CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)

09.MODIFIED RAOULT’S LAW: ACTIVITY COEFFICIENTS

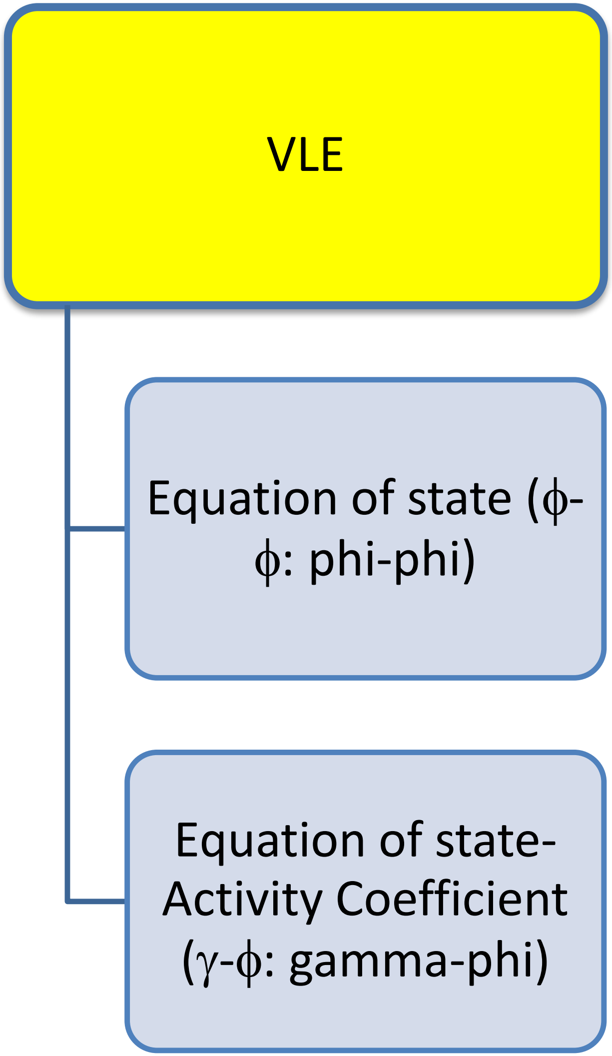
ALI KH. AL-MATAR (aalmatar@ju.edu.jo)

Chemical Engineering Department
University of Jordan
Amman 11942, Jordan

Outline

- General Approaches to VLE
- Assumptions in Raoult's Law
- Assumptions in Modified Raoult's Law
- Limitations and Exceptions
- Approaches to Activity Coefficient
- Definition of Activity Coefficients
- Gibbs-Duhem (G-D) Equation for γ
- One-Constant (Two-Suffix) Margules Equation
- van Laar Activity Coefficient Model
- VLE Experimental Data

General Approaches to VLE



VLE

Isofugacity condition: fugacity of each component in all phases is the same at equilibrium

$$f_i^L(T,P,\mathbf{x}) = f_i^V(T,P,\mathbf{y})$$

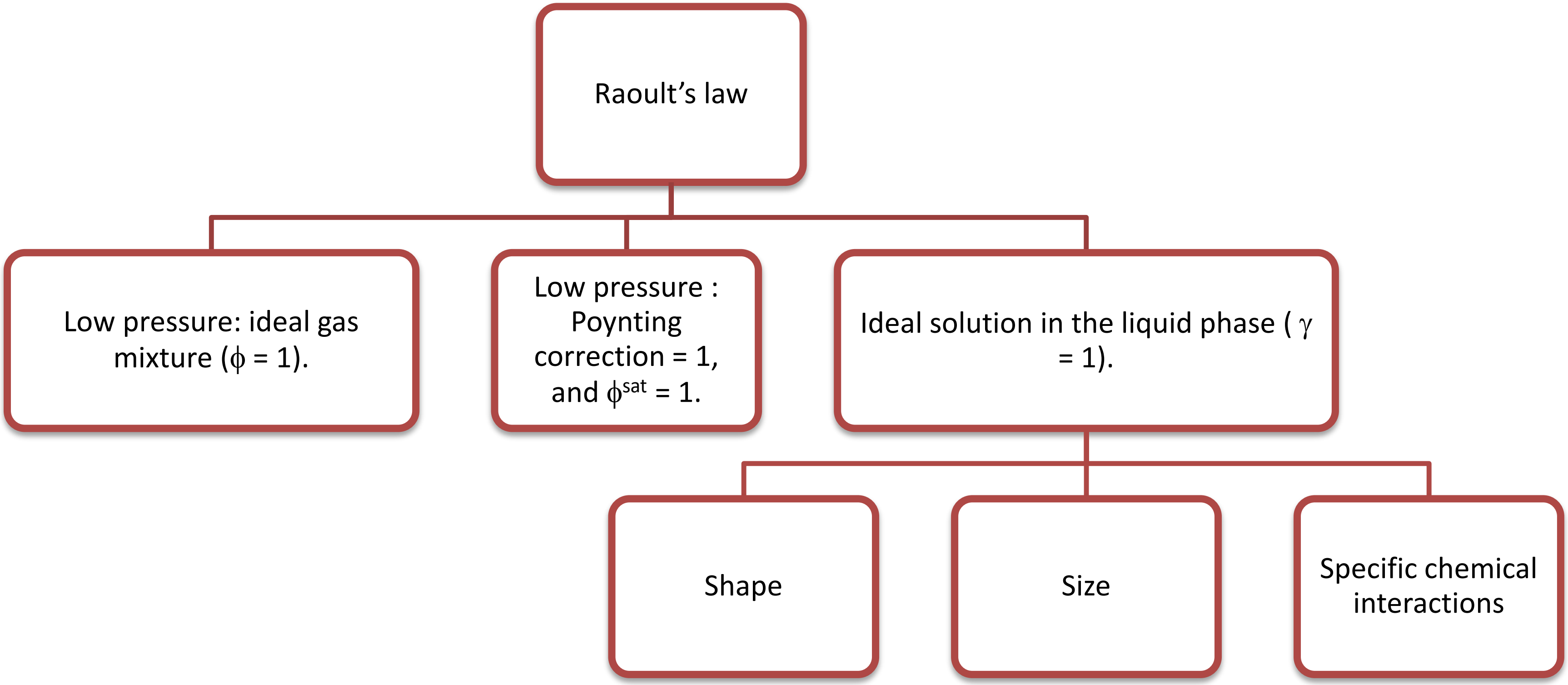
Equation of state (ϕ-ϕ: phi-phi)

$$x_i P \phi_i^L(T,P,\mathbf{x}) = y_i P \phi_i^V(T,P,\mathbf{y})$$

Equation of state-Activity Coefficient (γ-ϕ: gamma-phi)

$$x_i \gamma_i(T,P,\mathbf{x}) \phi_i^{\mathrm{L,sat}}(T,P_i^{\mathrm{sat}}) P_i^{\mathrm{sat}} \exp\left[\frac{v_i(P-P_i^{\mathrm{sat}})}{RT}\right] = y_i P \phi_i^V(T,P,\mathbf{y})$$

Assumptions in Raoult's Law

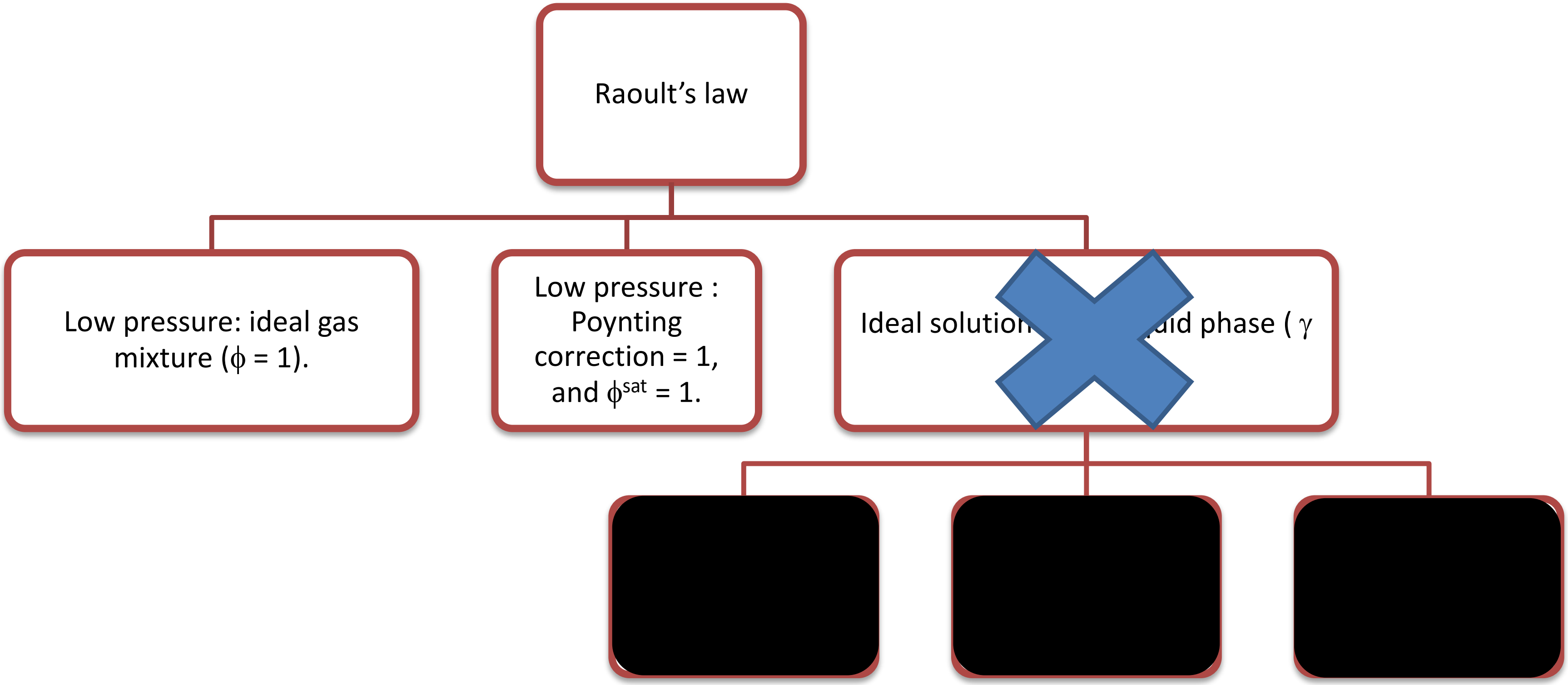


- Raoult's law
  - Low pressure: ideal gas mixture ($\phi = 1$).
  - Low pressure : Poynting correction = 1, and $\phi^{sat} = 1$.
  - Ideal solution in the liquid phase (γ = 1).
    - Shape
    - Size
    - Specific chemical interactions

$$x_i \gamma_i (T, P, \mathbf{x}) \phi_i^{\mathrm{L,sat}} (T, P_i^{\mathrm{sat}}) P_i^{\mathrm{sat}} \exp\left[\frac{v_i (P - P_i^{\mathrm{sat}})}{RT}\right] = y_i P \phi_i^V (T, P, \mathbf{y})$$

$$\rightarrow x_i P_i^{\mathrm{sat}} = y_i P$$

Assumptions in Modified Raoult's Law



Raoult's law

Low pressure: ideal gas mixture (ϕ = 1).

Low pressure : Poynting correction = 1, and ϕ^{sat} = 1.

Ideal solution uid phase (γ

[redacted]

[redacted]

[redacted]

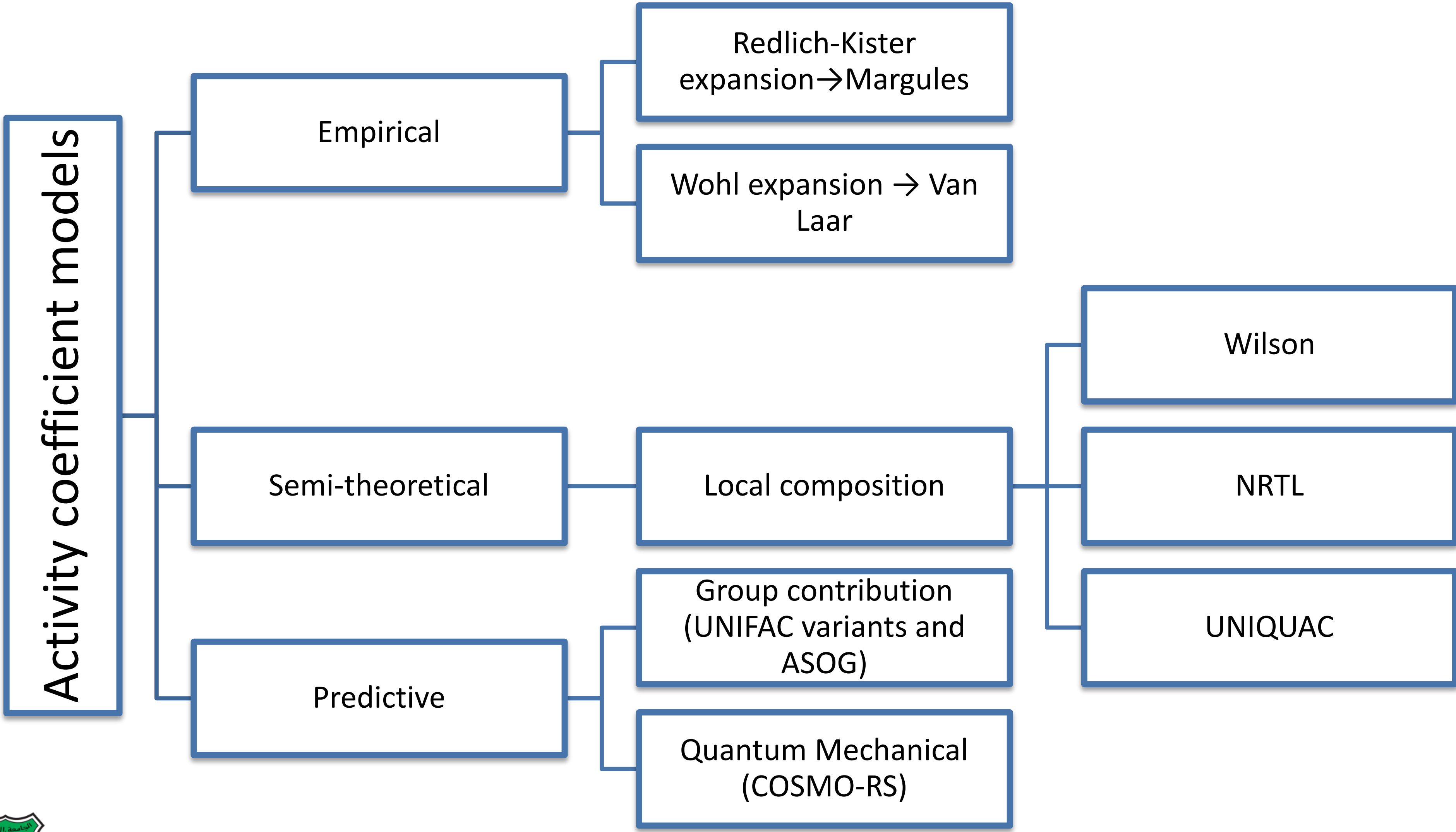
$$x_i \gamma_i (T, P, \mathbf{x}) \phi_i^{\mathrm{L,sat}} (T, P_i^{\mathrm{sat}}) P_i^{\mathrm{sat}} \exp\left[\frac{v_i (P - P_i^{\mathrm{sat}})}{RT}\right] = y_i P \phi_i^V (T, P, \mathbf{y})$$

$$x_i \gamma_i P_i^{\mathrm{sat}} = y_i P$$

Limitations and Exceptions

- Mixtures of strongly polar and/or hydrogen-bonding components.
- Mixtures of associating components e.g., acetic acid or hydrogen fluoride.
- Mixtures at cryogenic temperatures since gas phase corrections are usually significant.

Approaches to Activity Coefficient



Activity coefficient models

Empirical

Redlich-Kister expansion→Margules

Wohl expansion → Van Laar

Semi-theoretical

Local composition

Wilson

NRTL

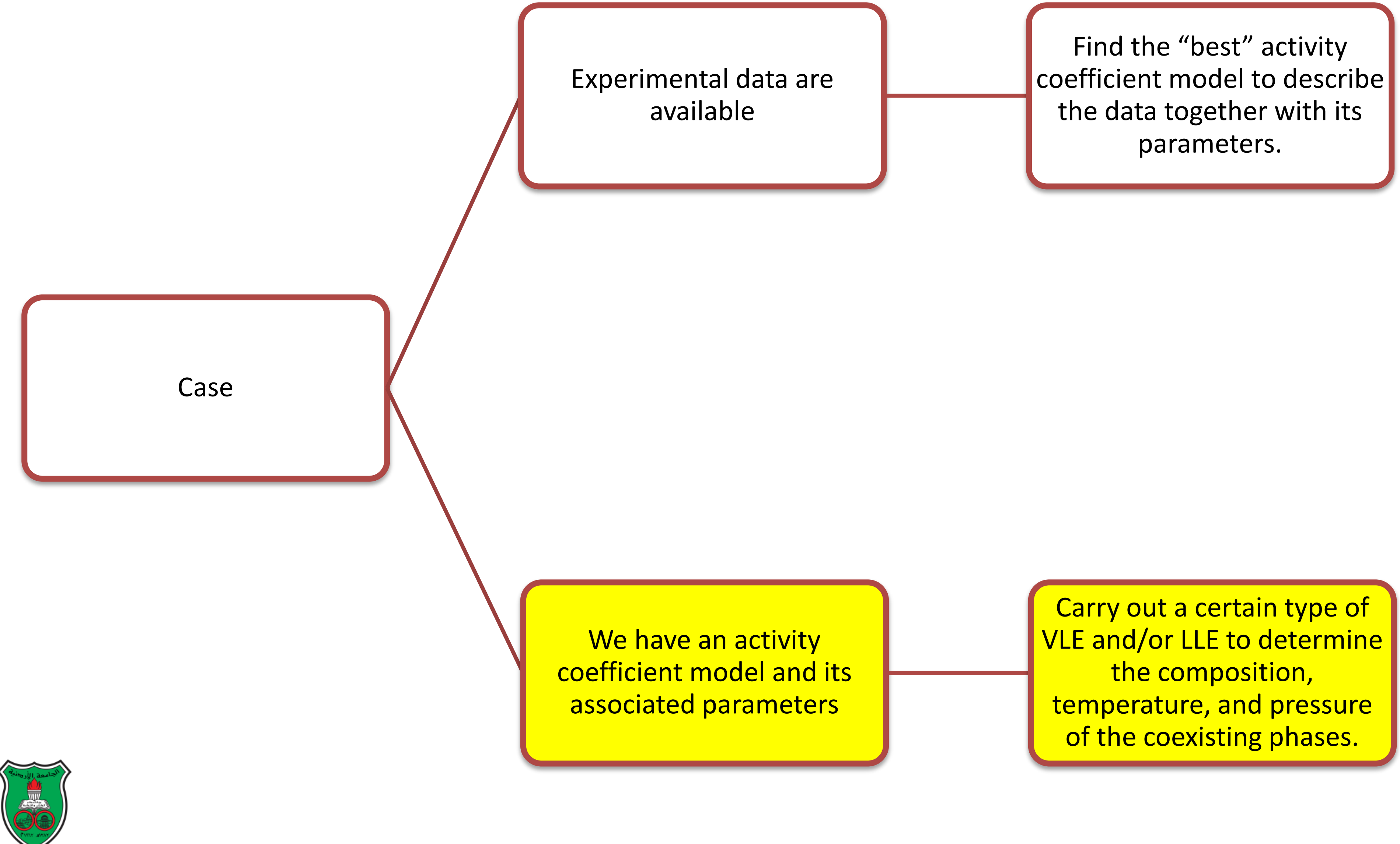
UNIQUAC

Predictive

Group contribution (UNIFAC variants and ASOG)

Quantum Mechanical (COSMO-RS)

Situations



Case

Experimental data are available

Find the "best" activity coefficient model to describe the data together with its parameters.

We have an activity coefficient model and its associated parameters

Carry out a certain type of VLE and/or LLE to determine the composition, temperature, and pressure of the coexisting phases.

Definition of Activity Coefficients

- Activity coefficient is defined as

$$RT\ln\gamma_i(T,P,\mathbf{x}) = \bar{g}_i^{\mathrm{ex}} = \left(\frac{\partial N g^{\mathrm{ex}}}{\partial N_i}\right)_{T,P,N_{j\neq i}}$$

- Unity for an ideal mixture (IM).
- Nonideal (real) mixtures given by:

$$\gamma_i(T,P,\mathbf{x}) = \exp\left(\frac{\bar{g}_i^{\mathrm{ex}}}{RT}\right) = \exp\left(\frac{1}{RT}\int_0^P \left[\bar{v}_i(T,P,\mathbf{x}) - v_i(T,P)\right]dP\right)$$

- Total excess Gibbs energy given by:

$$\frac{g^{\mathrm{ex}}}{RT} = \sum_{i=1}^{C} x_i \ln\gamma_i$$

Behavior of g^{ex} for Binary Mixtures

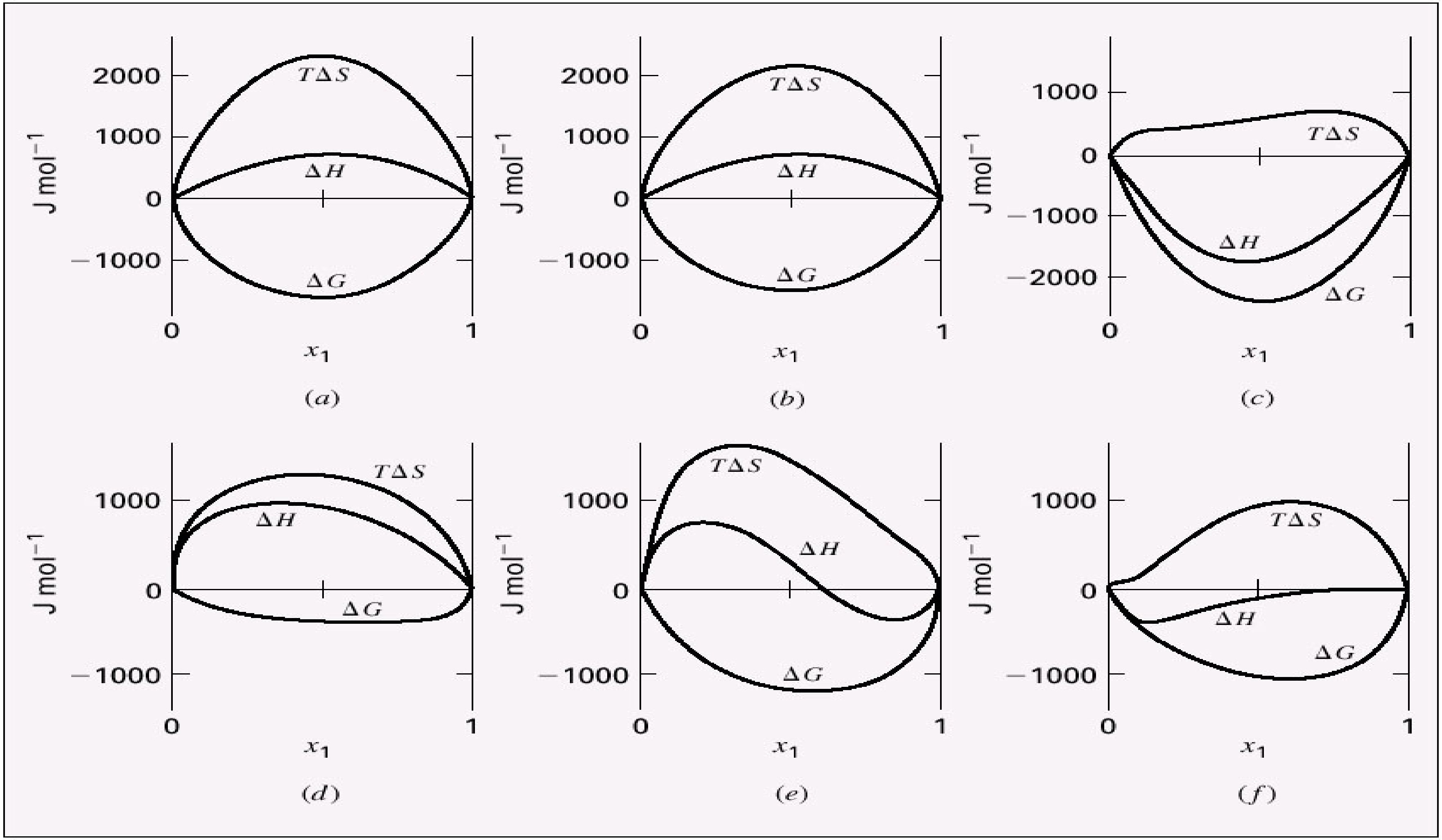


Figure 12.13: Property changes of mixing at 50°C for six binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

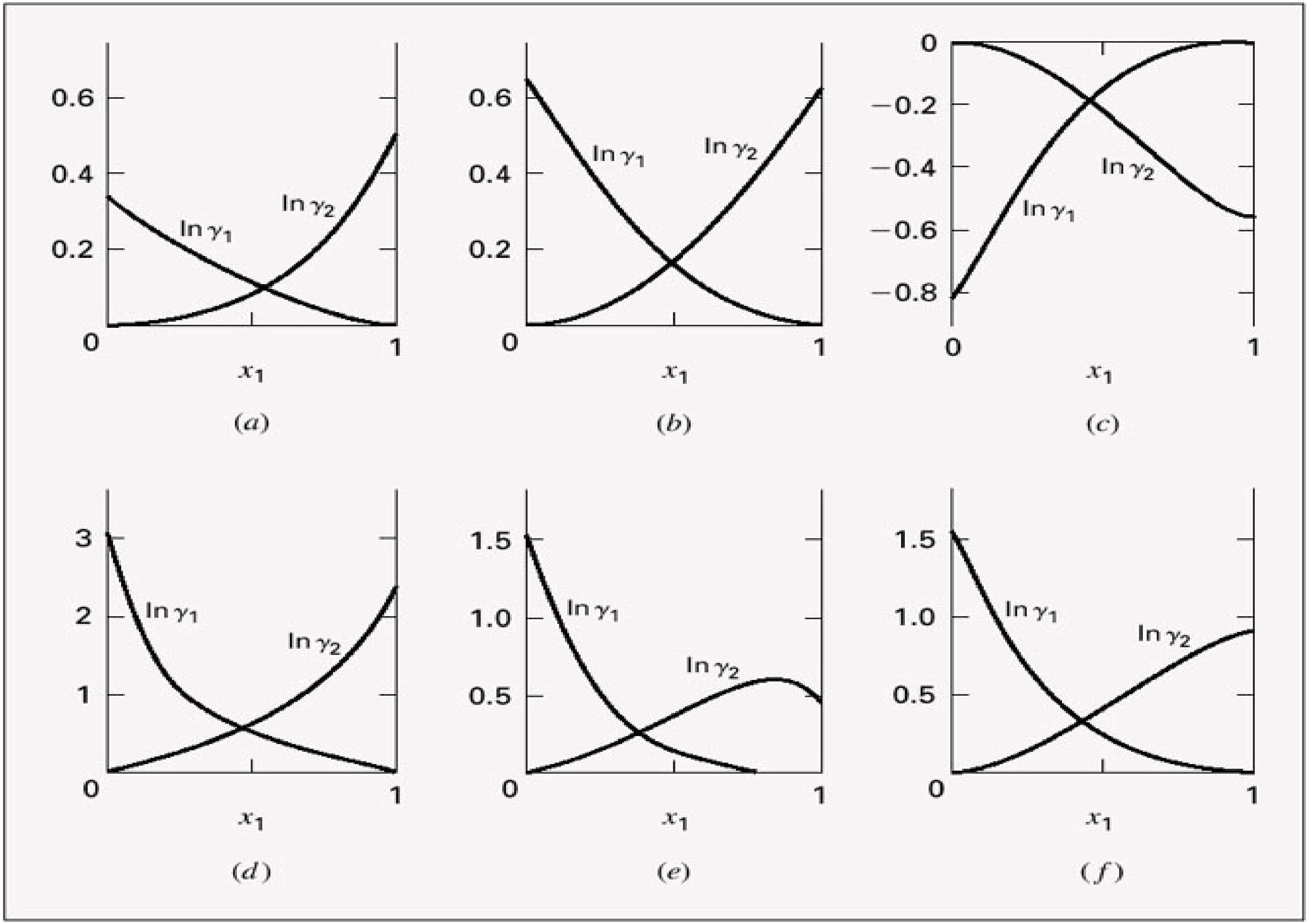


Figure 12.9: Logarithms of the activity coefficients at 50°C for six binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2).

Gibbs-Duhem (G-D) Equation for γ

- Gibbs-Duhem equation for excess properties

$$s^{\mathrm{ex}}dT - v^{\mathrm{ex}}dP + \sum_{i=1}^{C} x_i d\overline{g}_i^{\mathrm{ex}} = 0$$

- Use the definition of activity coefficients to obtain, at constant *T* and *P*,

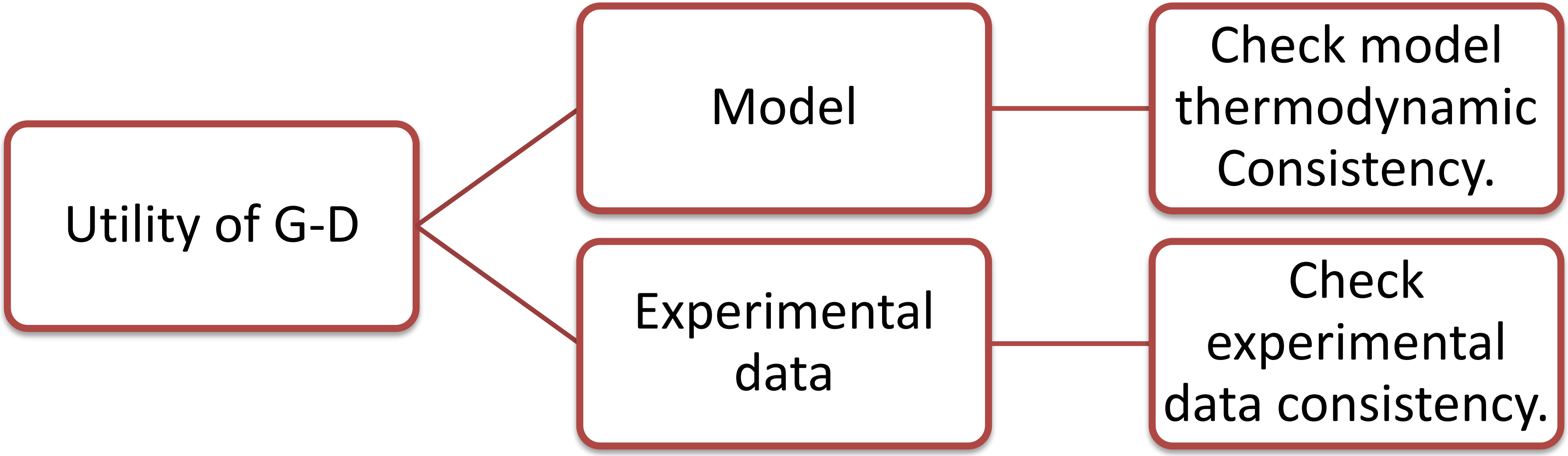
General G-D

$$\sum_{i=1}^{C} x_i d \ln \gamma_i \Big|_{T,P} = 0$$

G-D for Binary system

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} = 0$$

Why is G-D Equation Important?



Utility of G-D

Model

Check model thermodynamic Consistency.

Experimental data

Check experimental data consistency.

Self-read section 11-9 in Dahm 2014 and check the example there-within.

Model Consistency Using G-D Equation

- A model is proposed for the excess Gibbs energy as $\frac{g^{\text{ex}}}{RT}=Ax_1x_2$. Is this model thermodynamically consistent for a binary system?

$$RT\ \ln\gamma_1=\bar{g}_1^{\text{ex}}=\left(\frac{\partial Ng^{\text{ex}}}{\partial N_1}\right)_{T,P,N_2}=\left(\frac{\partial ANx_1x_2}{\partial N_1}\right)_{T,P,N_2}=\left(\frac{\partial A(N)\left(N_1N_2/N\right)^2}{\partial N_1}\right)_{T,P,N_2}$$

$$=A\left(\frac{\partial N_1N_2/\left(N_1+N_2\right)}{\partial N_1}\right)_{T,P,N_2}=A\left(\frac{N_2\left(N_1+N_2\right)-N_1N_2}{\left(N_1+N_2\right)^2}\right)=A\left(\frac{N_2\left(N_2\right)}{\left(N_1+N_2\right)^2}\right)=Ax_2^2$$

$$RT\ \ln\gamma_2=\bar{g}_2^{\text{ex}}=\left(\frac{\partial Ng^{\text{ex}}}{\partial N_2}\right)_{T,P,N_1}=A\left(\frac{\partial N_1N_2/\left(N_1+N_2\right)}{\partial N_2}\right)_{T,P,N_1}=A\left(\frac{N_1^2}{\left(N_1+N_2\right)^2}\right)=Ax_1^2$$

$$x_1\left(\frac{\partial\ln\gamma_1}{\partial x_1}\right)_{T,P}+x_2\left(\frac{\partial\ln\gamma_2}{\partial x_1}\right)_{T,P}=Ax_1\left(\frac{\partial x_2^2}{\partial x_1}\right)_{T,P}+Ax_2\left(\frac{\partial x_1^2}{\partial x_1}\right)_{T,P}=0?$$

$$-2x_1\left(1-x_1\right)+2x_2x_1=2x_1x_2-2x_1x_2=0$$

Consistent!

Quiz

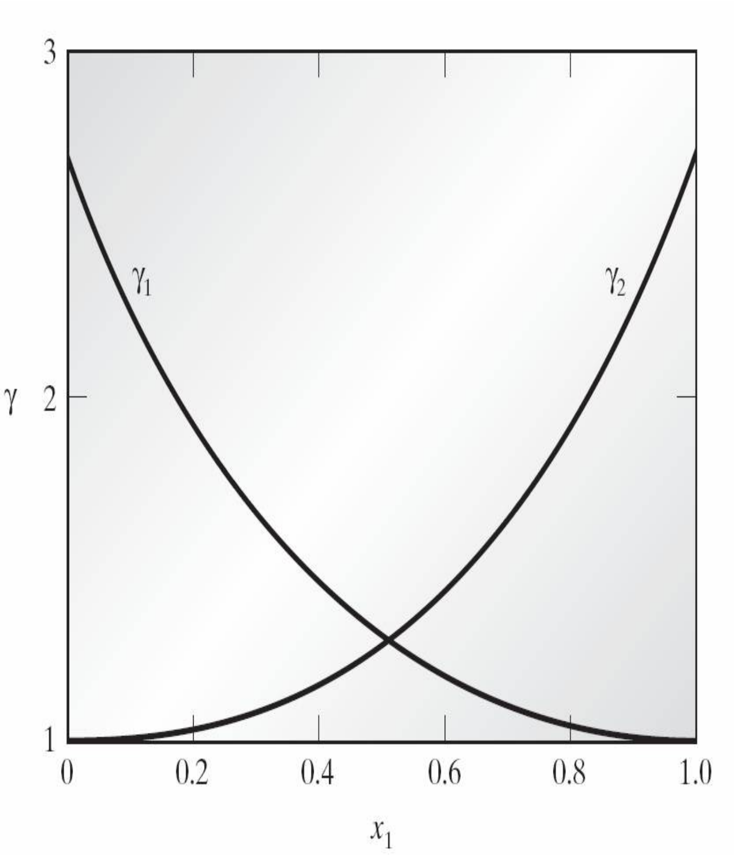
- Check the consistency of the following suggested model for the activity coefficients: $\ln\gamma_1 = Ax_1^2, \quad \ln\gamma_2 = Ax_2^2$

One-Constant (Two-Suffix) Margules Equation

- Probably, the simplest model for γ

$$\frac{g^{\text{ex}}}{RT} = Ax_1x_2$$

$$\ln\gamma_1 = Ax_2^2, \quad \ln\gamma_2 = Ax_1^2$$



  - The two species activity coefficients are mirror images of each other i.e. symmetrical.
  - In the limit of concentration approaching pure component; γ approaches unity.

$$\lim_{x_i \to 1} \gamma_i \to 1$$

- Parameter *A* can either be positive or negative
    - A > 0 leads to $\gamma > 1$; positive deviations from Raoult's law.
    - *A* < 0 leads to $\gamma < 1$; negative deviations from Raoult's law.
- Parameter *A* can be obtained from one experimental point.
- Parameter *A* is related to infinite dilution activity coefficient as:

$$\ln \gamma_1^{\infty} = \ln \gamma_2^{\infty} = A$$

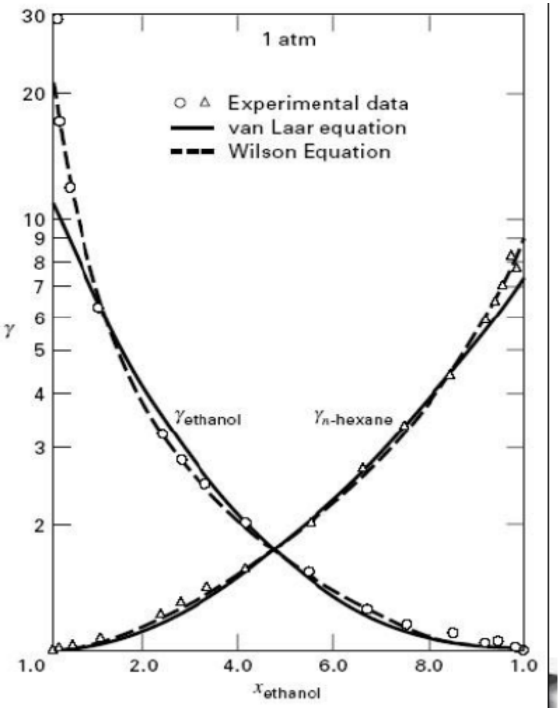
- satisfactory model for liquid mixtures containing constituents of similar size, shape, and chemical nature.
- Resort to more complicated models for dissimilar (asymmetrical) mixtures.

van Laar Activity Coefficient Model

- Used often to correlate vapor-liquid equilibrium (VLE) data.

$$\frac{g^{ex}}{RT}=x_1x_2\frac{AB}{Ax_1+Bx_2} \Rightarrow \ln\gamma_1=\frac{A}{\left[1+\frac{A}{B}\frac{x_1}{x_2}\right]^2},\quad \ln\gamma_2=\frac{B}{\left[1+\frac{B}{A}\frac{x_2}{x_1}\right]^2}$$

- Used for asymmetrical mixtures i.e., the activity coefficient of the first component is not a mirror image of the second component.
  - Close to symmetrical mixtures yields approximately the same values of A and B.
  - For higher asymmetry the values of A and B depart from each other.
  - General case for the two-suffix Margules equation when A = B.
- The parameters A and B are tabulated in many references e.g., Sandler, Perry’s and properties of gases and liquids.



gure 2.16 Liquid-phase activity coefficients for ethanol/hexane system.

van Laar Activity Coefficient Model

- The values of the parameters can be obtained from a single measurement.

$$A = \left[1 + \frac{x_2}{x_1}\frac{\ln\gamma_1}{\ln\gamma_2}\right]^2 \ln\gamma_1, \quad B = \left[1 + \frac{x_1}{x_2}\frac{\ln\gamma_1}{\ln\gamma_2}\right]^2 \ln\gamma_2$$

- Infinite dilution activity coefficients are given by:

$$\ln\gamma_1^\infty = A, \quad \ln\gamma_2^\infty = B$$

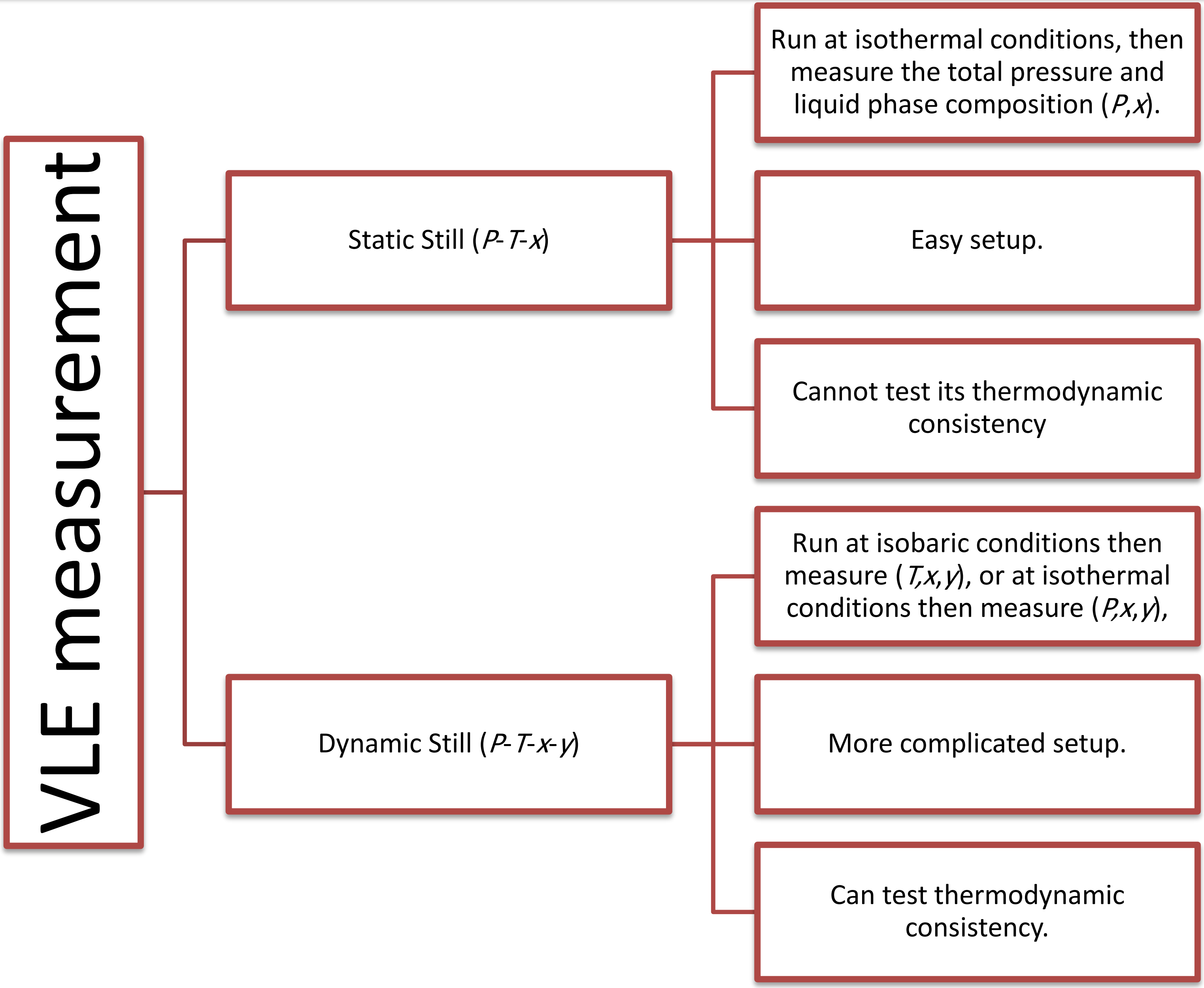
- Can fit systems with either positive or negative deviations from Raoult’s law.
  - Important in case of mixtures of self-associated polar molecules with nonpolar molecules such as hydrocarbons.
- Do not use for systems that exhibit minima or maxima
  - In the dilute region the predictions are poor.
  - May erroneously predict formation of two liquid phases when activity coefficients are larger than 7

Table 9.5-1 The van Laar Constants for Some Binary Mixtures

Component 1–Component 2	Temperature Range (°C)	α	β
Acetaldehyde–water	19.8–100	1.59	1.80
Acetone–benzene	56.1–80.1	0.405	0.405
Acetone–methanol	56.1–64.6	0.58	0.56
Acetone–water	25	1.89	1.66
	56.1–100	2.05	1.50
Benzene–isopropanol	71.9–82.3	1.36	1.95
Carbon disulfide–acetone	39.5–56.1	1.28	1.79
Carbon disulfide–Carbon tetrachloride	46.3–76.7	0.23	0.16
Carbon tetrachloride–benzene	76.4–80.2	0.12	0.11
Ethanol–benzene	67.0–80.1	1.946	1.610
Ethanol–cyclohexane	66.3–80.8	2.102	1.729
Ethanol–toluene	76.4–110.7	1.757	1.757
Ethanol–water	25	1.54	0.97
Ethyl acetate–benzene	71.1–80.2	1.15	0.92
Ethyl acetate–ethanol	71.7–78.3	0.896	0.896
Ethyl acetate–toluene	77.2–110.7	0.09	0.58
Ethyl ether–acetone	34.6–56.1	0.741	0.741
Ethyl ether–ethanol	34.6–78.3	0.97	1.27
n-Hexane–ethanol	59.3–78.3	1.57	2.58
Isobutane–furfural	37.8	2.62	3.02
	51.7	2.51	2.83
Isopropanol–water	82.3–100	2.40	1.13
Methanol–benzene	55.5–64.6	0.56	0.56
Methanol–ethyl acetate	62.1–77.1	1.16	1.16
Methanol–water	25	0.58	0.46
	64.6–100	0.83	0.51
Methyl acetate–methanol	53.7–64.6	1.06	1.06
Methyl acetate–water	57.0–100	2.99	1.89
n-Propanol–water	88.0–100	2.53	1.13
Water–phenol	100–181	0.83	3.22

Source: This table is an adaptation of one given in J. H. Perry, ed., *Chemical Engineers' Handbook,* 4th ed., McGraw-Hill, New York (1963), p. 13–7.

VLE Experimental Data



VLE measurement

Static Still (P-T-x)

Run at isothermal conditions, then measure the total pressure and liquid phase composition (P,x).

Easy setup.

Cannot test its thermodynamic consistency

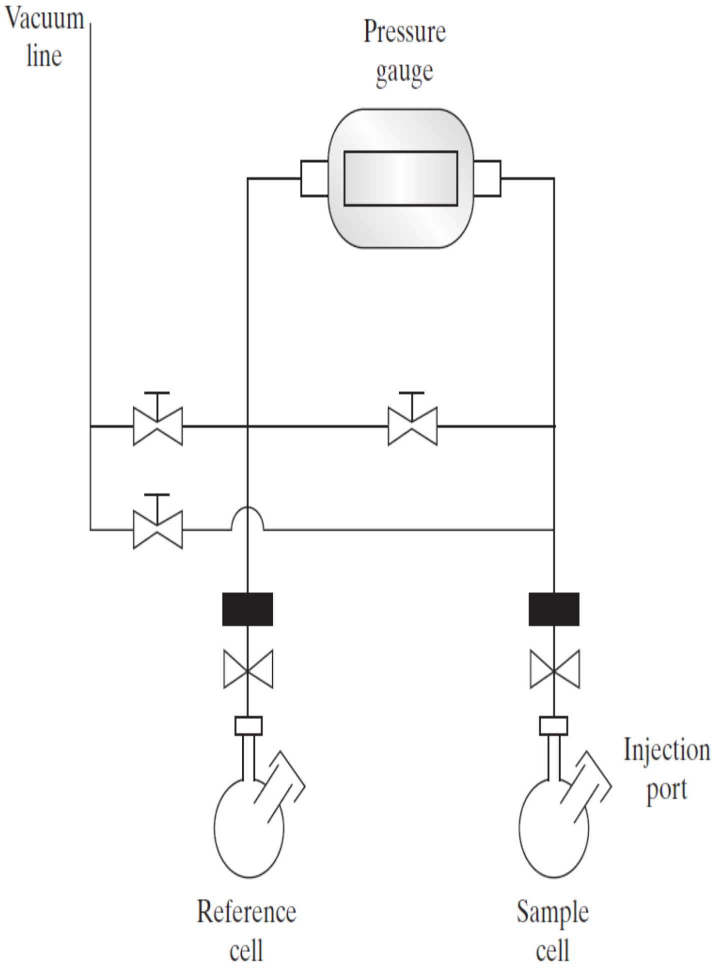
Dynamic Still (P-T-x-y)

Run at isobaric conditions then measure (T,x,y), or at isothermal conditions then measure (P,x,y),

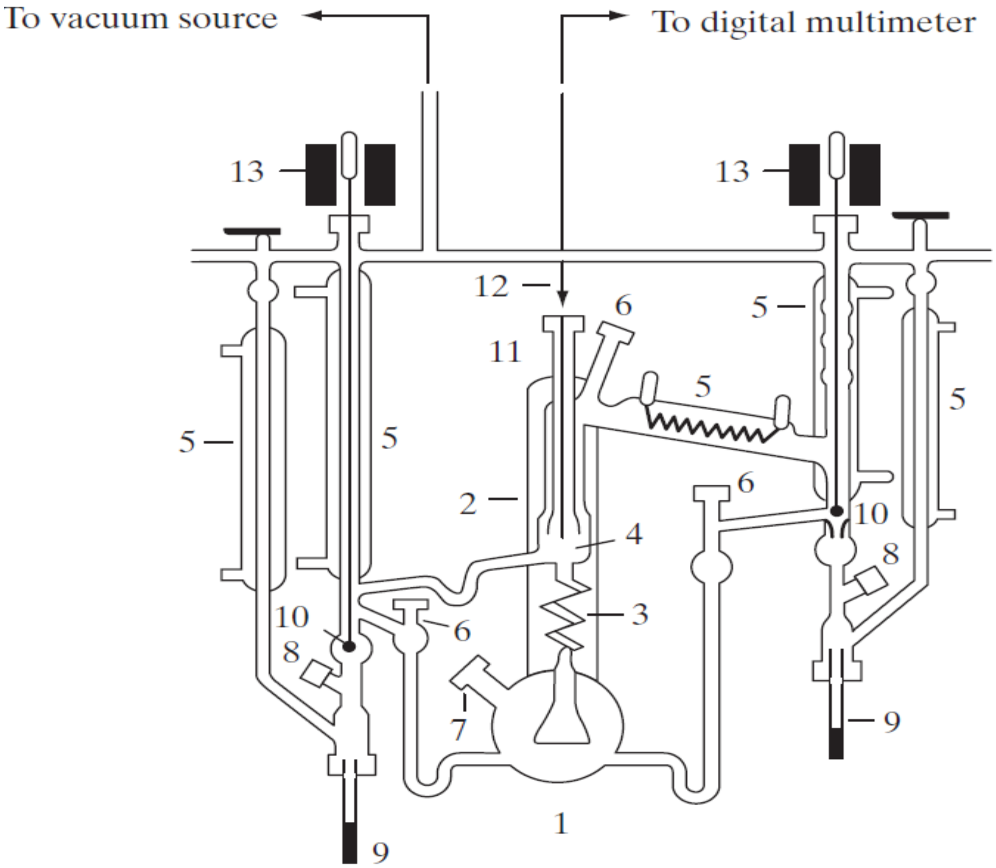
More complicated setup.

Can test thermodynamic consistency.

VLE Experimental Data



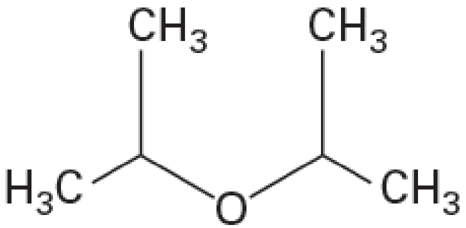
Static still



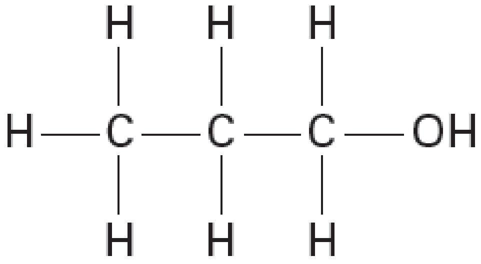
Schematic diagram of a dynamic still. In this figure, 1 is the boiling flask, 2 is a vacuum jacket so there is no heat loss from the equilibrium chamber, 3 is a device that forces the boiling vapor-liquid mixture into the equilibrium cell 4, items 5 are condensers to insure that no vapor is lost, items 6 are injection ports so that composition changes can be made, 7 is a thermometer port for the bath, items 8 and 10 are valves used to divert liquid to the sampling vials (9) for analysis and actuated by electromagnets (13), 11 is the thermometer well for the equilibrium chamber, and 12 is a very accurate platinum resistance thermometer to measure the temperature in the equilibrium cell.

Example 11-4 from Dahm (2014)

- Data reduction using Margules Equation: Perform a reduction of the data for the di-isopropyl ether (1)+1-propanol (2) system at 303.15 K using both the 1-parameter and 2-parameter Margules equations.



di-isopropyl ether



1-propanol

TABLE 11-1 Experimental *Pxy* data for the di-isopropyl ether (1) + 1-propanol (2) system at 303.15 K.

P (kPa)	x_1	y_1
3.77	0	0
5.05	0.0199	0.2671
6.15	0.0399	0.4090
7.22	0.0601	0.5061
8.29	0.0799	0.5783
10.60	0.1192	0.6847
12.16	0.1694	0.7346
14.07	0.2294	0.7822
15.62	0.2891	0.8133
16.81	0.3495	0.8343
17.91	0.4090	0.8524
18.77	0.4708	0.8659
19.51	0.5296	0.8774
20.23	0.5902	0.8890
20.71	0.6505	0.8974
21.35	0.7101	0.9093
21.92	0.7685	0.9209
22.62	0.8300	0.9372
23.20	0.8803	0.9521
23.59	0.9179	0.9637
23.80	0.9397	0.9709
23.99	0.9581	0.9785
24.19	0.9804	0.9885
24.36	1	1

Based on data from I. Hwang et al., J. Chem. Eng. Data, 52, 2503 (2007).

SOLUTION:

Step 1 *Obtain the experimental activity coefficients and the experimental excess molar Gibbs free energy*

We can obtain the experimental activity coefficients and the excess molar Gibbs free energy in a manner similar to the Example 11-2 by using the data in Table 11-1 and

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^{\text{sat}}}$$

$$\gamma_2 = \frac{(1 - y_1)P}{(1 - x_1)P_2^{\text{sat}}}$$

$$\frac{\underline{G}^{\text{E}}}{RT} = x_1 \ln[\gamma_1] + x_2 \ln[\gamma_2]$$

TABLE 11-2 Experimental activity coefficient data for the di-isopropyl (1) + 1-propanol (2) system at 303.15 K.

P (Kpa)	x_1	y_1	γ_1	γ_2	$\underline{G}^E/RT$
3.77	0	0	—	1	0
5.05	0.0199	0.2671	2.782	1.001	0.0213
6.15	0.0399	0.4090	2.587	1.003	0.0408
7.22	0.0601	0.5061	2.499	1.005	0.0597
8.29	0.0799	0.5783	2.464	1.006	0.0776
10.60	0.1192	0.6847	2.498	1.005	0.1135
12.16	0.1694	0.7346	2.165	1.030	0.1554
14.07	0.2294	0.7822	1.970	1.053	0.1953
15.62	0.2891	0.8133	1.804	1.087	0.2299
16.81	0.3495	0.8343	1.648	1.134	0.2564
17.91	0.4090	0.8524	1.533	1.185	0.2751
18.77	0.4708	0.8659	1.417	1.260	0.2864
19.51	0.5296	0.8774	1.327	1.346	0.2896
20.23	0.5902	0.8890	1.251	1.452	0.2850
20.71	0.6505	0.8974	1.173	1.611	0.2705
21.35	0.7101	0.9093	1.123	1.770	0.2479
21.92	0.7685	0.9209	1.078	1.984	0.2163
22.62	0.8300	0.9372	1.049	2.214	0.1748
23.20	0.8803	0.9521	1.030	2.460	0.1338
23.59	0.9179	0.9637	1.017	2.764	0.0989
23.80	0.9397	0.9709	1.009	3.047	0.0756
23.99	0.9581	0.9785	1.006	3.259	0.0552
24.19	0.9804	0.9885	1.001	3.750	0.0269
24.36	1	1	1	—	0

A reasonable objective function, therefore, looks like

$$\mathrm{OBJ} = \frac{1}{22}\sum_{i=1}^{22}\left[\frac{\left(\dfrac{\underline{\underline{G}}^{\mathrm{E}}}{RT}\right)_i^{\mathrm{Model}} - \left(\dfrac{\underline{\underline{G}}^{\mathrm{E}}}{RT}\right)_i^{\mathrm{Expt.}}}{\left(\dfrac{\underline{\underline{G}}^{\mathrm{E}}}{RT}\right)_i^{\mathrm{Expt.}}}\right]^2 \tag{11.93}$$

Here, OBJ will always be positive, and the terms are scaled so that they are the same order of magnitude. Note that the endpoints ($x_1 = 0$ and $x_1 = 1$) have been removed since the denominator of the objective function for both of those points will be zero and, thus, the objective function will become undefined.

If we minimize the objective function (OBJ) to find the best values for both models, we arrive at the following result, presented in Table 11-3.

TABLE 11-3 Model parameters for the di-isopropyl (1) + 1-propanol (2) system at 303.15 K.

Model	A	A_{12}	A_{21}	OBJ
1-parameter Margules	1.165			0.0653
2-parameter Margules		1.041	1.317	0.0065

P Effect on Activity Coefficients

- Effect on the activity coefficient

$$\gamma_i(T, P_2, \mathbf{x}) = \gamma_i(T, P_1, \mathbf{x}) \exp\left[\int_{P_1}^{P_2} \frac{\overline{v}_i^{\mathrm{ex}}(T, P, \mathbf{x})}{RT} dP\right]$$

- The second approximate equation makes use of the fact that the excess partial molar volume is pressure independent (close to incompressible fluid concept)!

$$\gamma_i(T, P_2, \mathbf{x}) \simeq \gamma_i(T, P_1, \mathbf{x}) \exp\left[\frac{\overline{v}_i^{\mathrm{ex}}(T, \mathbf{x})}{RT}(P_2 - P_1)\right]$$

T Effect on Activity Coefficients

- Temperature has a stronger effect on the activity coefficient compared to pressure

$$\gamma_i(T_2,P,\mathbf{x}) = \gamma_i(T_1,P,\mathbf{x})\exp\left[-\int_{T_1}^{T_2} \frac{\overline{h}_i^{\text{ex}}(T,P,\mathbf{x})}{RT^2}\,dT\right]$$

- For a **narrow temperature range**, or if the **excess partial molar enthalpy is temperature independent,**

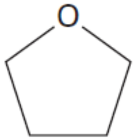
$$\gamma_i(T_2,P,\mathbf{x}) \simeq \gamma_i(T_1,P,\mathbf{x})\exp\left[\frac{\overline{h}_i^{\text{ex}}(\mathbf{x})}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\right]$$

the activity coefficients. For example, consider the system tetrahydrofuran (1) + 2,2,2-trifluoroethanol (2) at 298.15 K. The measured excess molar enthalpy for an equimolar mixture is about −2.0 kJ/mol, while the measured excess molar volume for an equimolar mixture is about 1 cm^3/mol (Perez et al., 2003). Plugging these values into Equations 11.111 and 11.114 (with proper choice of the universal gas constant) yields

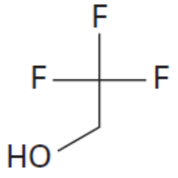
$$\frac{\partial}{\partial T}\left(\frac{\underline{G}^{\mathrm{E}}}{RT}\right)_{P,n_1,n_2} = \frac{2.7 \times 10^{-3}}{\mathrm{K}}$$

$$\frac{\partial}{\partial P}\left(\frac{\underline{G}^{\mathrm{E}}}{RT}\right)_{T,n_1,n_2} = \frac{4.03 \times 10^{-10}}{\mathrm{Pa}} = \frac{4.03 \times 10^{-5}}{\mathrm{bar}}$$

For the derivative with respect to temperature, we see that there is a change on the order of 10^{-3} per change in 1 Kelvin. For the derivative with respect to pressure, we see that there is a change on the order of 10^{-5} for every change in 1 bar. Thus, the impact of a change in temperature far exceeds that of pressure for the excess molar Gibbs free energy. Therefore, models for the excess molar Gibbs free energy will not normally include the effect of pressure and, accordingly, activity coefficients are often assumed to be independent of pressure.



Tetrahydrofuran



2,2,2-trifluoroethanol