

# Solution Thermodynamics

## Outline:

- Introduction of Solution thermodynamics
- Multicomponent Mixture
  - Partial Molar properties, Gibbs-Duhem Equation, Chemical Potential
  - Fugacity and Fugacity Coefficient
  - Estimation of pure gases through equation of state/compressibility factor correlation
- **Thermodynamics Properties of Real Gas Mixture:**
  - Mixing rule
  - P-V-T properties of real gas mixture, Departure function for real gas mixture
  - Fugacity and fugacity coefficient of real gas mixture
  - Fugacity of a component in a mixture, fugacity of liquid and solid
  - Stability and phase transition in thermodynamics system, stability criteria, phase transition in a pure substance, Gibbs phase rule

## Outline:

### ➤ Ideal Solution:

- Phase Equilibria, Phase equilibria for Ideal solution, Phase diagram for ideal solution
- Excess properties, Gibbs-Dehum relation
- Excess Gibbs Free Energy Model: Margules equation, Redlich- Kister equation, Wilson equation, Non-random two liquid (NRTL) equation, UNIQUAC equation, Henry's law

### ➤ Vapor Liquid Equilibrium (VLE):

- Basic equation for vapor-liquid equilibrium, Reduction of VLE data, VLE at low to moderate pressure
- Excess Gibbs free models, Azeotrope data, VLE at high pressure, Multicomponent VLE
- Bubble point, dew point calculation, Thermodynamics consistency test of VLE data

### ➤ Chemical-Reaction Equilibria

## Text Books

1. Introduction to Chemical Engineering Thermodynamics- J. M. Smith, H. C. Van Ness, M. M. Abbott, M.T. Swihart
2. Chemical Engineering Thermodynamics- Y. V. C. Rao

# Thermodynamics Properties

**Intensive Property:** Does not depend on mass of the system.

*Eg:* Temperature, pressure, density, specific volume, specific internal energy, specific enthalpy etc.

**Extensive Property:** Depend on mass of the system.

*Eg:* Mass, volume, internal energy, enthalpy, entropy etc.

➤ **Reference Property (  $P$ ,  $V$ ,  $T$ ,  $S$  )**

➤ **Energy Property: (  $U$ ,  $A$ ,  $G$ ,  $H$  )**

➤ **Derived Properties (  $C$ ,  $k$ ,  $\lambda$ ,  $\beta$  )**

**Internal Energy ( $U$ ):** it is the energy of the substance in the absence of effect due to capillary, external electric, magnetic or other field.

it indicate the total energy; potential or kinetic in a thermodynamics system.

# Energy Property: (U, A, G, H)

**Helmholtz Free Energy (A):** It measure the work of a closed system with constant temperature and volume. It predict the spontaneity, equilibrium state direction of change and maximum work for a system at constant temperature and volume.

$$A = U - TS \quad [ -\Delta A = -W_R \text{ (reversible work done)} ]$$

**Enthalpy (H):** It is the amount of total heat content in a system.

$$H = U + PV$$

Change in enthalpy determine whether a reaction is endothermic ( absorbed heat  $\Delta H = +ve$ ) or exothermic ( release heat  $\Delta H = -ve$ )

It is used to calculate the heat of reaction of a chemical process.

**Gibbs Free Energy (G):** It measure the maximum amount of work done in a thermodynamic system at constant temperature and pressure.

It determine whether a process will occur spontaneously or not.

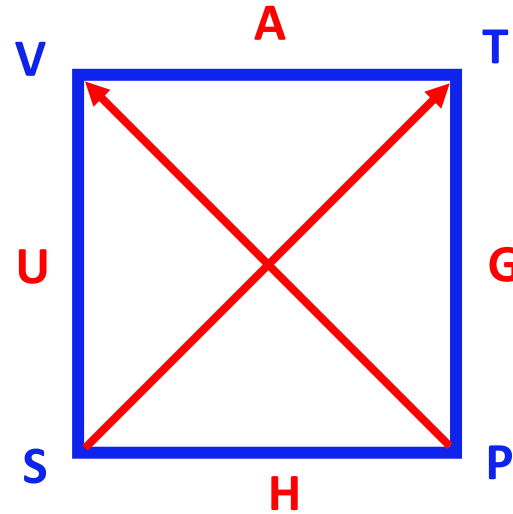
$$G = H - TS$$

# Maxwell Relations:

Energy Property:

A  
G  
H  
U

Variables ( V, T, P, S )



Born diagram

Maxwell equations:

$$1. dG = -SdT + VdP$$

$$2. dH = TdS + VdP$$

$$3. dU = TdS - PdV$$

$$4. dA = -PdV - SdT$$

$$1. \left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T$$

$$2. \left( \frac{\partial V}{\partial S} \right)_V = \left( \frac{\partial T}{\partial P} \right)_S$$

$$3. \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$4. \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$$

# **Solution Thermodynamics**

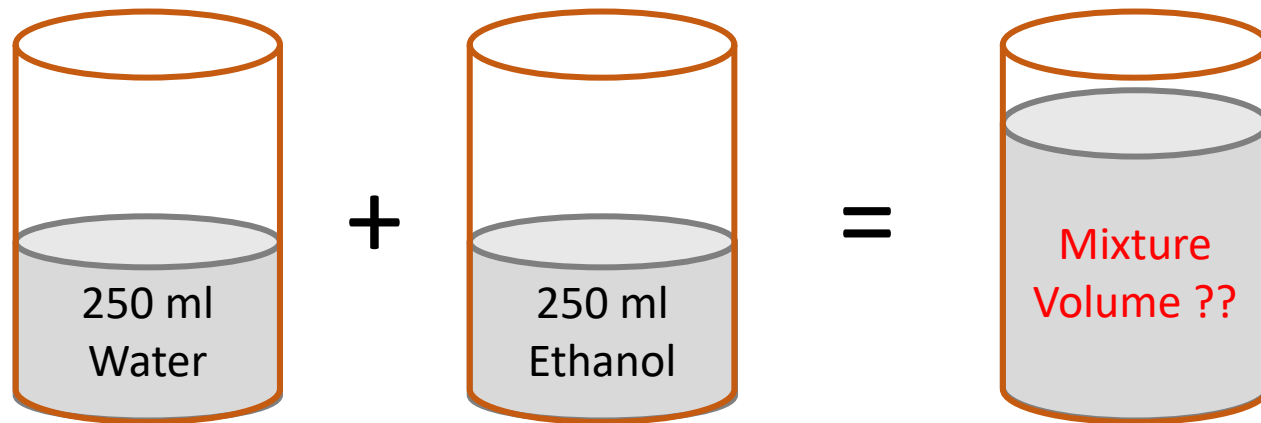
# Multicomponent Mixture:

## Content:

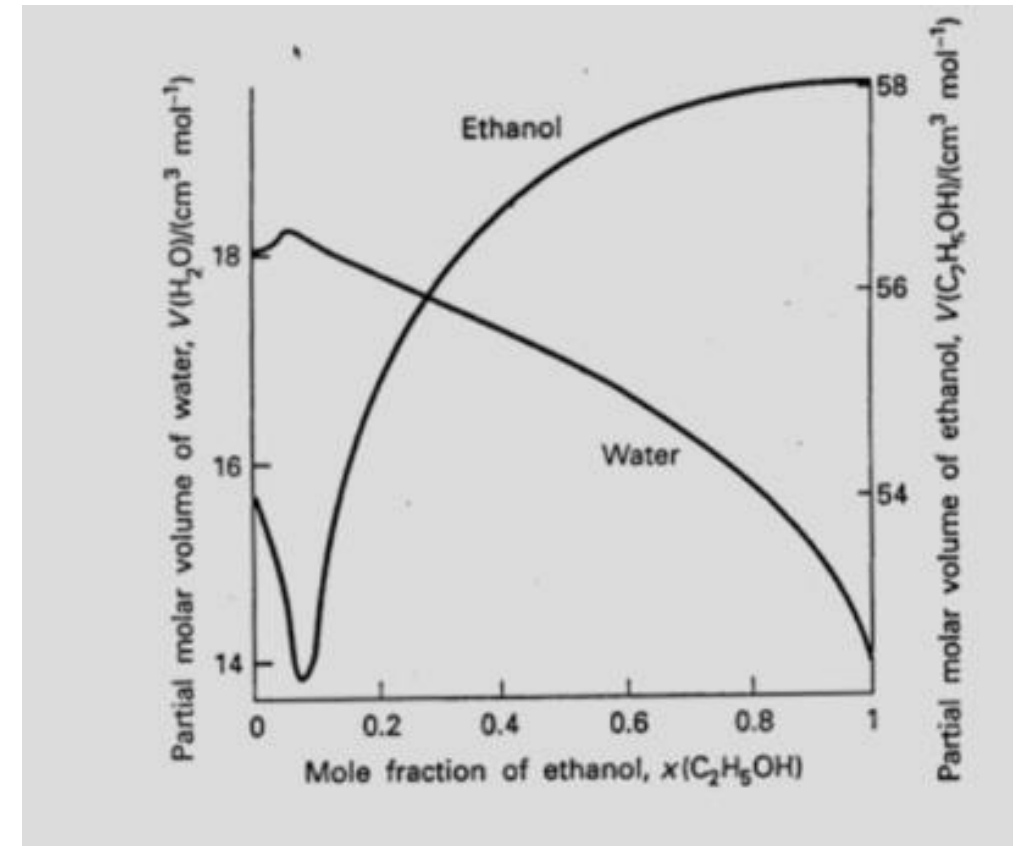
- *Partial Molar Properties*
- *Chemical Potential*
- *Fugacity and Fugacity Coefficient of pure gas*
- *Thermodynamics properties of real gas mixture*
- *Fugacity of a component in a mixture*
- *Fugacity of a liquid and solid*

## Multicomponent Mixture:

**Solution Thermodynamics:** *Study of solution and change its properties is known as solution thermodynamics*



Mixture Volume = 480 ml





# Multicomponent Mixture:

## Partial Molar Properties:

*Suppose we have  $n$  number of individual component in a solution. And at a particular temperature and pressure all the  $n$  number of component have their unique properties. However, after mixing they loose their identity (their properties changes in solution.*

*Now if in a mixture/solution, we changes the composition of any component by keeping  $T$  &  $P$  and other components const., then the properties of this particular component is known as **partial molar properties**.*

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

Some times it also called **response function**.

It is a measure of the response of total properties  $nM$  to the addition of an infinitesimal amount of species 'i' to the finite amount of solution at const. Temp. and Pressure

# Multicomponent Mixture:

## Measure of Composition:

Mass or mole fraction ( $x_i$ ):  $x_i = \frac{m_i}{m} = \frac{\dot{m}_i}{\dot{m}}$  or  $x_i = \frac{n_i}{n} = \frac{\dot{n}_i}{\dot{n}}$   $\dot{n}_i$

Molar concentration ( $C_i$ ):  $C_i = \frac{x_i}{V}$  or  $C_i = \frac{\dot{n}_i}{q}$

Molar mass ( $M$ ): It is define as mole fraction weighted sum of the molar mass of all species present

$$M = \sum x_i M_i$$

$M_i$  = Molar properties of species 'i'

$\overline{M}_i$  = Molar properties of pure species 'i' in solution or partial molar properties of species 'i'

$M$  = Molar properties of solution (intensive properties)

$M^t$  = Total properties of solution  $M^t = nM$  (extensive properties)

# Multicomponent Mixture:

## Fundamental properties for partial molar properties:

$$H_i, G_i, S_i, U_i, v_i, \dots$$

## Dependency of molar properties:

$$M = f(T, P, n_1, n_2, n_3, \dots, n_n)$$

1. Given  $V = 3x_1^2 + 2(1 - x_2) + 4x_1$ , then find out  $V_1$  and  $V_2$ .
2. Given  $\bar{G}_1 = 60x_1^2 + 40x_2$ , then find out  $G_1^a$ .
3.  $\bar{H}_1 = 2 - 60x_2^2 + 100x_1x_2^2$ ; find  $\bar{H}_1^a$ .

## Concept of Pure properties & Infinite Dilution:

### Pure Properties:

$$M_1 = \lim_{x_1 \rightarrow 1} M \quad \text{or} \quad M_1 = \lim_{x_2 \rightarrow 0} M$$

$$M_2 = \lim_{x_2 \rightarrow 1} M \quad \text{or} \quad M_2 = \lim_{x_1 \rightarrow 0} M$$

### Solution of infinite dilution:

$$M_1 = \lim_{x_1 \rightarrow 0} M \quad \text{or} \quad M_1 = \lim_{x_2 \rightarrow 1} M$$

$$M_2 = \lim_{x_2 \rightarrow 0} M \quad \text{or} \quad M_2 = \lim_{x_1 \rightarrow 1} M$$

**Partial Molar Properties:**

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

**Partial Molar volume:**

$$\overline{v}_i = \left( \frac{\partial(nv)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

**For binary system, phase rule**

$$\begin{aligned} \text{DOF} &= C - P + 2 && \text{Component, } C = 2 \\ &= 2 - 1 + 2 && \text{Phase, } P = 1 \text{ (gas/liquid)} \\ &= 3 \end{aligned}$$

*So, here we need to fixed three parameter ( $T$ ,  $P$ ,  $n_2$ ) to define the system*

# Derivation of Gibbs-Duhem Equation and Summability equation

We know that

$$nM = f(T, P, n_1, n_2, n_3, \dots, n_j, \dots, n_n)$$

$$d(nM) = \left(\frac{\partial(nM)}{\partial T}\right)_{P, n} dT + \left(\frac{\partial(nM)}{\partial P}\right)_{T, n} dP + \sum_i \left(\frac{\partial(nM)}{\partial n_i}\right)_{P, T, n_{i \neq j}} dn_i$$

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

At constant temperature and pressure,  $dT = 0$  and  $dP = 0$

$$d(nM) = \sum \bar{M}_i dn_i$$

We know that  $x_i = \frac{n_i}{n}$ ;  $n_i = x_i n$ ;

$$dn_i = x_i dn + n dx_i$$

So,

$$n dM + M dn = \sum \bar{M}_i x_i dn + \sum \bar{M}_i n dx_i$$

$$(M - \sum \bar{M}_i x_i) dn + n (dM - \sum \bar{M}_i dx_i) = 0$$

**So,  $(M - \sum \bar{M}_i x_i) = 0$ ; and  $(dM - \sum \bar{M}_i dx_i) = 0$**

From first part,

$$(M - \sum \bar{M}_i x_i) = 0$$

**$M = \sum \bar{M}_i x_i$  ..... Summability equation**

(M = molar properties)

$$nM = \sum \bar{M}_i n x_i \quad \text{as } n_i = x_i n$$

**$nM = \sum \bar{M}_i n_i$  ..... Summability equation**

For binary system

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

From part 2 at constant temp and pressure

$$(dM - \sum \bar{M}_i dx_i) = 0$$

$$dM = \sum \bar{M}_i dx_i$$

from Summability equation:  $M = \sum \bar{M}_i x_i$

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

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

$\sum x_i d\bar{M}_i = 0$  ..... Gibbs-Duhem relation (at constant T & P)

Or

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

**Gibbs-Duhem equation for binary system:**

$$\sum x_i d\bar{M}_i = 0$$

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

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

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

Similarly

$$\frac{d\bar{M}_2}{dx_2} = - \frac{x_1}{x_2} \frac{d\bar{M}_1}{dx_2}$$

Q1. If  $\bar{M}_2 = 5 x_1^2$ ; find  $\bar{M}_1 = ??$

Q2. The partial molar enthalpies of mixing (J/mol) for benzene (1) and cyclohexane (2) at 300 K and 1 bar are given by  $\Delta \bar{H}_1 = 3600 x_2^2$ ; and  $\Delta \bar{H}_2 = 3600 x_1^2$  where  $x_1$  and  $x_2$  are the mole fraction. What should be the enthalpy changes if one mole of benzene is added to 2 mol of cyclohexane?

## Partial Molar Properties of Binary mixture:

From Summability equation;  $M = x_1 \overline{M}_1 + x_2 \overline{M}_2$

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

.....(1)

From Gibbs -Duhem equation;  $x_1 d\overline{M}_1 + x_2 d\overline{M}_2 = 0$

.....(2)

So equation (1) become

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

$$dM = (\overline{M}_1 - \overline{M}_2) dx_1$$

$$\frac{dM}{dx_1} = (\overline{M}_1 - \overline{M}_2)$$

$$\overline{M}_1 = \left( \frac{dM}{dx_1} + \overline{M}_2 \right)$$

We know that  $M = x_1 \overline{M}_1 + x_2 \overline{M}_2$

$$M = \left( \frac{dM}{dx_1} + \overline{M}_2 \right) x_1 + x_2 \overline{M}_2$$

$$(x_1 + x_2) \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

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

Similarly,

$$\overline{M}_1 = M - x_2 \frac{dM}{dx_2}$$

Q3. At constant T & P, the molar density of a binary mixture is given by  $\rho = 1 + x_2$ , where  $x_2$  is the mole fraction of component 2. What should be the molar volume at infinite dilution for component 1,  $\overline{v}_1$ ?

Q4. At constant T & P, the molar enthalpy of a binary mixture is given by

$$h = 500x_1 + 1000x_2 + (50x_1 + 40x_2)x_1x_2, \quad \text{where } h \text{ in J/mol.}$$

a) Determine  $\bar{h}_1$  and  $\bar{h}_2$  as a function of  $x_1$  and numerical value of pure component enthalpies  $h_1$  and  $h_2$ .

b) Also determine the partial molar enthalpies at infinite dilution.



# Recap:

## Partial Molar Properties:

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

## Summability equation

$$M = \sum \overline{M}_i x_i$$

$$nM = \sum \overline{M}_i n_i$$

For binary system

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

## Partial Molar Properties of Binary mixture:

$$\overline{M}_1 = M - x_2 \frac{dM}{dx_2}$$

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

## Gibbs-Duhem relation

$$\sum x_i d\overline{M}_i = 0 \quad \text{..... (at constant T \& P)}$$

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

For binary system

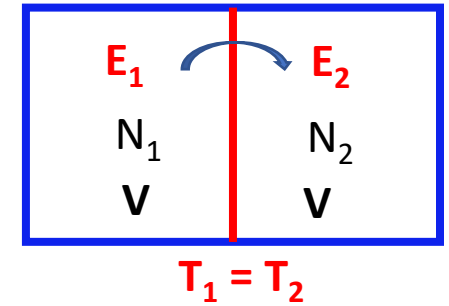
$$\frac{d\overline{M}_1}{dx_1} = - \frac{x_2}{x_1} \frac{d\overline{M}_2}{dx_1}$$

$$\frac{d\overline{M}_2}{dx_2} = - \frac{x_1}{x_2} \frac{d\overline{M}_1}{dx_2}$$

## Chemical Potential ( $\mu$ ):

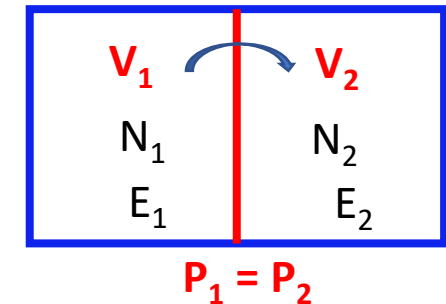
**Thermal Equilibrium:** Energy tends to flow from high energy (temperature) value to low energy (temperature) value until temperature of the both system are equal ( $T_1 = T_2$ ).

**Significant:** System have tendency to give energy



**Mechanical Equilibrium:** Here volume is transfer from high pressure value to low pressure value until pressure of the both system are equal ( $P_1 = P_2$ ).

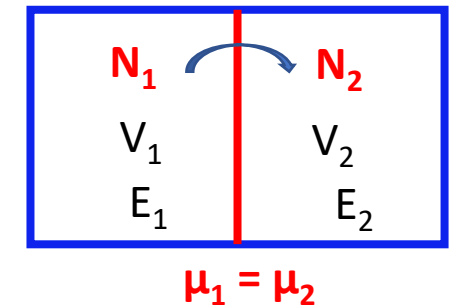
**Significant:** System have tendency to take volume



**Chemical Equilibrium:** Particles tends to flow from high potential value to low potential value until the chemical potential of both system are equal ( $\mu_1 = \mu_2$ ).

**Significant:** It measure the energy change if you add or remove  $dn_i$  particle of any component  $i$  while keeping the other components constant.

It helps to know the behaviours of any individual component in the system.



## Chemical Potential ( $\mu$ ):

**Chemical Potential ( $\mu$ )** is also known as **Partial Gibbs Free Energy** of any component  $i$  that can be add or remove during the reaction.

$$\mu_i = \overline{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

It tells about the effect of free energy (any terms of free energy) if we change the any component composition.

It measure the change of free energy

Chemical potential of a species is the energy that can be absorbed or released due to change in composition/particle number of the given species in a chemical reaction.

If the chemical potential of both the system are equal then there will be no reaction. Then the process is in chemical equilibrium.

# Chemical Potential ( $\mu$ ):

## Chemical Potential with Gibbs Free Energy:

We know that

$$\mu_i = \bar{G}_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T, P, n_j}$$

$$G = f(T, P, n_1, n_2, n_3, \dots, n_i, \dots)$$

$$d(G^t) = \left( \frac{\partial G^t}{\partial T} \right)_{P, n_j} dT + \left( \frac{\partial G^t}{\partial P} \right)_{T, n_j} dP + \sum_i \left( \frac{\partial G^t}{\partial n_i} \right)_{P, T, n_{i \neq j}} dn_i$$

$$d(G^t) = \left( \frac{\partial G^t}{\partial T} \right)_{P, n_j} dT + \left( \frac{\partial G^t}{\partial P} \right)_{T, n_j} dP + \sum \mu_i dn_i$$

At constant temp and pressure for a closed system

$$d(G^t) = \sum \mu_i dn_i$$

$$G^t = \sum \mu_i n_i$$

$$dG = -SdT + VdP$$

At const. temp

$$dG = VdP$$

$$V = \frac{dG}{dP}$$

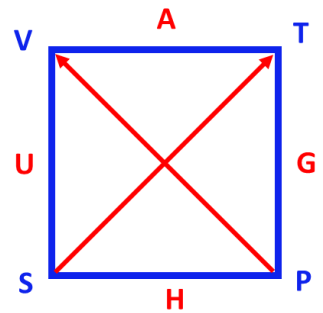
In terms of total Gibbs free energy

$$V^t = \frac{dG^t}{dP}$$

$$d(G^t) = -S^t dT + V^t dP + \sum \mu_i dn_i$$

For a binary system

$$G = \mu_1 x_1 + \mu_2 x_2$$



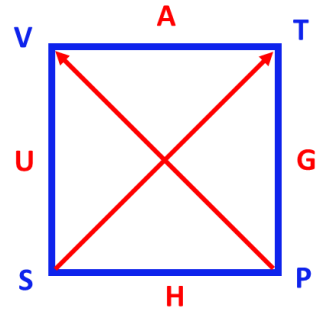
At const. Pressure

$$dG = -SdT$$

$$-S = \frac{dG}{dT}$$

$$-S^t = \frac{dG^t}{dT}$$

## Chemical Potential ( $\mu$ ):



### Chemical potential in terms of Helmholtz Free energy

$$dA = -SdT - PdV + \sum \mu_i dn_i$$

At const. temp and volume

$$dA = \sum \mu_i dn_i$$

$$\mu_i = \left( \frac{dA}{dn_i} \right)_{T, V}$$

### Chemical potential in terms of Internal energy

$$dU = TdS - PdV + \sum \mu_i dn_i$$

At const. entropy and volume

$$\mu_i = \left( \frac{dU}{dn_i} \right)_{S, V}$$

*In any system it is very difficult to keep constant to keep both entropy and volume constant together*

### Chemical potential in terms of Internal energy

$$dH = TdS + VdP + \sum \mu_i dn_i$$

At const. entropy and pressure

$$\mu_i = \left( \frac{dH}{dn_i} \right)_{S, P}$$

# Chemical Potential ( $\mu$ ):

## Effect of Temperature on Chemical Potential

$$\mu_i = G_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T, P, n_j} \dots\dots\dots (1)$$

$$-S^t = \left( \frac{\partial G^t}{\partial T} \right)_{P, n} \dots\dots\dots (2)$$

Differentiate eq<sup>n</sup> (1) w.r.t T (P, n constant)

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, n} = \left( \frac{\partial^2 G^t}{\partial T \partial n_i} \right)_{P, n} \dots\dots\dots (3)$$

Differentiate eq<sup>n</sup> (2) w.r.t  $n_i$  (P, n constant)

$$-\left( \frac{\partial S^t}{\partial n_i} \right)_{T, n} = \left( \frac{\partial^2 G^t}{\partial T \partial n_i} \right)_{P, n} \dots\dots\dots (4)$$

Compare (3) & (4)

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, n} = - \left( \frac{\partial S^t}{\partial n_i} \right)_{T, n}$$

$$\left( \frac{\partial \mu_i}{\partial T} \right)_{P, n} = - \bar{S}_i \dots\dots \text{Partial entropy}$$

$$\left( \frac{\partial \mu_{i/T}}{\partial T} \right)_{P, n} = \frac{T \left( \frac{\partial \mu_i}{\partial T} \right) - \mu_i}{T^2}$$

$$= \frac{T(-\bar{S}_i) - \bar{G}_i}{T^2}$$

$$= \frac{-T\bar{S}_i - \bar{G}_i}{T^2} = \frac{\bar{G}_i - \bar{H}_i - \bar{G}_i}{T^2}$$

$$\left( \frac{\partial \mu_{i/T}}{\partial T} \right)_{P, n} = - \frac{\bar{H}_i}{T^2}$$

# Chemical Potential ( $\mu$ ):

## Effect of Pressure on Chemical Potential

$$\mu_i = G_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T, P, n_j} \dots\dots\dots (1)$$

$$V^t = \left( \frac{\partial G^t}{\partial P} \right)_{T, n} \dots\dots\dots (2)$$

Differentiate eq<sup>n</sup> (1) w.r.t P (T, n constant)

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, n} = \left( \frac{\partial^2 G^t}{\partial P \partial n_i} \right)_{T, n} \dots\dots\dots (3)$$

Differentiate eq<sup>n</sup> (2) w.r.t  $n_i$  (T, n constant)

$$\left( \frac{\partial V^t}{\partial n_i} \right)_{T, P} = \left( \frac{\partial^2 G^t}{\partial P \partial n_i} \right)_{T, n} \dots\dots\dots (4)$$

Compare (3) & (4)

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, n} = - \left( \frac{\partial V^t}{\partial n_i} \right)_{T, P}$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T, P} = \bar{V}_i \dots\dots \text{Partial Volume}$$





## Partial Molar Properties:

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

## Summability equation

$$M = \sum \overline{M}_i x_i$$

$$nM = \sum \overline{M}_i n_i$$

For binary system

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

## Partial Molar Properties of Binary mixture:

$$\overline{M}_1 = M - x_2 \frac{dM}{dx_2} \quad \overline{M}_2 = M - x_1 \frac{dM}{dx_1}$$

## Recap:

### Gibbs-Duhem relation

$$\sum x_i d\overline{M}_i = 0 \quad \text{..... (at constant T \& P)}$$

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

For binary system

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

$$\frac{d\overline{M}_2}{dx_2} = - \frac{x_1}{x_2} \frac{d\overline{M}_1}{dx_2}$$

$$\text{Chemical Potential, } \mu_i = \overline{G}_i = \left( \frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j}$$

$$G = \sum \mu_i x_i$$

$$\mu_i = \left( \frac{dA}{dn_i} \right)_{T,V}$$

$$\mu_i = \left( \frac{dU}{dn_i} \right)_{S,V}$$

$$\mu_i = \left( \frac{dH}{dn_i} \right)_{S,P}$$

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

$$\left( \frac{\partial \mu_i / T}{\partial T} \right)_{P,n} = - \frac{\overline{H}_i}{T^2}$$

$$\left( \frac{\partial \mu_i}{\partial P} \right)_{T,P} = \overline{V}_i$$

# Ideal Gas-state Mixture Partial Properties Model

Ideal gas,  $PV = nRT$  (total volume,  $m^3$ )  
 $PV = RT$  (molar volume,  $m^3/mol$ )

Real gas,  $PV = ZnRT$   
 $PV = ZRT$   
 $Z$  = compressibility factor

For ideal gas,  $Z = 1$

$$Z = \frac{Pv^{real}}{RT} = \frac{v^{real}}{v^{ig}}$$

$$Pv^{ig} = RT \quad \text{or,} \quad v^{ig} = \frac{RT}{P}$$

**Partial Properties:**

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\overline{v}_i = \left( \frac{\partial(nv)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\overline{v}_i^{ig} = \left( \frac{\partial(n \frac{RT}{P})}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

For Ideal gas

$$\overline{v}_i^{ig} = \frac{RT}{P} \left( \frac{\partial(n)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\overline{v}_i^{ig} = \frac{RT}{P}$$

$$\overline{v}_i^{ig} = \frac{RT}{P} = v_i^{ig} = V^{ig}$$

$$p_i = y_i P = \frac{y_i RT}{V^{ig}}$$

$$\left( \frac{\partial(n)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\left( \frac{\partial n_1 + \partial n_2}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\left( \frac{\partial n_1}{\partial n_i} \right)_{T,P, n_{j \neq i}} = 1$$

# Ideal Gas-state Mixture Partial Properties Model

**Assumption:** Molecules have zero volume that do not interact.

So according to the ideal gas mixture model

$$\overline{M}_i^{ig}(T, P) = M_i^{ig}(T, p_i) \quad \overline{M}_i^{ig} \neq \overline{V}_i^{ig}$$

## Case 1: Enthalpy (H)

$$H^{ig} = f(T) = C_p dT \quad (\text{independent of pressure})$$

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

$$\text{So, } \overline{H}_i^{ig} = H_i^{ig}$$

## Case 2: Internal Energy (U)

$$U^{ig} = f(T) \quad (\text{independent of pressure})$$

$$\overline{U}_i^{ig}(T, P) = U_i^{ig}(T, p_i) = U_i^{ig}(T, P)$$

$$\overline{U}_i^{ig} = U_i^{ig}$$

## Case 3: Entropy (S)

$$S^{ig} = f(T, P)$$

From Maxwell equation we know that

$$dH = TdS + VdP$$

For ideal gas

$$TdS^{ig} = dH^{ig} - V^{ig}dP \quad (\text{At const. } T, dH^{ig} = C_p dT = 0)$$

$$dS^{ig} = -\frac{v^{ig}}{T} dP$$

$$\int_{S_i(P,T)}^{\overline{S}_i(p_i,T)} dS^{ig} = - \int_P^{p_i} \frac{v^{ig}}{T} dP$$

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

From ideal gas mixture model we know

$$\overline{S}_i^{ig}(T, P) = S_i^{ig}(T, p_i) \text{ or}$$

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

$$p_i = y_i P$$
$$y_i = \frac{p_i}{P}$$

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

# Ideal Gas-state Mixture Partial Properties Model

## Case 4: Gibbs free energy (g)

$$G^{ig} = f(T, P)$$

From Maxwell equation we know that

$$dG = VdP - SdT$$

(for real gas and At const.  $dT = 0$ )

$$dG^{ig} = v^{ig}dP = \frac{RT}{P}dP$$

$$\int_{G_i(P,T)}^{\overline{G}_i(p_i,T)} dG^{ig} = \int_P^{p_i} \frac{RT}{P} dP$$

$$G_i^{ig}(p_i, T) - G_i^{ig}(P, T) = RT \ln \frac{p_i}{P}$$

From ideal gas mixture model we know

$$\overline{G}_i^{ig}(T, P) = G_i^{ig}(T, p_i) \text{ or}$$

$$\overline{G}_i^{ig}(T, P) - G_i^{ig}(T, P) = RT \ln \frac{p_i}{P}$$

$$\boxed{\overline{G}_i^{ig} = G_i^{ig} + RT \ln y_i}$$

# Change in Properties of Mixing

$$\Delta M_{\text{mix}} = M - \sum M_i x_i$$

From Summability equation

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

$$\Delta M_{\text{mix}} = \sum \bar{M}_i x_i - \sum M_i x_i$$

$$\Delta M_{\text{mix}} = \sum x_i (\bar{M}_i - M_i)$$

## Case 1: Enthalpy (H)

$$\Delta H_{\text{mix}} = \sum x_i (\bar{H}_i - H_i)$$

For ideal gas

$$\Delta H_{\text{mix}}^{ig} = \sum y_i (\bar{H}_i^{ig} - H_i^{ig})$$

$$\Delta H_{\text{mix}}^{ig} = 0 \quad (\text{as } \bar{H}_i^{ig} = H_i^{ig})$$

## Case 2: Internal Energy (U)

$$\Delta U_{\text{mix}} = \sum x_i (\bar{U}_i - U_i)$$

For ideal gas

$$\Delta U_{\text{mix}}^{ig} = \sum y_i (\bar{U}_i^{ig} - U_i^{ig})$$

$$\Delta U_{\text{mix}}^{ig} = 0 \quad (\text{as } \bar{U}_i^{ig} = U_i^{ig})$$

## Case 3: Volume (V)

$$\Delta V_{\text{mix}} = \sum x_i (\bar{V}_i - V_i)$$

For ideal gas

$$\Delta V_{\text{mix}}^{ig} = \sum y_i (\bar{V}_i^{ig} - V_i^{ig})$$

$$\Delta V_{\text{mix}}^{ig} = 0 \quad (\text{as } \bar{V}_i^{ig} = V_i^{ig})$$

# Change in Properties of Mixing

## Case 4: Entropy (S)

$$\Delta S_{\text{mix}} = \sum y_i (\bar{S}_i - S_i)$$

For ideal gas

$$\Delta S_{\text{mix}}^{ig} = \sum y_i (\bar{S}_i^{ig} - S_i^{ig})$$

$$\Delta S_{\text{mix}}^{ig} = \sum y_i (-R \ln y_i)$$

$$\Delta S_{\text{mix}}^{ig} = -R \sum (y_i \ln y_i)$$

## Case 5: Gibbs Free Energy (g)

$$\Delta g_{\text{mix}} = \sum y_i (\bar{G}_i - G_i)$$

For ideal gas

$$\Delta G_{\text{mix}}^{ig} = \sum y_i (\bar{G}_i^{ig} - G_i^{ig})$$

$$\Delta G_{\text{mix}}^{ig} = \sum y_i (RT \ln y_i)$$

$$\Delta G_{\text{mix}}^{ig} = RT \sum (y_i \ln y_i)$$

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}}$$

## Recap:

$$\overline{v}_i^{ig} = \frac{RT}{P} = v_i^{ig} = V^{ig}$$

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

$$\text{So, } \overline{H}_i^{ig} = H_i^{ig}$$

$$\overline{U}_i^{ig} = U_i^{ig}$$

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

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

$$\Delta M_{\text{mix}} = \sum x_i (\overline{M}_i - M_i)$$

$$\Delta H_{\text{mix}}^{ig} = 0$$

$$\Delta U_{\text{mix}}^{ig} = 0$$

$$\Delta V_{\text{mix}}^{ig} = 0$$

$$\Delta S_{\text{mix}}^{ig} = -R \sum (y_i \ln y_i)$$

$$\Delta G_{\text{mix}}^{ig} = RT \sum (y_i \ln y_i)$$

$$\Delta G^{\text{mix}} = \Delta H^{\text{mix}} - T \Delta S^{\text{mix}}$$

**Problem:**

For a given binary system at const. temp and pressure the molar volume ( $\text{m}^3/\text{mol}$ ) is given by

$$v = 30x_A + 20x_B + x_Ax_B(15x_A - 7x_B)$$

Then what should be the total volume of mixing  $\Delta v_{\text{mix}}$  ( $\text{m}^3/\text{mol}$ ) at  $x_A = 0.5$  ?



## Excess Properties:

Any solution (**liquid**) is how much far from ideal solution is known as **Excess properties ( $M^E$ )**

$$M^E = M - M^{id}$$

**Residual Properties ( $M^R$ ):** Any solution (**gas**) is how much far from ideal solution

$$M^R = M - M^{id}$$

**Excess properties:**

$$M^E = M - M^{id}$$

$$\Delta M_{mix}^{id} = M^{id} - \sum M_i x_i$$

$$M^{id} = \Delta M_{mix}^{id} + \sum M_i x_i$$

$$M^E = M - \Delta M_{mix}^{id} - \sum M_i x_i$$

$$M = M^E + \Delta M_{mix}^{id} + \sum M_i x_i$$

**Case 1: Enthalpy**

$$H = H^E + \Delta H_{mix}^{id} + \sum H_i x_i$$

$$H = H^E + \sum H_i x_i \quad \Delta H_{mix}^{id} = 0$$

$$H^E = H - \sum H_i x_i = \Delta H_{mix}^{real}$$

## Excess Properties:

### Case 2: Internal Energy

$$U = U^E + \Delta U_{mix}^{id} + \sum U_i x_i$$

$$U = U^E + \sum H_i x_i \quad \Delta U_{mix}^{id} = 0$$

$$U^E = U - \sum U_i x_i = \Delta U_{mix}^{real}$$

### Case 3: Volume

$$V = V^E + \Delta V_{mix}^{id} + \sum V_i x_i$$

$$V = V^E + \sum V_i x_i \quad \Delta V_{mix}^{id} = 0$$

$$V^E = V - \sum V_i x_i = \Delta V_{mix}^{real}$$

### Case 4: Gibbs Free Energy

$$G = G^E + \Delta G_{mix}^{id} + \sum G_i x_i$$

$$G = G^E + \sum G_i x_i + RT \sum (x_i \ln x_i)$$

$$\Delta G_{mix}^{ig} = RT \sum (x_i \ln x_i)$$

$$G - \sum G_i x_i = G^E + RT \sum (x_i \ln x_i)$$

$$\Delta G_{mix}^{real} = G^E + RT \sum (x_i \ln x_i)$$

### Case 5: Entropy

$$S = S^E + \Delta S_{mix}^{id} + \sum S_i x_i$$

$$S = S^E + \sum S_i x_i - R \sum (x_i \ln x_i)$$

$$\Delta S_{mix}^{ig} = R \sum (x_i \ln x_i)$$

$$S - \sum S_i x_i = S^E - R \sum (x_i \ln x_i)$$

$$\Delta S_{mix}^{real} = S^E - R \sum (x_i \ln x_i)$$

## Problem:

A binary system at a constant pressure with species 1 & 2 is described by two-suffix Margules equation

$$\frac{g^E}{RT} = 3x_1x_2 \text{ (where } g^E \text{ is molar excess free energy, } R \text{ universal constant)}$$

At temperature  $T$ ,  $\frac{g_1}{RT} = 1$  and  $\frac{g_2}{RT} = 2$ , where  $g_1$  and  $g_2$  are molar Gibbs free energy. What is the value of  $\frac{g}{RT}$  for a binary mixture with 40 % of species 1?

## Fugacity (f)

$$\sum y_i (\overline{G}_i^{ig} - G_i^{ig}) = \Delta G_{mix}^{ig} = RT \sum (y_i \ln y_i)$$

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

- **Fugacity** define the escaping tendency of real gas in the heterogenous system  
Ex: LPG operation
- Fugacity also define as a particular pressure at which it changes it phases (liquid to gas or vice versa).
- When the escaping tendency of the both phases are same, then the system are in equilibrium

$$dG = v dP - S dT$$

At const. temp.

$$dG = v dP$$

For ideal gas,  $Pv = RT$

$$v = \frac{RT}{P}$$

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

For real gas

$$dG = RT \ln f$$

$$dG - dG^{ig} = RT \ln \frac{f}{P}$$

$$d(G - G^{ig}) = RT \ln \frac{f}{P}$$

$$dG^R = RT \ln \frac{f}{P}$$

**(GR = residual Gibbs free energy)**

$$\int_{G^R=0}^{G^R} dG^R = \int_{P \rightarrow 0}^P RT \ln \frac{f}{P}$$

$$G^R = RT \ln \frac{f}{P}$$

$$\frac{G^R}{RT} = \ln \frac{f}{P}$$

## Fugacity Coefficient ( $\Phi$ )

$$\Phi = \frac{f}{P} = \frac{\text{pressure of real gas}}{\text{pressure of ideal gas}}$$

$$\frac{G^R}{RT} = \ln \frac{f}{P} = \ln \Phi$$

### Problem:

*The vapor pressure of a pure substance at a temperature  $T$  is 30 bar. The actual and ideal gas values of  $\frac{g}{RT}$  for the saturated vapor at this temperature and pressure are 7.0 and 7.7 respectively. Here,  $g$  is the molar Gibbs free energy and  $R$  is the gas constant. What is the fugacity of the saturated liquid at this condition?*

## Fugacity in terms of Compressibility Factor:

$$Z = \frac{Pv}{RT} = \frac{v_{real}}{v_{ideal}}$$

$$v_{real} = Z v_{ideal}$$

$$dG = v dP - S dT$$

At const. temp.

$$dG = v dP$$

For ideal gas,  $Pv = RT$

$$dG - dG^{ig} = (v - v^{ig}) dP$$

$$\int_{G^R=0}^{G^R} dG^R = \int_{P \rightarrow 0}^P (v - v^{ig}) dP$$

$$\int_{G^R=0}^{G^R} dG^R = \int_{P \rightarrow 0}^P (Z v^{ig} - v^{ig}) dP$$

$$\int_{G^R=0}^{G^R} dG^R = \int_{P \rightarrow 0}^P (Z - 1) v^{ig} dP$$

$$G^R = \int_0^P (Z - 1) \frac{RT}{P} dP$$

$$\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P}$$

$$\frac{G^R}{RT} = \ln \frac{f}{P} = \ln \Phi = \int_0^P (Z - 1) \frac{dP}{P}$$

## Fugacity in terms of Residual Volume ( $V^R$ ):

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

$$dG = v dP - S dT$$

At const. temp.

$$dG = v dP$$

For ideal gas,  $Pv = RT$

$$dG - dG^{ig} = (v - v^{ig}) dP$$

$$\int_{G^R=0}^{G^R} dG^R = \int_{P \rightarrow 0}^P v^R dP$$

$$\frac{G^R}{RT} = \int_0^P \frac{v^R}{RT} dP$$

$$\frac{G^R}{RT} = \ln \frac{f}{P} = \ln \Phi = \int_0^P (Z - 1) \frac{dP}{P} = \int_0^P \frac{v^R}{RT} dP$$

$$Z = 1 + \frac{BP}{RT}$$

$$\frac{Z - 1}{P} = \frac{B}{RT}$$

$$\int_0^P (Z - 1) \frac{dP}{P} = \int_0^P \frac{B}{RT} dP = \frac{BP}{RT}$$

$$G^R = BP$$

## Problem:

A pure gas obeys the equation  $\frac{Pv}{RT} = 1 + \frac{BP}{RT}$  where  $P$  is pressure and  $T$  is absolute temperature,  $v$  is molar volume,  $R$  is gas constant and  $B$  is parameter depended of  $T$  &  $P$ . The residual Gibbs free energy is given by  $\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P}$

$Z$  is compressibility factor,  $B = 10^{-4} \text{ m}^3/\text{mol}$ . *Integral is evaluated at constant temperature.*

What is the residual molar enthalpy in (J/mol) of the gas at 1000 kPa at 300 K?

Given:  $\frac{G^R}{RT} = \frac{v^R}{RT} dP - \frac{H^R}{RT^2} dT$  *(at constant pressure)*



## Activity and Activity Coefficient

$$dG = vdP - SdT$$

At constant temp.

$$dG = vdP$$

For ideal liquid

$$d\bar{G}^{id} = RTd\ln\hat{f}_i^{id} \dots\dots (1)$$

For real liquid

$$d\bar{G} = RTd\ln\hat{f}_i \dots\dots\dots (2)$$

$$(2) - (1)$$

$$d(\bar{G} - \bar{G}^{id}) = RTd\ln\frac{\hat{f}_i}{\hat{f}_i^{id}}$$

$$\bar{G}^E = \int_0^{\hat{f}_i} RTd\ln\frac{\hat{f}_i}{\hat{f}_i^{id}}$$

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

$$\frac{\bar{G}^E}{RT} = \ln\frac{\hat{f}_i}{\hat{f}_i^{id}} = \ln\gamma_i \text{ (activity coefficient)}$$

$$\gamma_i = \frac{\text{fugacity in real solution}}{\text{fugacity in ideal solution}}$$

$$\text{Activity } (a_i) = \frac{\text{fugacity of species } i \text{ in real solution}}{\text{fugacity of pure species}}$$

$$(a_i) = \frac{\hat{f}_i}{f_i}$$

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{id}} = \frac{\hat{f}_i}{f_i \cdot x_i} = \frac{a_i}{x_i}$$

$$a_i = \gamma_i x_i$$

## Activity and Activity Coefficient

$$\overline{M}_i = \left( \frac{\partial(nM)}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

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

$$\frac{\overline{G}^E}{RT} = \left( \frac{\partial(n \frac{G^E}{RT})}{\partial n_i} \right)_{T,P, n_{j \neq i}}$$

$$\overline{M}_1 = M - x_2 \frac{dM}{dx_2}$$

$$\frac{\overline{G}^E}{RT} = \frac{G^E}{RT} - x_2 \frac{d \frac{G^E}{RT}}{dx_2}$$

$$\ln \gamma_1 = \frac{G^E}{RT} - x_2 \frac{d \frac{G^E}{RT}}{dx_2}$$

$$\ln \gamma_2 = \frac{G^E}{RT} - x_1 \frac{d \frac{G^E}{RT}}{dx_1}$$

$$\ln \gamma_1 = \left( \frac{\partial(n \frac{G^E}{RT})}{\partial n_1} \right)_{T,P, n_2}$$

$$\ln \gamma_2 = \left( \frac{\partial(n \frac{G^E}{RT})}{\partial n_2} \right)_{T,P, n_1}$$

### Problem:

Fugacity of component 1 in a binary liquid mixture of component 1 and 2 at 303 K and 10 bar is given by

$$\hat{f}_1 = 50 x_1 + 100 x_1 x_2 + 20 x_2^2$$

Find out the activity coefficient of component 1 for equimolar composition.



## Phase Equilibrium for Ideal Solution

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{\text{id}}} = \frac{\hat{f}_i}{f_i \cdot x_i}$$

For liquid system

$$\hat{f}_i^l = x_i \gamma_i^l f_i^l$$

For gas system

$$\hat{f}_i^v = y_i \Phi_i^v P$$

Now vapour phase is assume to be ideal gas state and liquid phase is an ideal solution

$$\gamma_i = \Phi_i = 1$$

And if the system is in equilibrium and the pressure of the liquid system will be saturated pressure ( $P_i^{\text{sat}}$ )

$$\hat{f}_i^l = \hat{f}_i^v$$

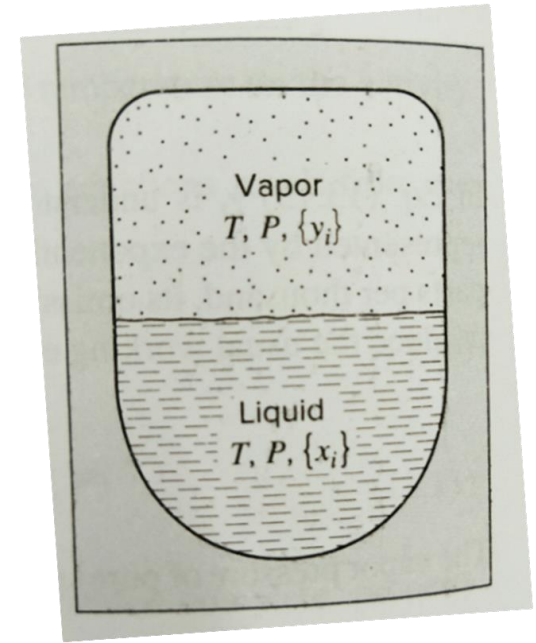
$$x_i \gamma_i^l f_i^l = y_i \Phi_i^v P$$

$$x_i \gamma_i^l \Phi_i^{\text{sat}} P_i^{\text{sat}} = y_i \Phi_i^v P$$

$$x_i \gamma_i^l P_i^{\text{sat}} = y_i \frac{\Phi_i^v}{\Phi_i^{\text{sat}}} P$$

$$x_i \gamma_i^l P_i^{\text{sat}} = y_i \Phi_i P$$

$$\hat{f}_i^{\text{id}} = f_i \cdot x_i \quad \text{Lewis and Randall Rule}$$



Limitation:

- Ideal solution
- Low to moderate pressure

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

**Modified Raoult's Law**

$$y_i P = x_i P_i^{\text{sat}}$$

..... Raoult's law

# Vapour Liquid Equilibrium (VLE)

- Vapour pressure depends on the temperature and quantity of liquid and vapour

Vapour pressure can be calculated from Clausius-Clapeyron equation or Antoine equation

Clausius-Clapeyron equation:

$$\ln\left(\frac{p^v}{p_1^v}\right) = \frac{\lambda}{R} \left( \frac{1}{T_1} - \frac{1}{T} \right)$$

$\lambda$  = molar latent heat

$p^v, p_1^v$  = vapour pressure in pascal

Antoine equation:

$$\ln p^v = A - \frac{B}{T+C}$$

Parameterisation for T in °C and P in mmHg

	A	B	C	T min. (°C)	T max. (°C)
Water	8.07131	1730.63	233.426	1	100
Water	8.14019	1810.94	244.485	99	374
Ethanol	8.20417	1642.89	230.300	-57	80
Ethanol	7.68117	1332.04	199.200	77	243

# T-x-y diagram at Constant Pressure:

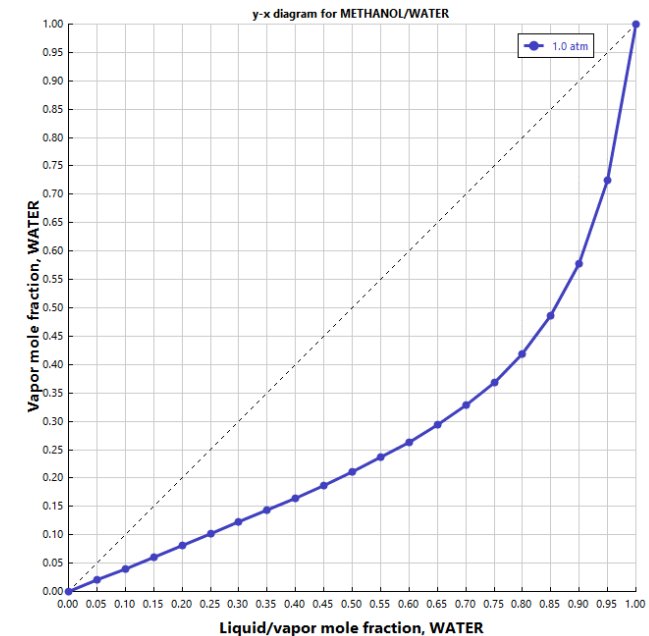
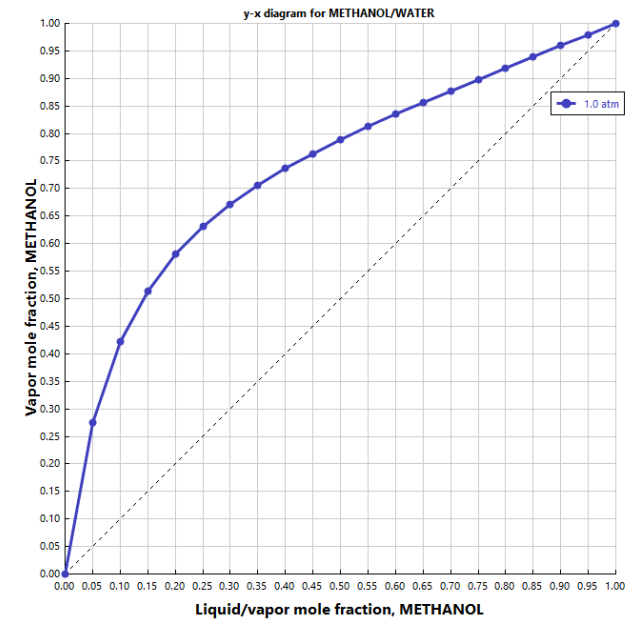
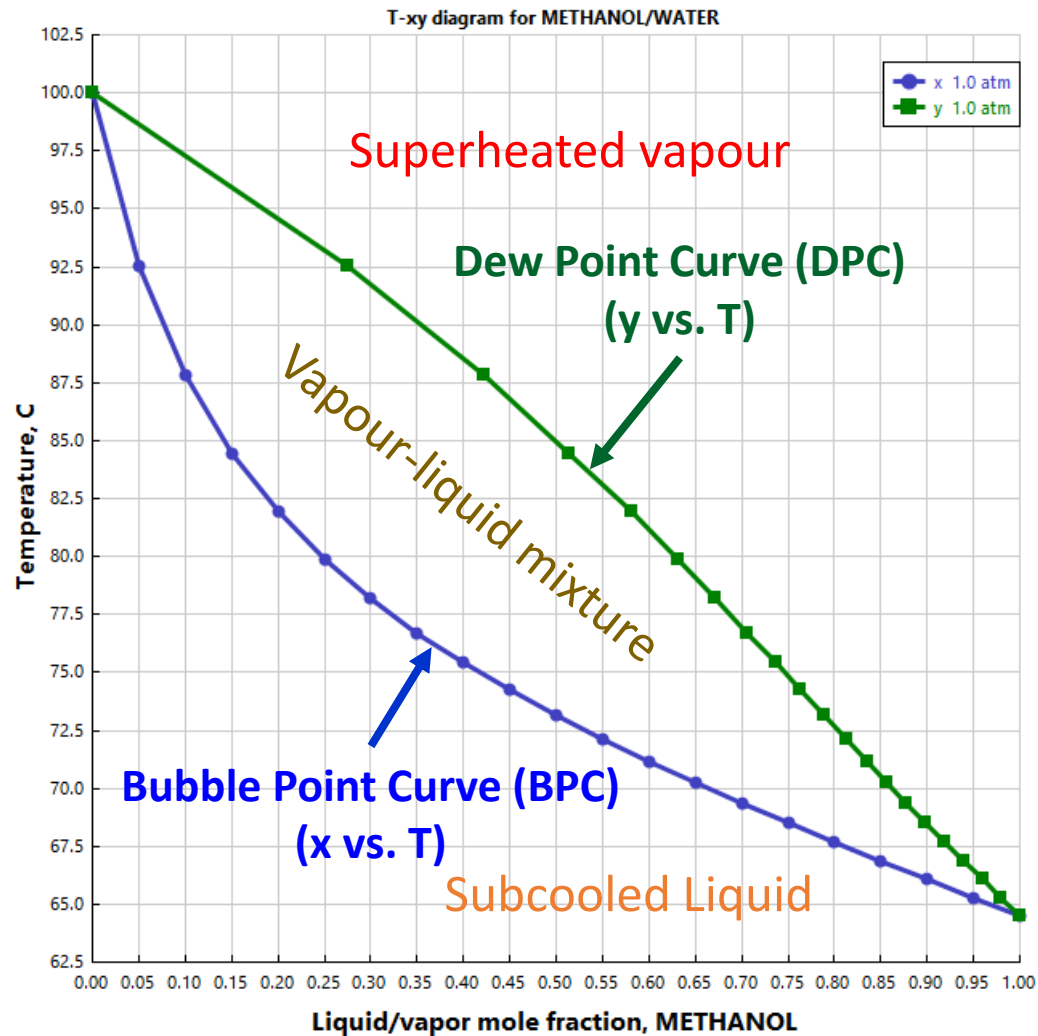
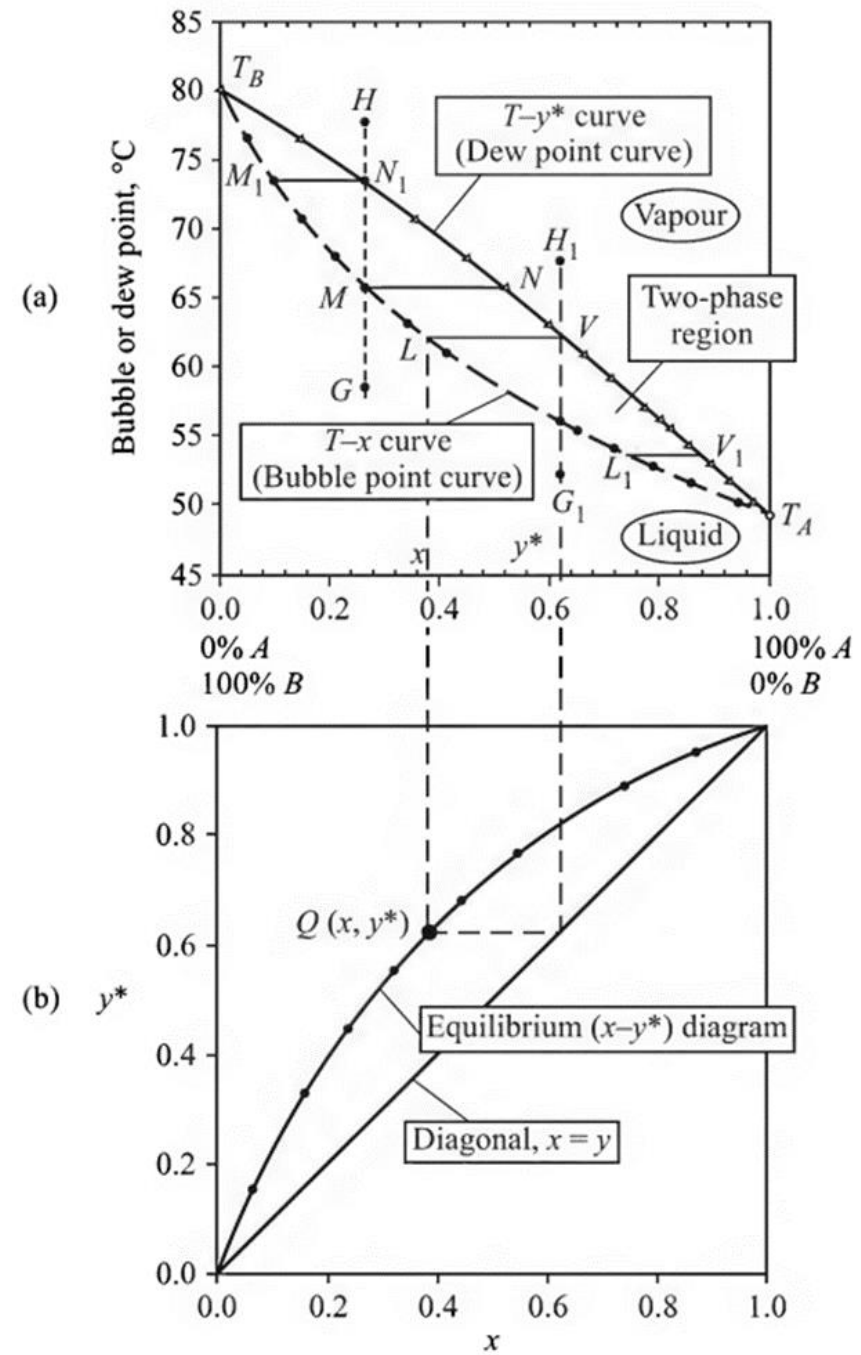


Fig. Constant pressure vapor liquid equilibria

# Constant pressure Binary T-x-y and x-y diagram



➤ Vapor-liquid equilibria at increased pressures

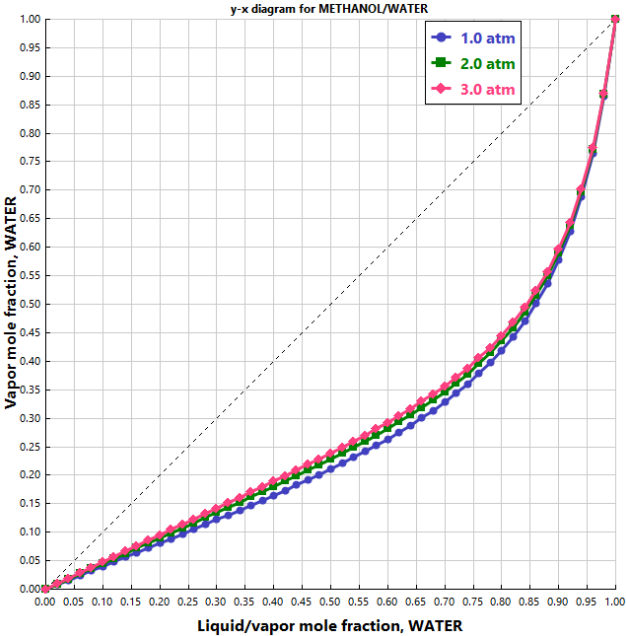
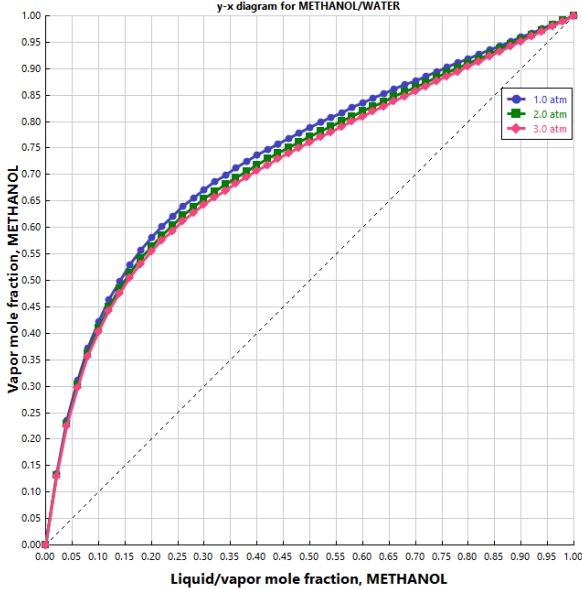
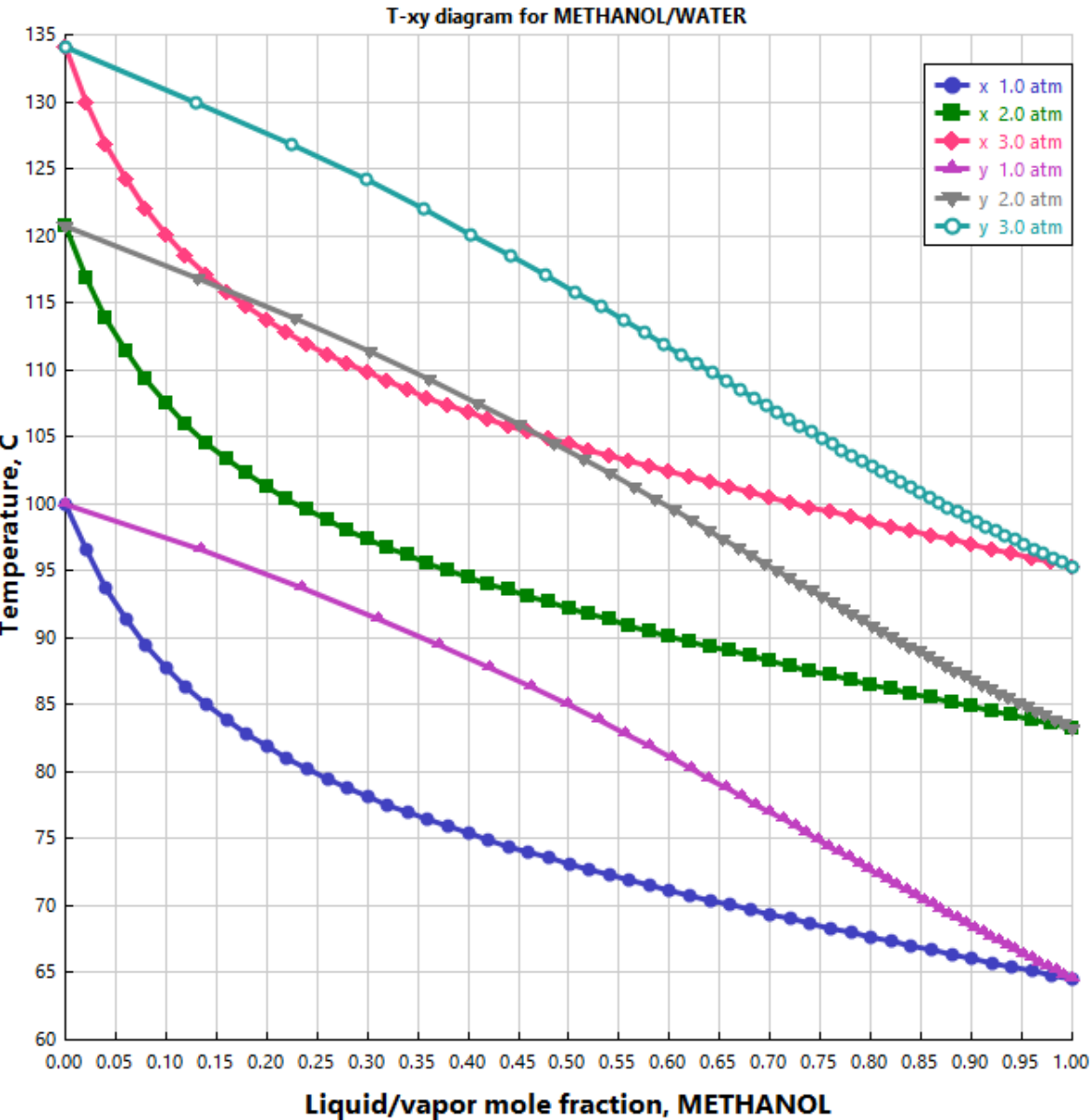


Fig. Vapor liquid equilibria at increased pressures



## Relative volatility ( $\alpha$ )

- This is the ratio of the concentration ratio of A and B in one phase to that in the other and is a measure of the separability.

$$\alpha = \frac{\frac{y^*}{(1-y^*)}}{\frac{x}{(1-x)}} = \frac{y^* (1-x)}{x (1-y^*)} \quad (1)$$

$$y^* = \frac{\alpha x}{1 + (\alpha - 1)x}$$

$x$  – mole fraction of the more volatile substance in the liquid

$y^*$  – mole fraction of the more volatile substance in the vapor

- The value of  $\alpha$  will ordinarily change as  $x$  varies from 0 to 1.
- If  $y^* = x$  (except at  $x = 0$  or 1),  $\alpha=1$  and no separation is possible.
- The larger the value of  $\alpha$  above unity, the greater the degree of separability.

## ➤ P-x-y diagram for methanol-water

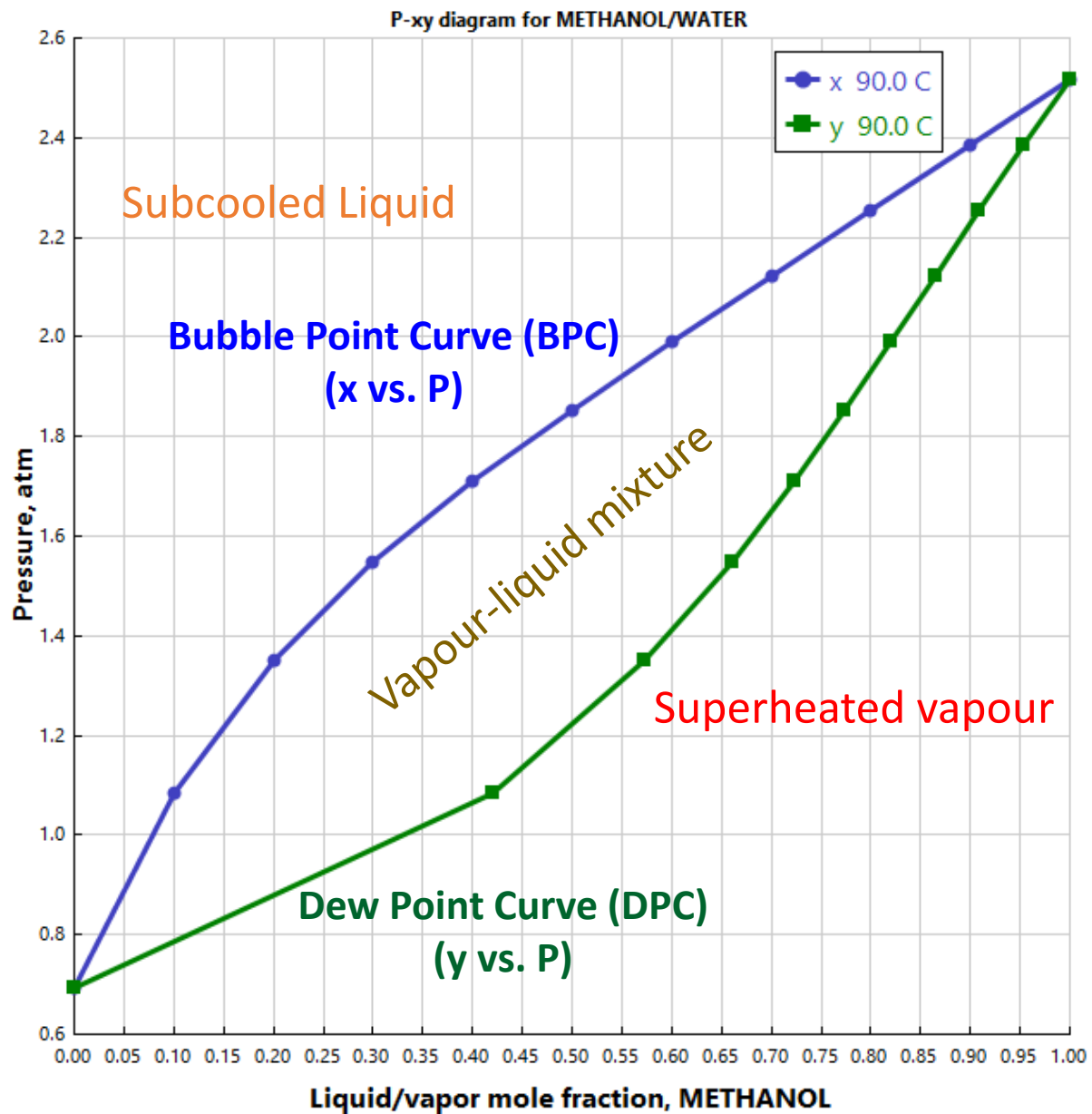
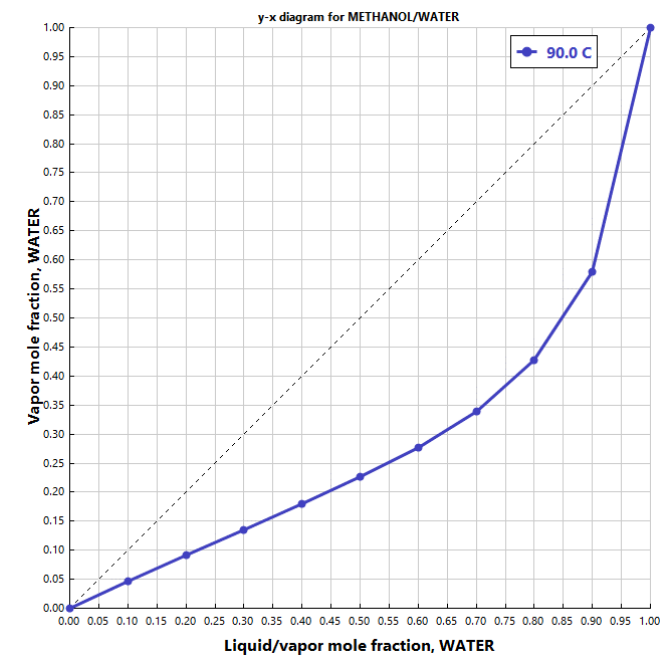
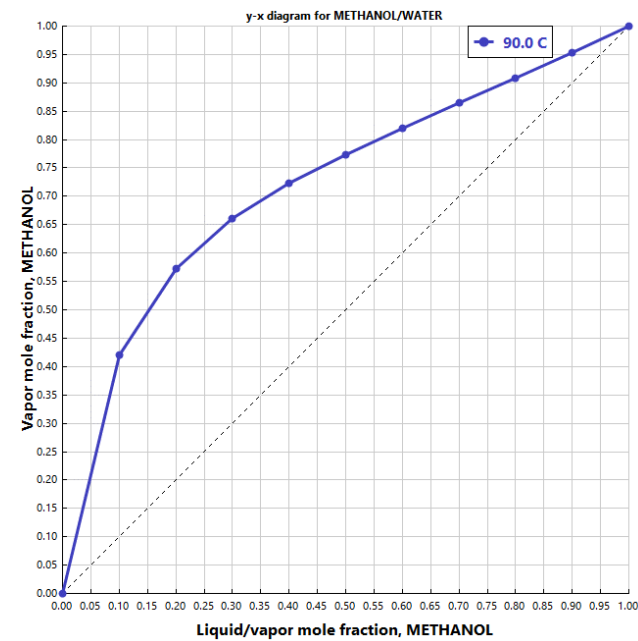


Fig. Constant temperature vapor liquid equilibria



## Raoult's Law: (Ideal gas-liquid system)

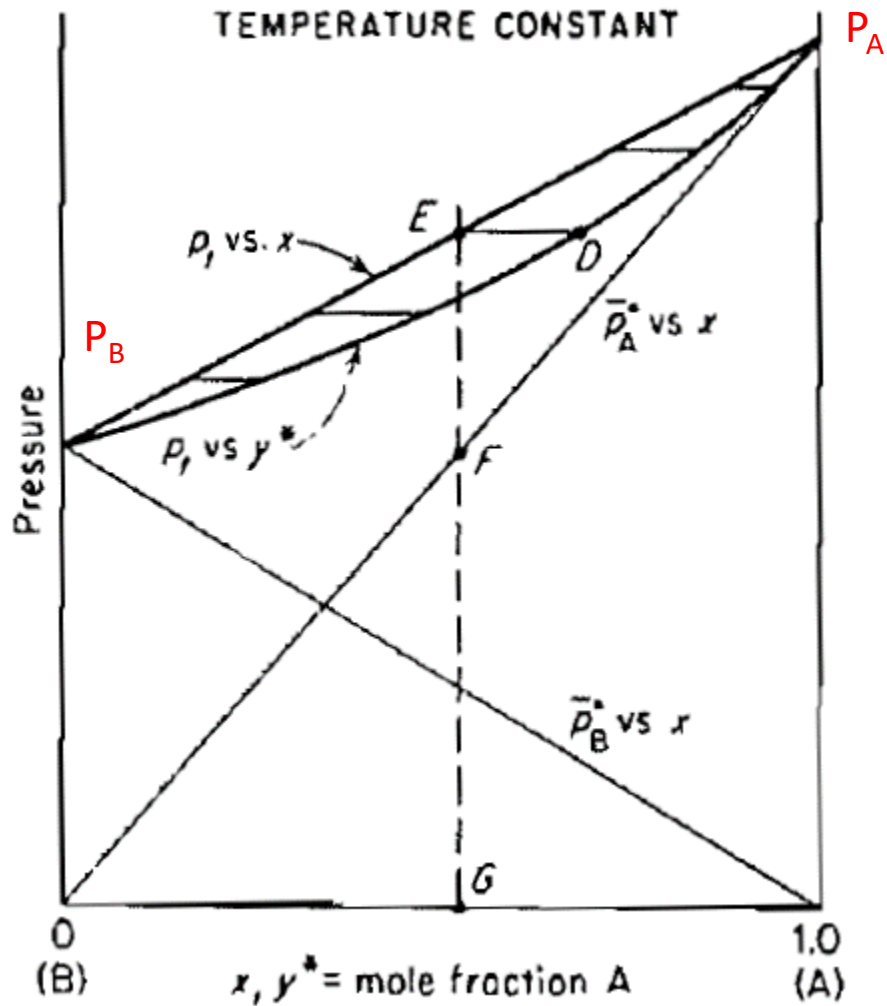


Fig. Ideal solutions

$$y^* = \frac{\text{distance FG}}{\text{distance EG}} = \frac{\overline{P}_A^*}{P_t} = \frac{P_A x}{P_t} \quad (5)$$

$$1 - y^* = \frac{\overline{P}_B^*}{P_t} = \frac{P_B (1 - x)}{P_t} \quad (6)$$

The relative volatility  $\alpha$  is, by substitution in equation (1)

$$\alpha = \frac{P_A}{P_B} \quad (7)$$

## ➤ Positive deviations from ideality

- A mixture whose total pressure is greater than that computed for ideality (eq. 4) is said to show positive deviations from Raoult's law.

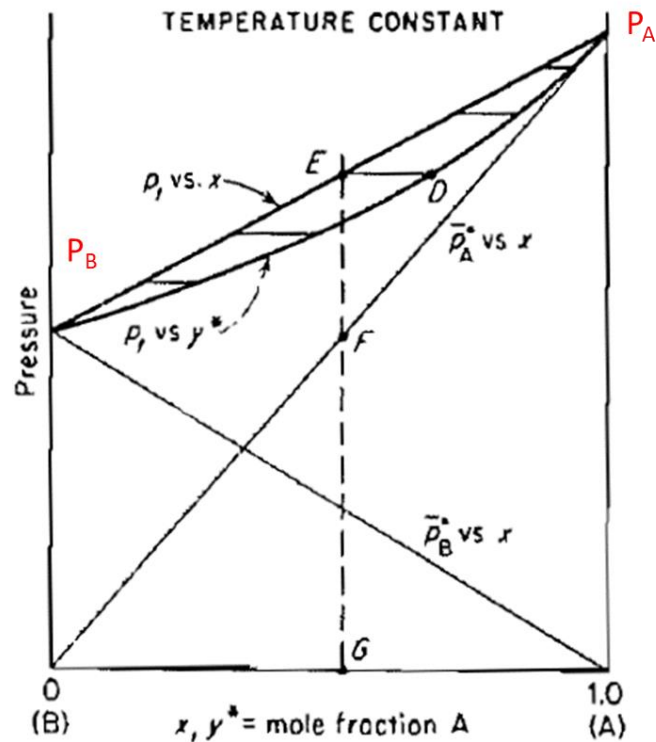
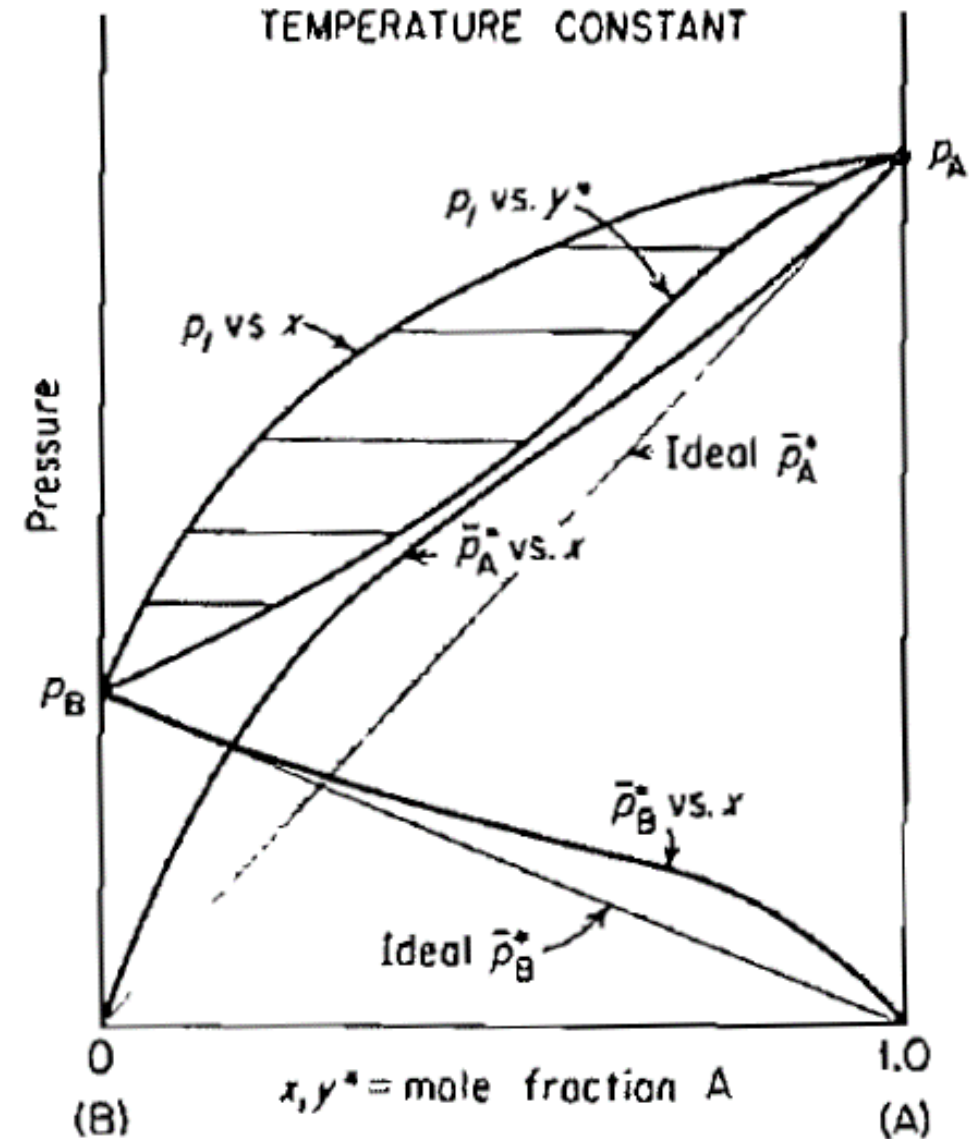
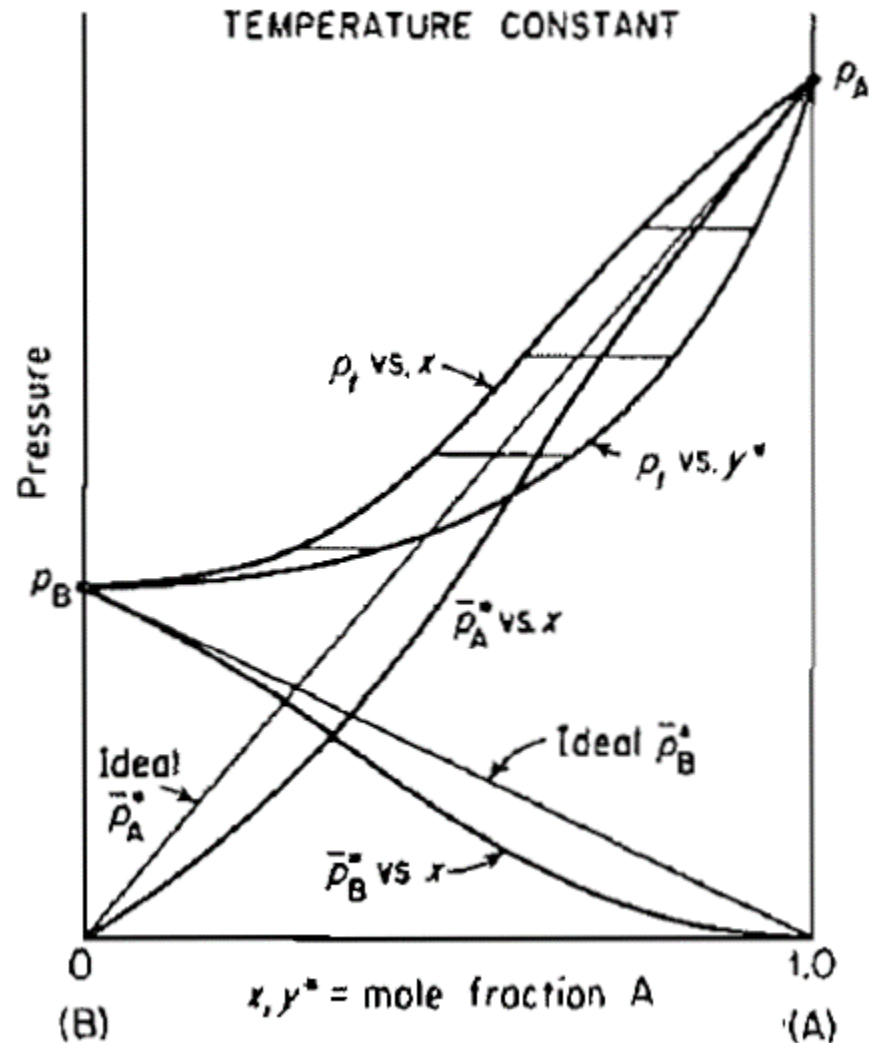


Fig. Ideal solutions

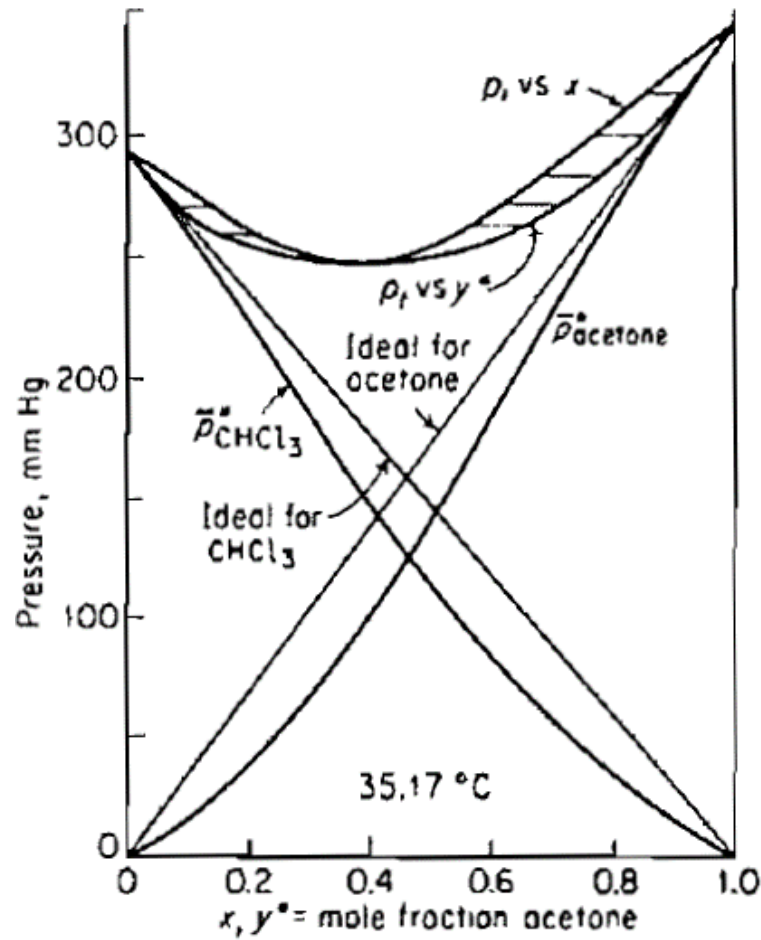


## ➤ Negative deviations from Ideality

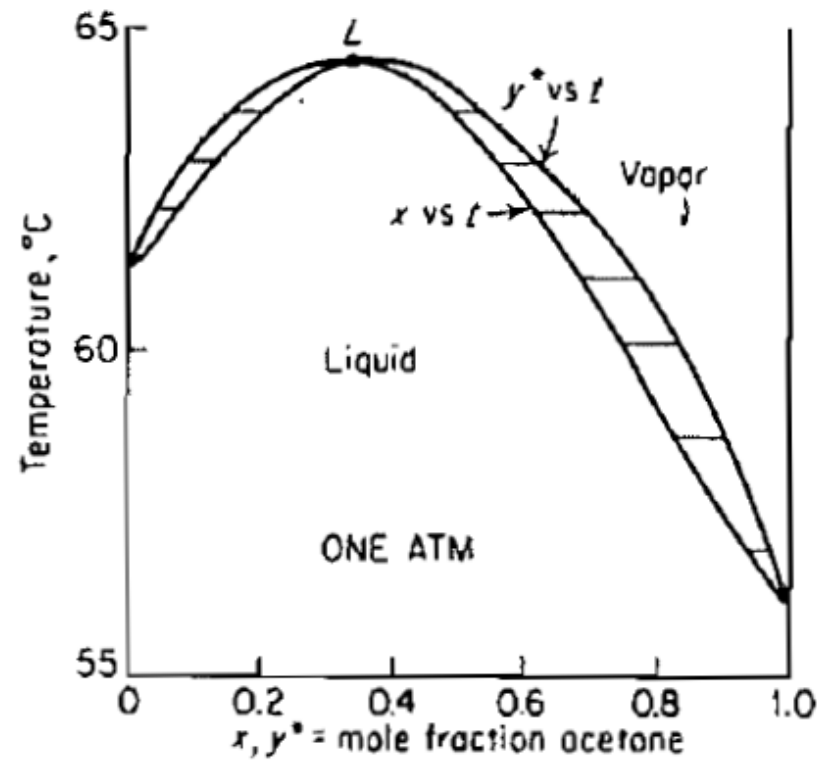
- When the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from Raoult's law.



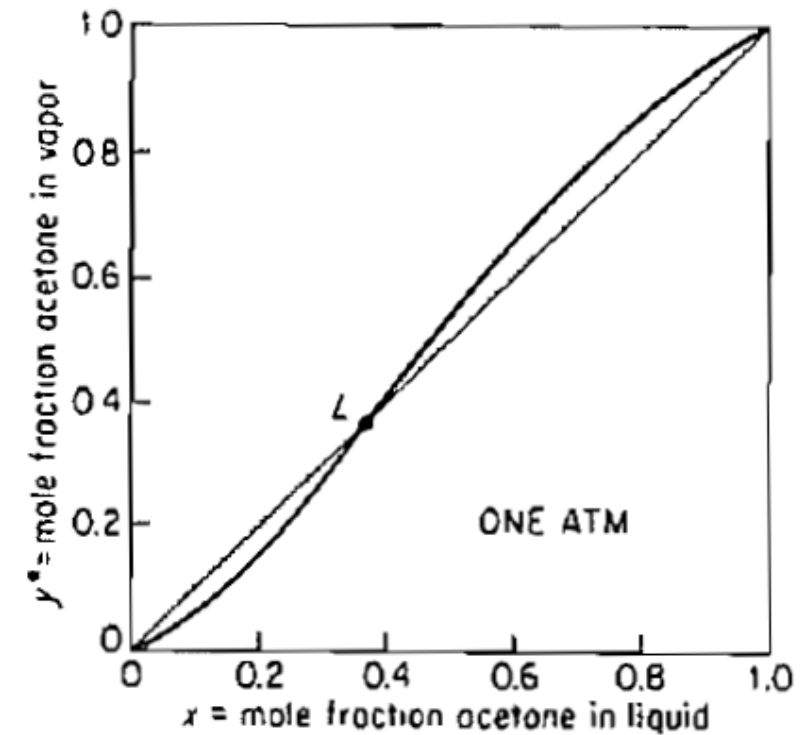
➤ Maximum boiling mixtures - azeotropes



(a)



(b)



(c)

Fig. Maximum-boiling azeotropism in the system acetone-chloroform: (a) at constant temperature; (b) and (c) at constant pressure.



# Enthalpy Concentration Diagram

○ 40 wt% ethanol water  
mixture at 84 °C

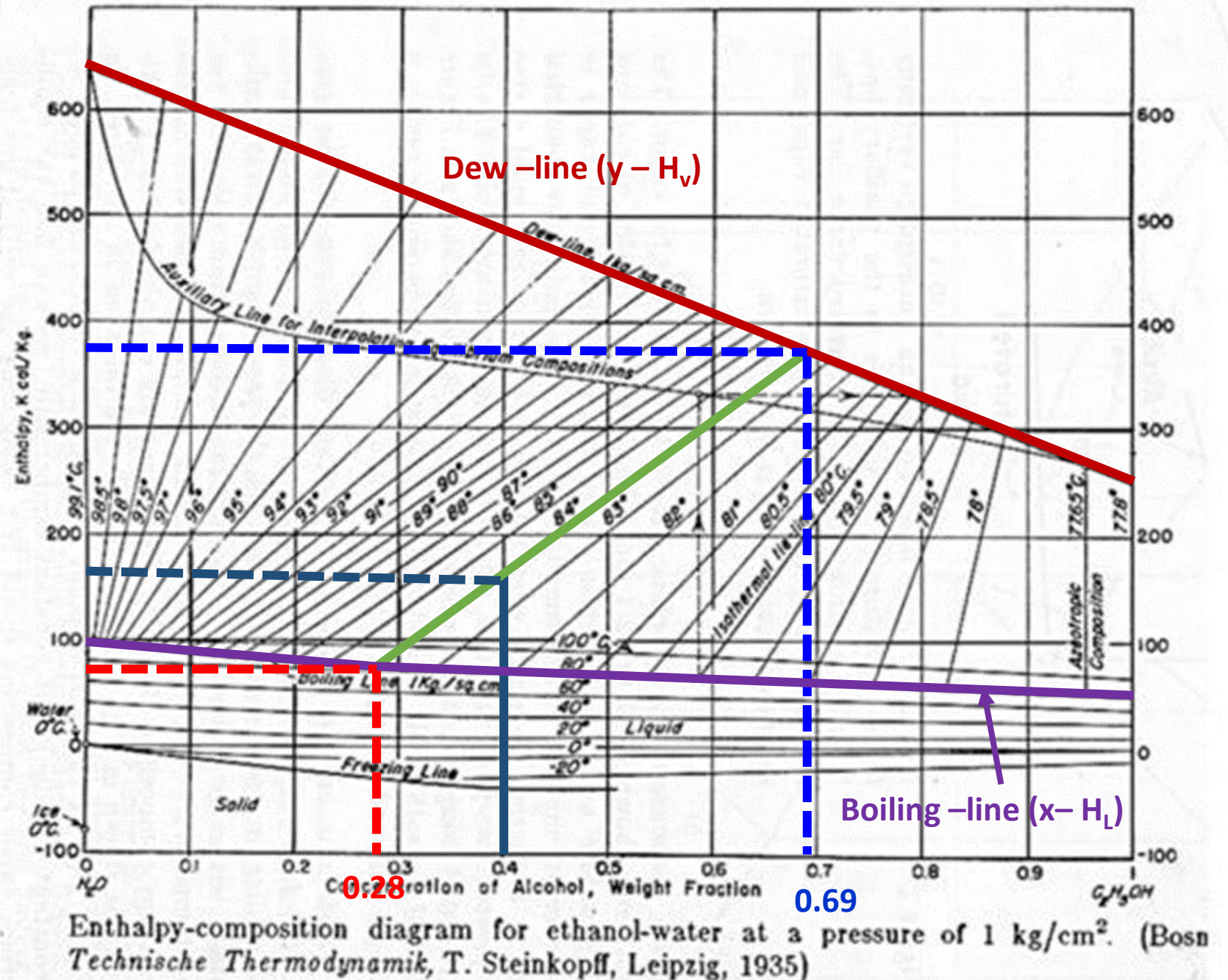
✓  $x_{\text{ethanol}} = 0.28$

✓  $y_{\text{ethanol}} = 0.69$

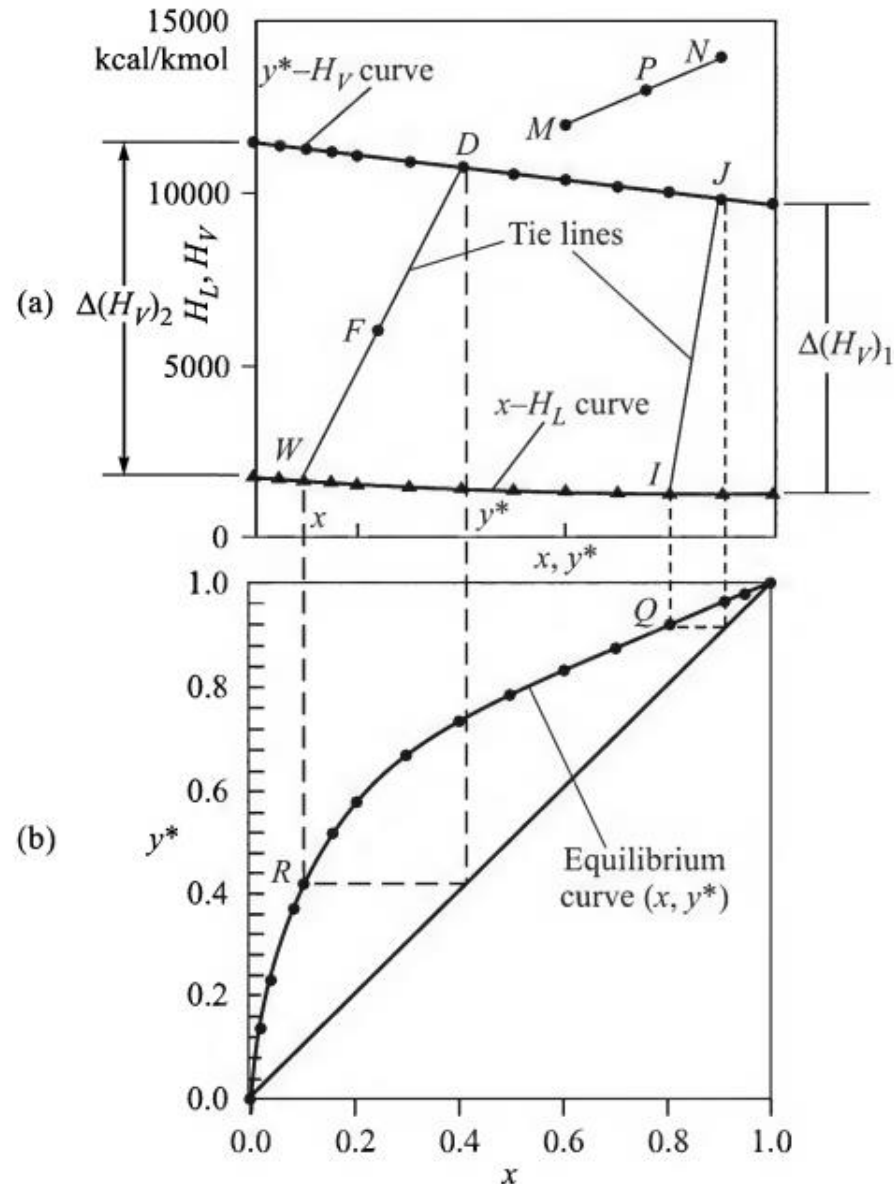
✓  $H_F = 165 \text{ Kcal/kg}$

✓  $H_v = 380 \text{ Kcal/kg}$

✓  $H_L = 70 \text{ Kcal/kg}$



# Enthalpy Concentration Diagram to Equilibrium Diagram



Total material balance:

Component A balance:

Enthalpy balance:

$$M + N = P$$

$$Mz_M + Nz_N = Pz_P$$

$$MH_M + NH_N = PH_P$$

$$\frac{M}{N} = \frac{z_N - z_P}{z_P - z_M}$$

$$\frac{M}{N} = \frac{H_N - H_P}{H_P - H_M}$$

$$\frac{H_N - H_P}{z_N - z_P} = \frac{H_P - H_M}{z_P - z_M}$$



### Problem 01:

A binary liquid mixture of n-pentane (1) and n-heptane (2) make a ideal solution. The vapor pressure of the pure component are given by Antoine equation. Prepare

- P-x-y diagram at 70 °C.
- T-x-y diagram at 10.325 kPa pressure.
- If the equimolar vapor mixture of this two at 90 °C is isothermally compressed till condensation starts. Determine the pressure at which condensation begins and composition of the liquid that form.

Components	A	B	C
n-pentane (1)	6.87633	1075.780	233.205
n-heptane (2)	6.89386	1264.370	216.640

# Excess Gibbs Free Energy Model (Binary Mixture)

*Behaviour of several liquid solution can not be express by equation of state to estimate the Gibbs free energy*

*Use empirical or semi empirical relation*

*For pure component activity coefficient,  $\gamma$  will be unity*

*Then  $\left(\frac{G^E}{RT}\right) \rightarrow 0$  (as,  $x_1 \rightarrow 1$  and  $x_2 \rightarrow 0$ )*

$$\frac{G^E}{RT} = \frac{G^E}{RT} (x_1, x_2)$$

*Then  $\left(\frac{G^E}{RT}\right) \rightarrow 0$  (as,  $x_1 \rightarrow 1$  and  $x_2 \rightarrow 0$ )*

$$\text{So } \left(\frac{G^E}{RT}\right) = 0 \text{ (as, } x_1 = 1 \text{ and } x_2 = 1)$$

## Models

1. Margules Equation
  - a. Two suffix Margules Equation
  - b. Three suffix Margules Equation
2. Redlich –Kister equation
3. Wohl's equation
4. Van Laar equation
5. Wilson and NRTL equation
6. UNIQUAC equation

# Excess Gibbs Free Energy Model (Binary Mixture)

## 1. Margules Equation

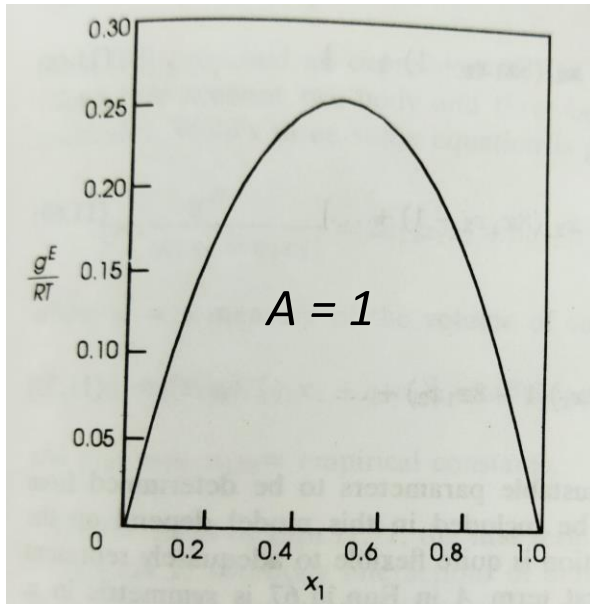
### a. Two suffix Margules Equation

$$\frac{G^E}{RT} = Ax_1x_2$$

$A$  = adjustable parameter

$$\ln \gamma_1 = Ax_2^2$$

$$\ln \gamma_2 = Ax_1^2$$

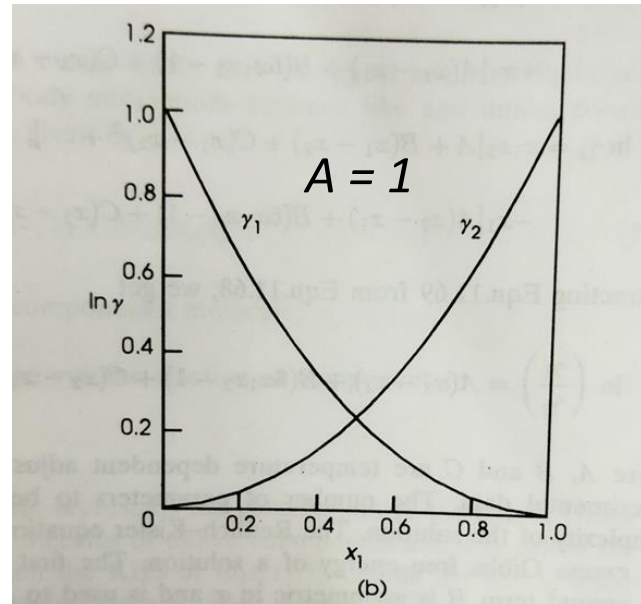


### b. Three suffix Margules Equation

$$\frac{G^E}{RT} = x_1x_2(A_2x_1 + A_1x_2)$$

$$\ln \gamma_1 = x_2^2 [A_1 - 2(A_2 - A_1)X_1]$$

$$\ln \gamma_2 = x_1^2 [A_2 - 2(A_1 - A_2)X_2]$$



➤ **Limitation:**

- Applicable for the components of similar size, shape and chemical nature
- Symmetric about  $x_1 = 0.5$  (activity coefficient is mirror image to each other)

# Excess Gibbs Free Energy Model (Binary Mixture)

## ○ Redlich –Kister equation

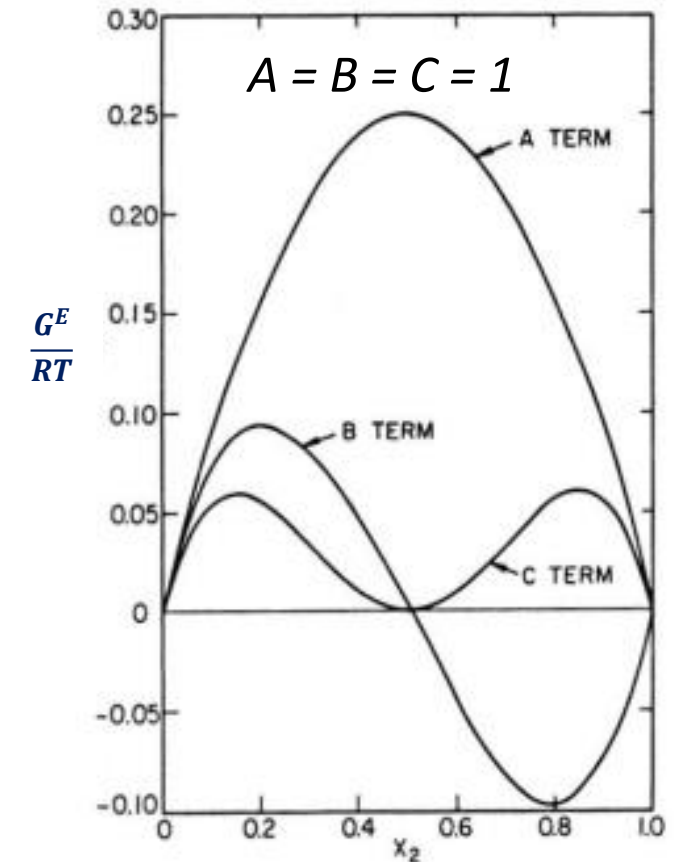
$$\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots]$$

$A, B, C = \text{temperature dependent adjustable parameter}$

$$\ln \gamma_1 = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] + x_2 [A(x_2 - x_1) + B(6x_1 x_2 - 1) + C(x_1 - x_2)(8x_1 x_2 - 1) + \dots]$$

$$\ln \gamma_2 = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] - x_1 [A(x_2 - x_1) + B(6x_1 x_2 - 1) + C(x_1 - x_2)(8x_1 x_2 - 1) + \dots]$$

$$\ln \frac{\gamma_1}{\gamma_2} = A(x_1 - x_2) + B(6x_1 x_2 - 1) + C(x_2 - x_1)(8x_1 x_2 - 1) + \dots]$$



### Problem 02:

A binary liquid mixture is in equilibrium with its vapour at 300 K temperature. The liquid mole fraction  $x_1$  is 0.4 and molar excess Gibbs free energy is 200 J/mol,  $R = 8.314$  J/mol/K and  $\gamma_1$  is liquid phase activity coefficient, where  $\ln \gamma_1 = 0.09$ . then find out the value of  $\gamma_2$ ?

### Problem 03:

The constant A and B of three suffix Margules equation for the system Ethanol (1)- toluene (2) at 85 °C are 1.6409 and 1.7540 respectively. Estimate  $\ln \gamma_1$  and  $\ln \gamma_2$  at  $x_1 = 0.1, 0.3, 0.5, 0.7, 0.9$  and plot  $\ln \gamma_1$  and  $\ln \gamma_2$  versus  $x_1$ . Compare the constant A and B with the values of  $\ln \gamma_1$  and  $\ln \gamma_2$  as  $x_1 \rightarrow 0$  and  $x_2 \rightarrow 0$ .

### Problem 04:

*The constant A, B and C of Redlich –Kister equation for the system methanol (1)- benzene (2) at 85 °C are 1.601, 1.704 and 1.025 respectively. Estimate bubble pressure and composition of vapour at  $x_1 = 0.4$  by using Redlich –Kister equation*

The Antoine constant of the components are

Components	A	B	C
Methanol (1)	8.08097	1582.271	239.726
Benzene (2)	6.89787	1196.760	219.161

# Excess Gibbs Free Energy Model (Binary Mixture)

## Wohl's equation:

*Gibbs free energy of binary liquid solution talking into account of **two-body** and **three-body** interaction between **like** and **unlike** constituent molecules.*

**two-body** interaction between **unlike** components  
is called two suffix term.

$$\frac{G^E}{RT(q_1x_1 + q_2x_2)} = 2a_{12}z_1z_2 + 3a_{112}z_1^2z_2 + 3a_{122}z_1z_2^2$$

..... Three suffix equation

**three-body** interaction between **unlike** components  
is called three suffix terms.

*Where  $q_i$  = a measure of volume of component  $i$  molecule*

$z_i = \frac{x_i q_i}{x_1 q_1 + x_2 q_2}$  = effective volume fraction of component  $i$

$a_{12}, a_{112}, a_{122}$  = empirical constant

# Excess Gibbs Free Energy Model (Binary Mixture)

Wohl's equation:

$$z_1 + z_2 = 1$$

$$\frac{G^E}{RT} = (x_1 + \frac{q_2}{q_1}x_2) z_1 z_2 \{z_1 q_1 (2a_{12} + 3a_{112}) + z_2 q_1 (2a_{12} + 3a_{122})\}$$

$$\frac{G^E}{RT} = (x_1 + \frac{q_2}{q_1}x_2) z_1 z_2 (z_1 q_1 B + z_2 q_1 A)$$

Now for  $q_1 = q_2$  this Wohl's equation reduce to three-suffix Margules equation

Where,  $A = q_1 (2a_{12} + 3a_{122})$

$$B = q_2 (2a_{12} + 3a_{112})$$

$$\frac{G^E}{RT} = (Bx_1 + Ax_2)x_1x_2 = (A_{21}x_1 + A_{12}x_2)x_1x_2$$

$$\ln \gamma_1 = z_2^2 [A + 2(B \frac{q_1}{q_2} - A) z_1]$$

$$\ln \gamma_2 = z_1^2 [B + 2(A \frac{q_1}{q_2} - B) z_2]$$

$$\ln \gamma_1 = x_2^2 [A + 2(B - A)x_1] = (2B - A)x_2^2 + 2(A - B)x_2^3$$

$$= x_2^2 [A_{12} + 2(A_{21} - A_{12})x_1]$$

$$\ln \gamma_2 = x_1^2 [B + 2(A - B)x_2] = (2A - B)x_1^2 + 2(B - A)x_1^3$$

$$= x_1^2 [A_{21} + 2(A_{12} - A_{21})x_2]$$



# Excess Gibbs Free Energy Model (Binary Mixture)

Wohl's equation:

If  $x_1 = 0$

$$\ln \gamma_1 = A \quad \text{and} \quad \ln \gamma_2 = 0$$

If  $x_2 = 0$

$$\ln \gamma_1 = 0 \quad \text{and} \quad \ln \gamma_2 = B$$

If  $A = B$  then

$$\begin{aligned} \ln \gamma_1 &= x_2^2 [A + 2(B - A)x_1] = Ax_2^2 \\ \ln \gamma_2 &= x_1^2 [B + 2(A - B)x_2] = Bx_1^2 \end{aligned}$$

*Margules two-suffix equation*

# Excess Gibbs Free Energy Model (Binary Mixture)

## Van Laar equation:

If  $q_1/q_2 = A/B$  then Wohl's equation become **Van Larr equation**

$$\frac{G^E}{RT} = \frac{Ax_1x_2}{x_1\frac{A}{B} + x_2}$$

$$\text{If } x_1 = 0$$

$$\ln\gamma_1 = A \quad \text{and} \quad \ln\gamma_2 = 0$$

$$\text{If } x_2 = 0$$

$$\ln\gamma_1 = 0 \quad \text{and} \quad \ln\gamma_2 = B$$

$$\ln\gamma_1 = Az_2^2 = \frac{A}{\left(1 + \frac{Ax_1}{Bx_2}\right)^2}$$

$$\ln\gamma_2 = bz_1^2 = \frac{B}{\left(1 + \frac{Bx_2}{Ax_1}\right)^2}$$

$$A = \ln\gamma_1 \left(1 + \frac{x_2 \ln\gamma_2}{x_1 \ln\gamma_1}\right)^2$$

$$B = \ln\gamma_2 \left(1 + \frac{x_1 \ln\gamma_1}{x_2 \ln\gamma_2}\right)^2$$

### Problem:

Ethanol (1) and benzene (2) system forms an azeotropes with 44.8 mol% ethanol with a boiling point of 68.24 °C at 760 torr. The saturation pressure of ethanol and benzene at 68.24 °C are 506 and 517 torr respectively. Estimate the Van Laar constants for the system and evaluate the activity coefficient for a solution containing 10 mol% ethanol.

# Excess Gibbs Free Energy Model (Binary Mixture)

## Wilson equation:

*The mixture in which component differ from each other in molecular size and interaction between unlike and like component are different*

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 - \Lambda_{21}x_1)$$

*Where  $\Lambda_{12}$  and  $\Lambda_{21}$  are two adjustable parameter which related to pure component molar volume and characteristic energy differences.  $\lambda$*

$$\Lambda_{12} = \frac{v_2}{v_1} \exp\left[-\frac{\lambda_{12} - \lambda_{11}}{RT}\right]$$

$$\Lambda_{21} = \frac{v_1}{v_2} \exp\left[-\frac{\lambda_{12} - \lambda_{22}}{RT}\right]$$

$v_i$  = molar volume of pure component 'i'

$\lambda_{ij}$  = energy of interaction between a molecule of component i and a component j.

# Excess Gibbs Free Energy Model (Binary Mixture)

## Wilson equation:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right]$$

### Advantage:

- It is applicable to several miscible binary system
- It predicts the temperature dependence of activity coefficient

### Disadvantage:

- It is not applicable in which  $\ln \gamma_i$  exhibits a maxima or minima
- Inability to predict limited miscibility.

*It is useful for completely miscible or partially miscible system in the region where only one liquid phase exists*

### Problem 02:

Wilson's parameter  $\Lambda_{12}$  and  $\Lambda_{21}$  for the nitromethane (1) and carbon tetrachloride (2) at 45 °C are 0.1156 and 0.2879 respectively. Calculate the activity coefficient for the solution at  $x_1 = 0.3$ .

# Excess Gibbs Free Energy Model (Binary Mixture)

## Non-random Two Liquid (NRTL) Equation:

Applicable for partially miscible and completely system.

$$\frac{G^E}{RT} = x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right]$$

$$\tau_{12} = \frac{G_{12} - G_{22}}{RT}$$

$$\tau_{21} = \frac{G_{21} - G_{11}}{RT}$$

$$G_{12} = \exp(-\alpha_{12} \tau_{12})$$

$$G_{21} = \exp(-\alpha_{12} \tau_{21})$$

$$\ln \gamma_1 = x_2^2 \left[ \tau_{21} \left( \frac{G_{21}}{x_1 + x_2 G_{21}} \right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2} \right]$$

$$\ln \gamma_2 = x_1^2 \left[ \tau_{12} \left( \frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2} \right]$$

- $0.20 < \alpha_{12} < 0.47$
- *General case  $\alpha_{12} = 0.3$  (no other information is there)*
- If  $\alpha_{12} = 0$  (mixture is completely random)
- NRTL equation reduce to two-suffix Margules equation

- $\alpha_{12}$  is a parameter specific to a particular pair of species.
- $\alpha_{12}$  is non – randomness of the mixture
- It is independent of composition and temperature

➤ No additional information over Margules and Van Laar equation for moderately non-ideal solution

# Excess Gibbs Free Energy Model (Binary Mixture)

## Universal Quasi Chemical (UNIQUAC) Equation:

$$\frac{G^E}{RT} = \frac{G^E}{RT} (\text{combinatorial}) + \frac{G^E}{RT} (\text{residual})$$

Where,

$$\frac{G^E}{RT} (\text{combinatorial}) = x_1 \ln \frac{\phi_1}{x_1} + x_2 \ln \frac{\phi_2}{x_2} + \frac{Z}{2} \left( q_1 x_1 \ln \frac{\theta_1}{\phi_1} + q_2 x_2 \ln \frac{\theta_2}{\phi_2} \right) \rightarrow \text{Composition, size and shape (pure component property only)}$$

$$\frac{G^E}{RT} (\text{residual}) = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \rightarrow \text{Intermolecular forces (contains two adjustable parameter)}$$

Where,

$$\phi_i = \text{segment or volume fraction of component } i = \left( \frac{x_i r_i}{\sum_j x_j r_j} \right)$$

( $r_i$  = relative molecular volume)

$$\theta_i = \text{area fraction of component } i = \left( \frac{x_i q_i}{\sum_j x_j q_j} \right)$$

$q_i$  = surface area parameter of component  $i$

$$\tau_{21} = \exp \left\{ -\frac{(u_{ji} - u_{ii})}{RT} \right\} = \exp \left( -\frac{a_{ji}}{T} \right) = \text{Adjustable parameter}$$

$u_{ji}$  = average interaction energy of  $i$  and  $j$ .

$Z$  = Coordination number  
(usually taken as 10)

# Excess Gibbs Free Energy Model (Binary Mixture)

## Universal Quasi Chemical (UNIQUAC) Equation:

$$\ln \gamma_i = \ln \gamma_i^c \text{ (combinatorial)} + \ln \gamma_i^R \text{ (residual)}$$

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{q_i}{x_i} \sum_j x_j l_j$$

$$\ln \gamma_i^R = q_i \left[ 1 - \ln \left( \sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right]$$

$$\text{Where, } l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1)$$

$$r_i = \sum_k v_k^i R_k$$

$$q_i = \sum_k v_k^i Q_k$$

$v_k^i$  = number of group of type k in a molecule of component i

### Advantage:

- It contains two adjustable parameter  $a_{12}$  and  $a_{21}$
- parameter  $a_{12}$  and  $a_{21}$  are less dependent on temperature
- It is applicable to the solution containing small as well as large molecules



**Problem:**

*Estimate the activity coefficient for the ethanol (1) and benzene (2) system at 345 K and at  $x_1 = 0.8$  using the QNQUAC equation.*

The group identification and  $R_k$  and  $Q_k$  of the groups are given bellow

Molecule i	Name	Main No	Sec No.	$v_k^i$	$R_k$	$Q_k$
Ethanol (1)	CH3	1	1	1	0.9011	0.848
	CH2	1	2	1	0.6744	0.540
	OH	5	14	1	1.0	1.20
Benzene (2)	ACH	3	9	6	0.5313	0.40

$$u_{12} - u_{22} = -241.2287 \text{ J/mol K}$$

$$u_{21} - u_{11} = 2799.5827 \text{ J/mol K}$$