimental difficulties, there are few reliable values of third virial coefficients. It is therefore not possible to make a truly meaningful comparison between calculated and observed third virial coefficients; not only are experimental data not plentiful, but frequently they are of low accuracy. Even when calculated from very good  $P$ - $V$ - $T$  data, the accuracy of third virial coefficients is about one order of magnitude lower than that for second virial coefficients. To the extent that a comparison could be made, Sherwood (1964) found that the Lennard-Jones potential (with nonadditivity correction) generally predicted third virial coefficients that were too high, especially for larger molecules (such as pentane or benzene) where the predictions were very poor. The three-parameter potentials (square-well, exp-6, and Kihara) gave much better predictions; however, in view of the uncertainties in the data, and because corrections for nonadditive repulsive forces have been neglected, it is not possible to give a quantitative estimate of agreement between theory and experiment.

Little work has been done on the third virial coefficient of mixtures. The cross-coefficients, assuming additivity, can be calculated by Eq. (5-24) and the nonadditivity correction to these cross-coefficients, based on the formula of Axilrod and Teller, can also be computed as shown by Kihara (1953, 1958, 1963). However, the results of such calculations cannot be presented in a general manner; the coefficient  $C_{ijk}$  (for  $i \neq j \neq k$ ) is a function of five independent variables for a two-parameter potential; for a three-parameter potential, eight independent variables must be specified.

An approximate method for calculating  $C_{ijk}$  was proposed by Orentlicher (1967), who showed that, subject to several simplifying assumptions, a reasonable estimate of  $C_{ijk}$  can be made based on Sherwood's numerical results for the third virial coefficient of pure gases.<sup>10</sup> Component  $i$  is chosen as a reference component; let  $C_{ii}(T)$  stand for the third virial coefficient of pure  $i$  at the temperature  $T$  of interest. Let the potential function between molecules  $i$  and  $j$  be characterized by the collision diameter  $\sigma_{ij}$  and the energy parameter  $\epsilon_{ij}$ . Similarly, the potential function for the  $i$ - $k$  pair is characterized by  $\sigma_{ik}$  and  $\epsilon_{ik}$ , and that for the  $j$ - $k$  pair by  $\sigma_{jk}$  and  $\epsilon_{jk}$ . Orentlicher's approximation is

<sup>10</sup> Orentlicher's approximation has been critically discussed by D. E. Stogryn, 1968, *J. Chem. Phys.*, 48: 4474.

$$\frac{C_{ijk}(T)}{C_{ii}(T)} = \left( \frac{\sigma_{ij}\sigma_{jk}\sigma_{ik}}{\sigma_{ii}^3} \right)^2 \frac{[C_{ij}^*(T_{ij}^*)C_{jk}^*(T_{jk}^*)C_{ik}^*(T_{ik}^*)]^{1/3}}{C_{ii}^*(T_{ii}^*)} \quad (5-48)$$

where  $T_{ij}^* = kT/\epsilon_{ij}$ , etc., and where the individual reduced coefficients  $C_{ij}^*$ , etc., are obtained from available tables for pure components using any one of several popular potential functions.<sup>11</sup> Orentlicher's formula appears to give good results for mixtures where the components do not differ much in molecular size and characteristic energy. The accuracy of the approximation is difficult to assess, but it is probably useful for mixtures at those temperatures where the third virial coefficient of each component has already passed its maximum. Table 5-6 gives some observed and calculated third-virial cross coefficients for binary mixtures. Because the uncertainty in the experimental results is probably at least  $\pm 100$  (cm<sup>3</sup> mol<sup>-1</sup>)<sup>2</sup>, agreement between calculated and experimental results is good for these particular mixtures.

Third virial coefficients for polar gases were calculated by Rowlinson (1951) using the Stockmayer potential and assuming additivity. Because experimental data are scarce and of low accuracy, it is difficult to make a meaningful comparison between calculated and experimental results.

**Table 5-6** Experimental and calculated third-virial cross coefficients for some binary mixtures (Orentlicher, 1967).

Component		Temperature (K)	$C_{112}$ (cm <sup>3</sup> mol <sup>-1</sup> ) <sup>2</sup>	
1	2		Experimental	Calculated
Ar	N <sub>2</sub>	273	1349	1510
		203	1706	1770
		163	2295	2420
N <sub>2</sub>	Ar	273	1399	1340
		203	1780	1750
		163	2397	2330
CF <sub>4</sub>	CH <sub>4</sub>	273	4900	5250
		373	3400	3360
		473	2600	2700
		573	2400	2400
N <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	323	2300	2300

<sup>11</sup>  $C_{ij}^*$  is a function of  $kT/\epsilon_{ij}$  and, perhaps, of some additional parameter such as  $a_{ij}^*$  for the Kihara potential. This function, however, is the same as that for  $C_{ii}^*$ , that in turn depends on  $kT/\epsilon_{ii}$  and, perhaps, on  $a_{ii}^*$ .

## 5.7 Virial Coefficients from Corresponding-States Correlations

Because there is a direct relation between virial coefficients and intermolecular potential, it follows from the molecular theory of corresponding states (Sec. 4.12) that virial coefficients can be correlated by data reduction with characteristic parameters such as critical constants. A few correlations are given in the following paragraphs.

The major part of this section is concerned with second virial coefficients for nonpolar gases. We cannot say much about third virial coefficients because of the scarcity of good experimental data and because of the nonadditivity problem mentioned in the preceding section. Further, our understanding of polar gases is not nearly as good as that of nonpolar gases, because again, good experimental data are not plentiful for polar gases, and because theoretical models, based on ideal dipoles, often provide poor approximations to the behavior of real polar molecules.

Equation (5-17) relates second virial coefficient  $B$  to intermolecular potential  $\Gamma$ . Following the procedure given in Sec. 4.12, we assume that the potential  $\Gamma$  can be written in dimensionless form by

$$\frac{\Gamma}{\epsilon} = F\left(\frac{r}{\sigma}\right) \quad (5-49)$$

where  $\epsilon$  is a characteristic energy parameter,  $\sigma$  is a characteristic size parameter, and  $F$  is a universal function of the reduced intermolecular separation. Upon substitution, Eq. (5-17) can then be rewritten in dimensionless form:

$$\frac{B}{2\pi N_A \sigma^3} = \int_0^\infty \left[ 1 - \exp\left(-\frac{\epsilon F(r/\sigma)}{kT}\right) \right] \left(\frac{r}{\sigma}\right)^2 d\left(\frac{r}{\sigma}\right) \quad (5-50)$$

If we set  $\sigma^3$  proportional to critical volume  $v_c$ , and  $\epsilon/k$  proportional to critical temperature  $T_c$ , we obtain an equation of the form

$$\frac{B}{v_c} = F_B\left(\frac{T}{T_c}\right) \quad (5-51)$$

where  $F_B$  is a universal function of reduced temperature.

Equation (5-51) says that the reduced second virial coefficient is a generalized function of reduced temperature; this function can either be determined by specifying the universal potential function  $\Gamma/\epsilon$  and integrating, as shown by Eq. (5-50), or by a direct correlation of experimental data for second virial coefficients.

At high densities, we must compute fugacity coefficients from mostly empirical equations of state or from *generalized correlations* such as those based on the theorem of corresponding states (Sec. 5.11). Research on the statistical mechanics of dense gases is progressing rapidly and we may expect practical results in the not-too-distant future; however, at present mostly empirical methods are more useful for most applications.

When applying an equation of state or a corresponding-states correlation to a gaseous mixture, flexibility in *mixing rules* is essential for good results. A mixing rule that is good for one system may not be good for another; mixing and combining rules should therefore contain one or two adjustable parameters determined, if possible, by a few data for the mixture under consideration. If no mixture data are available, they should be estimated by careful analysis of chemically similar systems where mixture data are at hand. Good estimates of fugacity coefficients can be made for constituents of dense gas mixtures that contain nonpolar (or slightly polar) components. However, for mixtures containing polar gases, or for any mixture near critical conditions, calculated fugacity coefficients are not likely to be highly accurate. Fugacity coefficients calculated from an equation of state are usually more sensitive to binary coefficients in mixing and combining rules than to any other detail in the equation of state, especially for those components that are dilute in the mixture.

In phase equilibria, the effect of gas-phase nonideality is particularly strong in those cases where a condensed component is sparingly soluble in a compressed gas. This solubility is strongly affected by the density and by the intermolecular forces between solute and gaseous solvent. In many cases, at high pressures, solubilities calculated with the assumption of ideal-gas behavior are in error by several orders of magnitude (Sec. 5.12).

We close this chapter by briefly repeating what we stressed at the beginning: Calculation of fugacities in gaseous mixtures is not a thermodynamic problem. The relations that express fugacity in terms of fundamental macroscopic properties are exact and well known; they easily lend themselves to numerical solution by computers. The difficulty we face lies in our inability to characterize and to predict with sufficient accuracy the configurational (essentially, volumetric) properties of pure fluids and even more, of mixed fluids; this inability, in turn, is a consequence of insufficient knowledge concerning intermolecular forces. To increase our knowledge, we require on the one hand new results from theoretical molecular physics and on the other, more accurate experimental data for equilibrium properties of dense mixtures, especially for those containing one or more polar components.

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<sup>25</sup> The equilibrium constants reported here are too large by a factor of 1.317. However, the enthalpies of complex-formation are not affected.

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## Problems

- Consider the following simple experiment: We have a container of fixed volume  $V$ ; this container, kept at temperature  $T$ , has in it  $n_1$  moles of gas 1. We now add isothermally to this container  $n_2$  moles of gas 2 and we observe that the pressure rise is  $\Delta P$ . Assume that the conditions are such that the volumetric properties of the gases and their mixture are adequately described by the virial equation neglecting the third and higher coefficients. The second virial coefficients of the pure gases are known. Find an expression that will permit calculation of  $B_{12}$ .
- At  $-100^\circ\text{C}$ , a gaseous mixture of one mole contains 1 mol %  $\text{CO}_2$  and 99 mol %  $\text{H}_2$ . The mixture is compressed isothermally to 60 bar. Does any  $\text{CO}_2$  precipitate? If so, approximately how much? [At  $-100^\circ\text{C}$ , the saturation (vapor) pressure of pure solid  $\text{CO}_2$  is 0.1392 bar and the molar volume of solid  $\text{CO}_2$  is  $27.6\text{ cm}^3\text{ mol}^{-1}$ .]
- A gaseous mixture containing 30 mol %  $\text{CO}_2$  and 70 mol %  $\text{CH}_4$  is passed through a Joule-Thomson expansion valve. The gas mixture enters the valve at 70 bar and  $40^\circ\text{C}$  and leaves at 1 bar. Does any  $\text{CO}_2$  condense? Assume that the heat capacities are independent of temperature. The data are as follows ( $1 = \text{CH}_4$ ;  $2 = \text{CO}_2$ ):