CH.6 Fugacities in Liquid Mixtures: Excess Functions

Calculation of fugacities from volumetric properties for condensed phases is often not practical because it requires volumetric data for the entire density range including the two-phase region.
For liquid solutions, usual practice is to describe deviations from ideal behavior in terms of excess function, which yield the activity coefficient.

$$f_i^L = \gamma_i x_i f_i^0 \qquad (6\text{-}1)$$

The activity coefficient γ_i has no significance unless f_i^0 the fugacity at the standard state is specified.
The solution ideality ($\gamma_i = 1$) is not complete without the choice of standard state.
Ideal solution in the sense of Raoult's law
Ideal solution in the sense of Henry's law

6.1 The Ideal Solution

In an ideal solution, fugacity is proportional to some suitable measure of its concentration, usually the mole fraction.

$$f_i^L = \Re_i x_i \qquad (6\text{-}1a)$$

where $\Re_i$ is dependent on T and P, but independent of composition.
Ideal solution in the sense of Raoult's law

$$f_i^0 = \Re_i \text{ , then } \gamma_i = 1$$

Ideal solution in the sense of Henry's law

If x_i is near zero, it is still possible to have an ideal solution without referring to the fugacity of pure liquid *i*.

For an ideal solution in the sense of Raoult's law

$$f_i(T,P,x) = f_{\text{pure } i}(T,P)x_i \qquad (6\text{-}2)$$

We use exact thermodynamic relations

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_{P,x} = -\frac{\bar{h}_i - h_i^+}{RT^2} \qquad \left(\frac{\partial \ln f_{\text{pure } i}}{\partial T}\right)_P = -\frac{h_i - h_i^+}{RT^2} \qquad (6\text{-}3)$$

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_{T,x} = -\frac{\bar{v}_i}{RT} \qquad \left(\frac{\partial \ln f_{\text{pure } i}}{\partial P}\right)_T = -\frac{v_i}{RT} \qquad (6\text{-}4)$$

h_i^+ is the enthalpy of pure *i* in the ideal-gas state,

Substituting (6-2) into (6-3) (6-4) we have

$$\bar{h}_i = h_i \qquad (6\text{-}5)$$ for ideal sol'n

$$\bar{v}_i = v_i \qquad (6\text{-}6)$$ for ideal sol'n

The formation of an ideal solution occurs without evolution or absorption of heat and without change of volume.

6.2 Fundamental Relations of Excess Functions

Excess functions are correction terms that relate the properties of real solutions to those of ideal solutions.

Excess functions are thermodynamic properties of solutions that are in excess of those of an ideal (or ideal dilute) solution at the same T, P and x.

The excess Gibbs energy is defined by

$$\boxed{G^E \equiv G_{(\text{actual solution at } T,P \text{ and } x)} - G_{(\text{ideal solution at same } T,P, \text{ and } x)}} \qquad (6\text{-}7)$$

Relations between the excess functions are the same as those between the total functions.

$$H^E = U^E + PV^E \qquad (6\text{-}8)$$

$$G^E = H^E - TS^E \qquad (6\text{-}9)$$

$$A^E = U^E - TS^E \qquad (6\text{-}10)$$

Partial derivative of excess functions are the same as those between the total functions.

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E \qquad (6\text{-}11)$$

$$\left(\frac{\partial G^E/T}{\partial T}\right)_{P,x} = -\frac{H^E}{T^2} \qquad (6\text{-}12)$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E \qquad (6\text{-}13)$$

Partial molar property is defined by

$$\boxed{\overline{m}_i \equiv \left(\frac{\partial M}{\partial n_i}\right)_{T,P,n_j}} \qquad (6\text{-}14)$$

Similarly, partial molar excess property is defined by

$$\overline{m}_i^E \equiv \left(\frac{\partial M^E}{\partial n_i}\right)_{T,P,n_j} \qquad (6\text{-}15)$$

From Euler’s theorem

$$M = \sum_i n_i \overline{m}_i \qquad (6\text{-}16)$$

Similarly, the excess property is given by

$$\boxed{M^E = \sum_i n_i \overline{m}_i^E} \qquad (6\text{-}17)$$

6.3 Activity and Activity Coefficients

The activity of *i* is defined as the ratio of the fugacity of *i* to that of *i* in the standard state

$$\boxed{a_i(T,P,x) \equiv \frac{f_i(T,P,x)}{f_i(T,P^0,x^0)}} \qquad (6\text{-}18)$$

The standard state is at the same T as that of mixture, and pressure P^0 and x^0 at some specified condtion.

The activity coefficient

$$\gamma_i \equiv \frac{a_i}{x_i} \qquad (6\text{-}19)$$

Relation between partial molar excess Gibbs energy and activity coefficient

From definition of fugacity at constant T and P

$$\bar{g}_{i(\mathrm{real})} - \bar{g}_{i(\mathrm{ideal})} = RT[\ln f_{i(\mathrm{real})} - \ln f_{i(\mathrm{ideal})}] \qquad (6\text{-}20)$$

$$\bar{g}_i^E = \bar{g}_{i(\mathrm{real})} - \bar{g}_{i(\mathrm{ideal})} \qquad (6\text{-}21)$$

$$\bar{g}_i^E = RT \ln \frac{f_{i(\mathrm{real})}}{f_{i(\mathrm{ideal})}} \qquad (6\text{-}22)$$

substituting (6-1a) of ideal solution

$$\bar{g}_i^E = RT \ln \frac{f_i}{\Re x_i} \qquad (6\text{-}23)$$

$$a_i = \gamma_i x_i = \frac{f_i}{\Re_i} \qquad (6\text{-}24)$$

ideal solution, $\gamma_i = 1$ and $a_i = x_i$

substituting (6-24) into (6-23)

$$\boxed{\bar{g}_i^E = RT \ln \gamma_i} \qquad (6\text{-}25)$$

partial molar excess Gibbs energy

$$\boxed{g^E = RT \sum_i x_i \ln \gamma_i} \qquad (6\text{-}26)$$

molar excess Gibbs energy

The temperature and pressure derivative of the activity coefficient

Case where the excess Gibbs energy is defined relative to an ideal solution in the sense of Raoult's law

$$\Re_i = f_i \text{ (pure liquid } i \text{ at } T \text{ and } P \text{ of solution)} \qquad (6\text{-}27)$$

$$\ln \gamma_i = \ln f_i - \ln x_i - \ln f_{\text{pure } i} \qquad (6\text{-}28)$$

$$\gamma_i = \frac{f_i}{x_i f_i^{pur}}$$

Differentiation with respect to T gives

$$\left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} = \frac{h_{\text{pure } i} - \bar{h}_i}{RT^2} = -\frac{\bar{h}_i^E}{RT^2} \qquad (6\text{-}29)$$

Differentiation with respect to P gives

$$\left(\frac{\partial \ln \gamma_i}{\partial P} \right)_{T,x} = \frac{\bar{v}_i - v_{\text{pure } i}}{RT} = -\frac{\bar{v}_i^E}{RT} \qquad (6\text{-}30)$$

Case where the excess Gibbs energy is defined relative to an ideal dilute solution in the sense of Henry's law

For example, consider a liquid mixture containing a gaseous solute (2).

If the critical temperature of solute 2 is lower than the temperature of mixture, a liquid phase cannot exist as $x_2 \to 1$. (a hypothetical standard state is needed in the Raoult's law)

Instead, the proportionality constant is determined from the condition of infinitely dilute solution.

For solute 2

$$\Re_2 = \lim_{x_2 \to 0} \frac{f_2}{x_2} = H_{2,1} \qquad (6\text{-}31)$$

Henry's constant

For solvent

$$\Re_1 = \lim_{x_2 \to 0} \frac{f_1}{x_1} = f_{\text{pure liquid 1}} \qquad (6\text{-}32)$$

The activity coefficient of solute is g

$$\gamma_2 = \frac{f_2}{x_2 H_{2,1}} \qquad (6\text{-}33)$$

The temperature derivative is

$$\left(\frac{\partial \ln \gamma_2}{\partial T}\right)_{P,x} = -\frac{\bar{h}_2^E}{RT^2} \qquad (6\text{-}34)$$

but has a different meaning

$$\bar{h}_2^E = \bar{h}_2 - \bar{h}_2^\infty \qquad (6\text{-}35)$$

where $\bar{h}_2^\infty$ is the partial molar enthalpy of solute 2 in an infinitely dilute solution.

The pressure derivative

$$\left(\frac{\partial \ln \gamma_2}{\partial P}\right)_{T,x} = \frac{\bar{v}_2 - \bar{v}_2^\infty}{RT} \qquad (6\text{-}36a)$$

6.4 Normalization of Activity Coefficients

If activity coefficients are defined in the sense of Raoult’s law, then

$$\gamma_i \to 1 \quad \text{as} \quad x_i \to 1 \qquad (6\text{-}37)$$

called symmetric convention for normalization

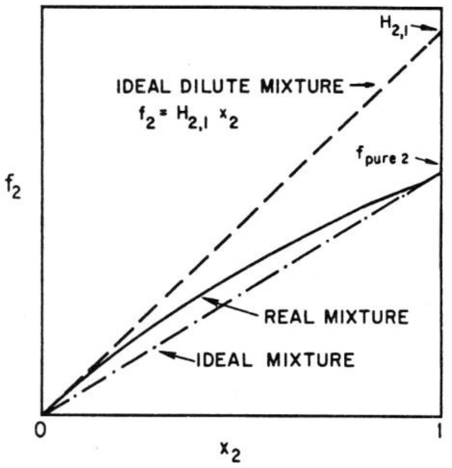
If activity coefficients are defined with reference to an ideal dilute solution, then

$$\begin{aligned} &\gamma_1 \to 1 \quad \text{as} \quad x_1 \to 1 \quad \text{(solvent)} \\ &\gamma_2 \to 1 \quad \text{as} \quad x_2 \to 0 \quad \text{(solute)} \end{aligned} \tag{6-38}$$

called unsymmetric convention for normalization

To distinguish, use * for solute

$$\begin{aligned} &\gamma_1 \to 1 \quad \text{as} \quad x_1 \to 1 \quad \text{(solvent)} \\ &\gamma_2^* \to 1 \quad \text{as} \quad x_2 \to 0 \quad \text{(solute)} \end{aligned} \tag{6-38a}$$



$$\gamma_2 \equiv \frac{f_2}{x_2 f_{\text{pure }2}} \qquad \text{and} \qquad \gamma_2^* \equiv \frac{f_2}{x_2 H_{2,1}}$$

$$\gamma_2 \to 1 \qquad\qquad \gamma_2^* \to 1$$

$$\text{as } x_2 \to 1 \qquad\qquad \text{as } x_2 \to 1$$

$$H_{2,1} = \lim_{x_2 \to 0} (f_2 / x_2)$$

Figure 6-1 Normalization of activity coefficients.

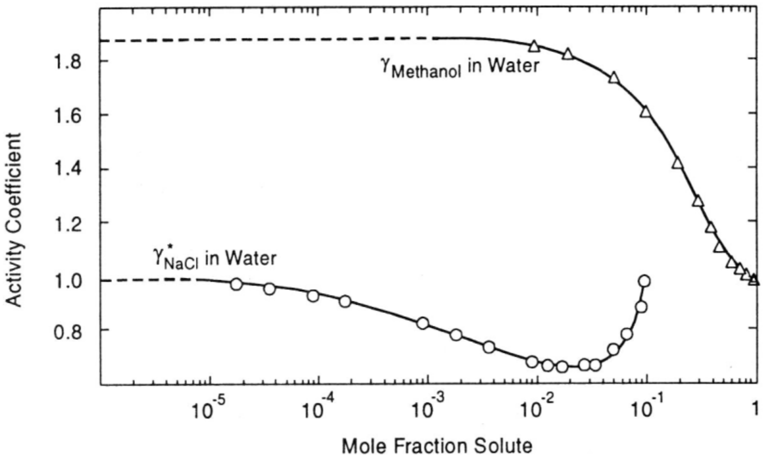


Figure 6-2 Symmetric and unsymmetric activity coefficient conventions. Experimental data at 25°C for the activity coefficients of methanol in water and sodium chloride in water (Ragal *et al.*, 1994). Solid lines are smooth data and dashed lines are extrapolations.

Ideal behavior of NaCl solution is approached at infinitely dilution.

Relation between symmetric and unsymmetric conventions

For binary mixture,

$$\gamma_2 = \frac{f_2}{x_2 f_{\text{pure }2}} \qquad (6\text{-}39)$$

$$\gamma_2^* = \frac{f_2}{x_2 H_{2,1}} \qquad (6\text{-}40)$$

$$\frac{\gamma_2}{\gamma_2^*} = \frac{H_{2,1}}{f_{\text{pure }2}} \qquad (6\text{-}41)$$

Because

$$\lim_{x_2 \to 0} \gamma_2^* = 1 \qquad (6\text{-}42)$$

We have

$$\lim_{x_2 \to 0} \gamma_2 = \frac{H_{2,1}}{f_{\text{pure } 2}} \tag{6-43}$$

$$\frac{\gamma_2}{\gamma_2^*} = \lim_{x_2 \to 0} \gamma_2 \tag{6-44}$$

physical situation

$$\frac{\gamma_2^*}{\gamma_2} = \lim_{x_2 \to 1} \gamma_2^* \tag{6-45}$$

physically unrealistic situation

6.5 Activity Coefficients from Excess Functions in Binary Mixtures

At a fixed temperature, the molar excess Gibbs energy g^E of a mixture depends on the composition.
The effect of pressure is negligible away from critical conditions.

For binary mixture (for which the standard state is pure liquid at the same T, P)
The molar excess Gibbs energy must obey the two boundary conditions

$$g^E = 0 \quad \text{when} \quad x_1 = 0$$
$$g^E = 0 \quad \text{when} \quad x_2 = 0$$

Two-suffix Margules Equations

The simplest expression

$$g^E = Ax_1x_2 \tag{6-46}$$

A is an empirical constant

To get activity coefficient

$$\boxed{RT\ln\gamma_i = \bar{g}_i^E = \left(\frac{\partial n_T g^E}{\partial n_i}\right)_{T,P,n_j}} \tag{6-47}$$

substituting (6-46) into (6-47)

$$\boxed{\ln\gamma_1 = \frac{A}{RT}x_2^2} \tag{6-48}$$

$$\boxed{\ln\gamma_2 = \frac{A}{RT}x_1^2} \tag{6-49}$$

A good representation for mixtures of molecules that are similar in size and chemical nature

At infinite dilution, the activity coefficients are equal.

$$\gamma_1^\infty \equiv \lim_{x_1 \to 0} \gamma_1 = \exp\left(\frac{A}{RT}\right) \tag{6-50}$$

$$\gamma_2^\infty \equiv \lim_{x_2 \to 0} \gamma_2 = \exp\left(\frac{A}{RT}\right) \tag{6-51}$$

Over a small temperature range, *A* is nearly constant or a weak function of *T*.

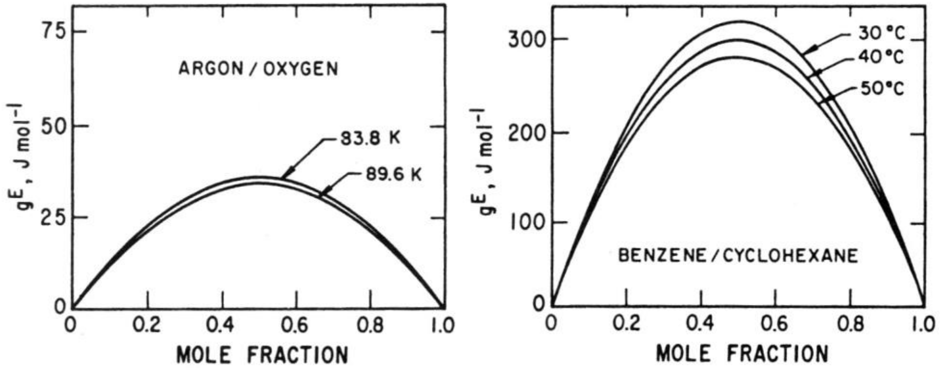


Figure 6-3 Applicability of two-suffix Margules equation to simple binary mixtures.

A usually falls with rising temperature for nonpolar solutions.

In general case,

$$g^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + D(x_1 - x_2)^3 + \dots] \tag{6-52}$$

[15] Redlich-Kister expansion

gives activity coefficient as

$$RT \ln \gamma_1 = a^{(1)} x_2^2 + b^{(1)} x_2^3 + c^{(1)} x_2^4 + d^{(1)} x_2^5 + \ldots \tag{6-53}$$

$$RT \ln \gamma_2 = a^{(2)} x_1^2 + b^{(2)} x_1^3 + c^{(2)} x_1^4 + d^{(2)} x_1^5 + \ldots \tag{6-54}$$

where

$$\begin{aligned} a^{(1)} &= A + 3B + 5C + 7D & a^{(2)} &= A - 3B - 5C - 7D \\ b^{(1)} &= -4(B + 4C + 9D) & b^{(2)} &= 4(B - 4C + 9D) \\ c^{(1)} &= 12(C + 5D) & c^{(2)} &= 12(C - 5D) \\ d^{(1)} &= -32D & d^{(2)} &= 32D \end{aligned}$$

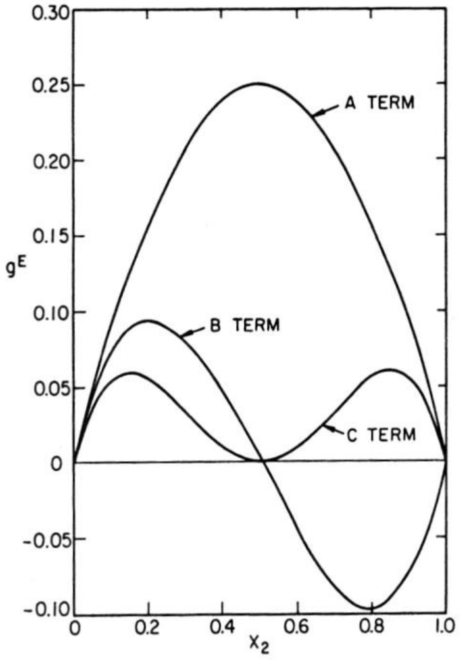


Figure 6-4 Contributions to g^E in Redlich-Kister equation (for $A = B = C = 1$).

Even-powered term to flatten or sharpen the parabola (A, C..)

Odd-powered term to skew the parabola (B, D..)

From (6-53) and (6-54)

$$RT\ln\frac{\gamma_1}{\gamma_2} = A(x_2 - x_1) + B(6x_1x_2 - 1) + C(x_1 - x_2)(8x_1x_2 - 1) + D(x_1 - x_2)^2(10x_1x_2 - 1) + \ldots \qquad (6\text{-}55)$$

can be used to classify different types of liquid solutions

Hexane / Toluene

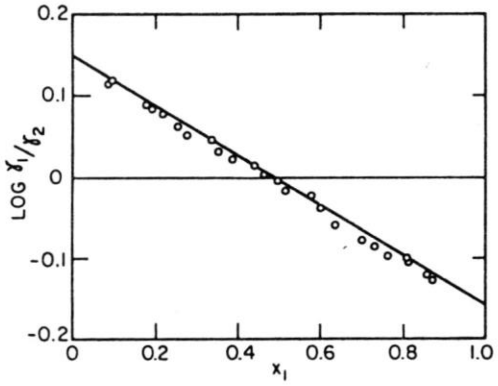


Figure 6-5 Activity-coefficient ratio for a simple mixture. Experimental data for *n*-hexane (1)/toluene (2) at 1.013 bar. The line is drawn to satisfy the area (consistency) test given by Eq. (6-92).

One parameter sufficient (linear)

Ration of molar volume (hexane/toluene) = 1.23

Isooctane / Benzene

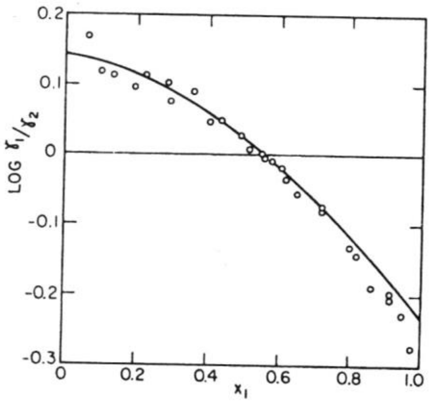


Figure 6-6 Activity-coefficient ratio for a mixture of intermediate complexity. Experimental data for benzene (1)/isooctane (2) at total pressures ranging from 0.981 to 1.013 bar.

Two parameters (A, B) are needed because of large size difference

Ration of molar volume (isooctane/benzene) = 1.86

Ethanol / Methylcyclohexane

Highly complex solution requiring 4 parameters

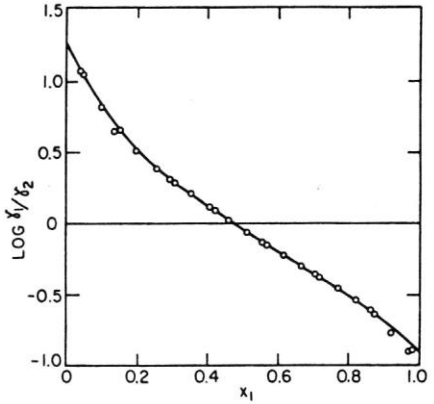


Figure 6-7 Activity-coefficient ratio for a highly complex mixture. Experimental data for ethanol (1)/methylcyclohexane (2) in the region 30-35°C.

The degree of hydrogen bonding of the alcohol is strongly dependent on the composition in the dilute region with respect to alcohol.

Most solutions are of intermediate complexity, requiring two or three parameters.

Acetic acid / Water

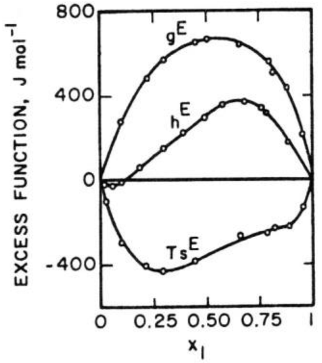


Figure 6-8 Excess functions for the acetic acid (1)/water (2) system at 25°C (R. Haase *et al.*, 1973, *Z. Naturforschung,* 28a: 1740).

The excess Gibbs energy is nearly a parabola, but is due to cancellation.

The excess enthalpy and the excess entropy show complexities.

6.6 Activity Coefficients for One Component from Those of the Other Components

The Gibbs-Duhem equation at constant temperature and pressure

$$\sum_i x_i d\overline{m}_i = 0 \qquad (6\text{-}56)$$

as this holds for ideal as well as real solutions

$$\sum_i x_i d\overline{m}_i^E = 0 \qquad (6\text{-}57)$$

Usage of (6-57)

To calculate activity coefficient of the other component

To check data for thermodynamic consistency

(6-57) in terms of activity coefficients becomes

$$\boxed{\sum_i x_i d\ln\gamma_i = 0 \qquad (\text{constant } T \text{ and } P)} \qquad (6\text{-}58)$$

For binary solution,

$$x_1 \frac{d\ln\gamma_1}{dx_1} = x_2 \frac{d\ln\gamma_2}{dx_2} \qquad (6\text{-}59)$$

Rewriting (6-59) for convenience

$$\frac{d\ln(\gamma_1/\gamma_2)}{dx_2} = \frac{1}{x_2}\frac{d\ln\gamma_1}{dx_2} \qquad (6\text{-}60)$$

Assuming an empirical equation of the form

$$\ln\gamma_1 = \sum_k \alpha_k x_2^{\beta_k} \qquad (\beta_k > 1) \qquad (6\text{-}61)$$

substituting into (6-60)

$$\frac{d\ln(\gamma_1/\gamma_2)}{dx_2} = \sum_k \alpha_k \beta_k x_2^{\beta_k - 2} \qquad (6\text{-}62)$$

Integrating

$$\ln\gamma_2 = \ln\gamma_1 - \sum_k \frac{\alpha_k\beta_k}{\beta_k - 1} x_2^{\beta_k - 1} - I \qquad (6\text{-}63)$$

Eliminating ln γ_1

$$\ln\gamma_2 = \sum_k \alpha_k x_2^{\beta_k} - \sum_k \frac{\alpha_k\beta_k}{\beta_k - 1} x_2^{\beta_k - 1} - I \qquad (6\text{-}64)$$

To determine I, use boundary condition that

$$\gamma_2 = 1 \quad \text{when} \quad x_2 = 1.$$

then

$$I = \sum_k \alpha_k - \sum_k \frac{\alpha_k\beta_k}{\beta_k - 1} \qquad (6\text{-}65)$$

Expression for ln γ_2 is

$$\ln\gamma_2 = \sum_k \alpha_k x_2^{\beta_k} - \sum_k \frac{\alpha_k}{\beta_k - 1}(\beta_k x_2^{\beta_k - 1} - 1) \qquad (6\text{-}66)$$

To illustrate, suppose the four-suffix Margules equation

$$\ln\gamma_1 = \alpha_2 x_2^2 + \alpha_3 x_2^3 + \alpha_4 x_2^4 \qquad (6\text{-}67)$$

α_i from experimental data

then

$$\ln\gamma_2 = (\alpha_2 + \tfrac{3}{2}\alpha_3 + 2\alpha_4)x_1^2 - (\alpha_3 + \tfrac{8}{3}\alpha_4)x_1^3 + \alpha_4 x_1^4 \qquad (6\text{-}68)$$

A useful common practice: when there is a large difference in volatility.
For example, the activity coefficient of polymer that is dissolved in benzene is calculated from the activity coefficient of benzene.

6.7 Partial Pressures from Isothermal Total-Pressure Data

Total pressures are measured as a function of composition of the liquid phase. The composition of the other phase is calculated by the Gibbs-Duhem equation. (Reducing experimental work!)

Barker's Numerical Method

The total pressure for a binary mixture is

$$P = \gamma_1 x_1 P_1^{s'} + \gamma_2 x_2 P_2^{s'} \qquad (6\text{-}71)$$

where $P_i^{S'}$ is corrected vapor pressure taking into account the second virial coefficients

$$P_1^{s'} \equiv P_1^s \exp\left[\frac{(v_1^L - B_{11})(P - P_1^s) - P\delta_{12} y_2^2}{RT}\right] \qquad (6\text{-}72)$$

$$P_2^{s'} \equiv P_2^s \exp\left[\frac{(v_2^L - B_{22})(P - P_2^s) - P\delta_{12} y_1^2}{RT}\right] \qquad (6\text{-}73)$$

$$\delta_{12} \equiv 2B_{12} - B_{11} - B_{22} \qquad (6\text{-}74)$$

Assumptions

The vapor phase is described by the volume-explicit virial equation terminated after the 2nd virial coefficients.

The pure component liquid volumes are incompressible and the liquid partial molar volume is invariant with composition.

We assume

$$\ln\gamma_1 = \alpha x_2^2 + \beta x_2^3 \tag{6-77}$$

It follows from the Gibbs-Duhem equation that

$$\ln\gamma_2 = \left(\alpha + \frac{3}{2}\beta\right)x_1^2 - \beta x_1^3 \tag{6-78}$$

Iterative calculations are required.

Benzene / cyclopentane

It is assumed that

$$\frac{g^E}{RT} = x_1 x_2 [A' + B'(x_1 - x_2)] \tag{6-79}$$

Activity coefficients are obtained from differentiation

$$\ln\gamma_1 = (A' + 3B')x_2^2 - 4B' x_2^3 \tag{6-80}$$

$$\ln\gamma_2 = (A' - 3B')x_1^2 + 4B' x_1^3 \tag{6-81}$$

Required data in Barker's method

Table 6-1 Second virial coefficients and liquid molar volumes* for benzene (1) and cyclopentane (2) (cm^3 mol^{-1}).

Temp. (°C)	v_1^L	v_2^L	B_{11}	B_{22}	B_{12}	δ_{12}
25	89.39	94.71	-1314	-1054	-1176	16
35	90.49	95.98	-1224	-983	-1096	15
45	91.65	97.29	-1143	-919	-1024	14

* Hermsen (1963).

Data (P, x_1) → calculated results (P, y_1)

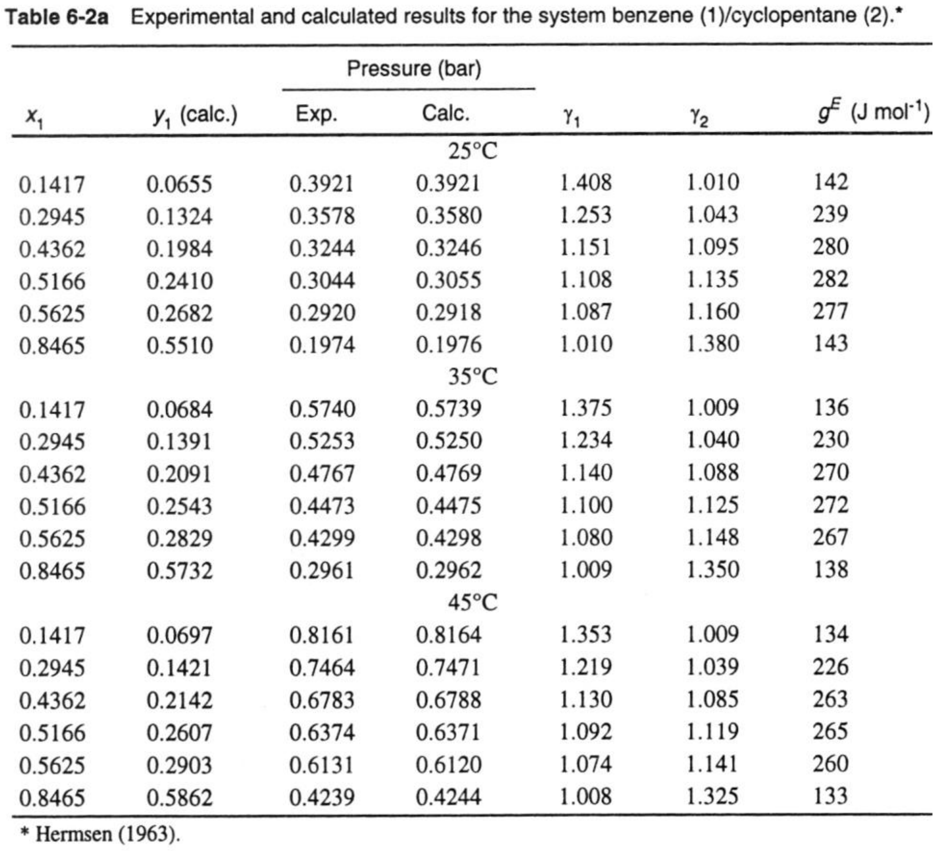


Table 6-2a Experimental and calculated results for the system benzene (1)/cyclopentane (2).*

x_1	y_1 (calc.)	Pressure (bar) Exp.	Pressure (bar) Calc.	γ_1	γ_2	g^E (J mol^{-1})
			25°C			
0.1417	0.0655	0.3921	0.3921	1.408	1.010	142
0.2945	0.1324	0.3578	0.3580	1.253	1.043	239
0.4362	0.1984	0.3244	0.3246	1.151	1.095	280
0.5166	0.2410	0.3044	0.3055	1.108	1.135	282
0.5625	0.2682	0.2920	0.2918	1.087	1.160	277
0.8465	0.5510	0.1974	0.1976	1.010	1.380	143
			35°C			
0.1417	0.0684	0.5740	0.5739	1.375	1.009	136
0.2945	0.1391	0.5253	0.5250	1.234	1.040	230
0.4362	0.2091	0.4767	0.4769	1.140	1.088	270
0.5166	0.2543	0.4473	0.4475	1.100	1.125	272
0.5625	0.2829	0.4299	0.4298	1.080	1.148	267
0.8465	0.5732	0.2961	0.2962	1.009	1.350	138
			45°C			
0.1417	0.0697	0.8161	0.8164	1.353	1.009	134
0.2945	0.1421	0.7464	0.7471	1.219	1.039	226
0.4362	0.2142	0.6783	0.6788	1.130	1.085	263
0.5166	0.2607	0.6374	0.6371	1.092	1.119	265
0.5625	0.2903	0.6131	0.6120	1.074	1.141	260
0.8465	0.5862	0.4239	0.4244	1.008	1.325	133

* Hermsen (1963).

Optimum values of *A*’ and *B*’ were found such that the calculated *P* is as closely as possible the experimental *P*.

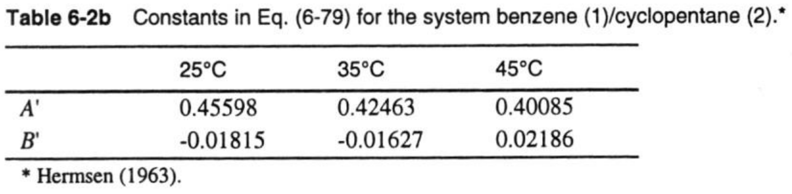


Table 6-2b Constants in Eq. (6-79) for the system benzene (1)/cyclopentane (2).*

	25°C	35°C	45°C
A'	0.45598	0.42463	0.40085
B'	-0.01815	-0.01627	0.02186

* Hermsen (1963).

Hydrocarbon / Polar solvent

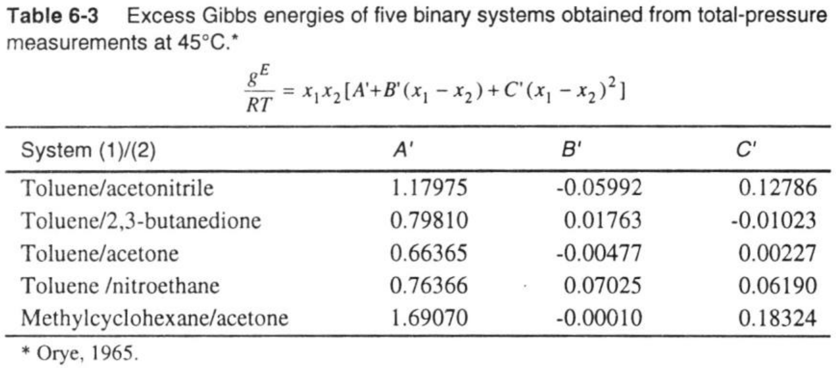


Table 6-3 Excess Gibbs energies of five binary systems obtained from total-pressure measurements at 45°C.*

$$\frac{g^E}{RT} = x_1 x_2 [A' + B'(x_1 - x_2) + C'(x_1 - x_2)^2]$$

System (1)/(2)	*A'*	*B'*	*C'*
Toluene/acetonitrile	1.17975	-0.05992	0.12786
Toluene/2,3-butanedione	0.79810	0.01763	-0.01023
Toluene/acetone	0.66365	-0.00477	0.00227
Toluene /nitroethane	0.76366	0.07025	0.06190
Methylcyclohexane/acetone	1.69070	-0.00010	0.18324

* Orye, 1965.

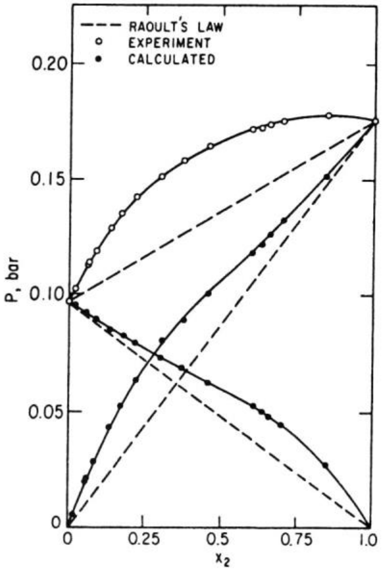
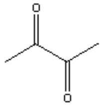


Figure 6-9 Total and partial pressures of toluene (1)/2,3-butanedione (2) at 45°C.



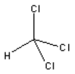
P-x measurements for14 binary systems

$$\frac{g^E}{RTx_1x_2} = A'x_2 + B'x_1 - D'x_1x_2 \qquad (6\text{-}82)$$

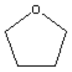
Table 6-4 Excess Gibbs energy from *P-x* measurements at 30°C.* [Constants in Eq. (6-82)].

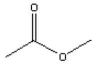
System (1)/(2)	*A'*	*B'*	*D'*
1. Carbon tetrachloride/THF†	-0.25704	-0.18188	0.04760
2. Chloroform/THF	-1.39352	-1.58092	0.58606
3. Dichloromethane/THF	-0.93341	0.87287	0.22232
4. Carbon tetrachloride/furan	0.28639	0.27034	0.01189
5. Chloroform/furan	-0.08350	-0.11890	0.02847
6. Dichloromethane/furan	0	0	0
7. THF/furan	-0.39970	-0.37125	-0.06410
8. Dichloromethane/methyl acetate	-0.42260	-0.63028	0.27851
9. Dichloromethane/acetone	0.58905	-0.76638	-0.11940
10. Dichloromethane/1,4-dioxane	-0.63128	-0.95516	-0.06863
11. Chloroform/1,4-dioxane	-0.75571	-1.58181	0.12739
12. Pyridine/acetone	0.19441	0.20447	0.02998
13. Pyridine/chloroform	-1.16104	-0.70714	0.37199
14. Pyridine/dichloromethane	-0.57919	-0.44873	0.03523

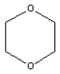
* Byer *et al.* (1973); † THF = tetrahydrofuran.

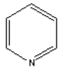
chloroform 

furan 

THF 

methyl acetate 

1,4-dioxane 

pyridine 

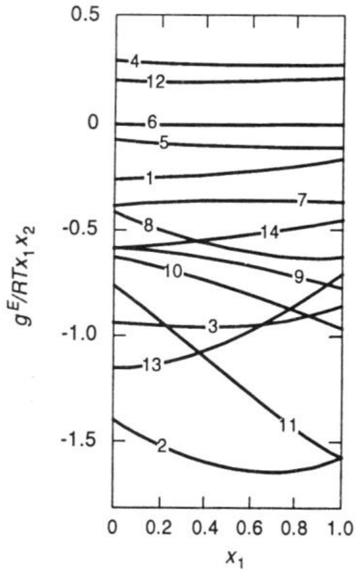


Figure 6-10 Excess Gibbs energies for 14 binary systems listed in Table 6-4.

No. 6 shows an ideal mixture behavior.

6.8 Partial Pressures from Isobaric Boiling-Point Data

Converting isobaric *T*-*x* data into *y*-*x* data is less useful because the Gibbs-Duhem equation contains a correction term proportional to the enthalpy of mixing.

It is easier to measure *y*-*x* data directly that to obtain enthalpy of mixing data.

For some practical applications, boiling-point measurement is easy.

We assume

The correction term for nonisothermal condition may be neglected.

The gas phase is ideal.

Two-suffix Margules equation is adequate.

$$RT \ln \gamma_1 = A x_2^2 \tag{6-83}$$

We assume that *A* is a constant independent of *T*, *P*, and *x*

$$RT \ln \gamma_2 = A x_1^2 \tag{6-84}$$

Total pressure is

$$P = \text{constant} = x_1 P_1^s \exp\left(\frac{A}{RT} x_2^2\right) + x_2 P_2^s \exp\left(\frac{A}{RT} x_1^2\right) \tag{6-85}$$

The value of *A* may be found by trial and error.

diisopropyl ether / 2-propanol

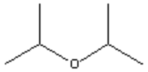
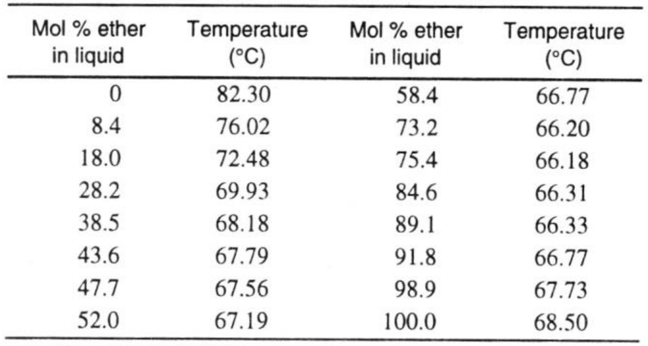


Table 6-5 Boiling points of diisopropyl ether/2-propanol mixtures at 1.013 bar.*



Mol % ether in liquid	Temperature (°C)	Mol % ether in liquid	Temperature (°C)
0	82.30	58.4	66.77
8.4	76.02	73.2	66.20
18.0	72.48	75.4	66.18
28.2	69.93	84.6	66.31
38.5	68.18	89.1	66.33
43.6	67.79	91.8	66.77
47.7	67.56	98.9	67.73
52.0	67.19	100.0	68.50

* Miller and Bliss (1940).

$A = (3.18 \pm 0.13)\ \mathrm{kJ\ mol^{-1}}$

diisopropyl ether

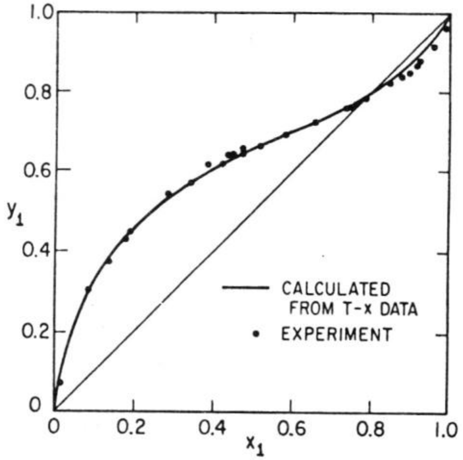


Figure 6-11 Vapor-liquid equilibrium for the diisopropyl ether (1)/2-propanol (2) system at 1.013 bar.

Good agreement!, but one should not assume that this will be always be the case.

Without the correction for the enthalpy of mixing, the boiling-point method is necessarily an approximation.

6.9 Testing Equilibrium Data for Thermodynamic Consistency

Consider binary mixture for which the Gibbs-Duhem equation is

$$x_1 \frac{d\ln\gamma_1}{dx_1} = x_2 \frac{d\ln\gamma_2}{dx_2} \qquad (6\text{-}59)$$

A theoretically simple technique is to test data directly with (6-59), "slope method" but it is of little value because experimental data inevitably show some scatter.
It is much easier to use an integral rather than a differential (slope) test.

Integral Test

The molar excess Gibbs energy is

$$\frac{g^E}{RT} = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \qquad (6\text{-}86)$$

Differentiating with respect to x_1

$$\frac{d(g^E/RT)}{dx_1} = x_1 \frac{\partial\ln\gamma_1}{\partial x_1} + \ln\gamma_1 + x_2 \frac{\partial\ln\gamma_2}{\partial x_1} + \ln\gamma_2 \frac{dx_2}{dx_1} \qquad (6\text{-}87)$$

Noting that $dx_1 = -dx_2$ and using (6-59) we obtain

$$\frac{d(g^E/RT)}{dx_1} = \ln\frac{\gamma_1}{\gamma_2} \qquad (6\text{-}88)$$

Integration with respect to x_1 gives

$$\int_0^1 \frac{d(g^E/RT)}{dx_1} dx_1 = \int_0^1 \ln\frac{\gamma_1}{\gamma_2} dx_1 = \frac{g^E}{RT}(\text{at } x_1 = 1) - \frac{g^E}{RT}(\text{at } x_1 = 0) \qquad (6\text{-}89)$$

If pure liquids are used as the standard states,

$$\begin{aligned} \ln\gamma_1 &\to 0 \quad \text{as} \quad x_1 \to 1 \\ \ln\gamma_2 &\to 0 \quad \text{as} \quad x_1 \to 0 \end{aligned} \tag{6-90}$$

and

$$\begin{aligned} \frac{g^E}{RT}(\text{at } x_1 = 1) &= 0 \\ \frac{g^E}{RT}(\text{at } x_1 = 0) &= 0 \end{aligned} \tag{6-91}$$

(6-89) becomes

$$\boxed{\int_0^1 \ln\frac{\gamma_1}{\gamma_2}\,dx_1 = 0} \tag{6-92}$$

Area test of phase-equilibrium data.

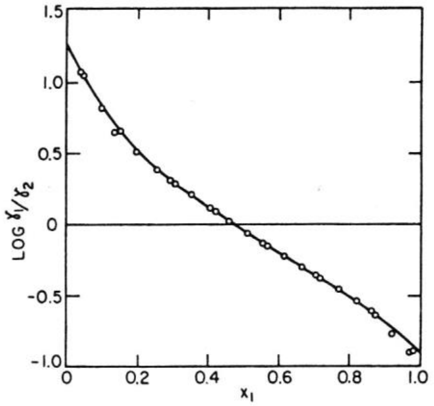


Figure 6-7 Activity-coefficient ratio for a highly complex mixture. Experimental data for ethanol (1)/methylcyclohexane (2) in the region 30-35°C.

The thermodynamic consistency is met if the area above the x-axis is equal to that below the x-axis.

Drawback: The area test does not utilize the most valuable (the most accurate) measurement, total pressure *P*

When the ratio of activity coefficients is calculated, the pressure cancels out

$$\frac{\gamma_1}{\gamma_2} = \frac{\varphi_1 y_1 / x_1 f_1^0}{\varphi_2 y_2 / x_2 f_2^0} \qquad (6\text{-}93)$$

Suggestion: Measure all *P*, *x*, *y* at constant *T*, select any two quantities and predict the third using the Gibbs-Duhem equation, and compare with the measured quantity.

Pyridine / Tetrachloroethylene

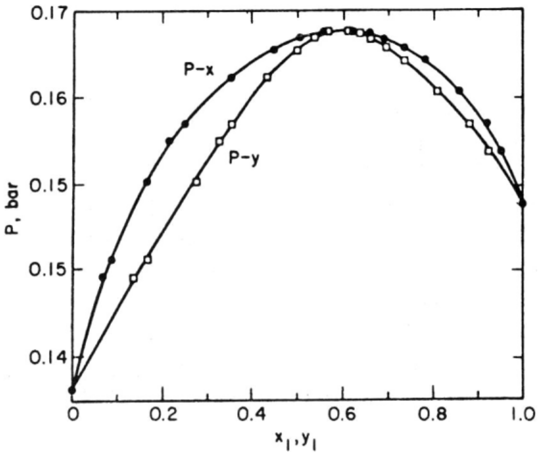


Figure 6-12 Experimental vapor-liquid equilibrium data for the system pyridine (1)/tetrachloroethylene (2) at 60°C.

The total pressures are so low that fugacity coefficients can be set to unity.
The standard-state fugacity is equal to vapor pressure.
There is only solution nonideality to be considered.

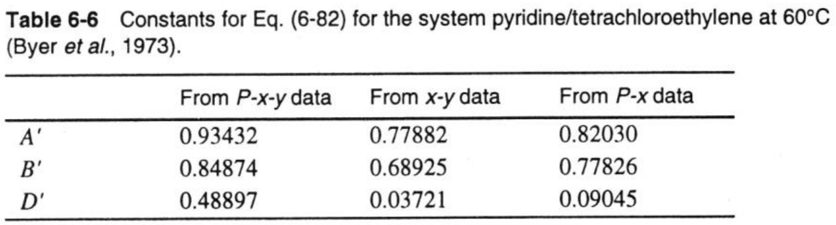


Table 6-6 Constants for Eq. (6-82) for the system pyridine/tetrachloroethylene at 60°C (Byer *et al.*, 1973).

	From P-x-y data	From x-y data	From P-x data
A'	0.93432	0.77882	0.82030
B'	0.84874	0.68925	0.77826
D'	0.48897	0.03721	0.09045

The coefficients depend significantly on the choice of data used.

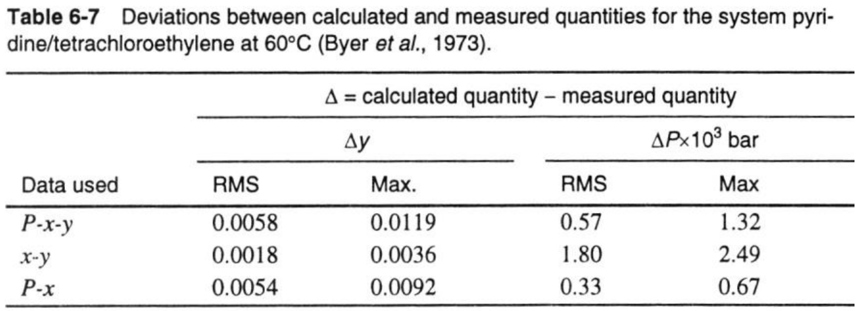


Table 6-7 Deviations between calculated and measured quantities for the system pyridine/tetrachloroethylene at 60°C (Byer *et al.*, 1973).

	Δ = calculated quantity – measured quantity			
	Δy		$\Delta P \times 10^3$ bar	
Data used	RMS	Max.	RMS	Max
P-x-y	0.0058	0.0119	0.57	1.32
x-y	0.0018	0.0036	1.80	2.49
P-x	0.0054	0.0092	0.33	0.67

When x-y data are used, RMS error in P is probably larger than the experimental error.

(One can measure pressure with high accuracy)

When p-x data are used, RMS error in y is probably within the experimental error of y.

6.10 Wohl's Expansion for the Excess Gibbs Energy

Wohl's expansion of the excess Gibbs energy of a binary solution

$$\frac{g^E}{RT(x_1q_1+x_2q_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2 + 4a_{1112}z_1^3z_2 + 4a_{1222}z_1z_2^3 + 6a_{1122}z_1^2z_2^2 + \dots \qquad (6\text{-}94)$$

where z_1 and z_2 are effective volume fractions

$$z_1 \equiv \frac{x_1q_1}{x_1q_1+x_2q_2} \qquad \text{and} \qquad z_2 \equiv \frac{x_2q_2}{x_1q_1+x_2q_2}$$

Two types of parameters:

q's are effective volumes of the molecules.

The ratio of *q*'s can be approximated as the ratio of the pure-component liquid molar volumes.

a's are interaction parameters in a rough way similar to that of virial coefficients (just crude analogy!)

As g^E must vanish as or becomes zero, terms of $z_1^2, z_1^3, \dots$ and $z_2^2, z_2^3, \dots$ do not explicitly appear in the expansion.

van Laar Equation

We consider a binary solution of two components that are not strongly dissimilar but that have different molecular sizes.

Example: Benzene / Isooctane

Molar volume (89 cm^3/mol at 25°C / 166 cm^3/mol at 25°C)

Truncating Whol’s expression after the first term,

$$\frac{g^E}{RT} = \frac{2a_{12}x_1x_2q_1q_2}{x_1q_1 + x_2q_2} \tag{6-96}$$

that is the van Laar equation.

The activity coefficients are

$$\boxed{\ln\gamma_1 = \frac{A'}{\left(1 + \frac{A'}{B'}\frac{x_1}{x_2}\right)^2}} \tag{6-97}$$

$$\boxed{\ln\gamma_2 = \frac{B'}{\left(1 + \frac{B'}{A'}\frac{x_2}{x_1}\right)^2}} \tag{6-98}$$

where $A' = 2q_1a_{12}$ and $B' = 2q_2a_{12}$.

The ratio of A' and B' are the ratio of q_1 and q_2

It is not necessary to know q_1 and q_2 separately because it is only their ratio that is important.

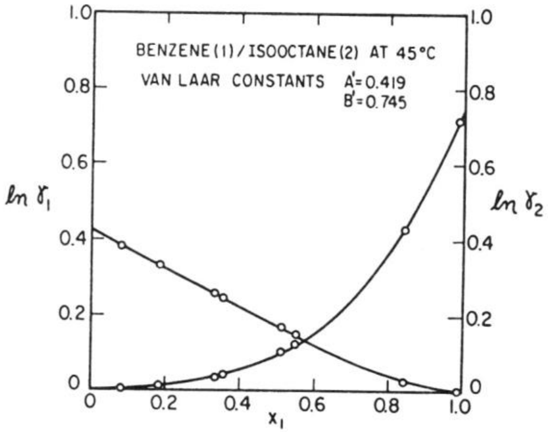


Figure 6-13 Application of van Laar's equations to a mixture whose components differ appreciably in molecular size.

For complex mixtures, the constants must be regarded as empirical parameters.

Propanol / Water

For an isobaric system, the temperature dependence is often not negligible. However, the assumption of temperature-invariant constants appears to be a good approximation provided that the temperature range is not large.

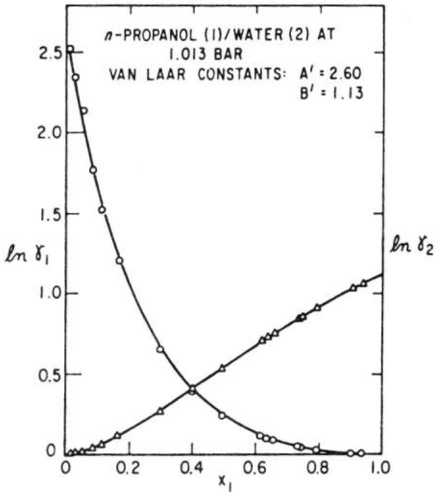


Figure 6-14 Application of van Laar's equations to an isobaric system. In this system the temperature varies only from 87.8 to 100°C.

A general empirical procedure at constant x is

$$\ln \gamma_i = c + dT^{-1} \tag{6-99}$$

When $d = 0$, we recover athermal solution behavior (h^E=0), and when $c = 0$, we recover regular solution behavior (s^E=0).

Margules Equations

We consider a binary solution of two components whose molecular sizes are not much different.

$q_1 = q_2$ in Wohl's equation

We obtain

$$\ln \gamma_1 = A' x_2^2 + B' x_2^3 + C' x_2^4 \tag{6-100}$$

$$\ln \gamma_2 = \left(A' + \frac{3}{2} B' + 2C'\right) x_1^2 - \left(B' + \frac{8}{3} C'\right) x_1^3 + C' x_1^4 \tag{6-101}$$

where

$$A' = q(2a_{12} + 6a_{112} - 3a_{122} + 12a_{1112} - 6a_{1122})$$

$$B' = q(6a_{122} - 6a_{112} - 24a_{1112} - 8a_{1222} + 24a_{1122})$$

$$C' = q(12a_{1112} + 12a_{1222} - 18a_{1122})$$

two-suffix Margules equations: $B' = C' = 0$

three-suffix Margules equations: $C' = 0$

four-suffix Margules equations: $C' \neq 0$

Examples of three-suffix Margules equations

	A'	*B'*
Acetone (1)/chloroform (2)	-0.553	-0.276
Acetone (1)/methanol (2)	0.334	0.368
Chloroform (1)/methanol (2)	2.89	-2.17

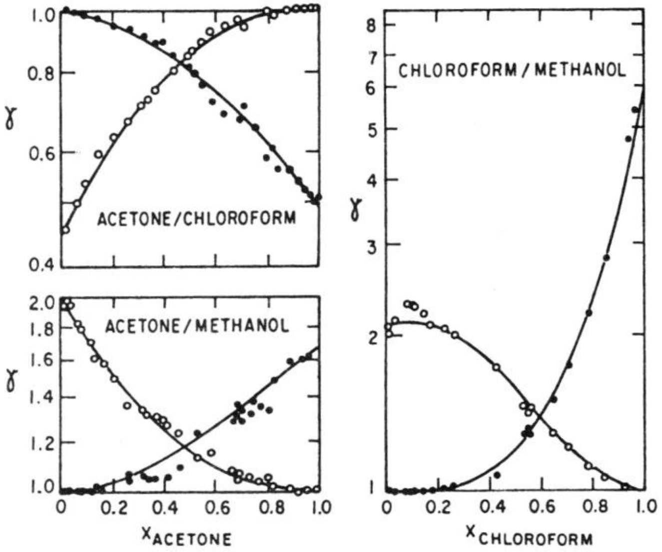


Figure 6-15 Activity coefficients for three binary systems at 50°C. Lines calculated from three-suffix Margules equations.

acetone/chloroform: strong negative deviations

acetone/methanol: strong positive deviations

methanol /chloroform: unusual behavior at the methanol-rich side

Scatchard-Hamer Equation

Instead of assuming $q_1 = q_2$, we assume that

$$\frac{q_1}{q_2} = \frac{v_1}{v_2}$$

where v_1 and v_2 are the molar volumes of the pure liquids.

Then, the activity coefficients are

$$\ln\gamma_1 = A' z_2^2 + B' z_2^3 \tag{6-102}$$

$$\ln\gamma_2 = \left(A' + \frac{3}{2}B'\right)\left(\frac{v_2}{v_1}\right) z_1^2 - B'\left(\frac{v_2}{v_1}\right) z_1^3 \tag{6-103}$$

where $A' = v_1(2a_{12} + 6a_{112} - 3a_{122})$ and $B' = v_1(6a_{122} - 6a_{112})$.

<u>Behavior of two-paramter model</u>

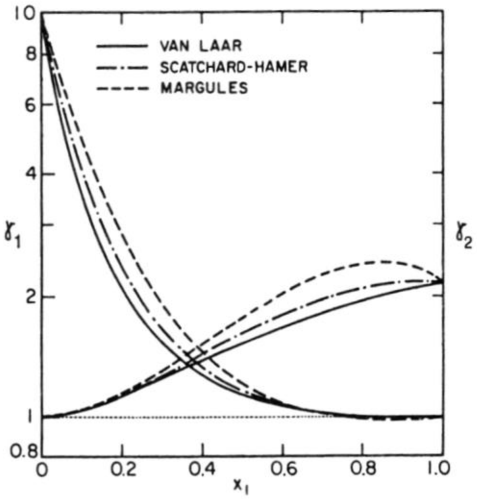


Figure 6-16 Activity coefficients according to three, two-parameter equations with $\gamma_1^\infty = 10$ and $\gamma_2^\infty = 2.15$. For the Scatchard-Hamer equation, $v_2 / v_1 = 2/3$.

The Scatchard-Hamer eq'n is intermediate between the van Laar eq'n and the three-suffix Margules eq'n.

6.11 Wilson, NRTL, and UNIQUAC Equations

Wilson Equation

The excess Gibbs energy of a binary solution

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \qquad (6\text{-}104)$$

The activity coefficients are derived as

$$\boxed{\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)} \qquad (6\text{-}105)$$

$$\boxed{\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right)} \qquad (6\text{-}106)$$

Eq (6-104) obeys the boundary condition that g^E vanishes as either x_1 or x_2 becomes zero.
Two adjustable parameters Λ_{12} and Λ_{21} (NOT the SAME!)

$$\Lambda_{12} \equiv \frac{v_2}{v_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT} \right) \qquad (6\text{-}107)$$

$$\Lambda_{21} \equiv \frac{v_1}{v_2} \exp\left(-\frac{\lambda_{21} - \lambda_{22}}{RT} \right) \qquad (6\text{-}108)$$

where v_i the molar volume of pure component i and λ's are energies of interaction
Wilson's equation gives an estimate of the variation of the activity coefficients with temperature.
It may provide a practical advantage in isobaric calculations where the temperature varies as composition changes.

Wilson equation is in many cases better than the three-suffix Margules equation and the van Laar equation.

Nitromethane / carbon tetrachloride

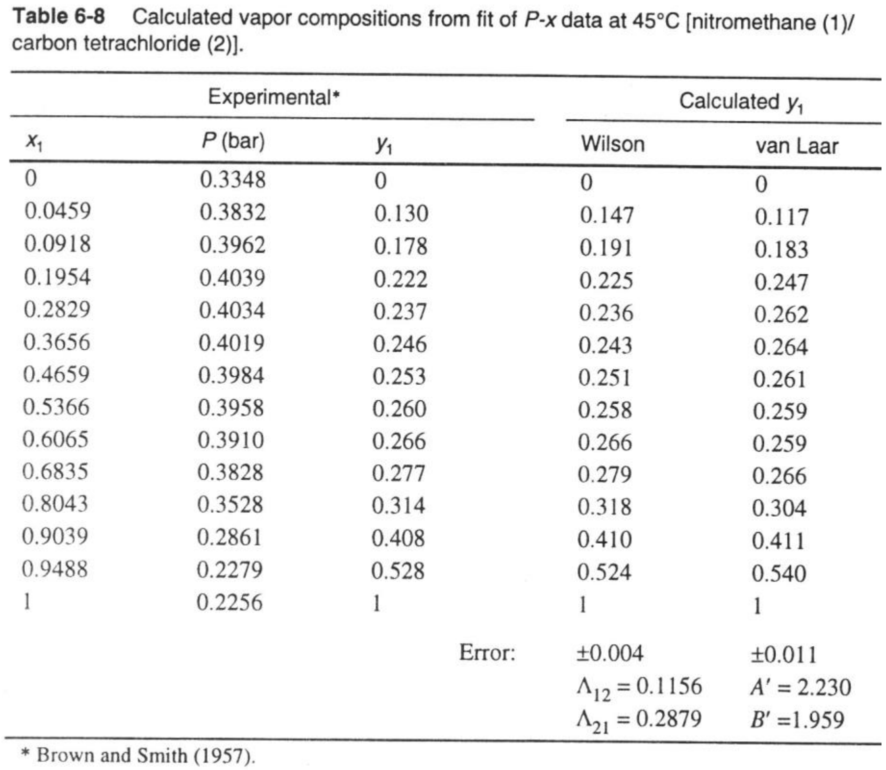


Table 6-8 Calculated vapor compositions from fit of *P-x* data at 45°C [nitromethane (1)/ carbon tetrachloride (2)].

Experimental*			Calculated y_1	
x_1	P (bar)	y_1	Wilson	van Laar
0	0.3348	0	0	0
0.0459	0.3832	0.130	0.147	0.117
0.0918	0.3962	0.178	0.191	0.183
0.1954	0.4039	0.222	0.225	0.247
0.2829	0.4034	0.237	0.236	0.262
0.3656	0.4019	0.246	0.243	0.264
0.4659	0.3984	0.253	0.251	0.261
0.5366	0.3958	0.260	0.258	0.259
0.6065	0.3910	0.266	0.266	0.259
0.6835	0.3828	0.277	0.279	0.266
0.8043	0.3528	0.314	0.318	0.304
0.9039	0.2861	0.408	0.410	0.411
0.9488	0.2279	0.528	0.524	0.540
1	0.2256	1	1	1
		Error:	±0.004	±0.011
			$\Lambda_{12} = 0.1156$	$A' = 2.230$
			$\Lambda_{21} = 0.2879$	$B' = 1.959$

* Brown and Smith (1957).

The average error in the predicted vapor composition is much less with Wilson equation.

Ethanol / Isooctane

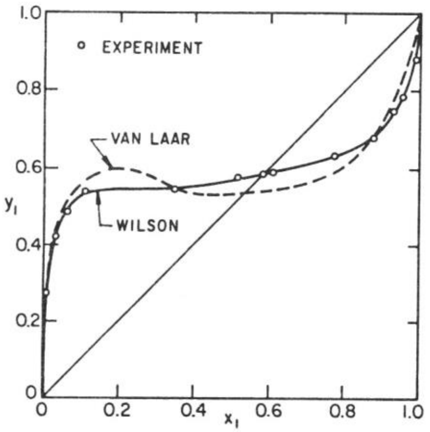


Figure 6-17 Vapor-liquid equilibrium for the ethanol (1)/ isooctane (2) system at 50°C. Lines calculated from *P-x* data. The van Laar equations erroneously predict partial immiscibility

Disadvantages of Wilson equation

Unable to describe maxima or minima of the activity coefficients.

Unable to predict limited miscibility of two liquid phases. (LLE×)

NRTL Equation (*n*on*r*andom, *t*wo *l*iquid)

Unlike Wioson's, NRTL equation is applicable to partially miscible as well as completely miscible system.

The excess Gibbs energy is

$$\frac{g^E}{RT} = x_1 x_2 \left(\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right) \qquad (6\text{-}109)$$

$$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \qquad \tau_{21} = \frac{g_{21} - g_{11}}{RT} \qquad (6\text{-}110)$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}) \qquad (6\text{-}111)$$

g_{ij} is an energy parameter characteristic of the *i*-*j* interaction

α_{12} indicates nonrandomness in the mixture. From experimental data reduction, α_{12} varies from 0.2 to 0.47. α_{12} can often be set to 0.3.

The activity coefficients are

$$\boxed{\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]} \qquad (6\text{-}112)$$

$$\boxed{\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]} \qquad (6\text{-}113)$$

The NRTL equation is good for strongly nonideal mixtures

Ethanol / Isooctane

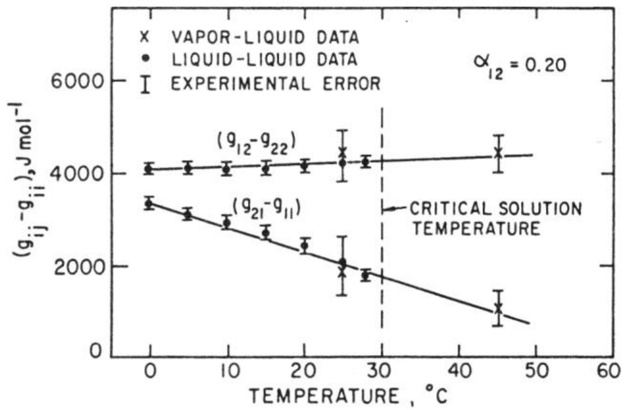


Figure 6-18 Parameters in NRTL equation for the nitroethane (1)/isooctane (2) system calculated from vapor-liquid and liquid-liquid equilibrium data.

This system has a miscibility gap below 30°C.

The parameters (g_{12}–g_{22}) and (g_{21}–g_{11}) appear to be linear functions of temperature showing no discontinuities near the critical solution temperature.

UNIQUAC Equation (*uni*versal *qua*si-*c*hemical theory from liquid theory on lattice)

g^E consists of two parts,

a combinatorial part to describe the entropic contribution, and

a residual part due to intermolecular forces that are responsible for the enthalpy of mixing.

$$\frac{g^E}{RT} = \left(\frac{g^E}{RT}\right)_{\text{combinatorial}} + \left(\frac{g^E}{RT}\right)_{\text{residual}} \qquad (6\text{-}114)$$

For a binary mixture

$$\left(\frac{g^E}{RT}\right)_{\text{combinatorial}} = x_1 \ln\frac{\Phi_1^*}{x_1} + x_2 \ln\frac{\Phi_2^*}{x_2} + \frac{z}{2}\left(x_1 q_1 \ln\frac{\theta_1}{\Phi_1^*} + x_2 q_2 \ln\frac{\theta_2}{\Phi_2^*}\right) \qquad (6\text{-}115)$$

The combinatorial part is determined by the composition, size and shape of molecules, requiring only pure-component data. The coordination number z is set to 10.

$$\left(\frac{g^E}{RT}\right)_{\text{residual}} = -x_1 q_1' \ln(\theta_1' + \theta_2' \tau_{21}) - x_2 q_2' \ln(\theta_2' + \theta_1' \tau_{12}) \qquad (6\text{-}116)$$

The residual part depends on intermolecular forces, and represented by two adjustable binary parameters, τ_{12} and τ_{21}

Segment fraction Φ^* and area fractions θ and θ' are

$$\Phi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad \Phi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \qquad (6\text{-}117)$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \qquad (6\text{-}118)$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'} \qquad \theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'} \qquad (6\text{-}119)$$

r, q, and q' are pure-component constants (dimensionless).

r for molecular size and q for external surface areas

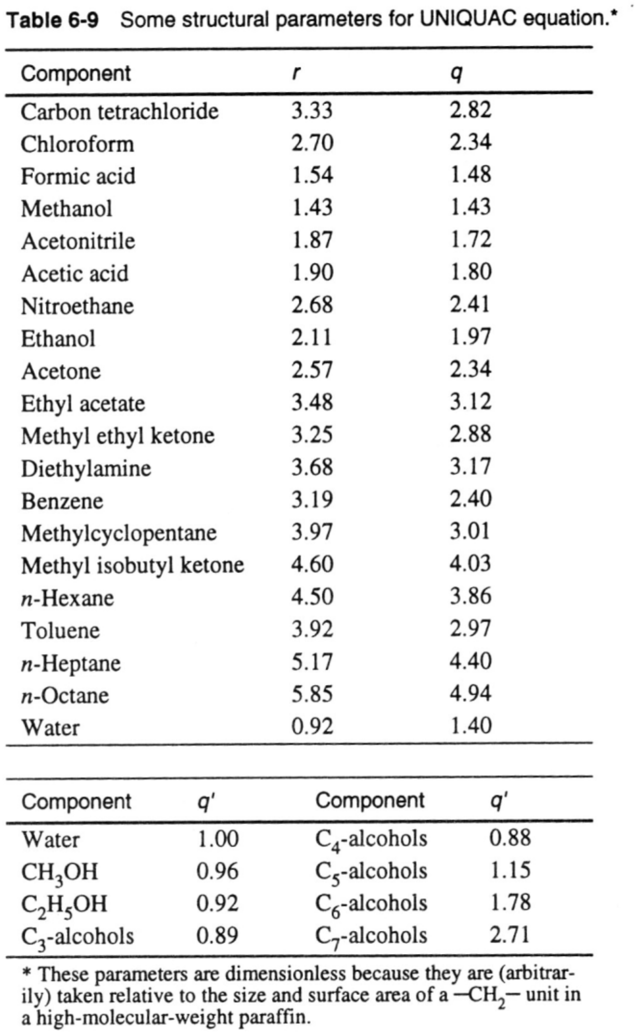


Table 6-9 Some structural parameters for UNIQUAC equation.*

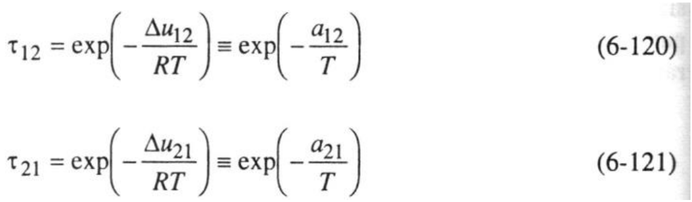
Component	r	q
Carbon tetrachloride	3.33	2.82
Chloroform	2.70	2.34
Formic acid	1.54	1.48
Methanol	1.43	1.43
Acetonitrile	1.87	1.72
Acetic acid	1.90	1.80
Nitroethane	2.68	2.41
Ethanol	2.11	1.97
Acetone	2.57	2.34
Ethyl acetate	3.48	3.12
Methyl ethyl ketone	3.25	2.88
Diethylamine	3.68	3.17
Benzene	3.19	2.40
Methylcyclopentane	3.97	3.01
Methyl isobutyl ketone	4.60	4.03
n-Hexane	4.50	3.86
Toluene	3.92	2.97
n-Heptane	5.17	4.40
n-Octane	5.85	4.94
Water	0.92	1.40

Component	q'	Component	q'
Water	1.00	C_4-alcohols	0.88
CH_3OH	0.96	C_5-alcohols	1.15
C_2H_5OH	0.92	C_6-alcohols	1.78
C_3-alcohols	0.89	C_7-alcohols	2.71

* These parameters are dimensionless because they are (arbitrarily) taken relative to the size and surface area of a $-CH_2-$ unit in a high-molecular-weight paraffin.

For fluids other than water or lower alcohols, $q = q'$

Two adjustable parameters τ_{12} and τ_{21} are



$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) \equiv \exp\left(-\frac{a_{12}}{T}\right) \tag{6-120}$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) \equiv \exp\left(-\frac{a_{21}}{T}\right) \tag{6-121}$$

(not equal to each other)

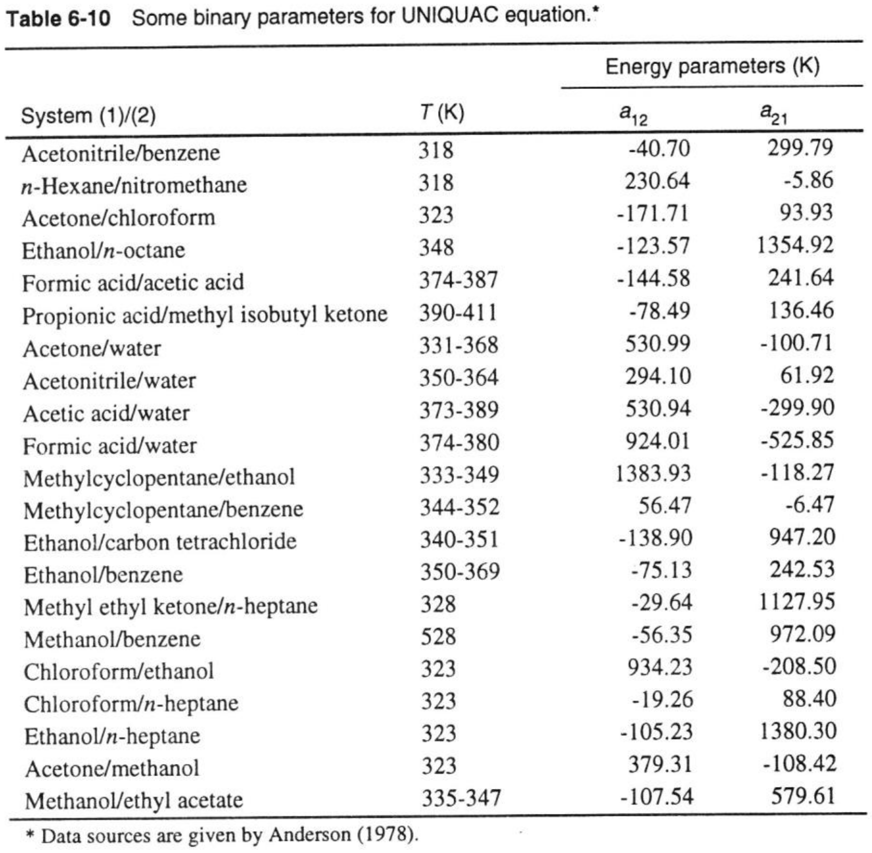


Table 6-10 Some binary parameters for UNIQUAC equation.*

System (1)/(2)	T (K)	Energy parameters (K) a_{12}	 a_{21}
Acetonitrile/benzene	318	-40.70	299.79
n-Hexane/nitromethane	318	230.64	-5.86
Acetone/chloroform	323	-171.71	93.93
Ethanol/*n*-octane	348	-123.57	1354.92
Formic acid/acetic acid	374-387	-144.58	241.64
Propionic acid/methyl isobutyl ketone	390-411	-78.49	136.46
Acetone/water	331-368	530.99	-100.71
Acetonitrile/water	350-364	294.10	61.92
Acetic acid/water	373-389	530.94	-299.90
Formic acid/water	374-380	924.01	-525.85
Methylcyclopentane/ethanol	333-349	1383.93	-118.27
Methylcyclopentane/benzene	344-352	56.47	-6.47
Ethanol/carbon tetrachloride	340-351	-138.90	947.20
Ethanol/benzene	350-369	-75.13	242.53
Methyl ethyl ketone/*n*-heptane	328	-29.64	1127.95
Methanol/benzene	528	-56.35	972.09
Chloroform/ethanol	323	934.23	-208.50
Chloroform/*n*-heptane	323	-19.26	88.40
Ethanol/*n*-heptane	323	-105.23	1380.30
Acetone/methanol	323	379.31	-108.42
Methanol/ethyl acetate	335-347	-107.54	579.61

* Data sources are given by Anderson (1978).

The activity coefficients are given by

$$\boxed{\begin{aligned}\ln\gamma_1 = \ln\frac{\Phi_1^*}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\Phi_1^*} + \Phi_2^*\left(l_1 - \frac{r_1}{r_2}l_2\right) \\ -q_1'\ln(\theta_1' + \theta_2'\tau_{21}) + \theta_2'q_1'\left(\frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}}\right)\end{aligned}} \tag{6-122}$$

$$\boxed{\begin{aligned}\ln\gamma_2 = \ln\frac{\Phi_2^*}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\Phi_2^*} + \Phi_2^*\left(l_2 - \frac{r_2}{r_1}l_1\right) \\ -q_2'\ln(\theta_2' + \theta_1'\tau_{12}) + \theta_1'q_2'\left(\frac{\tau_{12}}{\theta_2' + \theta_1'\tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2'\tau_{21}}\right)\end{aligned}} \tag{6-123}$$

where

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1) \tag{6-124}$$

$$l_2 = \frac{z}{2}(r_2 - q_2) - (r_2 - 1) \tag{6-125}$$

UNIQUAC parameters for many binary systems are given by DECHEMA.

Examples of UNIQUAC

Acetonitrile / benzene

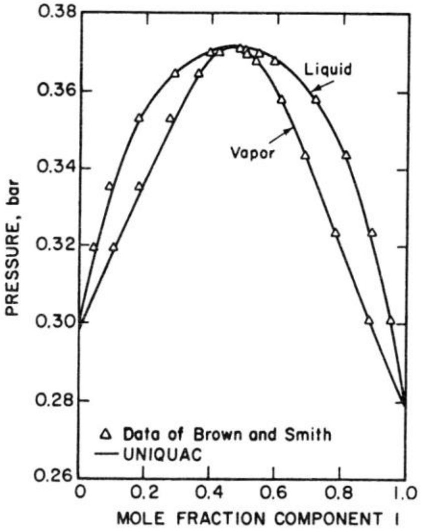


Figure 6-19 Moderate positive deviations from ideality. Vapor-liquid equilibria for the acetonitrile (1)/benzene (2) system at 45°C.

hexane / nitroethane

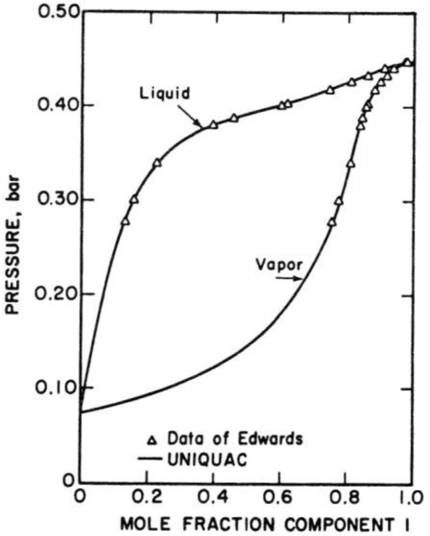


Figure 6-20 Strong positive deviations from ideality. Vapor-liquid equilibria for the *n*-hexane (1)/ nitroethane (2) system at 45°C.

acetone / chloroform

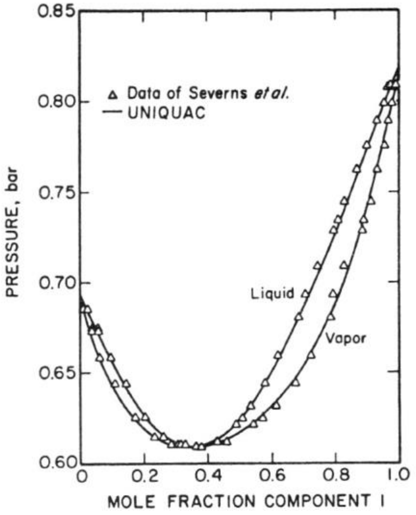


Figure 6-21 Negative deviations from ideality. Vapor-liquid equilibria for the acetone (1)/chloroform (2) system at 50°C.

Methanol / diethyamine

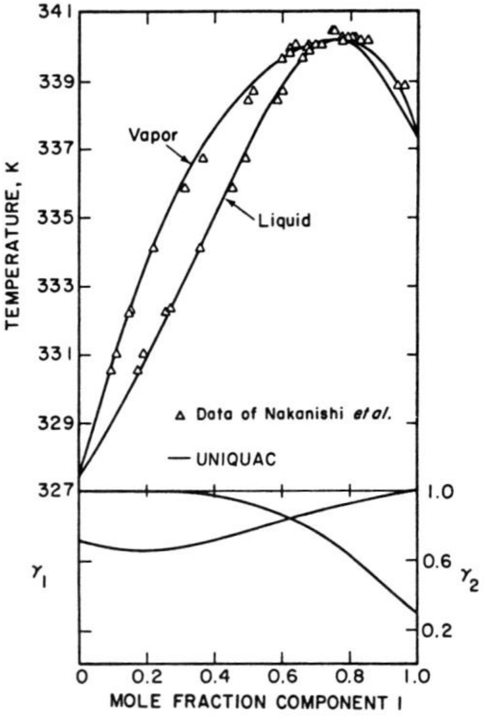


Figure 6-22 Vapor-liquid equilibria for a mixture containing two hydrogen-bonding components. Temperature-composition diagram for the system methanol (1)/diethylamine (2) at 0.973 bar.

Strong negative deviations

UNIQUAC equation reproduces a weak minima in the activity coefficient.

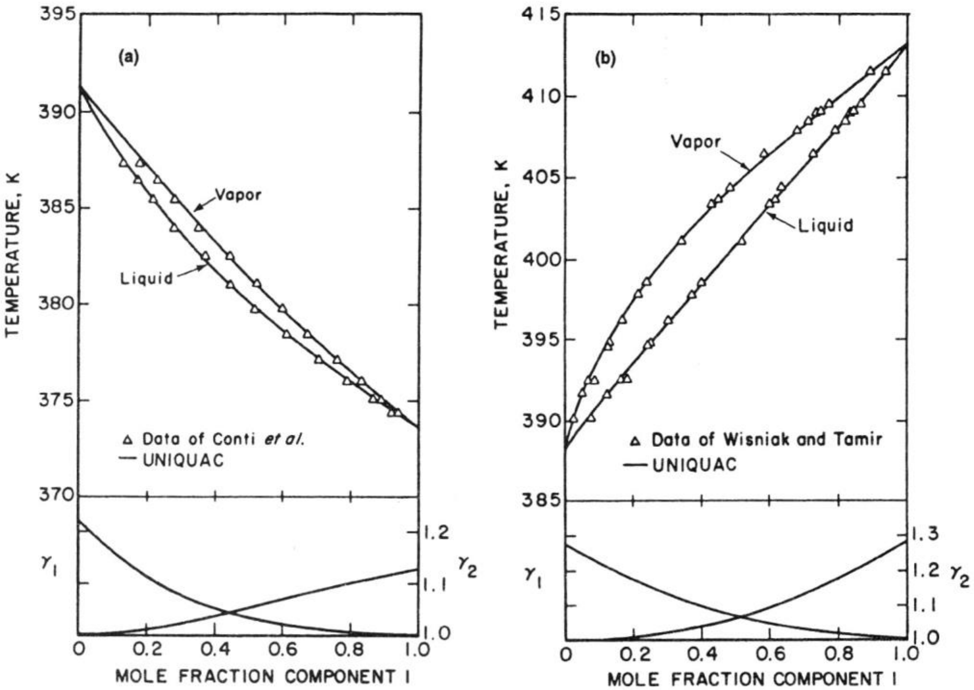
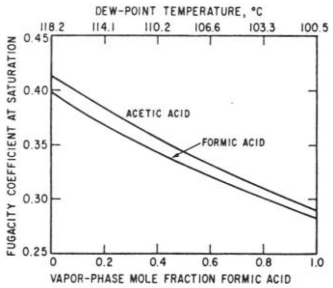


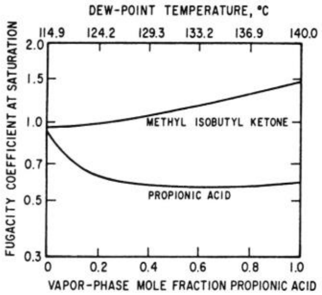
Figure 6-23 Vapor-liquid equilibria for binary systems containing two carboxylic acids or one carboxylic acid and one ketone. Temperature-composition diagrams and activity coefficients at 1.013 bar for the systems: (a) formic acid (1)/acetic acid (2); (b) propionic acid (1)/methyl isobutyl ketone (2).

The interesting feature of these systems is that the activity coefficients show only minor deviations from ideal-solution behavior.

The major contribution to nonideality occurs in the vapor phase.



Fugacity coefficients for saturated mixtures of two ca
ic acid (1)/acetic acid (2).



Fugacity coefficients for saturated mixtures of propionic a
ne (2) at 1 bar.

6.12 Excess Functions and Partial Miscibility

A liquid mixture splits into two separate liquid phases if it can lower its Gibbs energy.

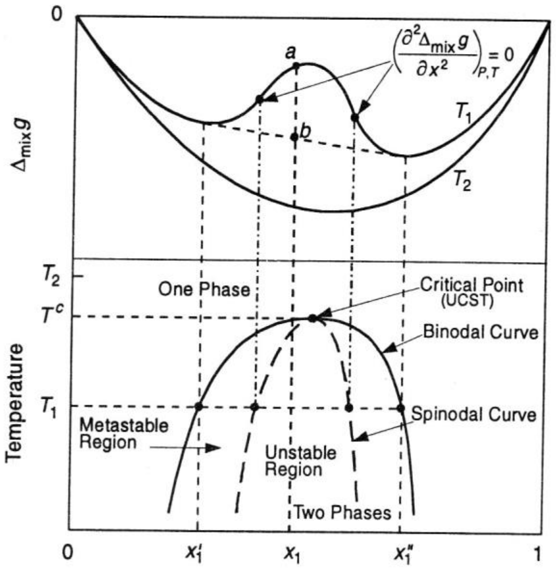


Figure 6-24 Molar Gibbs energy of mixing and *T*-*x* diagram of a mixture at constant pressure: T_1, partially miscible; T_2, totally miscible.

$$\Delta_{\text{mix}} g = g_{\text{mixt}} - (x_1\, g_{\text{pure }1} + x_2\, g_{\text{pure }2})$$

Homogeneous single liquid phase

$$\underset{(\text{at } a)}{g_{\text{mixt}}} = x_1 g_{\text{pure }1} + x_2 g_{\text{pure }2} + \Delta g_a \qquad (6\text{-}126)$$

Separated two liquid phase with overall composition the same as that of the homogeneous phase

$$\underset{(\text{at } b)}{g_{\text{mixt}}} = x_1 g_{\text{pure }1} + x_2 g_{\text{pure }2} + \Delta g_b \qquad (6\text{-}127)$$

As $g_{\text{mixt (at b)}} < g_{\text{mixt (at a)}}$, the liquid mixture splits into two phases each having mole fractions

x_1' and x_1''.

The condition for instability for a binary mixture is

$$\left(\frac{\partial^2 g_{\text{mixt}}}{\partial x^2}\right)_{T,P} < 0 \qquad (6\text{-}128)^{35}$$

equivalently,

$$\left(\frac{\partial^2 \Delta_{\text{mix}} g}{\partial x^2}\right)_{T,P} < 0 \qquad (6\text{-}129)$$

T^c the critical solution temperature (or the consolute temperature).

$T > T^c$ completely miscible

$T < T^c$ partially miscible

Binodal curve, the boundary between the one- and two-phase region

Spinodal curve, the boundary between unstable region and metastable region.

On the spinodal curve $\left(\frac{\partial^2 \Delta_{mix} g}{\partial x^2}\right)_{T,P} = 0$

If the overall mole fraction of the mixture falls within the unstable region, spontaneous demixing occurs.

The excess Gibbs energy of a mixture is

$$g^E \equiv g_{\text{mixt}} - RT(x_1 \ln x_1 + x_2 \ln x_2) - x_1 g_{\text{pure 1}} - x_2 g_{\text{pure 2}} \qquad (6\text{-}130)$$

Substituting into (6-128), the condition for instability becomes

$$\boxed{\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} + RT\left(\frac{1}{x_1}+\frac{1}{x_2}\right) < 0} \qquad (6\text{-}131)$$

For ideal solution, $g^E = 0$, LHS is always greater than zero.
Therefore, an ideal solution is always stable.

Suppose that

$$g^E = Ax_1x_2 \qquad (6\text{-}132)$$

(a large value of A will yield instability)

Then

$$\left(\frac{\partial^2 g^E}{\partial x_1^2}\right)_{T,P} = -2A \qquad (6\text{-}133)$$

Substituting into (6-131)

$$-2A < -RT\left(\frac{1}{x_1}+\frac{1}{x_2}\right) \qquad (6\text{-}134)$$

The condition for instability becomes

$$2A > RT\left(\frac{1}{x_1}+\frac{1}{x_2}\right) = \frac{RT}{x_1x_2} \qquad (6\text{-}135)$$

$1/(x_1x_2)$ has the minimum value of 4 at $x_1 = x_2 = 1/2$ (the most unstable composition)
The smallest value of A for instability is

$$A = 2RT \qquad (6\text{-}136)$$

Therefore, instability occurs whenever

$$\boxed{\frac{A}{RT} > 2} \qquad (6\text{-}137)$$

Incipient instability: the borderline between stability and instability

It corresponds to a critical state.

With the condition that

$$\left(\frac{\partial^2 g_{\text{mixt}}}{\partial x^2}\right)_{T,P} = 0 \qquad (6\text{-}138)$$

either x_1 or x_2

and

$$\left(\frac{\partial^3 g_{\text{mixt}}}{\partial x^3}\right)_{T,P} = 0 \qquad (6\text{-}139)$$

More useful characterization of incipient instability

In terms of activity

$$g_{\text{mixt}} = RT(x_1 \ln a_1 + x_2 \ln a_2) + x_1 g_{\text{pure }1} + x_2 g_{\text{pure }2} \qquad (6\text{-}140)$$

Substituting into (6-138) and (6-139), we obtain for incipient instability

$$\left(\frac{\partial \ln a_1}{\partial x_1}\right)_{T,P} = 0 \qquad (6\text{-}141)$$

use of Gibbs-Duhem eq’n

and

$$\left(\frac{\partial^2 \ln a_1}{\partial x_1^2}\right)_{T,P} = 0 \qquad (6\text{-}142)$$

Graphical illustration of instability

$$\ln a_1 = \ln \gamma_1 + \ln x_1 = \frac{A}{RT} x_2^2 + \ln x_1 \qquad (6\text{-}143)$$

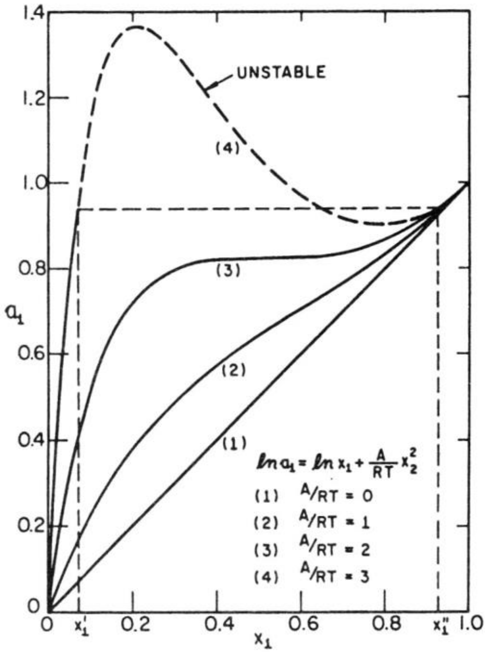


Figure 6-25 Activity of component 1 in a binary liquid solution for different values of *A*/*RT*. Curve (3) shows incipient instability.

When A/RT > 2, two stable liquid phases

When A/RT =2, incipient instability

When A/RT <2, only one stable liquid phase

Water / alcohol

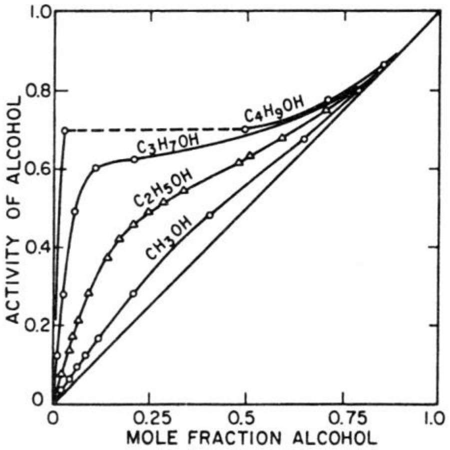


Figure 6-26 Activities of four alcohols in binary aqueous solution at 25°C. Data from Butler (1937).

Methyl and ethyl alcohols are completely miscible with water.

Propyl alcohol shows a point of inflection

Butyl alcohol is partially miscible with water.

6.13 Upper and Lower Consolute Temperatures (critical solution temperatures)

When one-parameter Margules equation is assumed

$$T^c = \frac{A}{2R} \qquad (6\text{-}144)$$

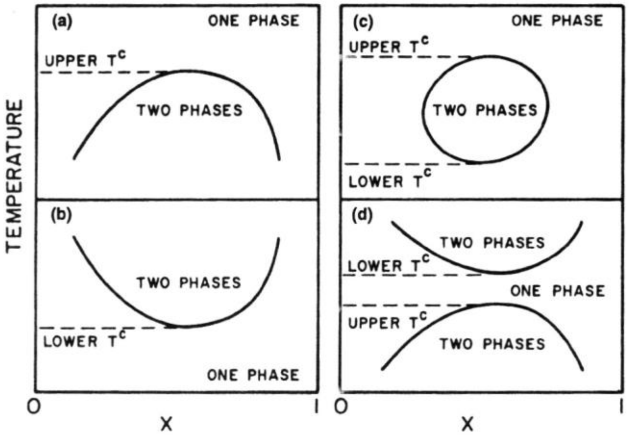


Figure 6-27 Phase stability in four binary liquid mixtures.

UCST (upper critical solution temperature) is more common than LCST (lower critical solution temperature).

LCST observed for mixture containing component that form hydrogen bonds or in polymers solutions.

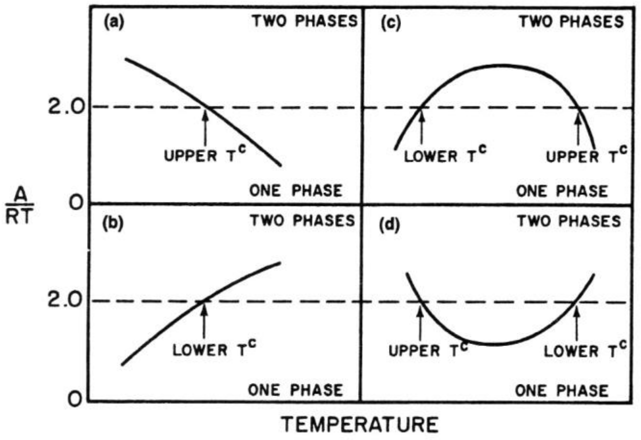


Figure 6-28 Phase stability in four binary liquid mixtures. For each, the excess Gibbs energy is given by a two-suffix Margules equation.

The value of A can be a function of temperature in practice.

When the excess Gibbs energy is given by

$$g^E = Ax_1x_2 \qquad (6\text{-}132)$$

Symmetric

The composition corresponding to T^c is $x_1 = x_2 = 1/2$

If the excess Gibbs energy is given by van Laar's equation

$$g^E = \frac{Ax_1x_2}{\frac{A}{B}x_1 + x_2} \qquad (6\text{-}145)$$

Upon substitution into (6-141) and (6-142), we obtain

$$T^c = \frac{2x_1x_2\frac{A^2}{B}}{R\left(\frac{A}{B}x_1 + x_2\right)^3}$$

$$x_1^c = \frac{\left[\left(\frac{A}{B}\right)^2 + 1 - \frac{A}{B}\right]^{1/2} - \frac{A}{B}}{1 - \frac{A}{B}} \qquad (6\text{-}146)$$

Case of the three-parameter Redlich-Kister series

$$g^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2] \qquad (6\text{-}147)$$

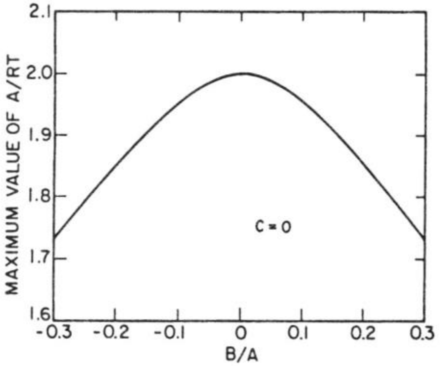


Figure 6-29 Effect of Redlich-Kister coefficient *B* on maximum values of *A/RT* for complete miscibility.

The lower region is for complete miscibility

Values of B tend to increase the tendency for phase separation.

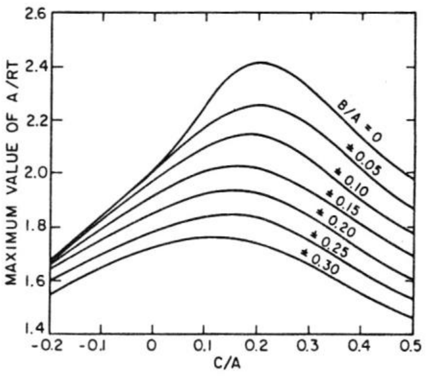


Figure 6-30 Effect of Redlich-Kister coefficient *C* on maximum values of *A/RT* for complete miscibility.

6.14 Excess Functions for Multicomponent Mixtures

Wohl's Equation

$$\begin{aligned}\frac{g^E}{RT(x_1q_1+x_2q_2+x_3q_3)} &= 2a_{12}z_1z_2+2a_{13}z_1z_3+2a_{23}z_2z_3 \\ &+3a_{112}z_1^2z_2+3a_{122}z_1z_2^2+3a_{113}z_1^2z_3 \\ &+3a_{133}z_1z_3^2+3a_{223}z_2^2z_3+3a_{233}z_2z_3^2 \\ &+6a_{123}z_1z_2z_3+\ldots\end{aligned} \tag{6-148}$$

Two-Suffix Margules Equation

Suppose that components are similar and of approximately the same size.
We assume that all q's are the same and that all three (and higher) body terms are neglected.

$$\frac{g^E}{RT} = 2qa_{12}x_1x_2+2qa_{13}x_1x_3+2qa_{23}x_2x_3 \tag{6-149}$$

The activity coefficients are

$$\ln\gamma_1 = A'_{12}x_2^2+A'_{13}x_3^2+(A'_{12}+A'_{13}-A'_{23})x_2x_3 \tag{6-150}$$

$$\ln\gamma_2 = A'_{12}x_1^2+A'_{23}x_3^2+(A'_{12}+A'_{23}-A'_{13})x_1x_3 \tag{6-151}$$

$$\ln\gamma_3 = A'_{13}x_1^2+A'_{23}x_2^2+(A'_{13}+A'_{23}-A'_{12})x_1x_2 \tag{6-152}$$

where $A'_{12}=2qa_{12}$, $A'_{13}=2qa_{13}$, and $A'_{23}=2qa_{23}$

All the constants may be obtained from binary data. (A great advantage!)

Van Laar Equation

We assume that all three (and higher) body terms are neglected.
But we do not assume that all q's are the same.

The molar excess Gibbs energy is given by

$$\frac{g^E}{RT} = \frac{2q_2 a_{12} x_1 x_2 + 2q_3 a_{13} x_1 x_3 + \frac{2q_2 q_3}{q_1} a_{23} x_2 x_3}{x_1 + \frac{q_2}{q_1} x_2 + \frac{q_3}{q_1} x_3} \qquad (6\text{-}153)$$

To simplify notation

$$A'_{12} = 2q_1 a_{12} \qquad A'_{21} = 2q_2 a_{12}$$

$$A'_{13} = 2q_1 a_{13} \qquad A'_{31} = 2q_3 a_{13}$$

$$A'_{23} = 2q_2 a_{23} \qquad A'_{32} = 2q_3 a_{23}$$

The activity coefficient for component 1 is

$$\ln \gamma_1 = \frac{x_2^2 A'_{12}\left(\frac{A'_{21}}{A'_{12}}\right)^2 + x_3^2 A'_{13}\left(\frac{A'_{31}}{A'_{13}}\right)^2 + x_2 x_3 \frac{A'_{21}}{A'_{12}} \frac{A'_{31}}{A'_{13}}\left(A'_{12} + A'_{13} - A'_{32}\right)\left(\frac{A'_{13}}{A'_{31}}\right)}{\left(x_1 + x_2 \frac{A'_{21}}{A'_{12}} + x_3 \frac{A'_{31}}{A'_{13}}\right)^2} \qquad (6\text{-}154)$$

For other components (see text)
All parameters may be obtained from binary data.

Three-Suffix Margules Equation

The molar excess Gibbs energy is

$$\frac{g^E}{RT} = 2qa_{12}x_1x_2 + 2qa_{13}x_1x_3 + 2qa_{23}x_2x_3 + 3qa_{112}x_1^2x_2$$
$$+3qa_{122}x_1x_2^2 + 3qa_{113}x_1^2x_3 + 3qa_{133}x_1x_3^2 + 3qa_{223}x_2^2x_3 \qquad (6\text{-}155)$$
$$+3qa_{233}x_2x_3^2 + 6qa_{123}x_1x_2x_3$$

All the constants may be obtained from binary data except qa_{123}.

To simplify notation

$$A'_{12} = q(2a_{12} + 3a_{122}) \qquad A'_{21} = q(2a_{12} + 3a_{112})$$

$$A'_{13} = q(2a_{13} + 3a_{133}) \qquad A'_{31} = q(2a_{13} + 3a_{113})$$

$$A'_{23} = q(2a_{23} + 3a_{233}) \qquad A'_{32} = q(a_{23} + 3a_{223})$$

$$Q' = \frac{3q}{2}(a_{122} + a_{112} + a_{133} + a_{113} + a_{233} + a_{223} - 4a_{123})$$ containing a ternary parameter

The activity coefficient for component 1 is

$$\ln\gamma_1 = A'_{12}x_2^2(1-2x_1) + 2A'_{21}x_1x_2(1-x_1) + A'_{13}x_3^2(1-2x_1)$$
$$+ 2A'_{31}x_1x_3(1-x_1) - 2A'_{23}x_2x_3^2 - 2A'_{32}x_2^2x_3 \qquad (6\text{-}156)$$
$$+ [\tfrac{1}{2}(A'_{12} + A'_{21} + A'_{13} + A'_{23} + A'_{32}) - Q'](x_2x_3 - 2x_1x_2x_3)$$

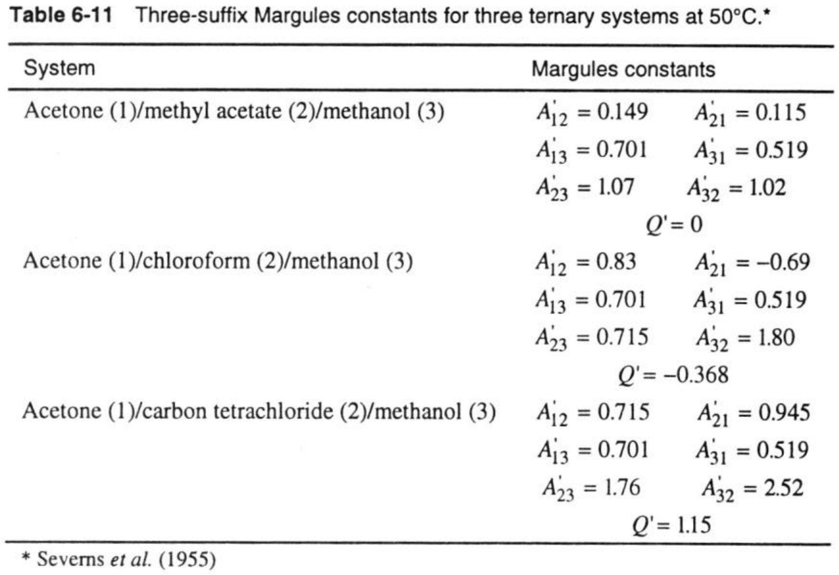


Table 6-11 Three-suffix Margules constants for three ternary systems at 50°C.*

System	Margules constants	
Acetone (1)/methyl acetate (2)/methanol (3)	$A'_{12} = 0.149$	$A'_{21} = 0.115$
	$A'_{13} = 0.701$	$A'_{31} = 0.519$
	$A'_{23} = 1.07$	$A'_{32} = 1.02$
	$Q' = 0$	
Acetone (1)/chloroform (2)/methanol (3)	$A'_{12} = 0.83$	$A'_{21} = -0.69$
	$A'_{13} = 0.701$	$A'_{31} = 0.519$
	$A'_{23} = 0.715$	$A'_{32} = 1.80$
	$Q' = -0.368$	
Acetone (1)/carbon tetrachloride (2)/methanol (3)	$A'_{12} = 0.715$	$A'_{21} = 0.945$
	$A'_{13} = 0.701$	$A'_{31} = 0.519$
	$A'_{23} = 1.76$	$A'_{32} = 2.52$
	$Q' = 1.15$	

* Severns *et al.* (1955)

In system III, the ternary constant Q' cannot be neglect.

6.15 Wilson, NRTL, and UNIQUAC Equations for Multicomponent Mixtures

Wilson Equation

$$\frac{g^E}{RT} = -\sum_{i=1}^{m} x_i \ln\left(\sum_{j=1}^{m} x_j \Lambda_{ij}\right) \tag{6-162}$$

$$\Lambda_{ij} \equiv \frac{v_j}{v_i} \exp\left(-\frac{\lambda_{ij} - \lambda_{ii}}{RT}\right) \tag{6-163}$$

$$\Lambda_{ji} \equiv \frac{v_i}{v_j} \exp\left(-\frac{\lambda_{ji} - \lambda_{jj}}{RT}\right) \tag{6-164}$$

The activity coefficient for component *k* is

$$\boxed{\ln \gamma_k = -\ln\left(\sum_{j=1}^{m} x_j \Lambda_{kj}\right) + 1 - \sum_{i=1}^{m} \frac{x_i \Lambda_{ik}}{\sum_{j=1}^{m} x_j \Lambda_{ij}}} \tag{6-165}$$

All parameters may be obtained from binary data.

Acetone / methyl acetate / methanol

Table 6-13 Parameters for Wilson and van Laar equations for the system acetone (1)/methyl acetate (2)/methanol (3) at 50°C (Orye, 1965a).

Wilson equation	van Laar equation*
$\Lambda_{12} = 0.5781$	$A'_{12} = 0.1839$
$\Lambda_{13} = 0.6917$	$A'_{13} = 0.5965$
$\Lambda_{21} = 1.3654$	$A'_{21} = 0.1106$
$\Lambda_{23} = 0.6370$	$A'_{23} = 0.9446$
$\Lambda_{31} = 0.7681$	$A'_{31} = 0.5677$
$\Lambda_{32} = 0.4871$	$A'_{32} = 1.0560$

* Eq. (6-154)

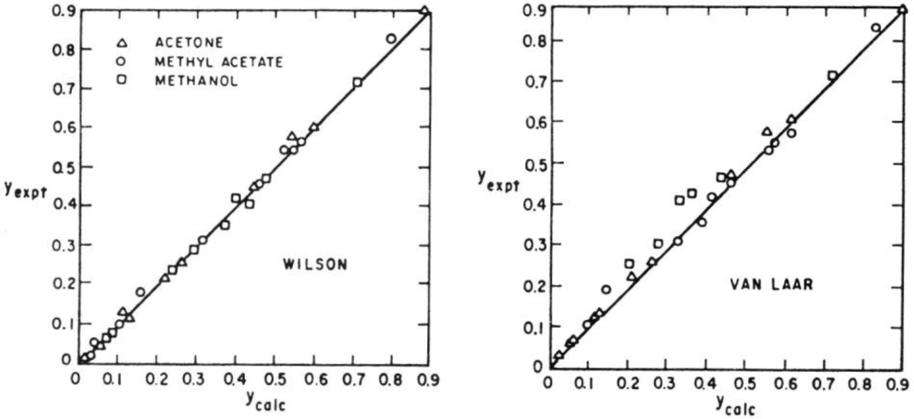


Figure 6-32 Experimental and calculated vapor compositions for the ternary system acetone/methyl acetate/methanol at 50°C. Calculations use only binary data.

Wilson equation gives a better prediction than van Laar equation.

Acetone / methanol / chloroform

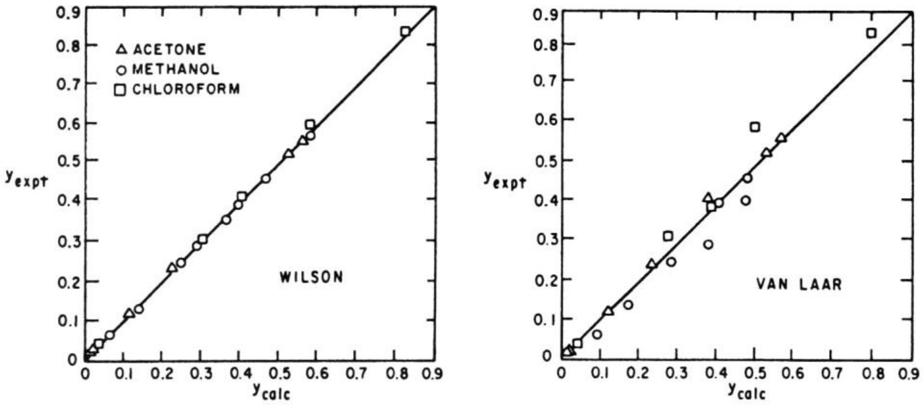


Figure 6-33 Experimental and calculated vapor compositions for the ternary system acetone/methanol/chloroform at 50°C. Calculations use only binary data.

Wilson equation gives a better prediction than van Laar equation.

Three-suffix Margules equation requires a ternary constant.

Ethanol / methylcyclopentane / benzene

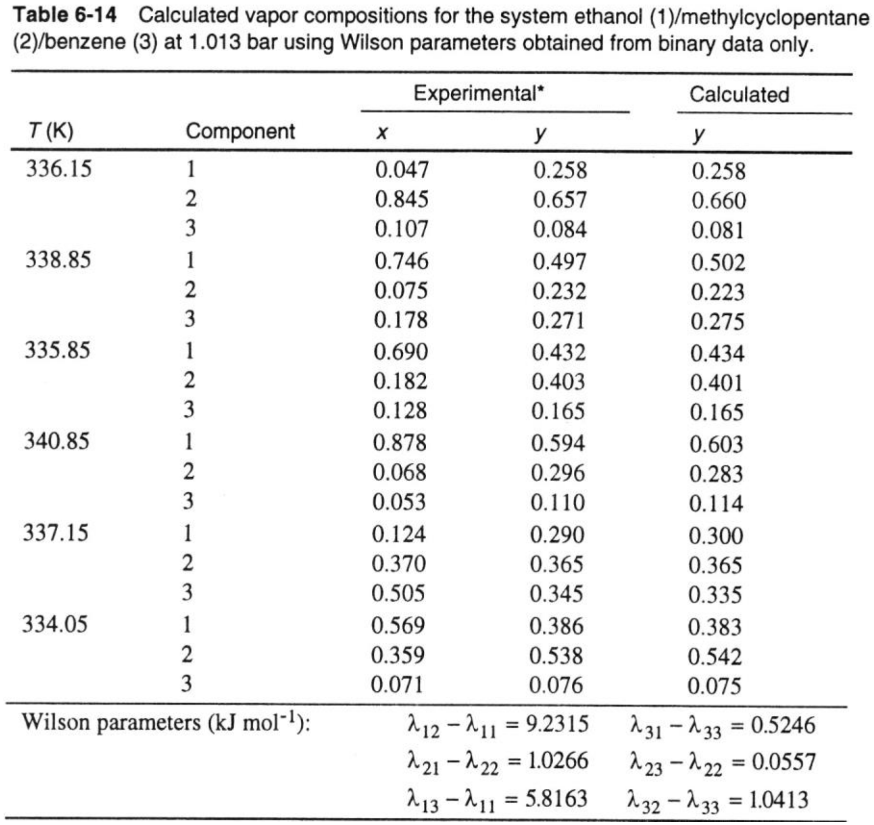


Table 6-14 Calculated vapor compositions for the system ethanol (1)/methylcyclopentane (2)/benzene (3) at 1.013 bar using Wilson parameters obtained from binary data only.

		Experimental*		Calculated
T (K)	Component	*x*	*y*	*y*
336.15	1	0.047	0.258	0.258
	2	0.845	0.657	0.660
	3	0.107	0.084	0.081
338.85	1	0.746	0.497	0.502
	2	0.075	0.232	0.223
	3	0.178	0.271	0.275
335.85	1	0.690	0.432	0.434
	2	0.182	0.403	0.401
	3	0.128	0.165	0.165
340.85	1	0.878	0.594	0.603
	2	0.068	0.296	0.283
	3	0.053	0.110	0.114
337.15	1	0.124	0.290	0.300
	2	0.370	0.365	0.365
	3	0.505	0.345	0.335
334.05	1	0.569	0.386	0.383
	2	0.359	0.538	0.542
	3	0.071	0.076	0.075

Wilson parameters (kJ mol^{-1}):

$\lambda_{12} - \lambda_{11} = 9.2315$ $\quad\lambda_{31} - \lambda_{33} = 0.5246$

$\lambda_{21} - \lambda_{22} = 1.0266$ $\quad\lambda_{23} - \lambda_{22} = 0.0557$

$\lambda_{13} - \lambda_{11} = 5.8163$ $\quad\lambda_{32} - \lambda_{33} = 1.0413$

NRTL Equation

$$\frac{g^E}{RT} = \sum_{i=1}^{m} x_i \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} \tag{6-166}$$

where

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT} \tag{6-167}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \qquad (\alpha_{ji} = \alpha_{ij}) \tag{6-168}$$

The activity coefficient for component *i* is

$$\boxed{\ln \gamma_i = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{j=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_{r=1}^{m} x_r \tau_{rj} G_{rj}}{\sum_{l=1}^{m} G_{lj} x_l} \right)} \tag{6-169}$$

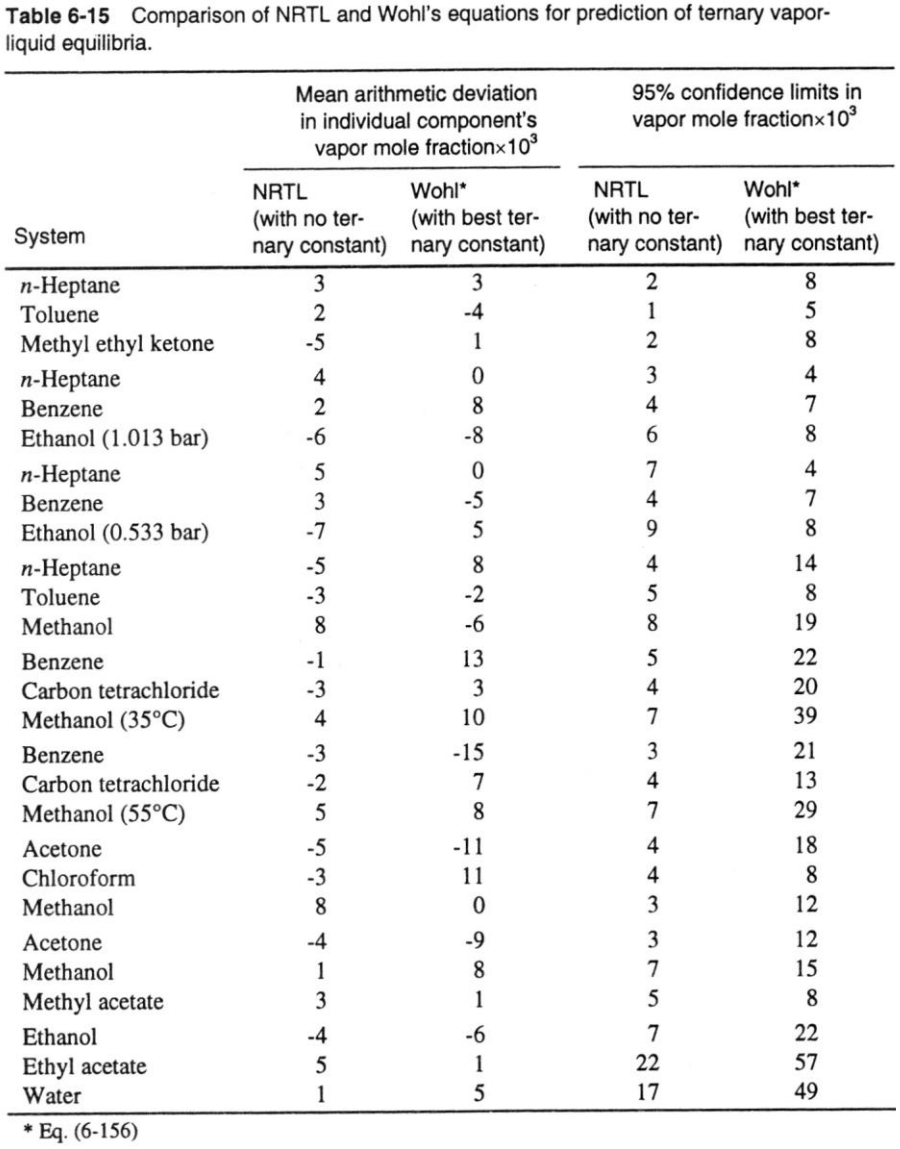


Table 6-15 Comparison of NRTL and Wohl's equations for prediction of ternary vapor-liquid equilibria.

System	Mean arithmetic deviation in individual component's vapor mole fraction×10^3		95% confidence limits in vapor mole fraction×10^3	
	NRTL (with no ternary constant)	Wohl* (with best ternary constant)	NRTL (with no ternary constant)	Wohl* (with best ternary constant)
n-Heptane	3	3	2	8
Toluene	2	-4	1	5
Methyl ethyl ketone	-5	1	2	8
n-Heptane	4	0	3	4
Benzene	2	8	4	7
Ethanol (1.013 bar)	-6	-8	6	8
n-Heptane	5	0	7	4
Benzene	3	-5	4	7
Ethanol (0.533 bar)	-7	5	9	8
n-Heptane	-5	8	4	14
Toluene	-3	-2	5	8
Methanol	8	-6	8	19
Benzene	-1	13	5	22
Carbon tetrachloride	-3	3	4	20
Methanol (35°C)	4	10	7	39
Benzene	-3	-15	3	21
Carbon tetrachloride	-2	7	4	13
Methanol (55°C)	5	8	7	29
Acetone	-5	-11	4	18
Chloroform	-3	11	4	8
Methanol	8	0	3	12
Acetone	-4	-9	3	12
Methanol	1	8	7	15
Methyl acetate	3	1	5	8
Ethanol	-4	-6	7	22
Ethyl acetate	5	1	22	57
Water	1	5	17	49

* Eq. (6-156)

*Whol = Three-suffix Margules equation

NRTL shows a better prediction.

UNIQUAC Equation

The molar excess Gibbs energy is given by the sum of

$$\frac{g^{E\,\text{(combinatorial)}}}{RT} = \sum_{i=1}^{m} x_i \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} \sum_{i=1}^{m} q_i x_i \ln \frac{\theta_i}{\Phi_i^*} \qquad \text{(6-170)}$$

and

$$\frac{g^{E\,\text{(residual)}}}{RT} = -\sum_{i=1}^{m} q'_i x_i \ln\left(\sum_{j=1}^{m} \theta'_j \tau_{ji} \right) \qquad \text{(6-171)}$$

where

$$\Phi_i^* = \frac{r_i x_i}{\sum_{j=1}^{m} r_j x_j} \qquad \theta_i = \frac{q_i x_i}{\sum_{j=1}^{m} q_j x_j} \qquad \theta'_i = \frac{q'_i x_i}{\sum_{j=1}^{m} q'_j x_j}$$

$$\tau_{ij} = \exp\left(-\frac{a_{ij}}{T} \right) \quad \text{and} \quad \tau_{ji} = \exp\left(-\frac{a_{ji}}{T} \right)$$

and $z = 10$

The activity coefficient for component *i* is

$$\begin{aligned}\ln \gamma_i = {} & \ln \frac{\Phi_i^*}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i^*} + l_i - \frac{\Phi_i^*}{x_i} \sum_{j=1}^{m} x_j l_j \\ & - q'_i \ln\left(\sum_{j=1}^{m} \theta'_j \tau_{ji} \right) + q'_i - q'_i \sum_{j=1}^{m} \frac{\theta'_j \tau_{ij}}{\sum_{k=1}^{m} \theta'_k \tau_{kj}} \end{aligned} \qquad \text{(6-172)}$$

where

$$l_j = \frac{z}{2}(r_j - q_j) - (r_j - 1) \qquad \text{(6-173)}$$

Eqn (6-172) requires only pure-component and binary parameters.

Table 6-16 Prediction of multicomponent vapor-liquid equilibrium with UNIQUAC equation using binary data only.*

System†	Number of data points	Pressure (bar); Temperature (°C)	Deviation in temperature or percent deviation in pressure Avg. (max)	Deviation in vapor composition (mol%) Avg. (max.)
MCP		1.013		0.51 (-3.03)
Ethanol	48	60-71	0.25 (0.31)°C	0.55 (2.99)
Benzene				0.35 (-1.25)
Acetic acid		1.013		1.00 (-2.08)
Formic acid	40	102-110	0.55 (-1.80)°C	1.60 (3.77)
Water				2.18 (-5.36)
Acetone		1.016		1.22 (3.24)
Acetonitrile	30	63-92	1.13 (-3.67)°C	1.27 (-3.45)
Water				1.53 (-4.68)
Methanol		0.8866-0.9559	0.11 (-0.27)%	0.44 (0.99)
CTC	8	55		0.39 (-0.89)
Benzene				0.09 (017)
MEK		1.013		0.79 (2.00)
n-Heptane	39	77-103	0.17 (-0.63)°C	0.52 (-1.31)
Toluene				0.38 (-1.18)
Chloroform		0.3493-0.6679		
Ethanol	92	50	1.57 (-3.30)%	‡
n-Heptane				
Chloroform		0.6173-0.8599		0.86 (1.03)
Acetone	29	50	1.10 (-3.12)%	0.77 (2.68)
Methanol				0.81 (1.03)
Chloroform		1.013		0.74 (2.06)
Methanol	72	56-72	0.36 (1.77)°C	1.11 (2.40)
Ethyl acetate				0.80 (2.47)
n-Hexane				0.31(0.60)
MCP	10	1.013		0.44 (0.95)
Ethanol		60-65	0.38 (-0.45)°C	0.55 (-1.13)
Benzene				0.44 (0.96)

UNIQUAC can be used with confidence to predict VLE of typical multicomponent systems of nonelectrolytes with reliable binary parameters.

However, it is often not possible for NRTL and UNIQUAC equation to predict multicomponent liquid-liquid equilibria using only binary data.