

Chemical Engineering Thermodynamics CHE F213

Solution Thermodynamics

Contents

- Chemical Potential
- Partial Properties
- Ideal Gas Mixtures
- Fugacity and Fugacity Coefficient: Pure species
- Fugacity and Fugacity Coefficient: Species in solution
- Ideal Mixtures

Solution Thermodynamics

- Real system in Chemical, Petroleum and Pharmaceutical industries usually contains multi-component gases and liquids undergoing composition changes
- Develop the theoretical foundation for applications of thermodynamics to gas mixtures and liquid solutions
- Introducing
 - Chemical Potential
 - Partial Properties
 - Fugacity
 - Excess Properties
 - Ideal Solution

Fundamental property relation

- The basic relation connecting the Gibbs energy to the temperature and pressure in any closed system:

$$d(nG) = \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} dT = (nV)dP - (nS)dT$$

- applied to a single-phase fluid in a closed system wherein no chemical reactions occur.
- Consider general case of a single-phase, open system:

$$d(nG) = \left[\frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nG)}{\partial T} \right]_{P,n} dT + \sum_i \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j} dn_i$$

Define the chemical potential:

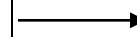
$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j}$$

The fundamental property relation for single-phase fluid systems of variable mass and composition:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

When $n = 1$,

$$dG = VdP - SdT + \sum_i \mu_i dx_i$$



$$G = G(P, T, x_1, x_2, \dots, x_i, \dots)$$

$$V = \left(\frac{\partial G}{\partial P} \right)_{T,x}$$

$$S = \left(\frac{\partial G}{\partial T} \right)_{P,x}$$

Solution properties, M
Partial properties, \bar{M}_i
Pure-species properties, M_i

Chemical potential & Phase Equilibria

- Consider a closed system consisting of two phases (α and β) in equilibrium:

$$d(nG)^\alpha = (nV)^\alpha dP - (nS)^\alpha dT + \sum_i \mu_i^\alpha dn_i^\alpha$$


$$d(nG)^\beta = (nV)^\beta dP - (nS)^\beta dT + \sum_i \mu_i^\beta dn_i^\beta$$

$$nM = (nM)^\alpha + (nM)^\beta$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i^\alpha dn_i^\alpha + \sum_i \mu_i^\beta dn_i^\beta$$

Since two-phase system is closed

$$d(nG) = (nV)dP - (nS)dT$$

Mass balance: $dn_i^\alpha = -dn_i^\beta$  $\mu_i^\alpha = \mu_i^\beta$

Multiple phases at the same T and P are in equilibrium when chemical potential of each species is the same in all phases.

Partial properties

- Define the partial molar property of species i:

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i} \right]_{P,T,n_j}$$

- the chemical potential and the partial molar Gibbs energy are identical: $\mu_i \equiv \bar{G}_i$

- Relation between Molar and Partial Molar Properties

$$nM = M(P, T, n_1, n_2, \dots, n_i, \dots)$$



$$d(nM) = \left[\frac{\partial(nM)}{\partial P} \right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T} \right]_{P,n} dT + \sum_i \bar{M}_i dn_i$$

$$d(nM) = n \left[\frac{\partial M}{\partial P} \right]_{T,x} dP + n \left[\frac{\partial M}{\partial T} \right]_{P,x} dT + \sum_i \bar{M}_i dn_i$$

Since $n_i = n x_i$
 $dn_i = x_i dn + n dx_i$
 $d(nM) = n dM + M dn$

$$ndM + Mdn = n \left[\frac{\partial M}{\partial P} \right]_{T,x} dP + n \left[\frac{\partial M}{\partial T} \right]_{P,x} dT + \sum_i \bar{M}_i (x_i dn + n dx_i)$$

$$\left[dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i \right] n + \left[M - \sum_i x_i \bar{M}_i \right] dn = 0$$

n and dn are independent

$$dM - \left(\frac{\partial M}{\partial P} \right)_{T,x} dP - \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i \bar{M}_i dx_i = 0$$

and

$$M = \sum_i x_i \bar{M}_i$$

$$dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$$

$$nM = \sum_i n_i \bar{M}_i$$

$$\left(\frac{\partial M}{\partial P} \right)_{T,x} dP + \left(\frac{\partial M}{\partial T} \right)_{P,x} dT - \sum_i x_i d\bar{M}_i = 0$$

The Gibbs/Duhem equation

Calculation of mixture properties from partial properties

Gibbs Duhem Equation

- General form:

$$\left(\frac{\partial M}{\partial P}\right)_{T,n} dP + \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum_i x_i d\bar{M}_i = 0$$

- For the changes at constant T and P,

$$\sum_i x_i d\bar{M}_i \Big|_{T,P} = 0$$

$$\sum_i n_i d\bar{M}_i \Big|_{T,P} = 0$$

A rationale for Partial Properties

- A solution/ mixture property is represented by the sum of its parts (partial properties \bar{M}_i)
- **Partial properties like solution properties are function of compositions**

- In the limit as a solution becomes pure i species, both M and \bar{M}_i approaches to pure-species

property M_i

$$\lim_{x_i \rightarrow 1} M = \lim_{x_i \rightarrow 1} \bar{M}_i \equiv M_i$$

- In the infinite-dilution limit i.e., mole fraction i approaches zero, no general statement is valid

$$\lim_{x_i \rightarrow 0} \bar{M}_i \equiv \bar{M}_i^\infty$$

Partial properties in binary solution

- For binary system

$$M = x_1 \bar{M}_1 + x_2 \bar{M}_2$$

$$dM = x_1 d\bar{M}_1 + \bar{M}_1 dx_1 + x_2 d\bar{M}_2 + \bar{M}_2 dx_2$$

Const. P and T, using Gibbs/Duhem equation

$$dM = \bar{M}_1 dx_1 + \bar{M}_2 dx_2$$

$$x_1 + x_2 = 1$$

$$\frac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$$

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1}$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1}$$

Partial properties in binary solution

- Gibbs/Duhem Equation for binary System:

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0$$

$$x_1 \frac{d\bar{M}_1}{dx_1} + x_2 \frac{d\bar{M}_2}{dx_1} = 0$$

$$\frac{d\bar{M}_1}{dx_1} = - \frac{x_2}{x_1} \frac{d\bar{M}_2}{dx_1}$$

- Given an expression for $\bar{M}_1(x_1)$, integration of above equation yields an expression for $\bar{M}_2(x_1)$ that satisfy Gibbs/Duhem equation.

Graphical representation of Partial properties

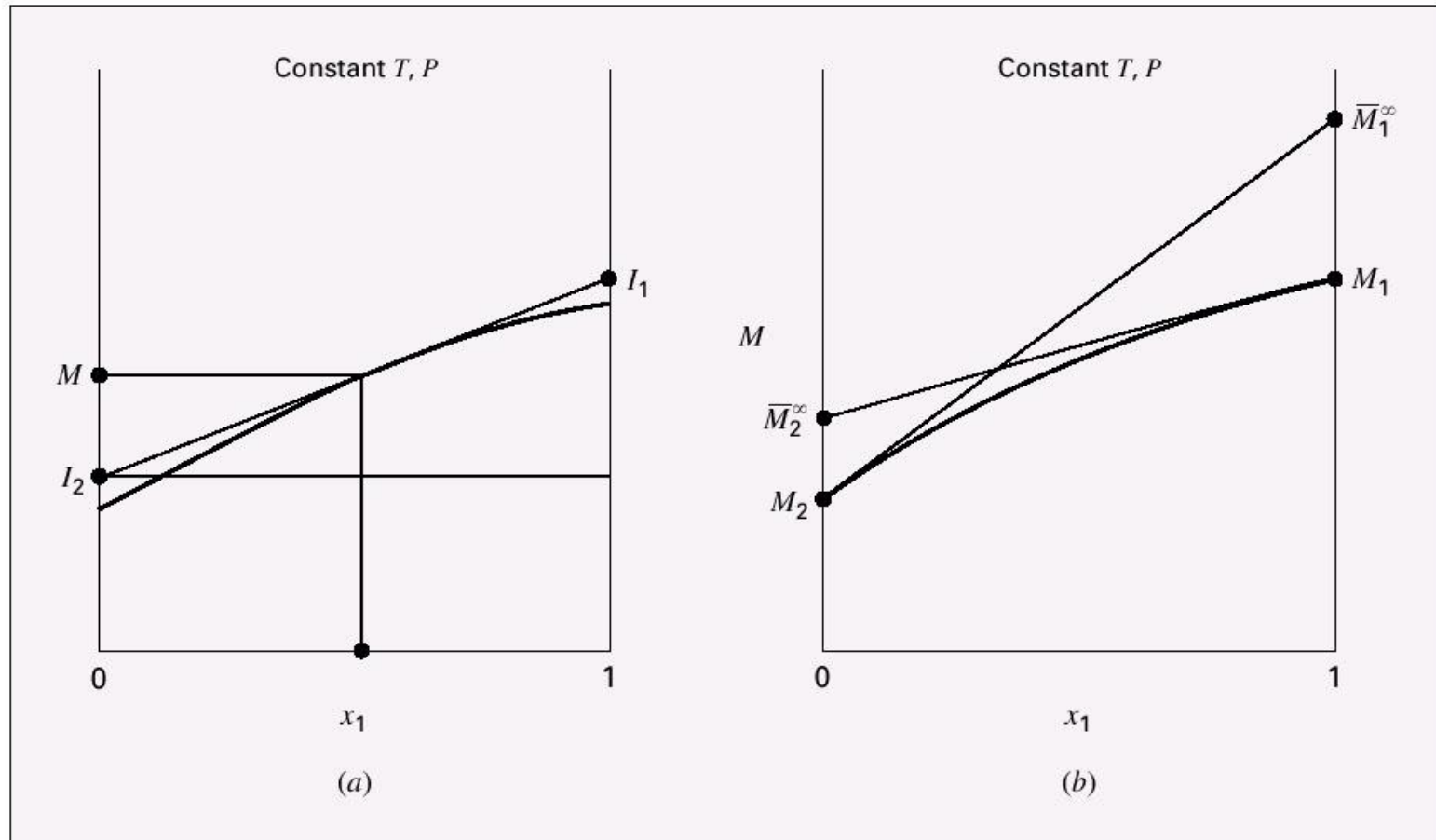


Figure 11.1: (a) Graphical construction of Example 11.2. (b) Infinite-dilution values of partial properties.

Illustration 1

If the molar density of binary mixture is given by the empirical expression:

$$\rho = a_0 + a_1x_1 + a_2x_1^2$$

Find the corresponding expressions for \bar{V}_1 and \bar{V}_2

Example 11.2, 3 and 4

Illustration 2

The molar volumes of a binary solution at 25°C are measured as given below:

x_1	0	0.2	0.4	0.6	0.8	1.0
$v \times 10^6$ m^3/mol	20	21.5	24	27.4	32	40

Calculate the partial molar volumes of components 1 and 2 at $x_1=0.5$ and $x_1=0.75$

Solution: Draw a tangent to the curve at $x_1=0.5$,
intercept at $x_1=0$ gives $\bar{v}_2 = 17 \times 10^{-6} \text{ m}^3/\text{mol}$ and $x_1=1$
gives $\bar{v}_1 = 33.8 \times 10^{-6} \text{ m}^3/\text{mol}$

Relations among partial properties

$$d(nG) = (nV)dP - (nS)dT + \sum_i \bar{G}_i dn_i$$

- Maxwell relation:

$$\left(\frac{\partial V}{\partial T} \right)_{P,n} = - \left(\frac{\partial S}{\partial P} \right)_{T,n}$$

$$\left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,n} = - \left[\frac{\partial (nS)}{\partial n_i} \right]_{P,T,n_j}$$

$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,n} = \left[\frac{\partial (nV)}{\partial n_i} \right]_{P,T,n_j}$$

$$\left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,x} = -\bar{S}_i$$

$$\left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,x} = \bar{V}_i$$

In a constant-composition solution, \bar{G}_i is a function of P and T, and therefore:

$$d\bar{G}_i = \left(\frac{\partial \bar{G}_i}{\partial P} \right)_{T,x} dP + \left(\frac{\partial \bar{G}_i}{\partial T} \right)_{P,x} dT$$

$$d\bar{G}_i = \bar{V}_i dP - \bar{S}_i dT$$

- Consider equation that defines Enthalpy:

$$H = U + PV$$

$$nH = nU + P(nV)$$

Differentiation with respect to n_i at constant T , P , and n_j yields:

$$\left[\frac{\partial(nH)}{\partial n_i} \right]_{P,T,n_j} = \left[\frac{\partial(nU)}{\partial n_i} \right]_{P,T,n_j} + P \left[\frac{\partial(nV)}{\partial n_i} \right]_{P,T,n_j}$$

This becomes:

$$\bar{H}_i = \bar{U}_i + P\bar{V}_i$$

Every equation that provides a linear relation among thermodynamic properties of a constant-composition solution has its counterpart an equation connecting the corresponding partial properties of each species in solution

The Ideal Gas Mixture Model

- The ideal gas mixture model provides a conceptual basis to build the structure of solution thermodynamics
 - It is simple and has a molecular basis
 - Applied in well defined limit of zero pressure
 - In an ideal gas mixture, the density is so low that it's molecules do not appreciably interact
 - The molar volume $V=RT/P$, regardless of nature of the gas (whether pure or mixed)

$$\bar{V}_i^{-ig} = \left[\frac{\partial(nV^{ig})}{\partial n_i} \right]_{P,T,n_j} = \left[\frac{\partial(nRT/P)}{\partial n_i} \right]_{P,T,n_j} = \frac{RT}{P} \left(\frac{\partial n}{\partial n_i} \right)_{n,j} = \frac{RT}{P}$$

$$\bar{V}_i^{-ig} = V_i^{ig} = V^{ig} = \frac{RT}{P}$$

Ideal-gas mixture

The partial pressure of species i in an ideal-gas mixture, denoted by p_i is defined as the pressure that species i would exert if it alone occupied the molar volume of the mixture.

$$p_i(n, V^t, T) = \text{Pressure}(n_i, V^t, T)$$

For the ideal gas mixture,

$$p_i = \frac{y_i RT}{V^{ig}} = y_i P \quad (i = 1, 2, \dots, N)$$

- **Gibbs's theorem**

- A partial molar property (other than volume) of a constituent species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at the mixture temperature but at a pressure equal to its partial pressure in the mixture.

$$\bar{M}_i^{ig} \neq \bar{V}_i^{ig}$$

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i)$$

Ideal Gas mixture Enthalpy and Internal Energy

$$\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, p_i) = H_i^{ig}(T, P)$$

Enthalpy and internal energy of ideal gas is independent of pressure

$$H^{ig} = \sum_i y_i H_i^{ig}$$

$$U^{ig} = \sum_i y_i U_i^{ig}$$

For ideal gas mixture, enthalpy change of mixing is zero

Ideal Gas mixture Entropy

$$dS_i^{ig} = -R d \ln P \quad (const.T)$$

$$S_i^{ig}(T, P) - S_i^{ig}(T, p_i) = -R \ln \frac{P}{p_i} = -R \ln \frac{P}{y_i P} = R \ln y_i$$

$$\bar{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i)$$

$$S_i^{ig}(T, P) - \bar{S}_i^{ig}(T, P) = R \ln y_i$$

$$S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$$S^{ig} - \sum_i y_i S_i^{ig} = R \sum_i y_i \ln \frac{1}{y_i}$$

Entropy change of mixing for ideal gases, always positive

Ideal Gas mixture Gibbs Energy

$$\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}$$

$$\bar{H}_i^{ig}(T, P) = H_i^{ig}(T, P)$$

$$S_i^{ig}(T, P) - \bar{S}_i^{ig}(T, P) = -R \ln y_i$$

$$\bar{G}_i^{ig} = H_i^{ig} - TS_i^{ig} + RT \ln y_i$$

$$\mu_i^{ig} \equiv \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i$$

$$G^{ig} = \sum_i y_i \bar{G}_i^{ig} = \sum_i y_i G_i^{ig} + RT \sum_i y_i \ln y_i$$

An alternative expression,

$$dG_i^{ig} = V_i^{ig} dP = \frac{RT}{P} dP = RT \ln P$$

Constant T

$$G_i^{ig} = \Gamma_i(T) + RT \ln P$$

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P$$

$$G^{ig} = \sum_i y_i \Gamma_i(T) + RT \sum_i y_i \ln y_i P$$

Ideal Gas Mixture

$$U^{ig} = \sum_i y_i U_i^{ig}$$

$$H^{ig} = \sum_i y_i H_i^{ig}$$

$$C_p^{ig} = \sum_i y_i C_{p_i}^{ig}$$

$$S^{ig} = \sum_i y_i S_i^{ig} - R \sum_i y_i \ln y_i$$

$$G^{ig} = \sum_i y_i G_i^{ig} + RT \sum_i y_i \ln y_i$$

$$\mu_i^{ig} = \bar{G}_i^{ig} = \Gamma_i(T) + RT \ln y_i P$$

Illustration (11.1)

What is the change in the entropy when 0.7 m³ of CO₂ and 0.3 m³ N₂ each at 1 bar and 298.15 K blend to form a gas mixture at the same conditions. Assume ideal gas mixture.

For an ideal gas mole fraction = volume fraction

CO₂ (1):

$$x_1 := 0.7$$

$$V_1 := 0.7 \text{ m}^3$$

N₂ (2):

$$x_2 := 0.3$$

$$V_2 := 0.3 \text{ m}^3$$

$$i := 1..2$$

$$P := 1 \text{ bar}$$

$$T := (25 + 273.15) \text{ K}$$

$$n := \frac{P \cdot \sum_i V_i}{R \cdot T} \quad n = 40.342 \text{ mol}$$

$$\Delta S := -n \cdot R \cdot \sum_i (x_i \cdot \ln(x_i))$$

$$\Delta S = 204.885 \frac{\text{J}}{\text{K}}$$

Illustration 2 (Problem 11.4)

What is the ideal work for the separation of an equimolar mixture of methane and ethane at 175°C and 3 bar in a steady-state flow process into product streams of the pure gases at 35°C and 1 bar if $T_\sigma = 300$ K?

Fugacity and fugacity coefficient

- **Fugacity:**

- The concept by introduced by G.N. Lewis and is used in solution thermodynamics to represent the behavior of the real fluid
- a quantity that takes the place of μ_i to facilitate the criteria for equilibrium

For a constant temperature process, the property relation :

$$dG = VdP$$

For 1 mol of an ideal gas, V may be replaced by $V=RT/P$

$$dG = RT \frac{dP}{P} = RTd(\ln P)$$

For a real fluid, the true pressure (for ideal gas case) can be replaced by an 'effective' pressure, which is called '**fugacity**' of gases

$$dG \equiv RT d(\ln f) \longrightarrow \text{With units of pressure}$$

$$G_i \equiv \Gamma_i(T) + RT \ln f_i$$

$$G_i^{ig} = \Gamma_i(T) + RT \ln P$$

$$G_i - G_i^{ig} = RT \ln \frac{f_i}{P}$$

Subscript i, for
pure species i

Residual Gibbs energy

$$G_i^R = RT \ln \phi_i$$

Fugacity coefficient

$$\phi_i = \frac{f_i}{P}$$

$$\lim_{P \rightarrow 0} \ln \phi_i = \lim_{P \rightarrow 0} \ln \left(\frac{f_i}{P} \right) = 0$$

and

$$\lim_{P \rightarrow 0} \phi_i = \lim_{P \rightarrow 0} \left(\frac{f_i}{P} \right) = 1$$

- Pressure Explicit Form

$$\ln \phi_i = \ln \frac{f_i}{P} = \int_0^P (Z_i - 1) \frac{dP}{P} \quad (\text{Constant } T)$$

- Volume Explicit Form

$$\ln \frac{f_i(T, P)}{P} = \frac{G_i^R}{RT} = \int_0^P (Z_i - 1) \frac{d\rho_i}{\rho_i} + Z_i - 1 - \ln Z_i$$

Like departure functions, there are different ways to estimate fugacity and fugacity coefficient

Fugacity from Generic Cubic Equation of State (for pure species)

Evaluation of fugacity coefficients through cubic EoS (e.g., van der Waals, R/K, S/R/K, P/R)

$$\frac{G_i^R}{RT} = \ln \phi_i = Z_i - 1 - \ln(1 - \rho_i b_i) Z_i - q_i I_i$$

$$\text{Case 1: } \varepsilon \neq \sigma \quad I = \frac{1}{\sigma - \varepsilon} \ln \left(\frac{1 + \sigma \rho_i b_i}{1 + \varepsilon \rho_i b_i} \right)$$

$$\text{Case 1: } \varepsilon = \sigma \quad I = \frac{\rho_i b_i}{1 + \varepsilon \rho_i b_i}$$

Application of these equations at a given T and P requires prior solution of an equation of state for Z_i

Generalized correlations for the fugacity coefficient (for pure species)

$$\ln \phi_i = \int_0^{P_r} (Z_i - 1) \frac{dP_r}{P_r} \quad (const. T_r)$$



$$Z = Z^0 + \omega Z^1$$

$$\ln \phi = \int_0^{P_r} (Z^0 - 1) \frac{dP_r}{P_r} + \omega \int_0^{P_r} Z^1 \frac{dP_r}{P_r} \quad (const. T_r)$$

or

$$\ln \phi = \ln \phi^0 + \omega \ln \phi^1 \quad \text{with}$$

$$\ln \phi^0 \equiv \int_0^{P_r} (Z^0 - 1) \frac{dP_r}{P_r} \quad \ln \phi^1 \equiv \int_0^{P_r} Z^1 \frac{dP_r}{P_r} \quad \text{For pure gas}$$

Table E1:E4

or

Table E13:E16

Fugacity Coefficient from Virial EoS

$$Z_i = 1 + \frac{B_{ii}P}{RT}$$

$$\ln \phi_i = \frac{B_{ii}}{RT} \int_0^P dP \quad (\text{Constant } T)$$

$$\ln \phi_i = \frac{B_{ii}P}{RT}$$

VLE for pure species

- Saturated vapor: $G_i^v = \Gamma_i(T) + RT \ln f_i^v$
 - Saturated liquid: $G_i^l = \Gamma_i(T) + RT \ln f_i^l$
-

$$G_i^v - G_i^l = RT \ln \frac{f_i^v}{f_i^l}$$

↓ VLE

$$G_i^v - G_i^l = RT \ln \frac{f_i^v}{f_i^l} = 0$$

↓

$$f_i^v = f_i^l = f_i^{sat}$$

$$\phi_i^v = \phi_i^l = \phi_i^{sat}$$

For a pure species coexisting liquid and vapor phases are in equilibrium when they have the same temperature, pressure, fugacity and fugacity coefficient.

Fugacity of a pure liquid

- The fugacity of pure species i as a compressed liquid:

$$f_i^l(P) = \underbrace{\frac{f_i^v(P_i^{sat})}{P_i^{sat}}}_{(A)} \underbrace{\frac{f_i^l(P_i^{sat})}{f_i^v(P_i^{sat})}}_{(B)} \underbrace{\frac{f_i^l(P)}{f_i^l(P_i^{sat})}}_{(C)} P_i^{sat}$$

Ratio (A) is ϕ_i^{sat} and given as

$$\ln \phi_i^{sat} = \int_0^{P_i^{sat}} (Z_i^v - 1) \frac{dP}{P} \quad (\text{Constant T})$$

Ratio (B) is unity at equilibrium

Fugacity of a pure liquid

- Ratio (C) reflects the effect of pressure on fugacity of pure liquid i,

$$G_i - G_i^{sat} = RT \ln \frac{f_i}{f_i^{sat}}$$

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^P V_i^l dP \quad (\text{isothermal process})$$

$$\ln \frac{f_i}{f_i^{sat}} = \frac{1}{RT} \int_{P_i^{sat}}^P V_i^l dP$$

Since V_i is a weak function of P

$$\ln \frac{f_i(P)}{f_i^{sat}(P_i^{sat})} = \frac{V_i^l (P - P_i^{sat})}{RT}$$

- Substituting three ratios in initial equation :

$$f_i^l(P) = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT}$$

The exponential is known as **Poynting factor**

For H₂O at a temperature of 300°C and for pressures up to 10,000 kPa (100 bar) calculate values of f_i and ϕ_i from data in the steam tables and plot them vs. P.

From steam table at T=300°C, P^{sat} = 8592.7 kPa

$$G_i = \Gamma_i(T) + RT \ln f_i$$

For a low pressure reference state:

$$G_i^* = \Gamma_i(T) + RT \ln f_i^*$$

$$\ln \frac{f_i}{f_i^*} = \frac{1}{R} \left[\frac{H_i - H_i^*}{T} - (S_i - S_i^*) \right]$$

$$G_i = H_i - TS_i$$

$$\ln \frac{f_i}{f_i^*} = \frac{1}{RT} (G_i - G_i^*)$$

The low pressure (say 1 kPa) at 300°C:

$$f_i^* = P^* = 1 \text{ kPa}$$

$$H_i^* = 3076.8 \text{ J/g}$$

$$S_i^* = 10.3450 \text{ J/gK}$$

For saturation pressure P = 8592.7 at 300°C

$$H_i = 2751.0 \text{ J/g}$$

$$S_i = 5.7081 \text{ J/gK}$$

$$\phi_i^{sat} = 0.7843$$

$$f_i^{sat} = 6738.9 \text{ kPa}$$

For different values of P up to the saturated pressure at 300°C , one obtains the values of f_i , and hence ϕ_i . Note, values of f_i and ϕ_i at 8592.7 kPa are obtained

Values of f_i and ϕ_i at higher pressure:

$$f_i = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^l (P - P_i^{sat})}{RT}$$

V_i^l can be taken as molar volume of saturated liquid water at 300°C

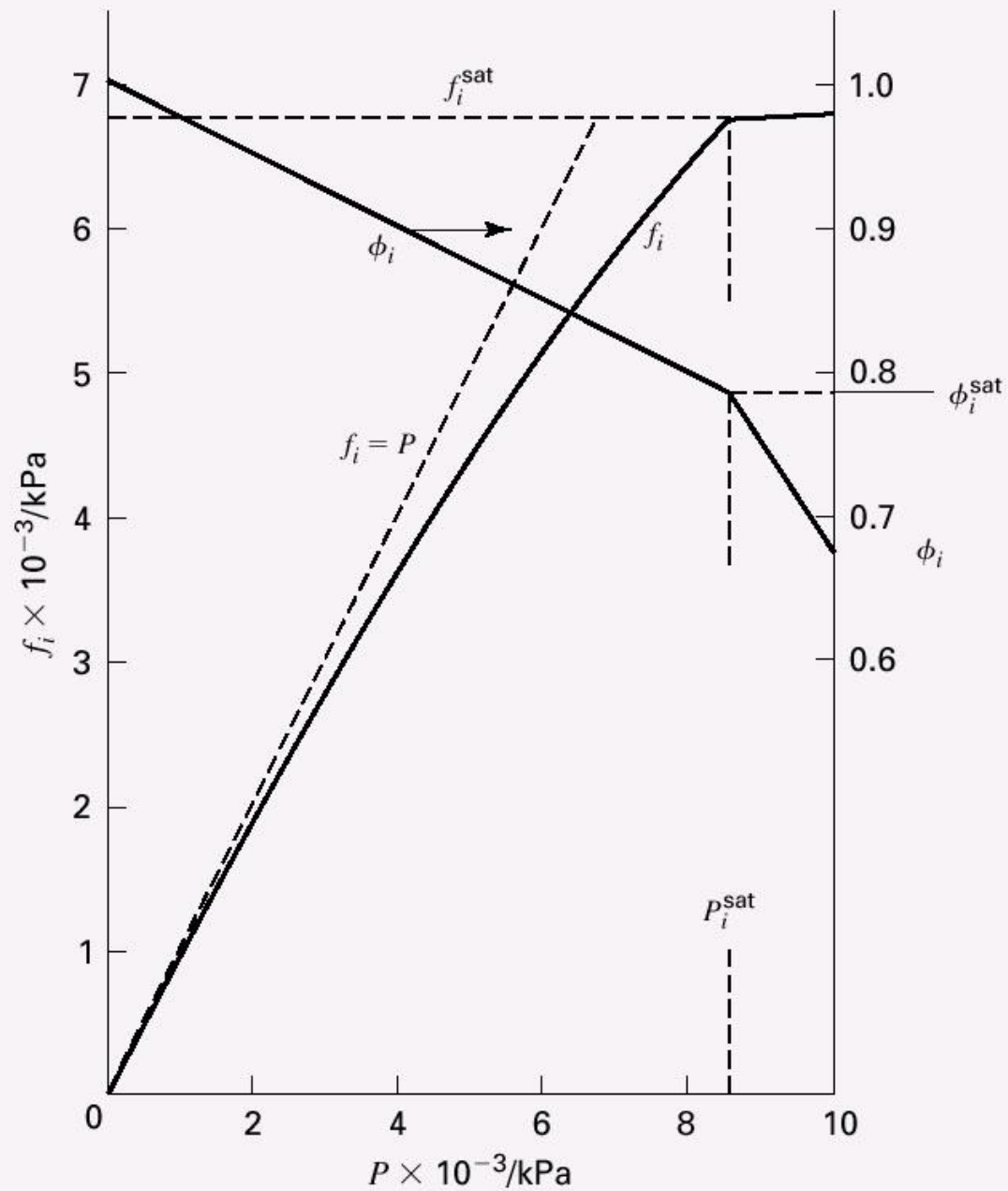
$$V_i^l = 25.28 \text{ cm}^3/\text{mol},$$

$$f_i = 6789.8 \text{ kPa}$$

$$\phi_i = 0.6790$$

Fig 11.3

Figure 11.3: Fugacity and fugacity coefficient of steam at 300°C.



Fugacity and fugacity coefficient: species in solution

- For species i in a mixture of real gases or in a solution of liquids:

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i$$

Fugacity of species i in solution
(replacing the partial pressure)

- Multiple phases at the same T and P are in equilibrium when the fugacity of each constituent species is the same in all phases:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta = \dots = \hat{f}_i^\pi$$

$$\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i$$

$$\mu_i^{ig} = \Gamma_i(T) + RT \ln y_i P$$

$$\mu_i - \mu_i^{ig} = RT \ln \frac{\hat{f}_i}{y_i P}$$

$$\bar{G}_i^R = RT \ln \hat{\phi}_i$$

The residual property:

$$G^R = G - G^{ig}$$

The partial residual property:

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig}$$

$$\mu_i \equiv \left[\frac{\partial(nG)}{\partial n_i} \right]_{P,T,n_j} = \bar{G}_i$$

$$\hat{\phi}_i \equiv \frac{\hat{f}_i}{y_i P}$$

The fugacity coefficient of species i in solution

For ideal gas,

$$\bar{G}_i^R = 0$$

$$\hat{\phi}_i = \frac{\hat{f}_i}{y_i P} = 1$$

$$\hat{f}_i = y_i P$$

Fundamental residual-property relation

$$d\left(\frac{nG}{RT}\right) = \frac{1}{RT} d(nG) - \frac{nG}{RT^2} dT$$

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$d\left(\frac{nG}{RT}\right) = \frac{nV}{RT} dP - \frac{nH}{RT^2} dT + \sum_i \frac{\bar{G}_i}{RT} dn_i \longrightarrow \frac{nG}{RT} = f(P, T, n_i)$$

G/RT as a function of its canonical variables allows evaluation of all other thermodynamic properties, and implicitly contains complete property information.

The residual properties:

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT} dP - \frac{nH^R}{RT^2} dT + \sum_i \frac{\bar{G}_i^R}{RT} dn_i$$

or

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT} dP - \frac{nH^R}{RT^2} dT + \sum_i \ln \hat{\phi}_i dn_i$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT} dP - \frac{nH^R}{RT^2} dT + \sum_i \frac{\bar{G}_i^R}{RT} dn_i$$

$$d\left(\frac{nG^R}{RT}\right) = \frac{nV^R}{RT} dP - \frac{nH^R}{RT^2} dT + \sum_i \ln \hat{\phi}_i dn_i$$

Fix T and composition:

$$\frac{V^R}{RT} = \left(\frac{\partial(G^R / RT)}{\partial P} \right)_{T,x}$$

Fix P and composition:

$$\frac{H^R}{RT} = -T \left(\frac{\partial(G^R / RT)}{\partial T} \right)_{P,x}$$

Fix T and P:

$$\ln \hat{\phi}_i = \left(\frac{\partial(nG^R / RT)}{\partial n_i} \right)_{P,T,n_j}$$

Illustration (11.20)

Justify the following equations

$$\left(\frac{\partial \ln \hat{\phi}_i}{\partial P} \right)_{T,x} = \frac{\bar{V}_i^R}{RT}$$

$$\left(\frac{\partial \ln \hat{\phi}_i}{\partial T} \right)_{P,x} = -\frac{\bar{H}_i^R}{RT^2}$$

$$\frac{G^R}{RT} = \sum_i x_i \ln \hat{\phi}_i$$

$$G^R = RT \ln \phi$$

$$\sum_i x_i d \ln \hat{\phi}_i = 0 \quad (\text{const } T, P)$$

Illustration

- Estimate the fugacity of gaseous mixture consisting of 30% component 1 and 70% component 2 by mole ,given that at 100°C and 50 bar the fugacity coefficients of components 1 and 2 in mixture are 0.7 and 0.85 respectively.

$$\ln \phi = \sum x_i \ln \hat{\phi}_i$$

$$\text{and } \phi = f/P$$

Answer: 40.124 bar

Develop a general equation for calculation of $\ln \hat{\phi}_i$ values from compressibility-factor data.

$$\ln \hat{\phi}_i = \left(\frac{\partial(nG^R / RT)}{\partial n_i} \right)_{P,T,n_j}$$

$$\frac{nG^R}{RT} = \int_0^P (nZ - n) \frac{dP}{P}$$

$$\ln \hat{\phi}_i = \int_0^P \left[\frac{\partial(nZ - n)}{\partial n_i} \right]_{P,T,n_j} \frac{dP}{P}$$

$$\frac{\partial n}{\partial n_i} = 1 \quad \frac{\partial(nZ)}{\partial n_i} = \bar{Z}_i$$

$$\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P}$$

Integration at constant temperature and composition

Properties of real gas mixtures

- So far we have dealt with pure species (focus on gases)
- Methods discussed earlier need to be modified by including an additional composition variable to predict properties of real gas mixtures
- Constants which appear in EOS which characterize pure species behavior can be averaged to get mixture constants
- Equations which express mixture constants in terms of pure species constants are called **MIXING RULES**

Mixing rules

A mixing rule expresses a mixture constant a_m in terms of composition expressed in mole fraction y_i and the pure component constant a_i , i.e. $a_m = \sum y_i y_j a_{ij}$

$a_{ii} = a_i$, $a_{jj} = a_j$, (based on interaction of like pairs of molecules) and a_{ij} is based on interaction of unlike pairs of molecules

Equations which provide the interaction constant in terms of pure component constants are called combining rules

$$\text{If } a_{ij} = (a_{ii} + a_{jj}) / 2 = (a_i + a_j) / 2 \text{ ----- } \sqrt{a_{ii} a_{jj}} = \sqrt{a_i a_j}$$

$$\downarrow$$
$$a_m = \sum y_i a_i$$

$$\downarrow$$
$$a_m = [\sum y_i \sqrt{a_i}]^2$$

Mixing Rules

For Cubic Equation of State (RK, SRK, PR)

$$a_{mix} = \sum_{i=1}^n \sum_{j=1}^n y_i y_j a_{ij}$$

$$b_{mix} = \sum_{i=1}^n y_i b_i$$

where a_{ii} and b_i are the parameters of pure components i ,
and combining rule

$$a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) = a_{ji}$$

- Here k_{ij} is known as the binary interaction parameter, which results in more accurate mixture equation of state calculations.
- It is found by fitting EoS to mixture data (VLE data). In the absence of data, k_{ij} can be set equal to zero

Fugacity coefficient in mixture from the virial E.O.S

- The virial equation:
$$Z = 1 + \frac{BP}{RT}$$
 - the mixture second virial coefficient B:
$$B = \sum_i \sum_j y_i y_j B_{ij}$$
 - for a binary mixture:
$$B = y_1 y_1 B_{11} + y_1 y_2 B_{12} + y_2 y_1 B_{21} + y_2 y_2 B_{22}$$

For species i in mixture,

$$\bar{Z}_i = \left[\frac{\partial(nZ)}{\partial n_i} \right]_{P,T,n_j} = 1 + \frac{P}{RT} \left[\frac{\partial(nB)}{\partial n_i} \right]_{P,T,n_j}$$

Fugacity coefficient of species i in mixture,

$$\ln \hat{\phi}_i = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P}$$

Fugacity coefficient from the virial E.O.S

Fugacity coefficient

$$\ln \hat{\phi}_1 = \frac{P}{RT} (B_{11} + y_2^2 \delta_{12})$$

$$\delta_{12} \equiv 2B_{12} - B_{11} - B_{22}$$

$$\ln \hat{\phi}_2 = \frac{P}{RT} (B_{22} + y_1^2 \delta_{12})$$

For multi-component gas mixture, the general form:

$$\ln \hat{\phi}_k = \frac{P}{RT} \left(B_{kk} + \frac{1}{2} \sum_i \sum_j y_i y_j (2\delta_{ik} - \delta_{ij}) \right)$$

where

$$\delta_{ik} \equiv 2B_{ik} - B_{ii} - B_{kk}$$

The Ideal Solution Model

- Serves as a standard to which real-solution behavior can be compared

From relation for ideal-gas mixture model

$$\mu_i^{ig} = \bar{G}_i^{ig} = G_i^{ig} + RT \ln y_i$$

$$\mu_i^{id} = \bar{G}_i^{id} = G_i + RT \ln x_i$$

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

$$M^{id} = \sum_i x_i \bar{M}_i^{id}$$

From fundamental property relation

$$\bar{S}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial T}\right)_{P,x} = -\left(\frac{\partial G_i}{\partial T}\right)_P - R \ln x_i$$

$$\bar{S}_i^{id} = S_i - R \ln x_i$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

$$\bar{V}_i^{id} = -\left(\frac{\partial \bar{G}_i^{id}}{\partial P}\right)_{T,x} = -\left(\frac{\partial G_i}{\partial P}\right)_T$$

$$\bar{V}_i^{id} = V_i$$

$$V^{id} = \sum_i x_i V_i$$

$$\bar{H}_i^{id} = \bar{G}_i^{id} + T\bar{S}_i^{id} = G_i + RT \ln x_i + TS_i - RT \ln x_i$$

$$\bar{H}_i^{id} = H_i$$

$$H^{id} = \sum_i x_i H_i$$

Ideal Solution/Mixture

$$V^{id} = \sum_i x_i V_i$$

$$H^{id} = \sum_i x_i H_i$$

$$G^{id} = \sum_i x_i G_i + RT \sum_i x_i \ln x_i$$

$$S^{id} = \sum_i x_i S_i - R \sum_i x_i \ln x_i$$

The Lewis/Randall Rule

- The composition dependence of the fugacity of a species in an ideal solution is simple.

$$\boxed{\mu_i \equiv \Gamma_i(T) + RT \ln \hat{f}_i} \longrightarrow \boxed{\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}}$$

Comparison with the equation $\boxed{\bar{G}_i^{id} = G_i + RT \ln x_i}$ where G_i can be replaced by, $\boxed{G_i \equiv \Gamma_i(T) + RT \ln f_i}$

$$\boxed{\hat{f}_i^{id} = x_i f_i} \xrightarrow{\text{Division both sides by } x_i P} \boxed{\hat{\phi}_i^{id} = \phi_i} \quad \text{The Lewis/Randall rule}$$

The fugacity coefficient of species i in an ideal solution is equal to the fugacity coefficient of pure species i in the same physical state as the solution and at the same T and P .

Excess properties

- The mathematical formalism of excess properties is analogous to that of the residual properties:

$$M^E \equiv M - M^{id}$$

- where M represents the molar (or unit-mass) value of any extensive thermodynamic property (e.g., V , U , H , S , G , etc.)
- Similarly, we have:

The fundamental excess-property relation

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$$

Table 11.1: Summary of Equations for the Gibbs Energy and Related Properties

M in Relation to G	M^R in Relation to G^R	M^E in Relation to G^E
$V = (\partial G / \partial P)_{T,x} \quad (11.4)$	$V^R = (\partial G^R / \partial P)_{T,x}$	$V^E = (\partial G^E / \partial P)_{T,x}$
$S = -(\partial G / \partial T)_{P,x} \quad (11.5)$	$S^R = -(\partial G^R / \partial T)_{P,x}$	$S^E = -(\partial G^E / \partial T)_{P,x}$
$H = G + TS$ $= G - T(\partial G / \partial T)_{P,x}$ $= -RT^2 \left[\frac{\partial(G/RT)}{\partial T} \right]_{P,x}$	$H^R = G^R + TS^R$ $= G^R - T(\partial G^R / \partial T)_{P,x}$ $= -RT^2 \left[\frac{\partial(G^R/RT)}{\partial T} \right]_{P,x}$	$H^E = G^E + TS^E$ $= G^E - T(\partial G^E / \partial T)_{P,x}$ $= -RT^2 \left[\frac{\partial(G^E/RT)}{\partial T} \right]_{P,x}$

The excess Gibbs energy and the activity coefficient

- The partial excess Gibbs energy is of particular interest:

$$\bar{G}_i^E \equiv \bar{G}_i - \bar{G}_i^{id}$$

$$\bar{G}_i = \Gamma_i(T) + RT \ln \hat{f}_i$$

$$\bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$$

$$\bar{G}_i^E = RT \ln \frac{\hat{f}_i}{x_i f_i}$$

$$\bar{G}_i^E = RT \ln \gamma_i$$

$$\bar{G}_i^R = RT \ln \hat{\phi}_i$$

The activity coefficient of species i in solution.

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}$$

A factor introduced into Raoult's law to account for liquid-phase non-idealities.

For ideal solution, $\bar{G}_i^E = 0, \quad \gamma_i = 1$

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \frac{\bar{G}_i^E}{RT} dn_i$$

$$d\left(\frac{nG^E}{RT}\right) = \frac{nV^E}{RT} dP - \frac{nH^E}{RT^2} dT + \sum_i \ln \gamma_i dn_i$$

$$\frac{V^E}{RT} = \left(\frac{\partial(G^E / RT)}{\partial P} \right)_{T,x}$$

$$\frac{H^E}{RT} = -T \left(\frac{\partial(G^E / RT)}{\partial T} \right)_{P,x}$$

$$\ln \gamma_i = \left(\frac{\partial(nG^E / RT)}{\partial n_i} \right)_{P,T,n_j}$$

Experimental accessible values:
activity coefficients from VLE data,
 V^E and H^E values come from mixing experiments.

$$\frac{G^E}{RT} = \sum_i x_i \ln \gamma_i$$

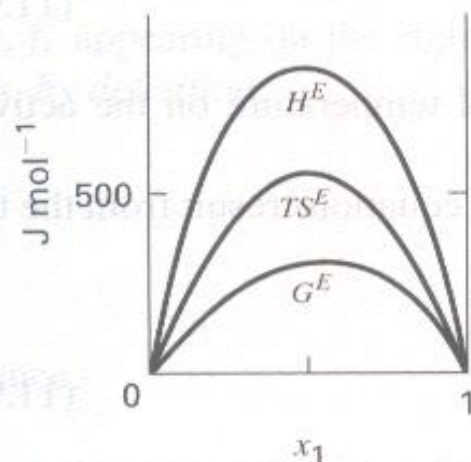
$$\sum_i x_i d \ln \gamma_i = 0 \quad (const. T, P)$$

Important application in phase-equilibrium thermodynamics.

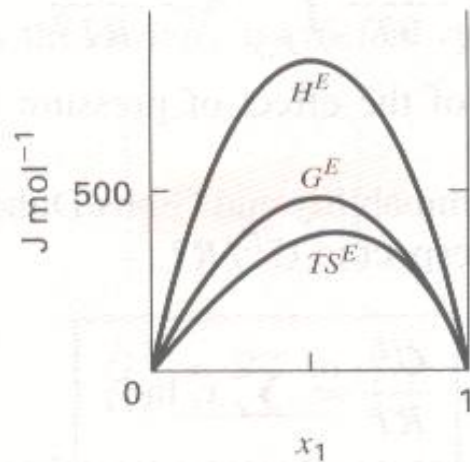
The nature of excess properties

- G^E : through reduction of VLE data
- H^E : from mixing experiment
- $S^E = (H^E - G^E) / T$
- [Fig 11.4](#)
 - Excess properties become zero as either species ~ 1 .
 - G^E is approximately parabolic in shape; H^E and TS^E exhibit individual composition dependence.
 - The extreme value of M^E often occurs near the equimolar composition.

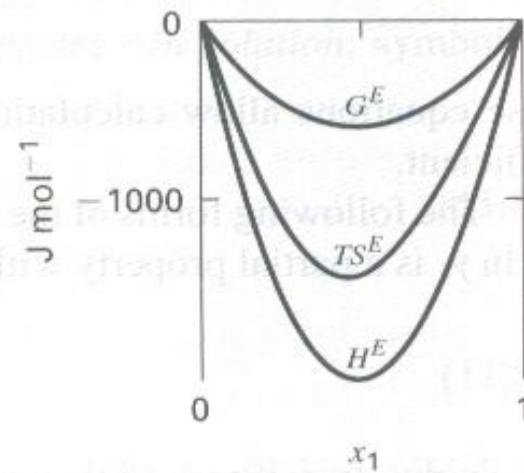
Fig 11.4



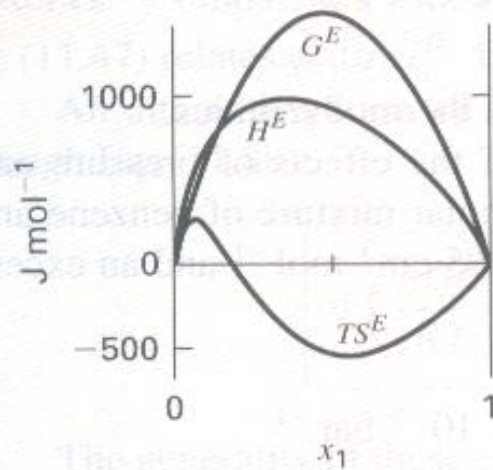
(a)



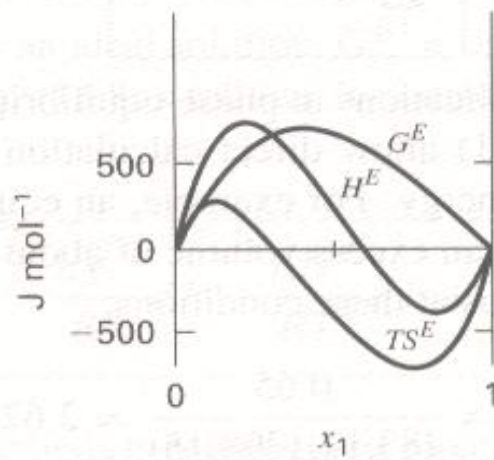
(b)



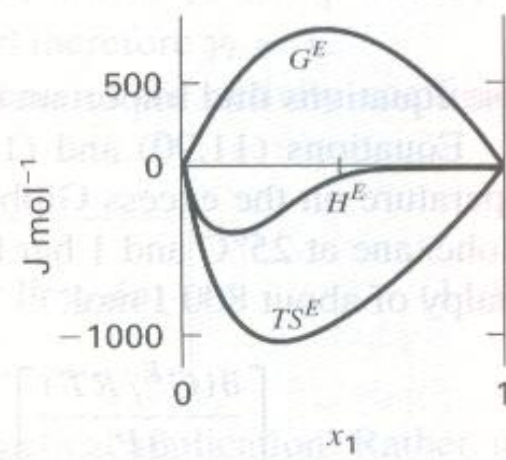
(c)



(d)



(e)



(f)

Models for the Excess Gibbs Energy

- In general G^E/RT is a function of T , P and compositions, but for liquids at low to moderate pressure, it is very weak function of P .
- Therefore, for data at constant T :

$$\frac{G^E}{RT} = g(x_1, x_2, \dots, x_n) \quad (\text{const } T)$$

- Margules Equation is an example of this functionality

$$\frac{G^E}{RT} = (A_{21}x_1 + A_{12}x_2)x_1x_2$$

- For binary system, the function more often represented by an equation is G^E/x_1x_2RT , which may be expressed as a power series :

$$\frac{G^E}{x_1x_2RT} = a + bx_1 + cx_1^2 + \dots$$

- Redlich/Kister expansion

$$\frac{G^E}{x_1x_2RT} = A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots$$

- Another well known equation results when the reciprocal expression x_1x_2RT/G^E , is expressed as a linear function of x_1 :

$$\frac{x_1x_2}{G^E / RT} = A' + B'(x_1 - x_2) + \dots$$

- van Laar equation

$$\frac{G^E}{x_1x_2RT} = \frac{A'_{12}A'_{21}}{A'_{12}x_1 + A'_{21}x_2}$$