CH.5 Fugacities in Gas Mixtures

Fugacity from volumetric data: (exact relations)

$$\ln \varphi_i = \frac{1}{RT}\int_0^P \left[\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP \qquad (5\text{-}1)$$

$$\ln \varphi_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right] dV - \ln z \qquad (5\text{-}2)$$

more useful

where the fugacity coefficient is defined by

$$\varphi_i \equiv \frac{f_i}{y_i P} \qquad (5\text{-}3)$$

$$V = F_V(T, P, n_1, \ldots) \qquad (5\text{-}4)$$

$$P = F_P(T, V, n_1, \ldots) \qquad (5\text{-}5)$$

Most forms of the equation of state are pressure explicit.

5.1 The Lewis Fugacity Rule

Fugacity of component i in a gas mixture is related to that of pure gas at the same temperature and pressure by

$$RT \ln \frac{f_i}{y_i f_{\text{pure } i}} = \int_0^P (\overline{v}_i - v_i)\, dP \qquad (5\text{-}6)$$

assuming Amagat's law $\bar{v}_i = v_i$ over the entire pressure range

$$f_i = y_i f_{\text{pure } i} \qquad \text{or} \qquad \varphi_i = \varphi_{\text{pure } i}$$

Lewis rule assumes that φ_i is a function only of temperature and pressure but not of composition

- A good approximation at low pressures where the gas phase is nearly ideal.
- A good approximation whenever *i* is present in excess (say, y_i>0.9). Exact in the limit as $y_i \rightarrow 1$
- A fair approximation whenever physical properties of all the components are nearly the same.

5.2 The Virial Equation of State

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.

Parameters in the virial equation of state are directly related to intermolecular forces. (a sound theoretical foundation!)

$$\boxed{z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \ldots} \qquad (5\text{-}9)$$

B is the second virial coefficient, *C* is the third virial coefficient..

Virial coefficients are independent of pressure and density. They depends on temperature.

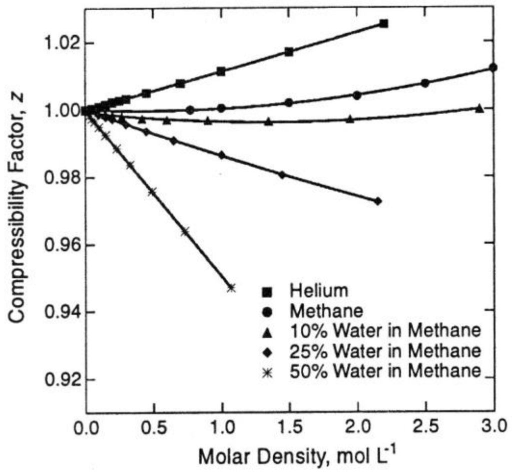


Figure 5-1 Compressibility factors for helium, methane and three water/methane mixtures as a function of density at 498.15 K (Joffrion and Eubank, 1988).

As a power series in the pressure

$$\boxed{z = \frac{Pv}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots} \tag{5-10}$$

Two sets of coefficients are related by

$$B' = \frac{B}{RT} \tag{5-11}$$

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

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

Eq (5-9) is better than (5-10) when truncated after the third term.

Experimentally, *B* is obtained from low-pressure PVT data by the definition

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

Similarly,

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

Reduction of PVT data to yield second and third virial coefficients

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

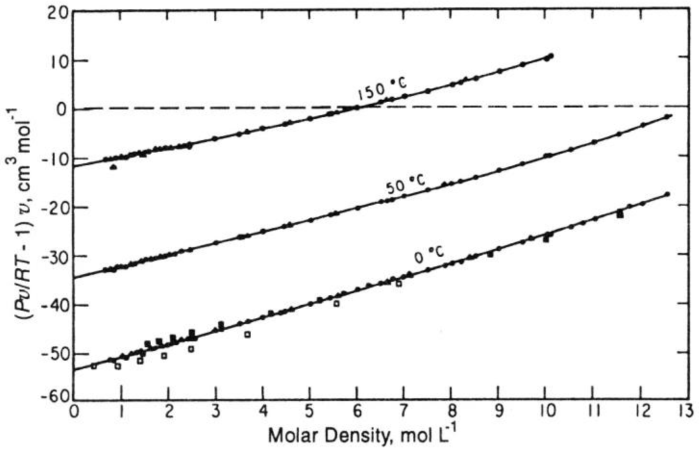


Figure 5-2 Reduction of *P-V-T* data for methane to yield second and third virial coefficients (data from various sources).

B from the intercept, *C* from the limiting slope

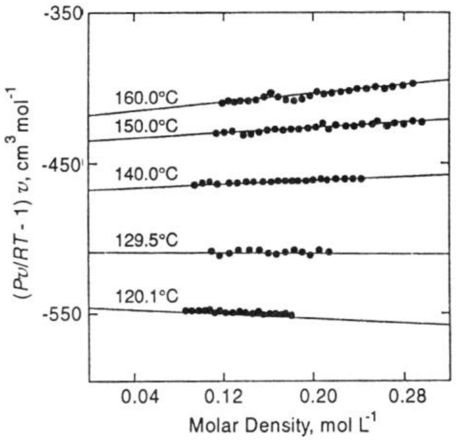
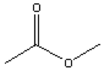


Figure 5-3 Reduction of *P-V-T* data for methanol/methyl acetate to yield second and third virial coefficients of approximately equimolar mixtures (Olf *et al.*, 1989).



methyl acetate

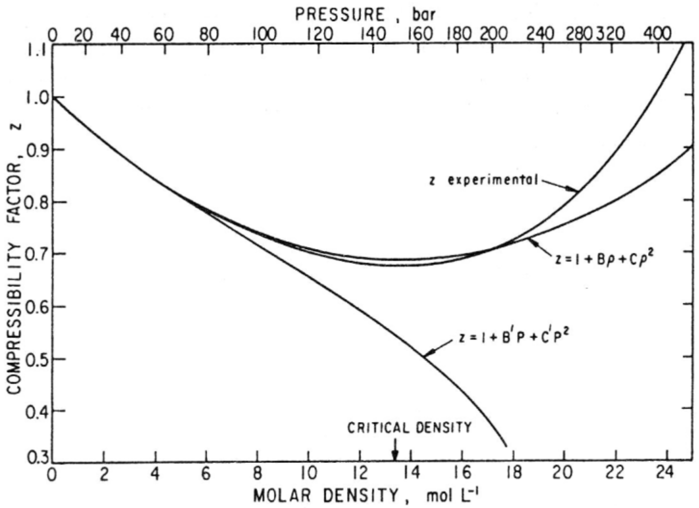


Figure 5-4 Compressibility factor for argon at -70°C.

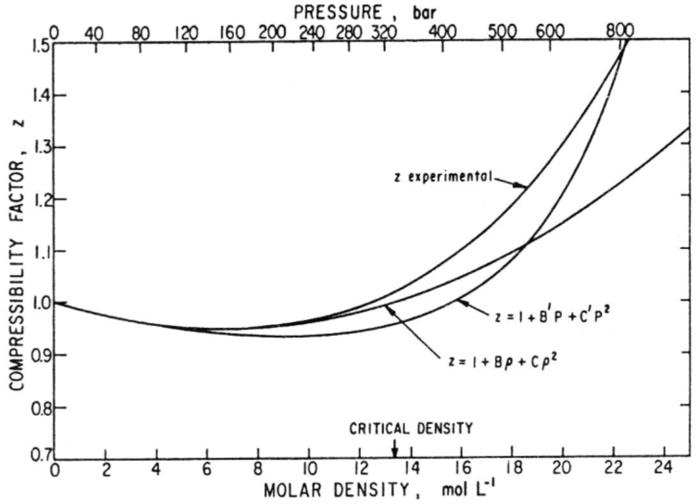


Figure 5-5 Compressibility factor for argon at 25°C.

The density series, Eq. (5-9) is more successful, and gives a good representation of the compressibility factor to about one half the critical density for many gases.

The second virial coefficient takes into account deviations from ideal behavior that result from interactions between two molecules.

The virial coefficients are given as an integral of intermolecular potential. For simple, spherical molecules

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

derived by Mayor

The third virial coefficient takes into account …. . from interactions of three molecules.

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

where $f_{ij} \equiv \exp(-\Gamma_{ij} / kT) - 1$, called May *f*-function

B and *C* are functions of temperature.

For complex molecules, the intermolecular potential depends not only on the distance but also on the relative orientation, and expressions for *B* and *C* become more complicated. (Monte Carlo calculations are often used.)

5.3 Extension to Mixtures

The composition dependence of virial coefficients are given by a generalization of the statistical-mechanical derivation.

The second virial coefficient corresponding to the *i-j* interaction is given by

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

B_{ii} and B_{jj} are those of pure components.

For a binary mixture, the second virial coefficient is

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

depending on compositions

For a mixture of *m* component, from a rigorous generalization

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

proof in advanced text

For the third virial coefficient for mixture

$$C_{ijk} = \frac{-8\pi^2 N_A^2}{3} \int_0^\infty \int_0^\infty \int_{|r_{ij} - r_{ik}|}^{r_{ij} + r_{ik}} f_{ij} f_{ik} f_{jk} r_{ij} r_{ik} r_{jk} dr_{ij} dr_{ik} dr_{jk} \qquad (5\text{-}24)$$

In a binary mixture, there are four C_{ijk} coefficients.

$$C_{\text{mixt}} = y_i^3 C_{iii} + 3 y_i^2 y_j C_{iij} + 3 y_i y_j^2 C_{ijj} + y_j^3 C_{jjj} \qquad (5\text{-}22)$$

For a mixture of *m* component

$$\boxed{C_{\text{mixt}} = \sum_{i=1}^{m} \sum_{j=1}^{m} \sum_{k=1}^{m} y_i y_j y_k C_{ijk}} \qquad (5\text{-}23)$$

If experimental data are available for several compositions, the cross coefficients can be Obtained from

$$\lim_{y_j \to 0} \left(\frac{\partial B_{\text{mixt}}}{\partial y_j} \right)_T = 2(B_{ij} - B_{ii}) \qquad \lim_{y_j \to 0} \left(\frac{\partial C_{\text{mixt}}}{\partial y_j} \right)_T = 3(C_{iij} - C_{iii})$$

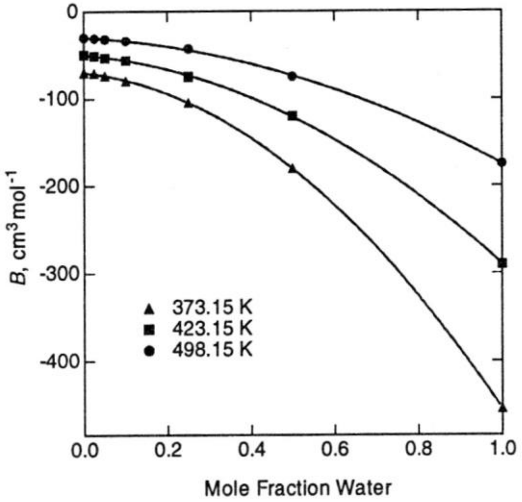


Figure 5-6 Experimental second virial coefficients for the CO_2/H_2O system as a function of the mole fraction of water, for various temperatures (Patel *et al.*, 1987).

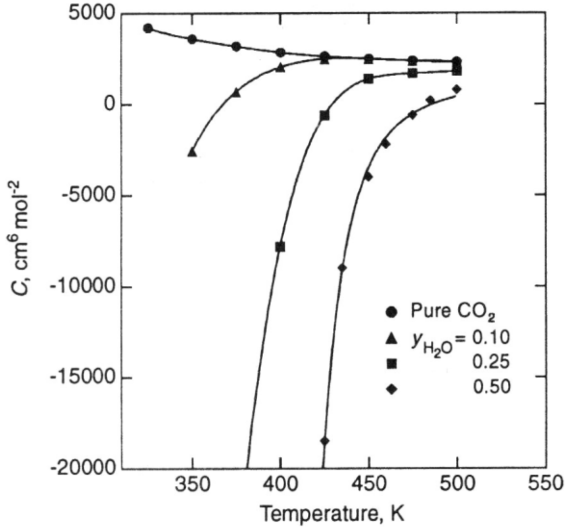


Figure 5-7 Experimental third virial coefficients for the CO_2/H_2O system as a function of temperature, for several mole fractions (Patel *et al.*, 1987).

In contrast, constants in empirical equation of state cannot be easily extended to mixtures with somewhat arbitrary mixing rules.

5.4 Fugacities from the Virial Equation

The viral equation for a mixture, truncated after the third term, is

$$z_{\text{mixt}} = \frac{Pv}{RT} = 1 + \frac{B_{\text{mixt}}}{v} + \frac{C_{\text{mixt}}}{v^2} \tag{5-27}$$

Substituting into

$$\ln \varphi_i = \frac{1}{RT} \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln z$$

we have

$$\boxed{\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{m} y_j B_{ij} + \frac{3}{2v^2} \sum_{j=1}^{m} \sum_{k=1}^{m} y_j y_k C_{ijk} - \ln z_{\text{mixt}}} \tag{5-28}$$

For a binary mixture

$$\ln \varphi_1 = \frac{2}{v}(y_1 B_{11} + y_2 B_{12}) + \frac{3}{2}\frac{1}{v^2}(y_1^2 C_{111} + 2y_1 y_2 C_{112} + y_2^2 C_{122}) - \ln z_{\text{mixt}} \tag{5-29}$$

$$\ln \varphi_2 = \frac{2}{v}(y_2 B_{22} + y_1 B_{12}) + \frac{3}{2}\frac{1}{v^2}(y_2^2 C_{222} + 2y_1 y_2 C_{122} + y_1^2 C_{112}) - \ln z_{\text{mixt}} \tag{5-30}$$

But (5-28) is limited to moderate densities.

Theoretical calculation of B and C is restricted to relatively simple substances.

Omitting the third virial coefficient

$$\boxed{\ln \varphi_i = \frac{2}{v} \sum_{j=1}^{m} y_j B_{ij} - \ln z_{\text{mixt}}} \tag{5-31}$$

where $z_{\text{mixt}} = 1 + \dfrac{B_{\text{mixt}}}{v}$ (5-32)

When the volume-explicit form of the virial equation is used

$$\boxed{\ln \varphi_i = \left(2 \sum_{j=1}^{m} y_j B_{ij} - B_{\text{mixt}} \right) \frac{P}{RT}} \tag{5-33}$$

which is more convenient because it uses pressure.

Both are valid only at low densities not exceeding (about) one-half the critical density.

5.5 Calculation of Virial Coefficients from Potential Functions

Ideal-Gas Potential

$\Gamma = 0$

virial coefficients = 0

ideal gas law

Hard-Sphere Potential

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

σ the hard-sphere diameter

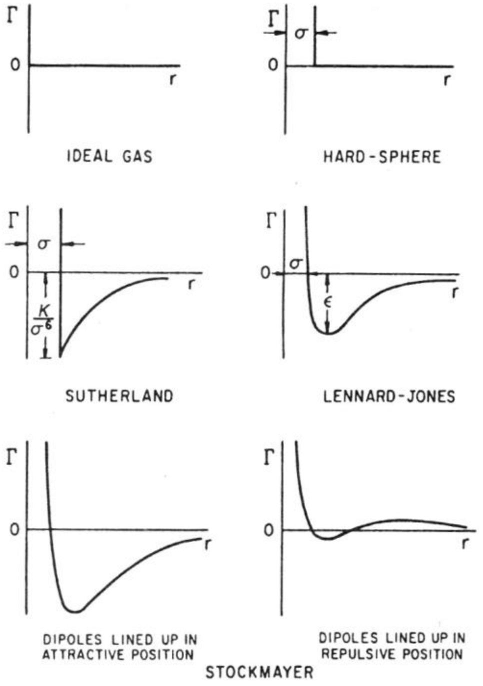


Figure 5-8 Potential functions with zero, one, or two adjustable parameters.

Substituting into (5-19)

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

pure component

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

mixture

The hard-sphere model is a highly oversimplified picture of real molecules because its second virial coefficient is independent of temperature.

Sutherland Potential (two parameter)

$$\Gamma = \begin{cases} \infty & \text{for} \quad r \le \sigma \\ \dfrac{-K}{r^6} & \text{for} \quad r > \sigma \end{cases} \tag{5-37}$$

reasonably successful in fitting experimental second virial coefficient data

Lennard-Jones Potential (the best known two parameter model)

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

where σ is size parameter (or the collision diameter) and

ε is energy parameter (the depth of the energy well).

B is obtained from numerical integration.

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

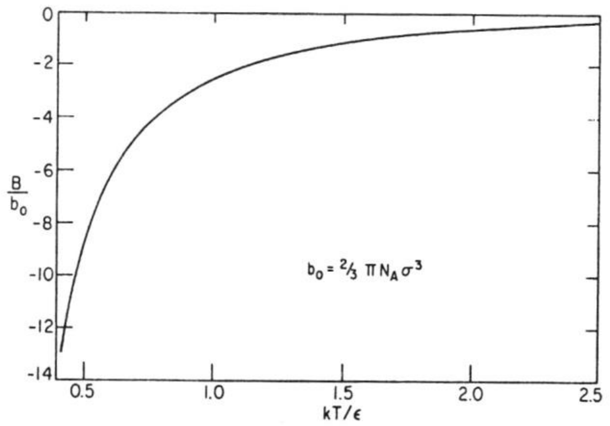


Figure 5-10 Second virial coefficients calculated from Lennard-Jones 6-12 potential.

reduced

(dimensionless)

LJ potential is only an approximate model.

One set of parameters (σ,ε) obtained from the second virial coefficient are not the same as another set of parameters (σ,ε) from viscosity data.

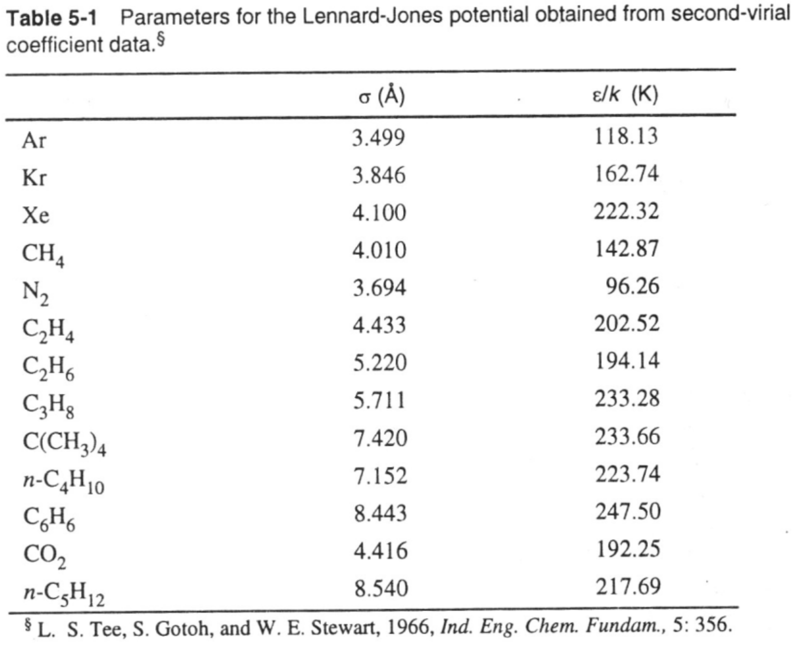


Table 5-1 Parameters for the Lennard-Jones potential obtained from second-virial coefficient data.[§]

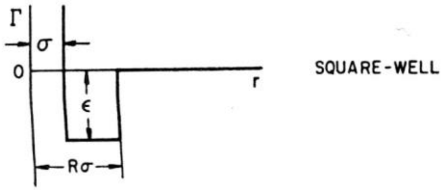
	σ (Å)	ε/k (K)
Ar	3.499	118.13
Kr	3.846	162.74
Xe	4.100	222.32
CH_4	4.010	142.87
N_2	3.694	96.26
C_2H_4	4.433	202.52
C_2H_6	5.220	194.14
C_3H_8	5.711	233.28
$C(CH_3)_4$	7.420	233.66
n-C_4H_{10}	7.152	223.74
C_6H_6	8.443	247.50
CO_2	4.416	192.25
n-C_5H_{12}	8.540	217.69

[§] L. S. Tee, S. Gotoh, and W. E. Stewart, 1966, *Ind. Eng. Chem. Fundam.*, 5: 356.

ε/k in units of temperature

The Square-Well Potential (three parameters)

$$\Gamma = \begin{cases} \infty & \text{for} \quad r \le \sigma \\ -\varepsilon & \text{for} \quad \sigma < r \le R\sigma \\ 0 & \text{for} \quad r > R\sigma \end{cases} \tag{5-39}$$



for example, R~ 1.5 for argon, methane

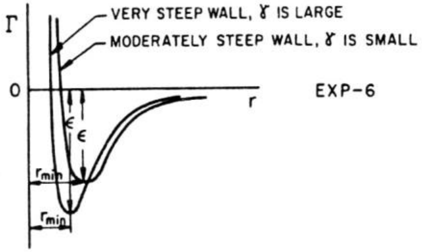
The second virial coefficient is analytically obtained as

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

Good agreement can often be obtained between calculated and experimental second virial coefficients.

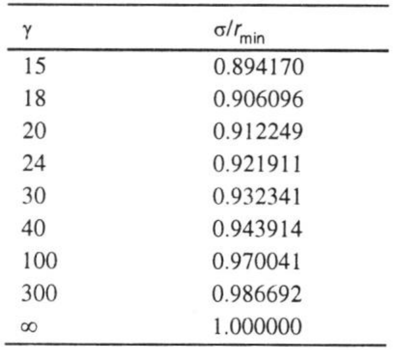
Exp-6 Potential (three parameters)

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



γ determines the steepness of the repulsive wall.

Table 5-2 Ratio σ/r_{min} for the exp-6 potential as a function of the repulsive steepness parameter γ.

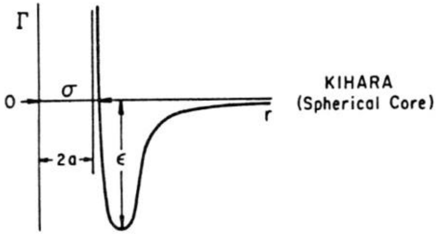


γ	σ/r_{min}
15	0.894170
18	0.906096
20	0.912249
24	0.921911
30	0.932341
40	0.943914
100	0.970041
300	0.986692
∞	1.000000

Kihara potential (three parameters)

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

where *a* is the radius of the spherical molecular core.



hard billiard ball with foam-rubber

Because it is a three-parameter function, Kihara's potential is successful in fitting thermodynamic data for a large number of nonpolar fluids.

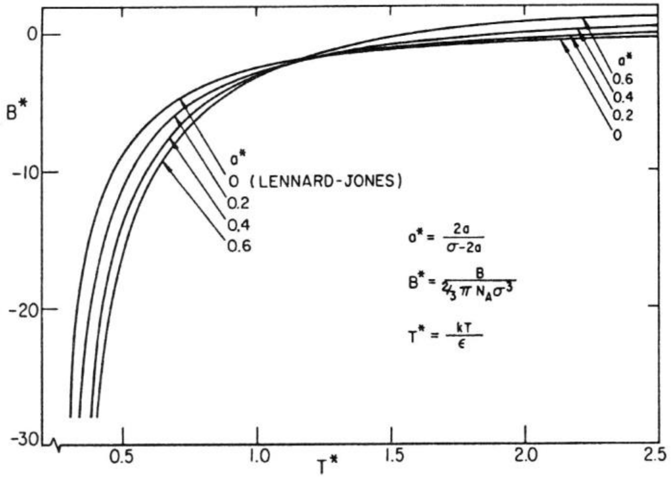


Figure 5-12 Second virial coefficients calculated from Kihara's potential with a spherical core of radius *a*.

a^* is the reduced core size. $a^* = \frac{2a}{\sigma - 2a}$

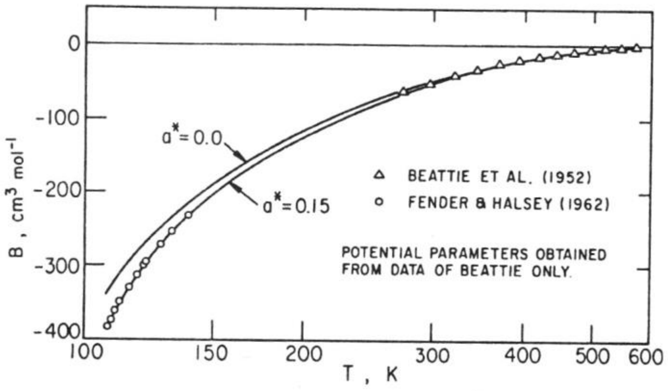


Figure 5-14 Second virial coefficients for krypton. Predictions at low temperatures based on Lennard-Jones potential ($a^* = 0$) and on Kihara potential.

superior to the LJ potential.

Table 5-3 Parameters for the Kihara potential (spherical core) obtained from second-virial-coefficient data.[§]

	a^*	σ (Å)	ε/k (K)
Ar	0.121	3.317	146.52
Kr	0.144	3.533	213.73
Xe	0.173	3.880	298.15
CH_4	0.283	3.565	227.13
N_2	0.250	3.526	139.2[†]
O_2	0.308	3.109	194.3[‡]
C_2H_6	0.359	3.504	496.69
C_3H_8	0.470	4.611	501.89
CF_4	0.500	4.319	289.7[‡]
$C(CH_3)_4$	0.551	5.762	557.75
$n\text{-}C_4H_{10}$	0.661	4.717	701.15
C_6H_6	0.750	5.335	832.0[†]
CO_2	0.615	3.760	424.16
$n\text{-}C_5H_{12}$	0.818	5.029	837.82

[§] L. S. Tee, S. Gotoh, and W. E. Stewart, 1966, *Ind. Eng. Chem. Fundam.*, 5: 363.

[†] A. E. Sherwood and *J. M.* Prausnitz, 1964, *J. Chem. Phys.*, 41: 429.

[‡] C. E. Hunt, unpublished results.

The difficulty of determining “true” potential

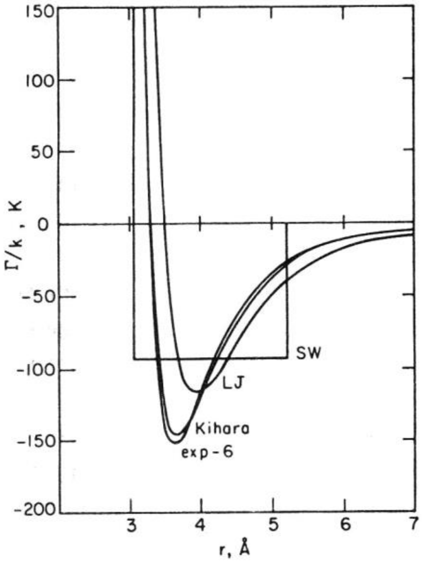


Figure 5-15 Potential functions for argon as determined from second-virial-coefficient data.

for argon

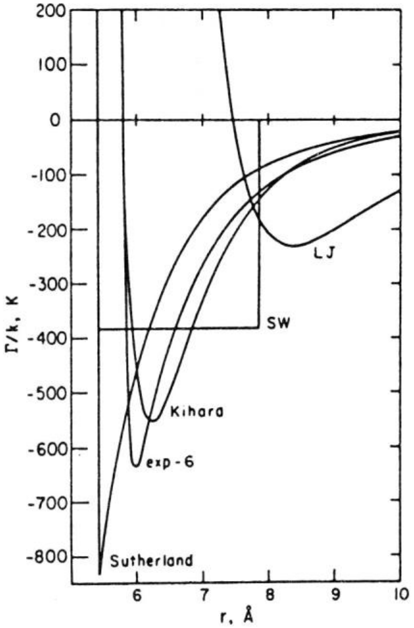


Figure 5-16 Potential functions for neopentane as determined from second-virial-coefficient data.

for neopentane

The various potential functions differ very much from one another.

Stockmayer Potential

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

$$\Gamma_{ij} = -\frac{\mu_i \mu_j}{4\pi\varepsilon_o r^3}\left[2\cos\theta_i \cos\theta_j - \sin\theta_i \sin\theta_j \cos(\phi_i - \phi_j)\right] \qquad (4\text{-}7)$$

in other form

$$U(\boldsymbol{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0 r_{ij}^3}\left[\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - \frac{3}{r_{ij}^2}(\boldsymbol{\mu}_i \cdot \boldsymbol{r}_{ij})(\boldsymbol{\mu}_j \cdot \boldsymbol{r}_{ij})\right]$$

Dipole moment is not a potential parameter. It is determined independently.

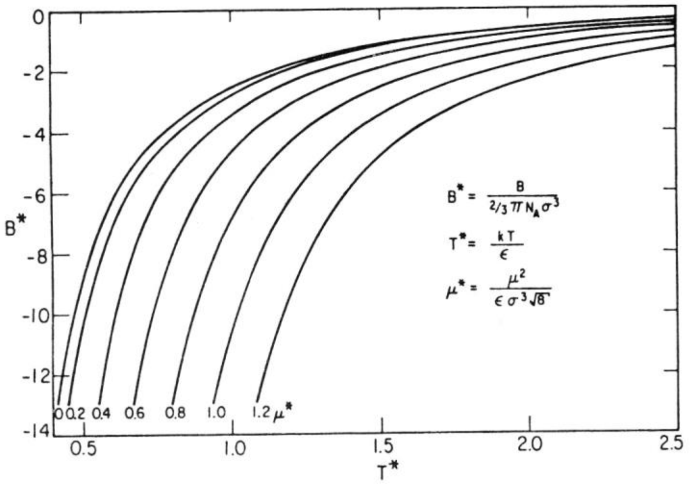


Figure 5-17 Second virial coefficients calculated from Stockmayer's potential for polar molecules.

The effect of polarity is to lower the second virial coefficient due to increased attractions.

Table 5-4 Parameters for Sockmayer'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.

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

Temperature	$-B$ (cm^3 mol^{-1})	
(°C)	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

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

In the derivation, pairwise additivity of potential was assumed such that

$$\Gamma_{ijk} = \Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk} \qquad (5\text{-}43)$$

because little is known about three (or higher) body forces.

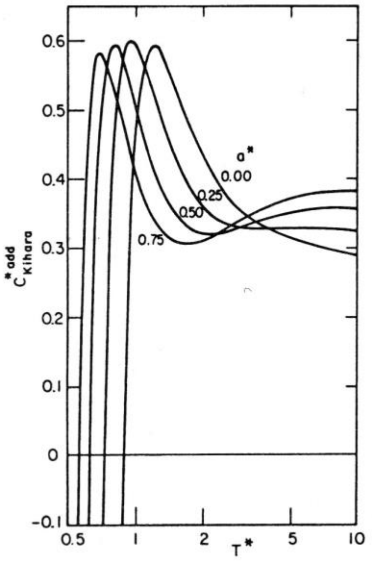


Figure 5-18 Third virial coefficient from Kihara potential assuming pairwise additivity.

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

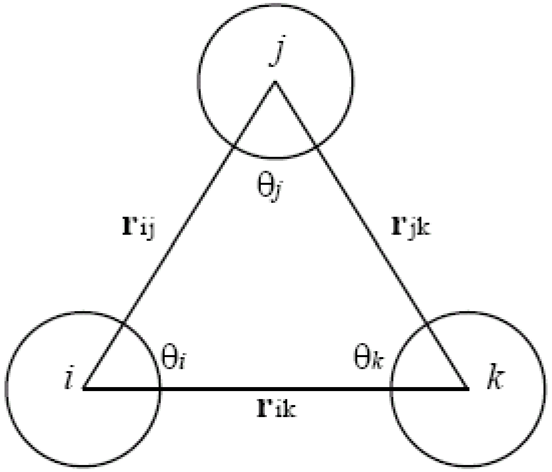
For $a^*=0$, the results are those obtained from LJ potential.

Nonadditive correction

The first-order correction (Axilrod-Teller correction)

$$\Gamma_{ijk} = \Gamma_{ij} + \Gamma_{ik} + \Gamma_{jk} + \Delta\Gamma_{ijk}$$

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



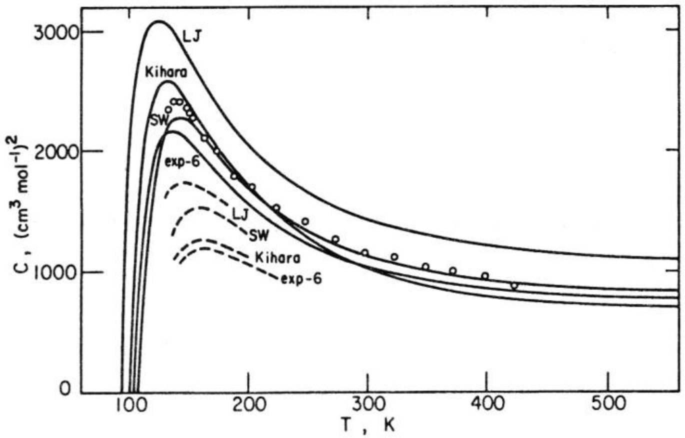


Figure 5-19 Calculated and observed third virial coefficients for argon. Solid lines include Axilrod-Teller nonadditivity corrections. Dashed lines show a portion of calculated results assuming additivity. Circles represent experimental data of Michels (1958).

with parameters determined from the second virial coefficient

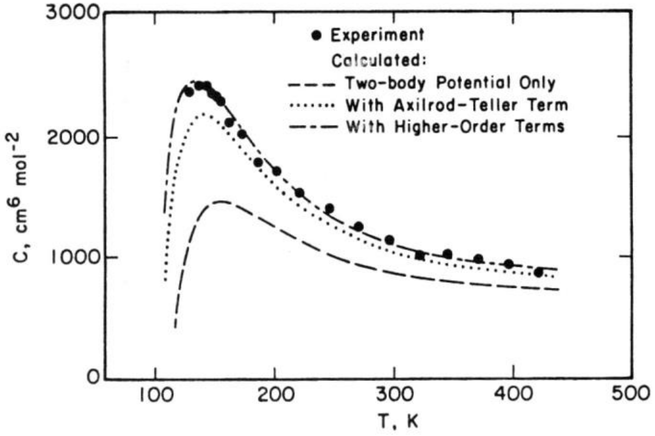


Figure 5-20 Third virial coefficients for argon (Barker and Henderson, 1976).

using unique two-body potential determined both from second virial coefficient and gas-phase transport properties.

Little work has been done on the third virial coefficient of mixture.

Experimental data of the third virial coefficient are scarce and of low accuracy, so it is difficult to

Make meaningful comparison between calculated and experimental results.