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

 $y_i P = x_i P_i^s$

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

$$g^E = u^E + Pv^E - Ts^E \tag{7-1}$$

Van Laar's assumptions corresponds to

$$g^E = u^E \tag{7-2}$$

A three-step isothermal thermodynamic cycle



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

 Δu is given by the sum of the three energy changes

$$\Delta u = u^E = \Delta u_{\rm I} + \Delta u_{\rm II} + \Delta u_{\rm III} \tag{7-3}$$

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

The energy change is given by the thermodynamic equation,

$$\left(\frac{\partial u}{\partial v}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_v - P \tag{7-4}$$

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

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

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

$$\left(\frac{\partial u}{\partial v}\right)_T = \frac{a}{v^2}$$
(7-5)

For one mole of mixture with x_1 moles of liquid 1 and x_2 moles of liquids

$$x_1(u_{\text{ideal}} - u)_1 = \int_{v_1^L}^{\infty} \frac{a_1 x_1}{v^2} dv - \frac{a_1 x_1}{v_1^L}$$
(7-6)

$$x_2(u_{\text{ideal}} - u)_2 = \int_{\nu_2}^{\infty} \frac{a_2 x_2}{\nu^2} d\nu = \frac{a_2 x_2}{\nu_2^2}$$
(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

$$\Delta u_1 = \frac{a_1 x_1}{b_1} + \frac{a_2 x_2}{b_2} \tag{7-8}$$

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

There is no change in energy

$$\Delta u_{\rm II} = 0 \tag{7-9}$$

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.

$$\Delta u_{\rm III} = -\frac{a_{\rm mixt}}{b_{\rm mixt}} \tag{7-10}$$

Constant a_{mixt} and b_{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)

$$b_{\rm mixt} = x_1 b_1 + x_2 b_2 \tag{7-12}$$

Adding up for Δu

$$g^{E} = \Delta u = \frac{a_{1}x_{1}}{b_{1}} + \frac{a_{2}x_{2}}{b_{2}} - \frac{x_{1}^{2}a_{1} + x_{2}^{2}a_{2} + 2x_{1}x_{2}\sqrt{a_{1}a_{2}}}{x_{1}b_{1} + x_{2}b_{2}}$$
$$g^{E} = \frac{x_{1}x_{2}b_{1}b_{2}}{x_{1}b_{1} + x_{2}b_{2}} \left(\frac{\sqrt{a_{1}}}{b_{1}} - \frac{\sqrt{a_{2}}}{b_{2}}\right)^{2}$$
(7-13)

The activity coefficients are obtained by differentiation

$$\ln \gamma_{1} = \frac{A'}{\left(1 + \frac{A'}{B'} \frac{x_{1}}{x_{2}}\right)^{2}}$$
(7-14)
$$\ln \gamma_{2} = \frac{B'}{\left(1 + \frac{B'}{A'} \frac{x_{2}}{x_{1}}\right)^{2}}$$
(7-15)

where

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

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

$$g^{E} = u^{E} + Pv^{E} - Ts^{E} \qquad \qquad g^{E} = u^{E}$$

$$RT \ln \gamma_i = \overline{g}_i^E = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j}$$
 independent of T

• The activity coefficients are always greater than unity (positive deviation from Raoult's law)

 $A' >\!\! 0 \;, \quad B' >\!\! 0 \quad \Longrightarrow \ln \gamma >\!\! 0$

If it were assumed that

 $a_{\rm mixt} = x_1 a_1 + x_2 a_2 \tag{7-21}$

Then we would have

 $\gamma_1 = \gamma_2 = 1 \quad \text{for all } x \tag{7-22}$

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 <u>no excess entropy of mixing</u> at constant temperature and at constant volume.

The cohesive energy density is defined by

$$c \equiv \frac{\Delta_{\text{vap}}u}{v^L}$$
(7-23)

where $\Delta_{vap}u$ 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,

$$-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mixt}} = \frac{c_{11}v_1^2x_1^2 + 2c_{12}v_1v_2x_1x_2 + c_{22}v_2^2x_2^2}{x_1v_1 + x_2v_2}$$
(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

$$\Phi_1 \equiv \frac{x_1 v_1}{x_1 v_1 + x_2 v_2} \tag{7-25}$$

$$\Phi_2 \equiv \frac{x_2 v_2}{x_1 v_1 + x_2 v_2} \tag{7-26}$$

Then (7-24) becomes

$$-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mixt}} = (x_1 \upsilon_1 + x_2 \upsilon_2)[c_{11} \Phi_1^2 + 2c_{12} \Phi_1 \Phi_2 + c_{22} \Phi_2^2]$$
(7-27)

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

$$\Delta_{\min} u = u^E \equiv u_{\min} - x_1 u_1 - x_2 u_2 \tag{7-28}$$

noting that
$$\Delta_{\text{mix}} u = u_{\text{ideal}}^E = 0$$
 (7-29)

$$u^{E} = (x_{1}v_{1} + x_{2}v_{2}) \left[c_{11}\Phi_{1}^{2} + 2c_{12}\Phi_{1}\Phi_{2} + c_{22}\Phi_{2}^{2} \right] - x_{1}u_{1} - x_{2}u_{2}$$

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

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

$$u^{E} = (c_{11} + c_{22} - 2c_{12})\Phi_{1}\Phi_{2}(x_{1}\upsilon_{1} + x_{2}\upsilon_{2})$$
(7-30)

As suggested by London's formula, it is assumed that

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

(7-30) becomes

$$u^{E} = (x_{1}\upsilon_{1} + x_{2}\upsilon_{2})\Phi_{1}\Phi_{2}(\delta_{1} - \delta_{2})^{2}$$
(7-32)

where δ is called the *solubility parameter*.

$$\delta_{1} = c_{11}^{1/2} = \left(\frac{\Delta_{\text{vap}}u}{v}\right)_{1}^{1/2}$$
(7-33)

$$\delta_2 \equiv c_{22}^{1/2} = \left(\frac{\Delta_{\text{vap}}u}{\upsilon}\right)_2^{1/2}$$
(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

$$RT \ln \gamma_1 = v_1 \Phi_2^2 (\delta_1 - \delta_2)^2 \qquad RT \ln \gamma_2 = v_2 \Phi_1^2 (\delta_1 - \delta_2)^2 \qquad (7-37)$$

that are the regular-solution equations.

The regular-solution equations always predicts $\gamma_i \ge 1$ (positive deviation from Raoult's law), which is a consequence of the geometric-mean assumption.

	v (cm ³ mol ⁻¹)	δ (J cm ⁻³) ^{1/2}
Liquefied gases at 90 K		
Nitrogen	38.1	10.8
Carbon monoxide	37.1	11.7
Argon	29.0	13.9
Oxygen	28.0	14.7
Methane	35.3	15.1
Carbon tetrafluoride	46.0	17.0
Ethane	45.7	19.4
Liquid solvents at 25 °C		
Perfluoro-n-heptane	226	12.3
Neopentane	122	12.7
Isopentane	117	13.9
n-Pentane	116	14.5
<i>n</i> -Hexane	132	14.9
1-Hexene	126	14.9
n-Octane	164	15.3
n-Hexadecane	294	16.3
Cyclohexane	109	16.8
Carbon tetrachloride	97	17.6
Ethyl benzene	123	18.0
Toluene	107	18.2
Benzene	89	18.8
Styrene	116	19.0
Tetrachloroethylene	103	19.0
Carbon disulfide	61	20.5
Bromine	51	23.5

Table 7-1 Molar liquid volumes and solubility parameters of some nonpolar liquids.*

The difference in solubility parameters provides a measure of solution nonideality.

For example, mixtures of aliphatic hydrocarbons with aromatics show appreciable nonideality.



Figure 7-2 Vapor-liquid equilibria for CO (1)/CH₄ (2) mixtures at 90.7 K.



Figure 7-3 Vapor-liquid equilibria for $C_6H_6(1)/n-C_7H_{16}(2)$ at 70°C.



Figure 7-4 Vapor-liquid equilibria for neo-C₅H₁₂ (1)/CCl₄ (2) at 0°C.

To relax the geometric-mean assumption

$$c_{12} = (1 - l_{12})(c_{11}c_{22})^{1/2}$$
(7-42)

The resulting activity coefficients are

$$\ln \gamma_{1} = \frac{\upsilon_{1} \Phi_{2}^{2}}{RT} \Big[(\delta_{1} - \delta_{2})^{2} + 2l_{12}\delta_{1}\delta_{2} \Big]$$
(7-43)
$$\ln \gamma_{2} = \frac{\upsilon_{2} \Phi_{1}^{2}}{RT} \Big[(\delta_{1} - \delta_{2})^{2} + 2l_{12}\delta_{1}\delta_{2} \Big]$$
(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 *I*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); 21. Toluene (2)/Methylcyclohexane (1); 23. Toluene (2)/2,2,4-Trimethylpentane (1); 24. Toluene (2)/Methylcyclohexane (1); 24. Toluene (2)/Methylcyclohexane (1); 24. Toluene (2)/Methylcyclohexane (1); 25. Toluene (2)/Methylcyclohexane (1); 26. Toluene (2)/Methylcyclohexane (1); 27. Toluene (2)/Methylcyclohexane (1); 28. Toluene (2)/2,2,4-Trimethylpentane (1); 29. Toluene (2)/Methylcyclohexane (1); 20. Toluene (2)/Methylcyclohexane (1); 21. Toluene (2)/Heptane (1); 23. Toluene (2)/2,2,4-Trimethylpentane (1); 24. Toluene (2)/Methylcyclohexane (1); 25. Toluene (2)/2,2,4-Trimethylpentane (1); 24. Toluene (2)/Methylcyclohexane (1); 25. Toluene (2)/2,2,4-Trimethylpentane (1); 26. Toluene (2)/Methylcyclohexane (1); 27. Toluene (2)/2,2,4-Trimethylpentane (1); 26. Toluene (2)/Methylcyclohexane (1); 27. Toluene (2)/2,2,4-Trimethylpentane (1); 26. Toluene (2)/2,2,4-Trimethylpentane (1); 27. Toluene (2)/2,2,4-Trimethylpentane (1).

Effect of l_{12} on VLE



Figure 7-7 Comparison of experimental volatilities with volatilities calculated by Scatchard-Hildebrand theory for 2,2-dimethylbutane (1)/benzene (2).

Extensions to hydrogen-bonded components are of little theoretical sense.

The multicomponent case

$$-(u_{\text{liquid}} - u_{\text{ideal gas}})_{\text{mixt}} = \frac{\sum_{i=j}^{m} \sum_{j=1}^{m} v_i v_j x_i x_j c_{ij}}{\sum_{i=1}^{m} x_i v_i}$$
(7-49)

The volume fraction is

$$\Phi_j \equiv \frac{x_j v_j}{\sum\limits_{i}^{m} x_i v_i}$$
(7-50)

The excess energy of mixing is defined by

$$u^E \equiv u_{\text{mixt}} - \sum_{i}^{m} x_i u_i \tag{7-51}$$

The cohesive-energy density is given by the geometric mean

$$c_{ij} = (c_{ii}c_{jj})^{1/2} \tag{7-52}$$

Assuming

$$s^E = v^E = 0 \tag{7-53}$$

Then

$$g^E = u^E \tag{7-54}$$

The activity coefficients are

$$RT \ln \gamma_j = \upsilon_j (\delta_j - \overline{\delta})^2$$

$$\overline{\delta} = \sum_{i}^{m} \Phi_i \delta_i$$
(7-56)

 $\overline{\delta}$ 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 suing 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 rises to nonvanishing **enthalpy of mixing**

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

Consider of 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

 $(v^{E}=0)$

$\begin{array}{c} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 &$	$\begin{array}{c} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 &$
2 2	00000 00000 00000 00000 00000 00000 0000
BEFORE	AFTER EXCHANGE

Figure 7-8 Physical significance of interchange energy. The energy absorbed in the process above is 2*w*. [See Eq. (7-71)].

z pairs of type 11, z pairs of type 22 \rightarrow 2z pairs of type 12 $z\Gamma_{11} + z\Gamma_{22}$ $2z\Gamma_{12}$ 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

$$zN_1 = 2N_{11} + N_{12}$$

$$zN_2 = 2N_{22} + N_{12}$$

(7-68)

$$\frac{z}{2} (N_1 + N_2) = N_{11} + N_{22} + N_{12}$$

The total potential energy is given by

$$U_t = N_{11}\Gamma_{11} + N_{22}\Gamma_{22} + N_{12}\Gamma_{12}$$
(7-69)

Eliminating N_{11} and N_{22} using (7-68)

$$U_t = \frac{z}{2} N_1 \Gamma_{11} + \frac{z}{2} N_2 \Gamma_{22} + \frac{w}{2} N_{12}$$
(7-70)

The last term of (7-70) is the energy of mixing *w* is the *interchange energy* defined by

$$w \equiv z \left[\Gamma_{12} - \frac{1}{2} (\Gamma_{11} + \Gamma_{22}) \right]$$

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

$$\Delta_{\text{mix}} A = A_{\text{mixt}} - (A_{\text{pure 1}} + A_{\text{pure 2}})$$
(7-73)

Since $A = -kT \ln Q$

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

$$N_{12}^{*} = \frac{zN_1N_2}{N_1 + N_2}$$
* indicate a completely random arrangement

$$= zN_1 \times \frac{N_2}{N_1 + N_2}$$
= (No. of neighbor sites of molecules of type 1)

× (Probability of randomly placing molecules of type 2 on the site)

$$g(N_1, N_2, N_{12}^*) = \frac{(N_1 + N_2)!}{N_1! N_2!}$$
(7-76)

Using Stirling's formula $\ln N! = N \ln N - N$, for N >> 1

$$\frac{\Delta_{\min}A}{kT} = N_1 \ln \frac{N_1}{N_1 + N_2} + N_2 \ln \frac{N_2}{N_1 + N_2} + \frac{w}{kT} \frac{N_1 N_2}{N_1 + N_2}$$
(7-77)
z disappeared!

In molar unit

$$\frac{\Delta_{\min}a}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{w}{kT} x_1 x_2$$
(7-78)

The molar excess Helmholtz energy is

$$\frac{a^E}{RT} = \frac{w}{kT} x_1 x_2 \tag{7-79}$$

Since *w* is assumed to be independent of temperature

$$\frac{\Delta_{\min}s}{R} = -\frac{1}{R} \left(\frac{\partial \Delta_{\min}a}{\partial T}\right)_{\upsilon} = -x_1 \ln x_1 - x_2 \ln x_2$$
(7-80)

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

$$s^E = 0$$

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

$$\ln \gamma_1 = \frac{w}{kT} x_2^2 \tag{7-82}$$

$$\ln \gamma_2 = \frac{w}{kT} x_1^2 \tag{7-83}$$

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

$$\begin{split} \left|\Gamma_{12}\right| \approx \sqrt{\left|\Gamma_{11}\right| \left|\Gamma_{22}\right|} &< \frac{1}{2} \left(\left|\Gamma_{11}\right| + \left|\Gamma_{22}\right|\right) \quad (\text{ geometric mean } < \text{arithmetic mean }) \\ \Gamma_{12} &> \frac{1}{2} \left(\Gamma_{11} + \Gamma_{22}\right) \quad \rightarrow \quad w > 0 \rightarrow \quad \gamma > 0 \end{split}$$

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

$$(1-1) + (2-2) \iff 2 \cdot (1-2)$$
 (7-91)

The equilibrium constant *K* is defined by

$$K = \frac{(N_{12})^2}{N_{11}N_{22}} \tag{7-92}$$

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

The temperature derivative of ln *K* is

$$\left[\frac{\partial \ln K}{\partial (1/T)}\right]_{U} = -\frac{\Delta_{\rm r} u}{R} \tag{7-93}$$

Assuming that the energy change of reaction is given by

$$\frac{\Delta_{\rm r}u}{R} = \frac{2w}{kz} \tag{7-94}$$

Integrating (7-93)

$$K = C \exp\left(-\frac{2w}{zkT}\right) \tag{7-95}$$

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)

$$z \frac{N_1}{N_{12}^*} = 2 \frac{N_{11}^*}{N_{12}^*} + 1 = \frac{N_1 + N_2}{N_2}$$
$$\frac{N_{11}^*}{N_{12}^*} = \frac{1}{2} \frac{N_1}{N_2} \qquad \frac{N_{22}^*}{N_{12}^*} = \frac{1}{2} \frac{N_2}{N_1} \qquad \text{then} \qquad \mathbf{C} = 4$$

The equilibrium constant *K* becomes

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

where $\eta \equiv \exp(w/zkT)$.

Introducing a parameter β

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

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

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

For random case, $\beta = 1$.

The excess energy of mixing is

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

where $u^{E^*} = N_A w x_1 x_2$

To obtain the excess Helmholtz energy

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

Integrating

$$\frac{a^E}{RT} = \frac{z}{2} \left[x_1 \ln \frac{\beta - 1 + 2x_1}{x_1(\beta + 1)} + x_2 \ln \frac{\beta - 1 + 2x_2}{x_2(\beta + 1)} \right]$$
(7-102)

To simplify further, we expand $\exp(2w/zkT)$ in power series. The molar excess functions are

$$\frac{g^E}{RT} = \left(\frac{w}{kT}\right) x_1 x_2 \left[1 - \frac{1}{2} \left(\frac{2w}{zkT}\right) x_1 x_2 + \dots\right]$$
(7-103)
$$\frac{h^E}{RT} = \left(\frac{w}{kT}\right) x_1 x_2 \left[1 - \left(\frac{2w}{zkT}\right) x_1 x_2 + \dots\right]$$
(7-104)
$$\frac{s^E}{R} = -\left(\frac{w}{kT}\right) x_1 x_2 \left[\frac{1}{2} \left(\frac{2w}{zkT}\right) x_1 x_2 + \dots\right]$$
(7-105)

The excess entropy is negative for any positive or negative *w*.



Figure 7-9 Effect of nonrandomness on excess Gibbs energies of binary mixtures.

The Gibbs energy with quasichemical approximation becomes lower.

Partial Miscibility

The criteria for instability is

$$\frac{\partial^2 \Delta_{\min} g}{\partial x^2} = \frac{\partial^3 \Delta_{\min} g}{\partial x^3} = 0$$
(7-106)

$$\Delta_{\min}g = RT(x_1 \ln x_1 + x_2 \ln x_2) + g^E \tag{7-107}$$

As in chapter 6, the upper consolute temperature is

$$T^c = \frac{w}{2k} \tag{7-108}$$

For the quasichemical approximation

$$T^{c} = \frac{w}{kz[\ln z - \ln(z - 2)]}$$
(7-109)

When z = 10,

$$T^c = \frac{w}{2.23k} \tag{7-110}$$

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



Figure 7-10 Effect of nonrandomness on Gibbs energy of mixing.

Methane / CF₄



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



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

$$M_{\rm mixt} = x_1 M^{(1)} + x_2 M^{(2)} \tag{7-111}$$

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^{conf} ,

$$\frac{h^{\text{conf}}}{RT} = F\left(\frac{kT}{\varepsilon}, \frac{P\sigma^3}{\varepsilon}\right)$$
(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)

 $\epsilon^{(1)} \, \text{and} \, \sigma^{(1)} \, \text{are composition averages for cells of type 1}$

$$\varepsilon^{(1)} = x_1 \varepsilon_{11} + x_2 \varepsilon_{12} \tag{7-114}$$

$$\sigma^{(1)} = x_1 \sigma_{11} + x_2 \sigma_{12} \tag{7-115}$$

 ε_{ij} and σ_{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)

$$\sigma^{(2)} = x_2 \sigma_{22} + x_1 \sigma_{12} \tag{7-118}$$

Then, the molar enthalpy of the mixture is given by

$$h_{\text{mixt}}^{\text{conf}} = x_1 h^{\text{conf}(1)} + x_2 h^{\text{conf}(2)}$$
(7-119) (Two-fluid theory)

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



Molecule Component

simple case with r = q = 1

Surface fractions:

 θ_{11} the local surface fraction of component 1 about central molecule 1

 θ_{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)

$$\frac{1}{2} z \left(\theta_{12} U_{12}^{(2)} + \theta_{22} U_{22}^{(2)} \right)$$

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

$$u^{E} = \frac{1}{2} z x_{1} N_{A} [q_{1}(\theta_{11}U_{11}^{(1)} + \theta_{21}U_{21}^{(1)} - U_{11}^{(0)})]$$

$$+ \frac{1}{2} z x_{2} N_{A} [q_{2}(\theta_{22}U_{22}^{(2)} + \theta_{12}U_{12}^{(2)} - U_{22}^{(0)})]$$
(7-120)
for any q in general

Conservation equation for the local surface fractions

$$\theta_{21} + \theta_{11} = 1$$

 $\theta_{12} + \theta_{22} = 1$
(7-121)

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

$$u^{E} = \frac{1}{2} z N_{A} [x_{1} \theta_{21} q_{1} (U_{21} - U_{11}) + x_{2} \theta_{12} q_{2} (U_{12} - U_{22})]$$
(7-122)
$$\frac{\theta_{21}}{\theta_{11}} = \frac{\theta_{2}}{\theta_{1}} \exp \left[\frac{-\frac{1}{2} z (U_{21} - U_{11})}{kT} \right]$$
(7-123)
$$\frac{\theta_{12}}{\theta_{22}} = \frac{\theta_{1}}{\theta_{2}} \exp \left[\frac{-\frac{1}{2} z (U_{12} - U_{22})}{kT} \right]$$
(7-124)

where θ is surface fraction

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{7-125}$$

note that

$$\frac{\theta_{21}}{\theta_{11}} = \frac{\theta_2}{\theta_1} \qquad \frac{\theta_{12}}{\theta_{22}} = \frac{\theta_1}{\theta_2}$$
 for random mixture

Rewriting (7-122)

$$u^{E} = x_{1}q_{1}\theta_{21}\Delta u_{21} + x_{2}q_{2}\theta_{12}\Delta u_{12}$$
(7-126)

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

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

where

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

To obtain the molar excess Helmholtz energy,

$$\frac{d(a^E/T)}{d(1/T)} = u^E$$
 (7-130)
at const volume and composition

Integration gives

$$\frac{a^E}{T} = \int_{1/T_0}^{1/T} u^E d(1/T) + \text{constant of integration}$$
(7-131)

At very high temperature $1/T_0 \rightarrow 0$, we have athermal mixture for which

$$\left(\frac{a^{E}}{RT}\right)_{\text{athermal}} = -\left(\frac{s^{E}}{R}\right)_{\text{combinatorial}}$$
(7-132)
$$= x_{1} \ln \frac{\Phi_{1}^{*}}{x_{1}} + x_{2} \ln \frac{\Phi_{2}^{*}}{x_{2}} + \frac{1}{2} z \left(q_{1}x_{1} \ln \frac{\theta_{1}}{\Phi_{1}^{*}} + q_{2}x_{2} \ln \frac{\theta_{2}}{\Phi_{2}^{*}}\right)$$
Guggenheim (1952)

where

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

segment fraction or volume fraction

Assuming that Δu_{21} and Δu_{12} are independent of temperature

and that $a^E \approx g^E$

Eq (7-131) gives

$$\left(\frac{a^E}{RT}\right)_{T,V} \approx \left(\frac{g^E}{RT}\right)_{T,P} = \left(\frac{g^E}{RT}\right)_{\text{combinatorial}} + \left(\frac{g^E}{RT}\right)_{\text{residual}}$$
 (7-134)

where

$$\left(\frac{g^E}{RT}\right)_{\text{combinatorial}} = x_1 \ln \frac{\Phi_1^*}{x_1} + x_2 \ln \frac{\Phi_2^*}{x_2} + \frac{1}{2}z \left(x_1 q_1 \ln \frac{\theta_1}{\Phi_1^*} + x_2 q_2 \ln \frac{\theta_2}{\Phi_2^*}\right) \quad (7-135)$$

$$\left(\frac{g^E}{RT}\right)_{\text{residual}} = -x_1 q_1 \ln \left[\theta_1 + \theta_2 \exp\left(\frac{-\Delta u_{21}}{RT}\right)\right] - x_2 q_2 \ln \left[\theta_2 + \theta_1 \exp\left(\frac{-\Delta u_{12}}{RT}\right)\right] \quad (7-136)$$

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-Contribution 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.



omn = 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 γ_i consists of two contributions, γ_i^C and γ_i^R where superscript 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 Φ and surface fraction θ ; F^{R} is a specified function of group composition, structure and interaction energies: X, Q and a_{mn} . 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: am and am.

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

$$nB \implies B_n$$

dimerization of acetic acid



Solvation

$$nA + mB \implies A_nB_m$$

solvation of chloroform an diethyl ether due to hydrogen bonding

$$C_3 - C - H + O C_2 H_5 \implies C_3 - C - H - \cdots O C_2 H_5$$

charge-transfer complex between nitrobenzene and mesitylene



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

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

$$Q(T, V, N) = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N (q_{\rm rep})^N (q_{\rm att})^N (q_{\rm r,v})^N$$
(7-212)³¹

where

 $\Lambda = h(2\pi m kT)^{-1/2}$ de Broglie wavlength

 q_{rep} molecular partition function contributed from repulsive intermolecular forces

q_{att} contributed from attractive intermolecular forces

 q_{EV} contributed from rotational and vibrational degrees of freedom

$$q_{\rm rep} = \frac{V_f}{V} \tag{7-213}$$

$$V_f < V$$

 V_f is the free volume available to the center of mass of a molecule as it moves, holding the other molecules fixed.

$$q_{\text{att}} = \exp\left(\frac{-E_{\text{o}}}{2kT}\right) \tag{7-214}$$

$$E_o < 0$$

 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

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

The rough approximation used by van der Waals

$$V_{f} = V - \frac{N}{N_{A}}b$$

$$(7-216)$$

$$b = (2/3)\pi N_{A}\sigma^{3}$$

$$E_{o} = -\frac{2aN}{VN_{A}^{2}}$$

$$(7-217)$$

$$\propto \frac{N}{V}$$

a is a constant representing the strength of attraction assuming $q_{r,v}$ 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

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv}$$
(7-218)

For large, polyatomic molecules, $q_{r,v}$ is assumed to be factored into

$$q_{\rm r,v} = q_{\rm ext}(V)q_{\rm int}(T) \tag{7-219}$$

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

Following Prigogine's idea

3c is "effective" external degrees of freedom per molecule (1 < c < r) *r* is the number of segments in a molecule

(7-221)

(7-222)

$$q_{\text{ext}}(V) = \left(\frac{V_f}{\Lambda^3}\right)^{c-1}$$
(7-220)

but it does not obey the ideal-gas limit.

To remedy this defect, some other forms were proposed

$$q_{\text{ext}}(V) = \left(\frac{V_f}{V}\right)^{c-1}$$

by Beret

 $q_{\text{ext}}(V,T) = \left[\frac{V_f}{V} \exp\left(\frac{-E_o}{2kT}\right)\right]^{c-1}$

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 $\eta = \eta_{cp}(v_0/v)$ and $v_0 = (\sigma^3/\sqrt{2})N_A$ The upper limit of η is $\eta_{cp} = \pi\sqrt{2}/6 = 0.7405$,

'cp' for closed packing, *v*_o is the closed-packed volume.

or
$$\eta = \frac{\pi N \sigma^3}{6V} = \frac{\pi N_A \sigma^3}{6v} = \frac{b}{4v}$$

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

$$= \exp\left[-\frac{\text{Reversible Work}}{kT}\right] = \exp\left[-\frac{A^{ex}/N}{kT}\right] \qquad \qquad \frac{A^{ex}}{N k T} = -\frac{\eta(3\eta - 4)}{(1 - \eta)^2}$$

The potential energy E_o is from molecular simulation of Alder (1972) for square-well fluids $\frac{E_o}{2kT} = \sum_{n=1}^{4} \sum_{m=1}^{M} \frac{mA_{nm}}{\tilde{T}^n \tilde{v}^m}$ (7-224)

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

$$\widetilde{T} = \frac{T}{T^*} = \frac{ckT}{\varepsilon q}$$
 $\widetilde{v} = \frac{v}{rv^*} = \frac{\sqrt{2}v}{r\sigma^3 N_A}$, r is the number of segments per molecule

The perturbed-hard-chain equation of state is

$$\frac{\widetilde{P}\widetilde{\upsilon}}{\widetilde{T}} = \frac{1}{c} + \frac{4\eta - 2\eta^2}{(1-\eta)^3} + \frac{1}{\widetilde{T}\widetilde{\upsilon}} \sum_{n=1}^{4} \sum_{m=1}^{M} \left(\frac{mA_{nm}}{\widetilde{\upsilon}^{m-1}}\right) \left(\frac{1}{\widetilde{T}^{n-1}}\right)$$
(7-225)

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

$$z = \frac{P}{\rho RT} = z_{ref} + z_{pert} = \left(\frac{P}{\rho RT}\right)_{ref} + \left(\frac{P}{\rho RT}\right)_{pert}$$
(7-226)
$$\rho = N / (VN_A),$$

$$z_{ref} = z_{HSC}$$

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).

⁴⁰ 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 connnectivity*, from *dispersion* (attraction), and from *association*

$$a^{R} = a_{\rm hs} + a_{\rm chain} + a_{\rm disp} + a_{\rm assoc} \tag{7-227}^{41}$$



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

$$\frac{a_{\rm hs}}{RT} = r \frac{\dot{a}_{\rm hs}}{RT} = r \frac{4\eta - 3\eta^2}{(1 - \eta)^2}$$
(7-228)

for a hard-sphere chain containing *r* hard spheres.

$$\eta = \frac{\pi N_A}{6} \rho r d^3 \tag{7-229}^{42}$$

 ρ is the molar density of chain molecules $\frac{N_{chain}}{N_A V}$

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

$$\frac{a_{\text{chain}}}{RT} = (1-r)\ln\frac{2-\eta}{2(1-\eta)^3}$$

$$= -(r-1)\ln g(\sigma) \qquad g(r) \text{ is the radial distribution function of hard sphere fluid}$$

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

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

$$\frac{a_{\text{disp}}}{RT} = r \sum_{n} \sum_{m} D_{nm} \left(\frac{u}{kT}\right)^{n} \left(\frac{\eta}{\eta_{\text{cp}}}\right)^{m}$$
(7-233)

 $\eta_{cp} = \pi \sqrt{2} / 6$ $u = \varepsilon (1 + e / kT)$ semiempirical, e/k = 0 for small molecules like argon The association contribution a_{assoc} is obtained from Wertheim's theory.



1

Figure 7-31 Models for a hard-sphere (monomer) and a hard-chain molecule (*r*-mer; \bullet are chemical bonds), with two association sites *A* and *B*. The chain model can represent nonspherical molecules. For example, if sites A and B attract each other, various associated complexes can be formed. This picture is not altered by converting hard spheres to soft spheres according to Eq. (7-230).

$$\frac{a_{\rm assoc}}{RT} = \sum_{S} \left(\ln X^{S} - \frac{X^{S}}{2} \right) + \frac{M}{2}$$
(7-235)⁴⁷

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** honded at site S given by

$$X^{S} = \left\{ 1 + N_{A} \sum_{Y} \rho X^{Y} \frac{2 - \eta}{2(1 - \eta)^{3}} (\sigma^{3} \kappa^{SY}) \left[\exp\left(\frac{\varepsilon^{SY}}{kT}\right) - 1 \right] \right\}^{-1}$$
(7-236)

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

 ε^{SY} and κ^{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
$$z = \rho \frac{\partial}{\partial \rho} \left(\frac{a}{RT} \right)_{T}$$

$$z = \frac{P}{\rho RT} = z^{\text{id}} + z_{\text{hs}} + z_{\text{chain}} + z_{\text{disp}} + z_{\text{assoc}} \qquad (7-237)$$

$$z_{\text{hs}} = r z_{\text{hs}}^{*} = r \frac{4\eta - 2\eta^{2}}{(1-\eta)^{3}} \qquad (7-238)^{48}$$

$$z_{\text{chain}} = (1-r) \frac{5\eta - 2\eta^{2}}{(1-\eta)(2-\eta)} \qquad (7-239)$$

$$z_{\text{disp}} = r \sum_{n} \sum_{m} m D_{nm} \left(\frac{u}{kT} \right)^{n} \left(\frac{\eta}{\eta_{\text{cp}}} \right)^{m} \qquad (7-240)$$

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

$$v_{\rm o} = \frac{\pi N_A}{6\eta_{\rm cp}} \sigma^3$$

equivalent to specifying σ

 ε the depth of the square-well potential for segment-segment interactions two additional parameters ε^{SY} and κ^{SY} for associating fluids.

For mixtures

The equation of states for hard-sphere mixtures

$$z_{\rm hs} = \frac{6}{\pi N_A \rho} \left[\frac{\xi_0 \xi_3}{1 - \xi_3} + \frac{3\xi_1 \xi_2}{(1 - \xi_3)^2} + \frac{(3 - \xi_3) \xi_2^3}{(1 - \xi_3)^3} \right]$$
(7-242)

with

$$\xi_k = \frac{\pi N_A \rho}{6} \sum_{i=1}^m x_i r_i (d_i)^k \qquad k = 0, 1, 2, 3$$
(7-243)

for pure fluids $\eta = \xi_3 = \xi_2 d$

The contribution accounting for the formation of chains is

$$z_{\text{chain}} = \sum_{i=1}^{m} x_i (1 - r_i) L(d_i)$$
(7-244)

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

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

The contribution for the association is

$$z_{\text{assoc}} = \rho \sum_{i=1}^{m} x_i \left[\sum_{S_i} \left(\frac{1}{X^{S_i}} - \frac{1}{2} \right) \frac{\partial X^{S_i}}{\partial \rho} \right]$$
(7-245)
$$X^{S_i} = \left(1 + N_{\text{Av}} \sum_{j=1}^{m} \sum_{Y_j} x_j \rho X^{Y_j} W_{ij} \right)^{-1}$$
(7-246)

$$W_{ij} = \left[\frac{1}{1 - \xi_3} + \frac{3d_i d_j}{d_i + d_j} \frac{\xi_2}{(1 - \xi_3)^2} + 2\left(\frac{d_i d_j}{d_i + d_j}\right)^2 \frac{\xi_2^2}{(1 - \xi_3)^3}\right] (\sigma_{ij} \kappa^{S_i Y_j}) \left[\exp\left(\frac{\varepsilon^{S_i Y_j}}{kT}\right) - 1\right]$$

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

For dispersion term for mixtures, mixing rules are necessary. See Huang and Radoz (1990, 1991).



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).