CH.7 Fugacities in Liquid Mixtures: Models and Theories of Solutions

The aim of solution theory is to express the properties of liquid mixture in terms of intermolecular forces and liquid structure.

The simplest theory of liquid solutions: Raoult’s law

\[ y_i P = x_i P^e_i \]

Its failure for real solutions is due to differences in molecular size, shape, and intermolecular forces.

7.1 The Theory of van Laar

Consider a mixture of two liquids at constant temperature and pressure

In mixing the two pure components, Van Laar assumed that

1. No volume change, \( v^E = 0 \)
2. The entropy of mixing is ideal, \( s^E = 0 \)

Since at constant pressure and temperature

\[ g^E = u^E + P v^E - T s^E \]  \hspace{1cm} (7-1)

Van Laar’s assumptions corresponds to

\[ g^E = u^E \]  \hspace{1cm} (7-2)
A three-step isothermal thermodynamic cycle

Figure 7-1  Thermodynamic cycle for forming a liquid mixture from the pure liquids at constant temperature.

\[ \Delta u \] is given by the sum of the three energy changes

\[ \Delta u = u^E = \Delta u_I + \Delta u_{II} + \Delta u_{III} \]  \hspace{1cm} (7-3)

**Step I.** Pure liquids are vaporized to the ideal-gas state at constant T.

The energy change is given by the thermodynamic equation,

\[ \left( \frac{\partial u}{\partial v} \right)_T = T\left( \frac{\partial P}{\partial T} \right)_v - P \]  \hspace{1cm} (7-4)

Van Laar assumed the van der Waals equation for the volumetric properties of the pure liquids

\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]

\[ \left( \frac{\partial u}{\partial v} \right)_T = T \left( \frac{R}{v-b} \right) - \frac{RT}{v-b} + \frac{a}{v^2} \]

\[ \left( \frac{\partial u}{\partial v} \right)_T = \frac{a}{v^2} \]  \hspace{1cm} (7-5)
For one mole of mixture with \( x_1 \) moles of liquid 1 and \( x_2 \) moles of liquids

\[
x_1 (u_{\text{ideal}} - u)_1 = \int_0^{\infty} \frac{a_1 x_1}{v_1^2} dv - \frac{a_1 x_1}{v_1^2}
\]

(7-6)

\[
x_2 (u_{\text{ideal}} - u)_2 = \int_0^{\infty} \frac{a_2 x_2}{v_2^2} dv - \frac{a_2 x_2}{v_2^2}
\]

(7-7)

According to the VDW theory, the molar volume of a liquid well below the critical temperature is approximated by the constant \( b \). Thus

\[
\Delta u_1 = \frac{a_1 x_1}{b_1} + \frac{a_2 x_2}{b_2}
\]

(7-8)

**Step II. Mixing of gases at very low pressure (i.e., ideal gases)**

There is no change in energy

\[
\Delta u_{\text{II}} = 0
\]

(7-9)

**Step III. The ideal gas mixture is compressed isothermally to the original pressure.**

As in the step I, the change in energy is given by the VDW EOS.

\[
\Delta u_{\text{III}} = - \frac{a_{\text{mixt}}}{b_{\text{mixt}}}
\]

(7-10)

Constant \( a_{\text{mixt}} \) and \( b_{\text{mixt}} \) in terms of those of the pure components

\[
a_{\text{mixt}} = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 \sqrt{a_1 a_2}
\]

(7-11)

\[
b_{\text{mixt}} = x_1 b_1 + x_2 b_2
\]

(7-12)
Adding up for $\Delta u$

$$g^E = \Delta u = \frac{a_1x_1 + a_2x_2}{b_1 + b_2} - \frac{x_1^2a_1 + x_2^2a_2 + 2x_1x_2\sqrt{a_1a_2}}{x_1b_1 + x_2b_2}$$

$$g^E = \frac{x_1x_2b_1b_2}{x_1b_1 + x_2b_2} \left( \frac{\sqrt{a_1}}{b_1} - \frac{\sqrt{a_2}}{b_2} \right)^2$$

(7-13)

The activity coefficients are obtained by differentiation

$$\ln \gamma_1 = \frac{A'}{\left(1 + \frac{A'x_1}{B'x_2}\right)^2}$$

(7-14)

$$\ln \gamma_2 = \frac{B'}{\left(1 + \frac{B'x_2}{A'x_1}\right)^2}$$

(7-15)

where

$$A' = \frac{b_1}{RT} \left( \frac{\sqrt{a_1}}{b_1} \frac{\sqrt{a_2}}{b_2} \right)^2$$

$$B' = \frac{b_2}{RT} \left( \frac{\sqrt{a_1}}{b_1} \frac{\sqrt{a_2}}{b_2} \right)^2$$

- $\ln \gamma$ is proportional to $T^{-1}$ because $s^E = 0$

$$g^E = u^E + p\gamma^E - Ts^E \quad \Rightarrow \quad g^E = u^E$$

$$RT \ln \gamma_i = \bar{g}_i^E = \left( \frac{\partial n_T g^E}{\partial n_i} \right)_{T,P,n_i} \quad \text{independent of } T$$
The activity coefficients are always greater than unity (positive deviation from Raoult’s law)

\[ A' > 0, \quad B' > 0 \quad \Rightarrow \ln \gamma > 0 \]

If it were assumed that

\[ a_{\text{mix}} = x_1a_1 + x_2a_2 \quad (7-21) \]

Then we would have

\[ \gamma_1 = \gamma_2 = 1 \quad \text{for all } x \quad (7-22) \]

The rules to express the constants for a mixture have a large influence.

- Quantitative agreement between van Laar’s equations and experimental results is not good because of VDW equation and the mixing rules used

- Van Laar equations are useful empirical relations if we regard \( A' \) and \( B' \) as adjustable parameters.

7.2 The Schtchard-Hildebrand Theory

Hildebrand (1929) defined a regular solution as one with no excess entropy of mixing at constant temperature and at constant volume.

The cohesive energy density is defined by

\[ \varepsilon = \frac{\Delta_{\text{vap}L}}{\nu^L} \quad (7-23) \]

where \( \Delta_{\text{vap}L} \) is the energy change on the vaporization of the saturated liquid to the ideal-gas state.
Hildebrand and Scatchard generalized (7-23) to a binary liquid mixture,

\[-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mix}} = \frac{c_{11}x_1^2 + 2c_{12}x_1x_2 + c_{22}x_2^2}{x_1v_1 + x_2v_2}\]  

(7-24)

The energy of a liquid mixture is assumed to be a quadratic function of the volume fraction. The volume of a liquid mixture is assumed to be given by the mole fraction average. \(c_{11}\) and \(c_{22}\) are for pure saturated liquids, which are functions only of temperature.

To simplify notation, volume fractions defined by

\[\Phi_1 = \frac{x_1v_1}{x_1v_1 + x_2v_2}\]  

(7-25)

\[\Phi_2 = \frac{x_2v_2}{x_1v_1 + x_2v_2}\]  

(7-26)

Then (7-24) becomes

\[-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mix}} = (x_1v_1 + x_2v_2)[c_{11}\Phi_1^2 + 2c_{12}\Phi_1\Phi_2 + c_{22}\Phi_2^2]\]  

(7-27)

The molar energy change of mixing (= excess energy of mixing) is

\[\Delta_{\text{mix}}u = u^E = u_{\text{mix}} - x_1u_1 - x_2u_2\]  

(7-28)

noting that \(\Delta_{\text{mix}}u = u^E_{\text{ideal}} = 0\)  

(7-29)

\[u^E = (x_1v_1 + x_2v_2)\left[c_{11}\Phi_1^2 + 2c_{12}\Phi_1\Phi_2 + c_{22}\Phi_2^2\right] - x_1u_1 - x_2u_2\]

since \(x_1u_1 = x_1c_{11}v_1 = (x_1v_1 + x_2v_2)c_{11}\Phi_1\)

\[u^E = (x_1v_1 + x_2v_2)\left[c_{11}\Phi_1^2 + 2c_{12}\Phi_1\Phi_2 + c_{22}\Phi_2^2 - c_1\Phi_1 - c_2\Phi_2\right]\]
As suggested by London’s formula, it is assumed that

\[ c_{12} = (c_{11}c_{22})^{1/2} \tag{7-31} \]

(7-30) becomes

\[ u^E = (x_1v_1 + x_2v_2)\Phi_1\Phi_2(\delta_1 - \delta_2)^2 \tag{7-32} \]

where \( \delta \) is called the solubility parameter.

\[ \delta_1 = c_{11}^{1/2} = \left( \frac{\Delta_{vap}^H}{v} \right)_{1}^{1/2} \tag{7-33} \]

\[ \delta_2 = c_{22}^{1/2} = \left( \frac{\Delta_{vap}^H}{v} \right)_{2}^{1/2} \tag{7-34} \]

As in the van Laar theory, we assume there are no excess entropy and no excess volume

\[ g^E = u^E \]

The activity coefficients are given by

\[ RT \ln \gamma_1 = v_1\Phi_2^2(\delta_1 - \delta_2)^2 \]

\[ RT \ln \gamma_2 = v_2\Phi_1^2(\delta_1 - \delta_2)^2 \tag{7-37} \]

that are the regular-solution equations.

The regular-solution equations always predicts \( \gamma_i \geq 1 \) (positive deviation from Raoult’s law), which is a consequence of the geometric-mean assumption.
The difference in solubility parameters provides a measure of solution nonideality.
For example, mixtures of aliphatic hydrocarbons with aromatics show appreciable nonideality.

<table>
<thead>
<tr>
<th>Liquefied gases at 90 K</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>Nitrogen</td>
<td>38.1</td>
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<tr>
<td>Carbon monoxide</td>
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<td>11.7</td>
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<tr>
<td>Argon</td>
<td>29.0</td>
<td>13.9</td>
</tr>
<tr>
<td>Oxygen</td>
<td>28.0</td>
<td>14.7</td>
</tr>
<tr>
<td>Methane</td>
<td>35.3</td>
<td>15.1</td>
</tr>
<tr>
<td>Carbon tetrafluoride</td>
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<td>17.0</td>
</tr>
<tr>
<td>Ethane</td>
<td>45.7</td>
<td>19.4</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Liquid solvents at 25°C</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Perfluoro-n-heptane</td>
<td>226</td>
<td>12.3</td>
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<tr>
<td>Neopentane</td>
<td>122</td>
<td>12.7</td>
</tr>
<tr>
<td>Isopentane</td>
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<td>13.9</td>
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<td>n-Pentane</td>
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<tr>
<td>n-Hexane</td>
<td>132</td>
<td>14.9</td>
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<tr>
<td>1-Hexene</td>
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<tr>
<td>n-Octane</td>
<td>164</td>
<td>15.3</td>
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<tr>
<td>n-Hexadecane</td>
<td>294</td>
<td>16.3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>109</td>
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<tr>
<td>Carbon tetrachloride</td>
<td>97</td>
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<td>Ethyl benzene</td>
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<td>Toluene</td>
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<td>Benzene</td>
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<tr>
<td>Styrene</td>
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<td>Tetrachloroethylene</td>
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<tr>
<td>Carbon disulfide</td>
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<tr>
<td>Bromine</td>
<td>51</td>
<td>23.5</td>
</tr>
</tbody>
</table>
Figure 7-2  Vapor-liquid equilibria for CO (1)/CH₄ (2) mixtures at 90.7 K.

Figure 7-3  Vapor-liquid equilibria for C₆H₆ (1)/n-C₇H₁₆ (2) at 70°C.
To relax the geometric-mean assumption

\[ c_{12} = (1 - l_{12})c_{12_2}c_{2_2} \]  

(7-42)

The resulting activity coefficients are

\[ \ln \gamma_1 = \frac{v_1 \Phi_2^2}{RT} \left[ (\delta_1 - \delta_2)^2 + 2l_{12} \delta_1 \delta_2 \right] \]  

(7-43)

\[ \ln \gamma_2 = \frac{v_2 \Phi_1^2}{RT} \left[ (\delta_1 - \delta_2)^2 + 2l_{12} \delta_1 \delta_2 \right] \]  

(7-44)

if the solubility parameters are close to each other, a small value of \( l_{12} \) can significantly affect activity coefficients.
The $l_{12}$ is an essentially empirical parameter, and efforts to correlate $l_{12}$ are of little success.

Figure 7-6  Binary parameter $l_{12}$ for aromatic-saturated hydrocarbon mixtures at 50°C. Binary systems shown are: 1. Benzene (2)/Pentane (1); 2. Benzene (2)/Neopentane (1); 3. Benzene (2)/Cyclopentane (1); 4. Benzene (2)/Hexane (1); 5. Benzene (2)/2-Methylpentane (1); 6. Benzene (2)/2,2-Dimethylbutane (1); 7. Benzene (2)/2,3-Dimethylbutane (1); 8. Benzene (2)/Cyclohexane (1); 9. Benzene (2)/Methylcyclopentane (1); 10. Benzene (2)/Heptane (1); 11. Benzene (2)/3-Methylhexane (1); 12. Benzene (2)/2,4-Dimethylpentane (1); 13. Benzene (2)/2,2,3-Trimethylbutane (1); 14. Benzene (2)/Methylcyclohexane (1); 15. Benzene (2)/Octane (1); 16. Benzene (2)/2,2,4-Trimethylpentane (1); 17. Toluene (2)/Hexane (1); 18. Toluene (2)/3-Methylpentane (1); 19. Toluene (2)/Cyclohexane (1); 20. Toluene (2)/Methylcyclopentane (1); 21. Toluene (2)/Heptane (1); 22. Toluene (2)/Methylcyclohexane (1); 23. Toluene (2)/2,2,4-Trimethylpentane (1).
Effect of $l_{12}$ on VLE

The multicomponent case

\[
-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mixt}} = \frac{\sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j c_{ij}}{\sum_{i=1}^{m} x_i v_i}
\]  

\text{(7-49)}

The volume fraction is

\[
\Phi_j = \frac{\sum_{i=1}^{m} x_i v_i}{\sum_{i=1}^{m} x_i v_i}
\]  

\text{(7-50)}

Extensions to hydrogen-bonded components are of little theoretical sense.
The excess energy of mixing is defined by

\[ u^E = u_{\text{mix}} - \sum_{i} x_i u_i \]  \hspace{1cm} (7-51)

The cohesive-energy density is given by the geometric mean

\[ c_{ij} = (c_{ii} c_{jj})^{1/2} \]  \hspace{1cm} (7-52)

Assuming

\[ s^E = u^E = 0 \]  \hspace{1cm} (7-53)

Then

\[ g^E = u^E \]  \hspace{1cm} (7-54)

The activity coefficients are

\[ \frac{RT \ln \gamma_j}{v_j (\bar{\delta} - \bar{\delta})^2} = \frac{\Phi_i \delta_i}{\sum_{i} \Phi_i \delta_i} \]  \hspace{1cm} (7-55)

\[ \bar{\delta} = \sum_{i} \Phi_i \delta_i \]  \hspace{1cm} (7-56)

\( \bar{\delta} \) is a volume-fraction average of the solubility parameter of all the components.

The regular-solution theory is attractive because of its simplicity, and it can correlate liquid-phase activity coefficients using only one adjustable parameter.

7.4 The Lattice Model

The liquid state is in some sense intermediate between the gaseous state and the crystalline state. The lattice model considers a liquid to be solid-like or quasicrystalline. It supposes molecules to sit in a regular array in space, called a lattice.
Deviations from ideal behavior in liquid solutions are due to:

Attractive forces between unlike molecules different from those between like molecules, which gives rise to nonvanishing enthalpy of mixing.

If the unlike molecules differ significantly in size or shape, giving rise to a nonideal entropy of mixing.

Consider a mixture of simple liquids 1 and 2.
Molecules are spherical, and the ratio of their sizes is close to unity.
All the molecules are situated on lattice points.
There are no vacant holes, and the lattice spacings for pure liquids and for the mixture are the same ($\nu^E = 0$).

\begin{align*}
z & \text{pairs of type 11, } z \text{ pairs of type 22} \rightarrow 2z \text{ pairs of type 12} \\
z\Gamma_{11} + z\Gamma_{22} & = 2z\Gamma_{12}
\end{align*}

*Figure 7-8* Physical significance of interchange energy. The energy absorbed in the process above is $2\nu$. [See Eq. (7-71)].
We assume that the potential energy is pairwise additive and
that only nearest neighbors need be considered (short-range interaction)
Consider \(N_1\) molecules of type 1 and \(N_2\) molecules of type 2.
Each molecule has \(z\) nearest neighbors; empirically, \(z\) is close to 10 for liquids.

The total number of nearest neighbors = \(\frac{z}{2}(N_1 + N_2)\) (avoiding double counting)

Three types of nearest neighbors: 11, 22, and 12
\(N_{11}\) is the number of nearest-neighbor pairs of type 11.
\(N_{22}\) \(N_{12}\)
They are related by
\[
\begin{align*}
\frac{z}{2}N_1 &= 2N_{11} + N_{12} \\
\frac{z}{2}N_2 &= 2N_{22} + N_{12} \\
\frac{z}{2}(N_1 + N_2) &= N_{11} + N_{22} + N_{12}
\end{align*}
\]

The total potential energy is given by
\[
U_t = N_{11} \Gamma_{11} + N_{22} \Gamma_{22} + N_{12} \Gamma_{12}
\]
Eliminating \(N_{11}\) and \(N_{22}\) using (7-68)
\[
U_t = \frac{z}{2} N_1 \Gamma_{11} + \frac{z}{2} N_2 \Gamma_{22} + \frac{w}{2} N_{12}
\]

The last term of (7-70) is the energy of mixing
\(w\) is the *interchange energy* defined by
\[
w = z \left[ \Gamma_{12} - \frac{1}{2}(\Gamma_{11} + \Gamma_{22}) \right]
\]
is energy change accompanied when \(z\) pairs of type 12 are formed.
The canonical partition function of the lattice is given by

\[ Q_{\text{lattice}} = \sum_{N_{12}} g(N_1, N_2, N_{12}) \exp \left( -\frac{U_t}{kT} \right) \]  

(7-72)

g is the combinatorial factor (degeneracy), the number of ways of arranging \( N_1 \) and \( N_2 \) molecules each giving the potential energy \( U_t \) (or giving \( N_{12} \) pairs, equivalently).

\( g = 1 \) for a pure component

We retain only the maximum term (p771, maximum term method).

The Helmholtz energy change of mixing is

\[ \Delta_{\text{mix}} A = A_{\text{mix}} - (A_{\text{pure}_1} + A_{\text{pure}_2}) \]  

(7-73)

Since \( A = -kT \ln Q \)

\[ \Delta_{\text{mix}} A = -kT \ln \left[ g(N_1, N_2, N_{12}) \exp \left( -\frac{wN_{12}}{kT} \right) \right] \]  

(7-74)

\( w/z \) is energy change per each pair of type 12.

We assume a completely random mixture for which all possible arrangement of the molecules are equally probable.

The number of dissimilar pairs is

\[ N^*_{12} = \frac{zN_1N_2}{N_1 + N_2} \quad * \text{indicate a completely random arrangement} \]

\[ = zN_1 \times \frac{N_2}{N_1 + N_2} \]

\[ = ( \text{No. of neighbor sites of molecules of type 1} ) \times ( \text{Probability of randomly placing molecules of type 2 on the site} ) \]

and
Using Stirling’s formula \( \ln N! = N \ln N - N, \) for \( N \gg 1 \)

\[
\frac{\Delta_{\text{mix}}}{kT} = N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} + \frac{w}{kT} \frac{N_1 N_2}{N_1 + N_2}
\]

(7-77)

In molar unit

\[
\frac{\Delta_{\text{mix}}}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{w}{kT} x_1 x_2
\]

(7-78)

The molar excess Helmholtz energy is

\[
\frac{a^E}{RT} = \frac{w}{kT} x_1 x_2
\]

(7-79)

Since \( w \) is assumed to be independent of temperature

\[
\frac{\Delta_{\text{mix}}}{R} = -\frac{1}{R} \left( \frac{\partial a^E}{\partial T} \right)_p = -x_1 \ln x_1 - x_2 \ln x_2
\]

(7-80)

is the entropy of mixing for an ideal solution. (We assumed a completely random arrangement)

\[ s^E = 0 \]

We assumed also that

\[ v^E = 0 \]

The mixture we considered is a regular solution:

\[
g^E = a^E = h^E = u^E = N_A w x_1 x_2
\]

(7-81) \( N_A \) Avogadro’s number

The activity coefficients are given by
The same form as with the two-suffix Margules equation.

If \( \Gamma_{12} = \frac{1}{2} (\Gamma_{11} + \Gamma_{22}) \rightarrow w = 0 \rightarrow \gamma = 0 \)

But for nonpolar molecules

\[
|\Gamma_{12}| \approx \sqrt{|\Gamma_{11}| |\Gamma_{22}|} < \frac{1}{2} (|\Gamma_{11}| + |\Gamma_{22}|) \quad \text{(geometric mean < arithmetic mean)}
\]

\( \Gamma_{12} > \frac{1}{2} (\Gamma_{11} + \Gamma_{22}) \rightarrow w > 0 \rightarrow \gamma > 0 \)

Positive deviations in agreement with experiment.

**7.6 Nonrandom Mixtures of Simple Molecules**

A completely random mixture can only result if intermolecular forces are the same for all the possible molecular pairs 11, 22, and 12.

Strictly, only an ideal mixture can be completely random.

Guggenheim constructed a lattice theory that is not necessarily random, which is called the **quasichemical approximation**.
Consider the reaction

\[(1-1) + (2-2) \rightleftharpoons 2 \cdot (1-2) \]  

(7-91)

The equilibrium constant \(K\) is defined by

\[
K = \frac{(N_{12})^2}{N_{11}N_{22}} \]  

(7-92)

The energy change for the reaction is \(2w/z\) by (7-71).

The temperature derivative of \(\ln K\) is

\[
\left[ \frac{\partial \ln K}{\partial (1/T)} \right]_V = -\frac{\Delta \mu}{R} \]  

(7-93)

Assuming that the energy change of reaction is given by

\[
\frac{\Delta \mu}{R} = \frac{2w}{kz} \]  

(7-94)

Integrating (7-93)

\[K = C \exp \left( -\frac{2w}{zkT} \right) \]  

(7-95)

When \(w = 0\), mixing is completely random

\[K^* = C = \frac{(N_{12}^*)^2}{N_{11}^*N_{22}^*} \]  

(7-96)

* designates random mixing

Using (7-68) and (7-75)

\[
\frac{N_i}{N_{12}} = 2 \frac{N_{11}^*}{N_{12}^*} + 1 = \frac{N_i + N_2}{N_2} \\
\frac{N_{12}^*}{N_{12}} = \frac{1}{2} \frac{N_1}{N_2} \quad \frac{N_{22}^*}{N_{12}^*} = \frac{1}{2} \frac{N_2}{N_1} \]

then \(C = 4\)
The equilibrium constant $K$ becomes

$$\frac{(N_{12})^2}{N_{11}N_{22}} = 4 \exp\left(-\frac{2w}{z\kappa T}\right) = \frac{4}{\eta^2} \quad (7-97)$$

where $\eta = \exp(w / z\kappa T)$.

Introducing a parameter $\beta$ determined from (7-68) and (7-97)

$$N_{12} = N_{12}^* \left(\frac{2}{\beta + 1}\right) = \frac{zN_1N_2}{N_1 + N_2} \left(\frac{2}{\beta + 1}\right) \quad (7-98)$$

$$\beta = [1 + 4x_1x_2(\eta^2 - 1)]^{1/2} \quad (7-99)$$

determined from (7-68) and (7-97)

For random case, $\beta = 1$.

The excess energy of mixing is

$$u^E = u^{E*} \left(\frac{2}{\beta + 1}\right) \quad (7-100)$$

where $u^{E*} = N_1\omega_{11}x_{12}$

To obtain the excess Helmholtz energy

$$\left[\frac{\partial (a^E / T)}{\partial (1/T)}\right]_{V,x} = u^E \quad (7-101)$$

Integrating

$$\frac{a^E}{RT} = \frac{z}{2} \left[ x_1 \ln \frac{\beta - 1 + 2x_1}{x_1(\beta + 1)} + x_2 \ln \frac{\beta - 1 + 2x_2}{x_2(\beta + 1)} \right] \quad (7-102)$$
To simplify further, we expand $\exp(2w/zkT)$ in power series.

The molar excess functions are

$$
\frac{g^E}{RT} = \left( \frac{w}{kT} \right) x_1 x_2 \left[ 1 - \frac{1}{2} \left( \frac{2w}{zkT} \right) x_1 x_2 + \ldots \right] \quad (7-103)
$$

$$
\frac{h^E}{RT} = \left( \frac{w}{kT} \right) x_1 x_2 \left[ 1 - \left( \frac{2w}{zkT} \right) x_1 x_2 + \ldots \right] \quad (7-104)
$$

$$
\frac{s^E}{k} = -\left( \frac{w}{kT} \right) x_1 x_2 \left[ \frac{1}{2} \left( \frac{2w}{zkT} \right) x_1 x_2 + \ldots \right] \quad (7-105)
$$

The excess entropy is negative for any positive or negative $w$. 
The Gibbs energy with quasichemical approximation becomes lower.

**Partial Miscibility**

The criteria for instability is

\[
\frac{\partial^2 \Delta_{\text{mix}}}{\partial x^2} = \frac{\partial^3 \Delta_{\text{mix}}}{\partial x^3} = 0 \quad (7-106)
\]

\[
\Delta_{\text{mix}} = RT(x_1 \ln x_1 + x_2 \ln x_2) + g^E \quad (7-107)
\]
As in chapter 6, the upper consolute temperature is

\[ T^c = \frac{w}{2k} \]  

(7-108)

For the quasichemical approximation

\[ T^c = \frac{w}{kz[\ln z - \ln(z-2)]} \]  

(7-109)

When \( z = 10 \),

\[ T^c = \frac{w}{2.23k} \]  

(7-110)

\( T^c \) is 10\% lower than in the case of random mixing.

Figure 7-10  Effect of nonrandomness on Gibbs energy of mixing.
Methane / CF$_4$

Figure 7-11 Excess Gibbs energy of methane/carbon tetrafluoride system.
Figure 7-12  Liquid-liquid coexistence curve for the methane/carbon tetrafluoride system.
7.7 The Two-Liquid Theory

One-fluid theory: a mixture is considered to be a hypothetical pure fluid
(in microscopic view) whose characteristic molecular size and potential energy are composition
averages of those of its components
(in macroscopic view) whose effective critical properties are composition averages of
component critical properties

Two-fluid theory uses two pure reference fluids.

Consider a binary mixture

![Diagram](image)

Figure 7-13  Essential idea of the two-fluid theory of binary mixtures. Hypothetical fluid (1) has a molecule 1 at the center. Hypothetical fluid (2) has a molecule 2 at the center.

A cell is referred to as an immediate region around any molecule.
There are two types of cells: One type contains molecule 1 at its center and the other contains
molecule 2 at its center.
The two-fluid theory assumes that the property \( M \) of the mixture is given by

\[
M_{\text{mixt}} = x_1 M^{(1)} + x_2 M^{(2)}
\]  

(7-111)

where \( M^{(1)} \) is the property \( M \) of a hypothetical fluid consisting only of cells of type 1,

\( M^{(2)} \) is the property \( M \) of a hypothetical fluid consisting only of cells of type 2.

For example, let \( M \) stand for the (configurational) enthalpy \( h_{\text{conf}} \),

\[
\frac{h_{\text{conf}}}{RT} = F \left( \frac{kT}{\varepsilon}, \frac{P_2 \sigma^3}{\varepsilon} \right)
\]  

(7-112)

For reference fluid 1, the same form is assumed that

\[
\frac{h_{\text{conf}(1)}}{RT} = F \left( \frac{kT}{\varepsilon^{(1)}}, \frac{P_{\sigma^{(1)}3}}{\varepsilon^{(1)}} \right)
\]  

(7-113)

\( \varepsilon^{(1)} \) and \( \sigma^{(1)} \) are composition averages for cells of type 1

\[
\varepsilon^{(1)} = x_1 \varepsilon_{11} + x_2 \varepsilon_{12}
\]  

(7-114)

\[
\sigma^{(1)} = x_1 \sigma_{11} + x_2 \sigma_{12}
\]  

(7-115)

\( \varepsilon_{ij} \) and \( \sigma_{ij} \) are for \( i-j \) interactions

Similarly,

\[
\frac{h_{\text{conf}(2)}}{RT} = F \left( \frac{kT}{\varepsilon^{(2)}}, \frac{P_{\sigma^{(2)}3}}{\varepsilon^{(2)}} \right)
\]  

(7-116)

\[
\varepsilon^{(2)} = x_2 \varepsilon_{22} + x_1 \varepsilon_{12}
\]  

(7-117)

\[
\sigma^{(2)} = x_2 \sigma_{22} + x_1 \sigma_{12}
\]  

(7-118)

Then, the molar enthalpy of the mixture is given by
The UNIQUAC equation is a two-fluid theory.

We consider a process in which one molecule of component 1 is vaporized from its pure liquid (0), and then condensed into the center of cell [ hypothetical fluid (1) ]

The energy of vaporization per molecule is \( \frac{1}{2} z U_{11}^{(0)} \) (factor 1/2 considering double counting)

\( U_{11}^{(0)} \) is the potential energy of two neighbors in pure liquid 1

simple case with \( r = q = 1 \)

Surface fractions:

\( \theta_{11} \) the local surface fraction of component 1 about central molecule 1
\( \theta_{21} \) the local surface fraction of component 2 about central molecule 1

\( \theta_{11} + \theta_{21} = 1 \)

The central molecule in hypothetical fluid (1) is surrounded by \( z \theta_{11} \) molecules of component 1 and \( z \theta_{22} \) molecules of component 2.

The energy released by the condensation process around a central molecule in hypothetical fluid (1)

\[ \frac{1}{2} z \left( \theta_{11} U_{11}^{(1)} + \theta_{21} U_{21}^{(1)} \right) \]

The energy released by the condensation process around a central molecule in hypothetical fluid (2)
\[
\frac{1}{2} z \left( \theta_2 U_{12}^{(2)} + \theta_2 U_{22}^{(2)} \right)
\]

For a mixture consisting of \(x_1\) moles of hypothetical fluid (1) and \(x_2\) moles of hypothetical fluid (2)

\[
u^E = \frac{1}{2} z x_1 N_A \left[ q_1 (\theta_1 U_{11}^{(1)} + \theta_2 U_{21}^{(2)} - U_{11}^{(0)}) \right] + \frac{1}{2} z x_2 N_A \left[ q_2 (\theta_2 U_{22}^{(2)} + \theta_1 U_{12}^{(2)} - U_{22}^{(0)}) \right]
\]

(7-120) for any \(q\) in general

Conservation equation for the local surface fractions

\[
\begin{align*}
\theta_{21} + \theta_{11} &= 1 \\
\theta_{12} + \theta_{22} &= 1
\end{align*}
\]

(7-121)

assuming that \(U_{11}^{(1)} = U_{11}^{(0)}\) and \(U_{22}^{(2)} = U_{22}^{(0)}\)

\[
u^E = \frac{1}{2} z N_A \left[ x_1 \theta_{21} q_1 (U_{21} - U_{11}) + x_2 \theta_{12} q_2 (U_{12} - U_{22}) \right]
\]

(7-122)

\[
\begin{align*}
\frac{\theta_{21}}{\theta_{11}} &= \frac{\theta_2}{\theta_1} \exp \left[ -\frac{1}{2} \frac{z (U_{21} - U_{11})}{kT} \right] \\
\frac{\theta_{12}}{\theta_{22}} &= \frac{\theta_1}{\theta_2} \exp \left[ -\frac{1}{2} \frac{z (U_{12} - U_{22})}{kT} \right]
\end{align*}
\]

(7-123)

(7-124)

where \(\theta\) is surface fraction

\[
\begin{align*}
\theta_1 &= \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \\
\theta_2 &= \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}
\end{align*}
\]

(7-125)

note that
\[
\begin{align*}
\frac{\theta_{21}}{\theta_{11}} &= \frac{\theta_2}{\theta_1} \\
\frac{\theta_{12}}{\theta_{22}} &= \frac{\theta_1}{\theta_2}
\end{align*}
\]
for random mixture

Rewriting (7-122)

\[
u^E = x_1 q_1 \theta_{21} \Delta u_{21} + x_2 q_2 \theta_{12} \Delta u_{12} \tag{7-126}
\]

\[
\theta_{21} = \frac{\theta_2 \exp(-\Delta u_{21} / RT)}{\theta_1 + \theta_2 \exp(-\Delta u_{21} / RT)} \tag{7-127}
\]

\[
\theta_{12} = \frac{\theta_1 \exp(-\Delta u_{12} / RT)}{\theta_2 + \theta_1 \exp(-\Delta u_{12} / RT)} \tag{7-128}
\]
local compositions

where

\[
\Delta u_{21} = \frac{1}{2} z (U_{21} - U_{11}) N_A \\
\Delta u_{12} = \frac{1}{2} z (U_{12} - U_{22}) N_A \tag{7-129}
\]

To obtain the molar excess Helmholtz energy,

\[
\frac{d(a^E / T)}{d(1/T)} = \nu^E \tag{7-130}
\]
at const volume and composition

Integration gives

\[
\frac{\Delta a^E}{T} = \int_{1/T_0}^{1/T} \nu^E d(1/T) + \text{constant of integration} \tag{7-131}
\]

At very high temperature \(1/T_0 \to 0\), we have athermal mixture for which
\[
\left( \frac{a^E}{RT} \right)_{\text{athermal}} = -\left( \frac{s^E}{R} \right)_{\text{combinatorial}} \\
= x_1 \ln \frac{\Phi_1^*}{x_1} + x_2 \ln \frac{\Phi_2^*}{x_2} + \frac{1}{2} \left( q_1 x_1 \ln \frac{\theta_1}{\Phi_1^*} + q_2 x_2 \ln \frac{\theta_2}{\Phi_2^*} \right)
\]

Guggenheim (1952)

Where
\[
\Phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \quad \text{and} \quad \Phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \quad (7-133)
\]

Assuming that \( \Delta u_{21} \) and \( \Delta u_{12} \) are independent of temperature and that \( a^E \approx g^E \)

Eq (7-131) gives
\[
\left( \frac{a^E}{RT} \right)_{T,V} \approx \left( \frac{g^E}{RT} \right)_{T,P} = \left( \frac{g^E}{RT} \right)_{\text{combinatorial}} + \left( \frac{g^E}{RT} \right)_{\text{residual}} \quad (7-134)
\]

Where
\[
\left( \frac{g^E}{RT} \right)_{\text{combinatorial}} = x_1 \ln \frac{\Phi_1^*}{x_1} + x_2 \ln \frac{\Phi_2^*}{x_2} + \frac{1}{2} \left( x_1 q_1 \ln \frac{\theta_1}{\Phi_1^*} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2^*} \right) \quad (7-135)
\]
\[
\left( \frac{g^E}{RT} \right)_{\text{residual}} = -x_1 q_1 \ln \left[ \theta_1 + \theta_2 \exp \left( \frac{-\Delta u_{21}}{RT} \right) \right] - x_2 q_2 \ln \left[ \theta_2 + \theta_1 \exp \left( \frac{-\Delta u_{12}}{RT} \right) \right] \quad (7-136)
\]

The UNIQUAC equation is a good empirical representation for a large variety of liquid mixtures. Molecular simulation suggests that the nonrandomness factors in (7-123) and (7-124) is too large.
7.8 Activity Coefficients from Group-Contribition Methods

Often necessary to estimate activity coefficients for mixtures
Group-contribution method
   A molecule is divided into functional groups.
   The number of possible distinct functional groups is much smaller than the number of distinct molecules
   Each functional group is assumed to be independent entity.

\[ \ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \]

\[ \ln \gamma_i^C (\text{as in UNIQAC}) = F^C(x, \Phi, \theta) \]

\[ \ln \gamma_i^R = F^R(x, Q, \sigma_{nm}) \]

\[ X = \text{GROUP MOLE FRACTION}, \quad Q = \text{GROUP EXTERNAL SURFACE AREA} \]
\[ \sigma_{nm} = \text{INTERACTION ENERGY BETWEEN GROUPS m AND n} \]

**Figure 7-14** Activity coefficients from group contribution illustrated for a mixture of acetone and toluene. Acetone has two groups and toluene has six, as shown. For a component \( i \), activity coefficient \( \gamma_i \) consists of two contributions, \( \gamma_i^C \) and \( \gamma_i^R \) where subscript \( C \) stands for configurational and superscript \( R \) stands for residual. Here \( F^C \) is a specified function of molecular composition and structure: mole fraction \( x \), volume fraction \( \Phi \) and surface fraction \( \theta \); \( F^R \) is a specified function of group composition, structure and interaction energies: \( X \), \( Q \) and \( \sigma_{nm} \). Both functions \( F^C \) and \( F^R \) are obtained from the UNIQUAC model. The key parameters are the group-group interaction parameters for all pairs of groups \((n,m)\) in the solution. In UNIFAC, for each pair, we use two parameters: \( a_{nm} \) and \( a_{nm}^{pr} \)

UNIFAC (UNIquac Functional Activity Coefficient) method
Numerous modifications and extensions have appeared since the work of Fredenslund, Jones, and Prausnitz (1975). (one of the most cited chem. eng. papers )
(Homework)

1. Use the UNIFAC model to predict the activity coefficients of benzene and 2,2,4-trimethyl pentane in their mixtures at 55°C. Predict activity coefficients as functions of compositions and Pressure-composition curves.

2. Use the UNIFAC model to predict the activity coefficients of water and acetone in their mixtures at 298K. Predict activity coefficients as functions of compositions and Pressure-composition curves.

Note: The program is based on the modified version of UNIFAC (Gmehling et al., 1993)
7.9 Chemical Theory  (Dolezalek, 1908)

Molecules in a liquid solution interact with each other to form new chemical species and solution nonideality, therefore, is a consequence of chemical reactions.

**Association**

\[ nB \rightleftharpoons B_n \]

dimerization of acetic acid

![Dimerization of Acetic Acid](image)

**Solvation**

\[ nA + mB \rightleftharpoons A_n B_m \]

solvation of chloroform an diethyl ether due to hydrogen bonding

![Solvation](image)

charge-transfer complex between nitrobenzene and mesitylene

![Charge-Transfer Complex](image)
A weak chemical bond is formed because mesitylene is a good electron donor (Lewis base) and nitrobenzene is a good electron acceptor (Lewis acid).

The chemical theory of solutions has little predictive value. 
Inability to assign equilibrium constants without experimental data. 
It cannot give quantitative predictions of solution behavior from pure-component data alone.
7.15 The Generalized van der Waals Partition Function

An approximate theory based on the canonical partition function

For a binary mixture, the equation of state is related to the partition function \( Q \) through

\[
P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N_1,N_2} \tag{7-209}
\]

and the chemical potentials are

\[
\mu_1 = kT \left( \frac{\partial \ln Q}{\partial N_1} \right)_{T,V,N_2} \tag{7-210}
\]

\[
\mu_2 = kT \left( \frac{\partial \ln Q}{\partial N_2} \right)_{T,V,N_1} \tag{7-211}
\]

The partition function is approximated by

\[
Q(T,V,N) = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N (q_{\text{rep}})^N (q_{\text{att}})^N (q_{r,v})^N \tag{7-212}
\]

where

\( \Lambda = h(2\pi mkT)^{1/2} \)  de Broglie wavelength

\( q_{\text{rep}} \)  molecular partition function contributed from repulsive intermolecular forces

\( q_{\text{att}} \)  contributed from attractive intermolecular forces

\( q_{r,v} \)  contributed from rotational and vibrational degrees of freedom

\[
q_{\text{rep}} = \frac{V_f}{V} \tag{7-213}
\]

\( V_f < V \)

\( V_f \) is the free volume available to the center of mass of a molecule as it moves, holding the other molecules fixed.
$q_{at} = \exp \left( \frac{-E_o}{2kT} \right)$  \hspace{1cm} (7-214) \hspace{1cm} E_o < 0

$E_o$ is the intermolecular potential energy experienced by one molecule due to the attractive forces from all other molecules.

The generalized van der Waals partition function is

$$Q(T,V,N) = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N \left( \frac{V_f}{V} \right)^N \left[ \exp \left( \frac{-E_o}{2kT} \right) \right]^N (q_{ee})^N$$  \hspace{1cm} (7-215)

The rough approximation used by van der Waals

$$V_f = V - \frac{N}{N_A} b$$  \hspace{1cm} (7-216)

$$b = (2/3)\pi N_A \sigma^3$$

4 times the volume of sphere

$$E_o = \frac{2aN}{VN_A^2}$$  \hspace{1cm} (7-217) \hspace{1cm} \propto \frac{N}{V}

$a$ is a constant representing the strength of attraction

assuming $q_{ee}$ is independent of volume

substituting into the partition function and using (7-209)

$$P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N_1,N_2}$$

We obtain the well-known van der Waals equation of state

$$\frac{PV}{RT} = \frac{v}{v-b} - \frac{a}{RTv}$$  \hspace{1cm} (7-218)
For large, polyatomic molecules, \( q_{r,v} \) is assumed to be factored into

\[
q_{r,v} = q_{\text{ext}}(V) q_{\text{int}}(T)
\]  

(7-219)

‘ext’ represents contributions from external rotations and vibrations, which depends on density.

Following Prigogine’s idea

3\( c \) is “effective” external degrees of freedom per molecule ( \( 1 < c < r \) )

\( r \) is the number of segments in a molecule

\[
q_{\text{ext}}(V) = \left( \frac{V_f}{A^3} \right)^c
\]  

(7-220)

but it does not obey the ideal-gas limit.

To remedy this defect, some other forms were proposed

\[
q_{\text{ext}}(V) = \left( \frac{V_f}{V} \right)^c
\]  

(7-221)  

by Beret

\[
q_{\text{ext}}(V,T) = \left( \frac{V_f}{V} \exp \left( \frac{-E_{c,v}}{2kT} \right) \right)^c
\]  

(7-222)  

by Donohue
7.16 Perturbed-Hard-Chain Theory

The free volume valid at low and at high densities (verified by computer simulation) is

\[ V_f = V \exp \left[ \frac{\eta (3\eta - 4)}{(1 - \eta)^2} \right] \]  

(7-223)

where \( \eta = \eta_{cp}(v_o/v) \) and \( v_o = (\sigma^3/\sqrt{2})N_A \)

The upper limit of \( \eta \) is \( \eta_{cp} = \pi \sqrt{2}/6 = 0.7405 \),

‘cp’ for closed packing, \( v_o \) is the closed-packed volume.

\[ \eta = \frac{\pi N \sigma^3}{6V} = \frac{\pi N_A \sigma^3}{6V} = \frac{b}{4V} \]

\[ \frac{V_f}{V} \] Probability of inserting a molecule into a system without overlap with existing ones

\[ = \exp \left[ - \frac{\text{Reversible Work}}{kT} \right] = \exp \left[ - \frac{A_{ex}/N}{kT} \right] \]

\[ A_{ex} = \frac{\eta (3\eta - 4)}{(1 - \eta)^2} \]

The potential energy \( E_o \) is from molecular simulation of Alder (1972) for square-well fluids

\[ \frac{E_o}{2kT} = \sum_{n=1}^{4} \sum_{m=1}^{M} \frac{m A_{nm}}{T^n \sigma^m} \]  

(7-224)

\( A_{nm} \)'s are fitting constants of simulation data.

\[ \tilde{T} = \frac{T}{T^*} = \frac{ckT}{\varepsilon q} \quad \tilde{\nu} = \frac{\nu}{r\sigma^3 N_A}, \quad r \text{ is the number of segments per molecule} \]

The perturbed-hard-chain equation of state is
\[
\frac{\tilde{P} \tilde{V}}{\tilde{T}} = \frac{1}{c} + \frac{4 \eta - 2 \eta^2}{(1 - \eta)^3} + \frac{1}{\tilde{T} \tilde{V}} \sum_{n=1}^{4} \sum_{m=1}^{M} \left( \frac{m A_{nm}}{\tilde{v}^m - 1} \right) \left( \frac{1}{T^{n-1}} \right)
\]
7.17 Hard-Sphere-Chain Models

Hard-sphere-chain (HSC) models take into account significant features of real fluids including excluded volume effects and chain connectivity. Freely-jointed tangent hard-sphere chains

HSC can be used as the reference system in the perturbation theory. The equation of state is written as

\[
\frac{z}{\rho RT} = z_{\text{ref}} + z_{\text{pert}} = \left( \frac{P}{\rho RT} \right)_{\text{ref}} + \left( \frac{P}{\rho RT} \right)_{\text{pert}}
\]  

(7.226)

\[
\rho = N / (V N_A)
\]

\[
z_{\text{ref}} = z_{\text{HSC}}
\]

The reference equation of state can be extended to mixtures without using mixing rules. Only attractive terms require mixing rules.
Statistical Associated-Fluid Theory  (SAFT)

The SAFT is based on the first-order thermodynamic perturbation theory (TPT) of Wertheim (1987). The literature on SAFT is complex and confusing. The original article by Wertheim, while brilliant, is essentially incomprehensible. Much patience is required to understand what SAFT is, what it can and what it cannot do.

The residual (or excess) molar Helmholtz energy $a^R$ has contributions from hard spheres, from chain connectivity, from dispersion (attraction), and from association

$$a^R = a_{hs} + a_{\text{chain}} + a_{\text{disp}} + a_{\text{assoc}}$$

(7-227)\(^1\)

![Diagram](image)

Figure 7-30  Three steps to form chain molecules and association complexes from hard spheres in the SAFT model.

The hard-sphere Helmholtz energy (in excess of that of ideal gas) is
\[
\frac{a_{hs}}{RT} = r \frac{a'_{hs}}{RT} = r \frac{4\eta - 3\eta^2}{(1-\eta)^2}
\]  
(7-228)

for a hard-sphere chain containing \( r \) hard spheres.

\[
\eta = \frac{\pi N_A}{6} \rho r d^3
\]
(7-229)

\( \rho \) is the molar density of chain molecules \( \frac{N_{\text{chain}}}{N_A V} \)

\( d \) is the temperature-dependent effective segment diameter

\[
d = \sigma [1 - C \exp(-3\varepsilon / kT)]
\]
(7-230) semiempirical relation with \( C = 0.12 \)

The Helmholtz energy for chain formation is

\[
\frac{\alpha_{\text{chain}}}{RT} = (1 - r) \ln \frac{2 - \eta}{2(1-\eta)^3}
\]
(7-232)

\[
= -\left( r - 1 \right) \ln g(\sigma) \quad g(r) \text{ is the radial distribution function of hard sphere fluid}
\]

\[
= \left[ \text{The number of bonds in a molecule} \right] \left[ \text{Reversible work to form each bond} \right]
\]

For the dispersion term, an expression obtained by Alder et al. for the square-well fluid is used

\[
\frac{\alpha_{\text{disp}}}{RT} = r \sum_n \sum_m D_{nm} \left( \frac{u}{kT} \right)^n \left( \frac{\eta}{\eta_{cp}} \right)^m
\]
(7-233)

\( \eta_{\text{cp}} = \pi \sqrt{2} / 6 \)

\( u = \varepsilon (1 + \varepsilon / kT) \) semiempirical, \( \varepsilon / k = 0 \) for small molecules like argon
The association contribution $a_{assoc}$ is obtained from Wertheim’s theory.

\[
\frac{a_{assoc}}{RT} = \sum_S \left( \ln X^S - \frac{X^S}{2} \right) + \frac{M}{2} \tag{7-235}^a
\]

$S$ represents association site (e.g., $A$ or $B$),

$M$ is the number association sites on each molecule (e.g., $M=2$)

$X^S$ is the mole fraction of molecules not bonded at site $S$, given by

\[
X^S = \left\{ 1 + N_A \sum_Y \rho_{XY} \frac{2 - \eta}{2(1 - \eta)^3} \left( \sigma^{3\kappa^{SY}} \right)^{\frac{1}{2}} \left( \frac{e^{SY}}{kT} \right)^{\frac{1}{2}} - 1 \right\}^{-1} \tag{7-236}
\]

where summation is over all association sites, $A$, $B$, ....

$e^{SY}$ and $\kappa^{SY}$ are the association energy and the association volume between sites $S$ and $Y$. 
From the residual molar Helmholtz energy $a^R$, the compressibility factor of a real fluid is obtained by

$$z = \rho \frac{\partial \left( \frac{a}{RT} \right)}{\partial \rho}$$

$$z = \frac{P}{\rho RT} = z^d + z_{hs} + z_{\text{chain}} + z_{\text{disp}} + z_{\text{assoc}}$$

(7-237)

$$z_{hs} = rz_{hs} = r \frac{4\eta - 2\eta^2}{(1-\eta)^3}$$

(7-238)

$$z_{\text{chain}} = (1-r) \frac{5\eta - 2\eta^2}{(1-\eta)(2-\eta)}$$

(7-239)

$$z_{\text{disp}} = r \sum_n \sum_m (\frac{1}{kT}) \left( \frac{\eta}{\eta_{cp}} \right)^n$$

(7-240)

$$z_{\text{assoc}} = \rho \sum_n \left( \frac{1}{X^3 - \frac{1}{2}} \frac{\partial X}{\partial \rho} \right)$$

(7-241)

Adjustable parameters for pure chain fluids

$r$ is the number of segments per molecule

$v_o$ is the segment (sphere) molar volume at closest packing

$$v_o = \frac{\pi N_A}{6 \eta_{cp}} \sigma^3$$

equivalent to specifying $\sigma$

$\varepsilon$ the depth of the square-well potential for segment-segment interactions

two additional parameters $\varepsilon^{SY}$ and $\kappa^{SY}$ for associating fluids.
For mixtures

The equation of states for hard-sphere mixtures

$$z_{hs} = \frac{6}{\pi N_A \rho} \left[ \frac{\xi_0 \xi_3}{1 - \xi_3} + \frac{3 \xi_1 \xi_2 + (3 - \xi_3) \xi_3^2}{(1 - \xi_3)^2} \right]$$

(7-242)

with

$$\xi_k = \frac{\pi N_A \rho}{6} \sum_{i=1}^{m} x_i \eta_i (d_i)^k \quad k = 0, 1, 2, 3$$

(7-243)

for pure fluids  \( \eta = \xi_3 = \xi_2 d \)

The contribution accounting for the formation of chains is

$$z_{\text{chain}} = \sum_{i=1}^{m} x_i (1 - \eta_i) L(d_i)$$

(7-244)

$$L(d_i) = \frac{2 \xi_3 + 3d_i \xi_2 - 4 \xi_3^3 + 2d_i^2 \xi_2^2 + 2 \xi_3^3 + d_i^2 \xi_2 \xi_3 - 3d_i \xi_2 \xi_3^2}{(1 - \xi_3)(2 - 4 \xi_3 + 3d_i \xi_2 + 2 \xi_3^2 + d_i^2 \xi_2^2 - 3d_i \xi_2 \xi_3)}$$

No mixing rules are necessary for the hard-sphere-chain reference system.

The contribution for the association is

$$z_{\text{assoc}} = \rho \sum_{i=1}^{m} x_i \left[ \frac{1}{X_i} \sum_{j} \left( \frac{1}{X_j} - \frac{1}{2} \frac{\partial X_j}{\partial \rho} \right) \right]$$

(7-245)

$$X_i = \left( 1 + N_A \sum_{j=1}^{m} \sum_{y_j} x_j \rho X_j W_{ij} \right)^{-1}$$

(7-246)
\[ W_{ij} = \frac{1}{1 - \xi_3} + \frac{3d_i d_j}{d_i + d_j (1 - \xi_3)^2} \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^3} \left( \sigma_{ij}^* \right)^{\frac{5}{2}} \left[ \exp \left( \frac{\xi_3^* X_j}{kT} \right) - 1 \right] \]

where \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \)

Figure 7-32  Vapor-liquid equilibria at 323 K for the mixture propanol/n-heptane (Fu and Sandler, 1995).
Figure 7.33 Vapor-liquid equilibria at 298 K and 394 K for the system CO$_2$/2-propanol. SAFT calculations were performed with the volume-fraction mixing rule (Huang and Radosz, 1991).