

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 , λ , β)**

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.

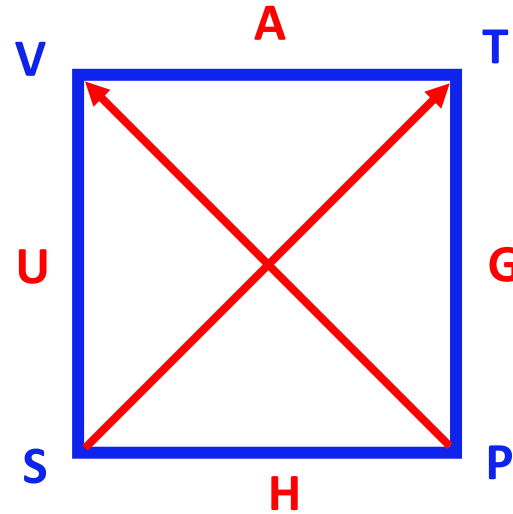
$$G = H - TS$$

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

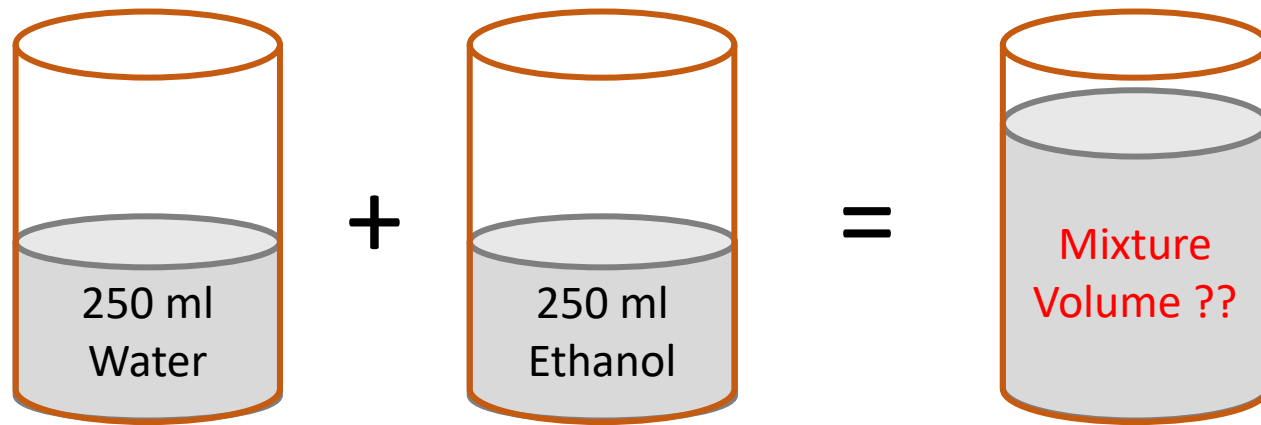
Multicomponent Mixture:

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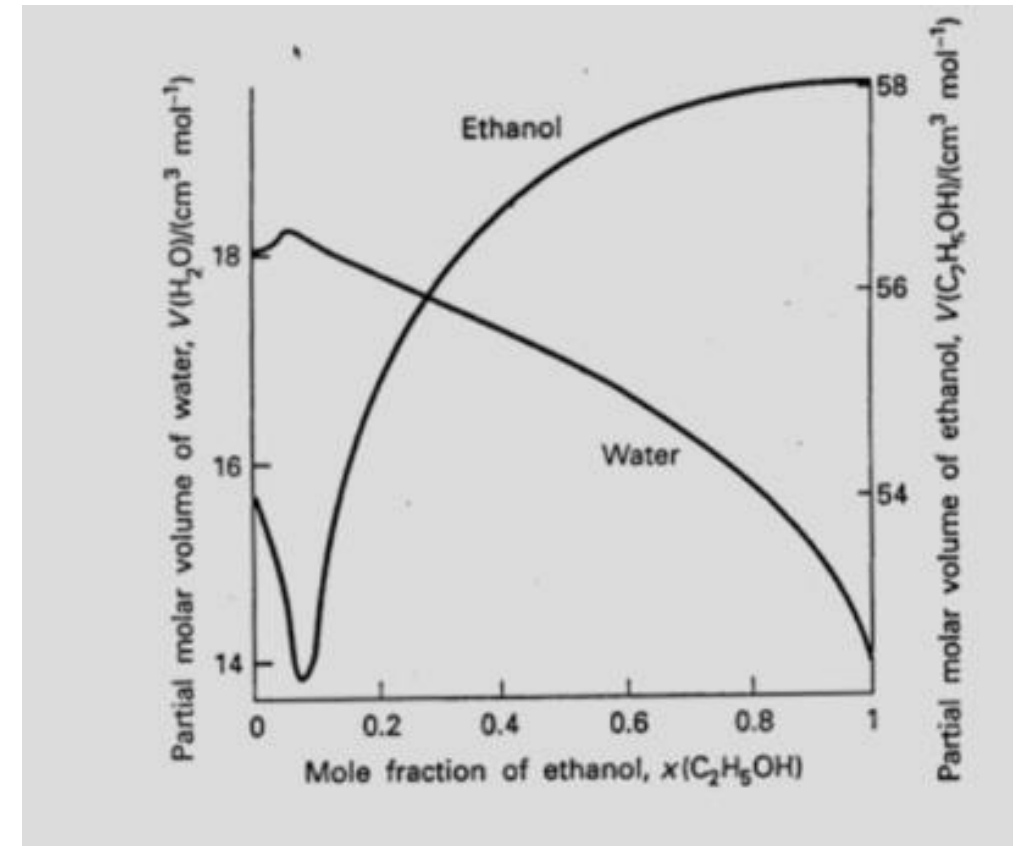
- *Partial Molar Properties*
- *Chemical Potential*
- *Fugacity and Fugacity Coefficient of pure gas*
- *Thermodynamics properties of real gas mixture*
- *Fugacity of a component in a mixture*
- *Fugacity of a liquid and solid*

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

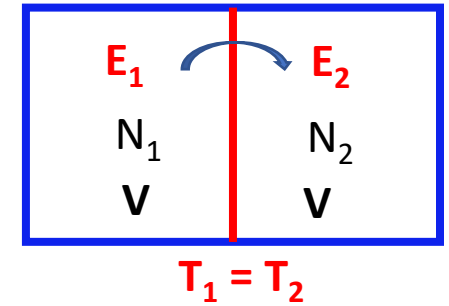
$$\frac{d\overline{M}_1}{dx_1} = - \frac{x_2}{x_1} \frac{d\overline{M}_2}{dx_1}$$

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

Chemical Potential (μ):

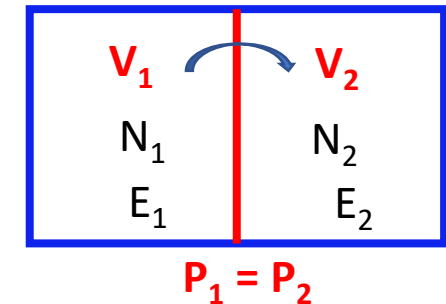
Thermal Equilibrium: Energy tends to flow from high energy (temperature) value to low energy (temperature) value until temperature of the both system are equal ($T_1 = T_2$).

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 ($P_1 = P_2$).

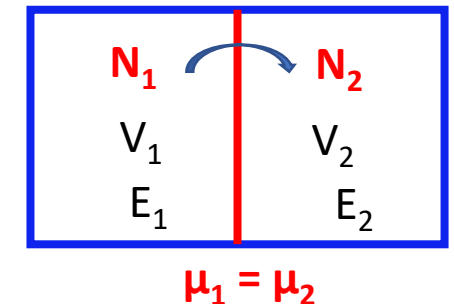
Significant: System have tendency to take volume



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 (μ):

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

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

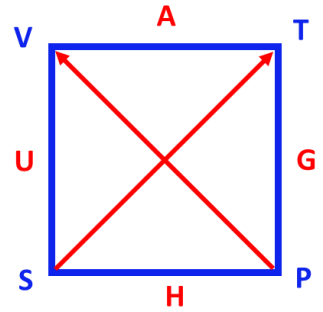
It tells about the effect of free energy (any terms of free energy) if we change the any component composition.

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 (μ):



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

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

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

At const. Pressure

$$dG = -SdT$$

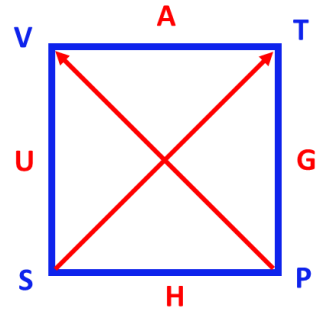
$$-S = \frac{dG}{dT}$$

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

For a binary system

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

Chemical Potential (μ):



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 (μ):

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 eqⁿ (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 eqⁿ (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 (μ):

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 eqⁿ (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 eqⁿ (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:

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

Summability equation

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

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

For binary system

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

Partial Molar Properties of Binary mixture:

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

Recap:

Gibbs-Duhem relation

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

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

For binary system

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

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

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

$$G = \sum \mu_i x_i$$

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

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

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

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

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

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

Ideal Gas-state Mixture Partial Properties Model

Ideal gas, $PV = nRT$ (total volume, m³)
 $PV = RT$ (molar volume, m³/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

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

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

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

Case 5: Gibbs Free Energy (g)

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

For ideal gas

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

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

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

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

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 (m^3/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 Δv_{mix} (m^3/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 (Φ)

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

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

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:

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

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

$$dG = vdP - SdT$$

At const. temp.

$$dG = vdP$$

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

$$\frac{G^E}{RT} = \frac{v^E}{RT} dP - \frac{H^E}{RT^2} dT$$

Activity and Activity Coefficient

$$dG = v dP - S dT$$

At constant temp.

$$dG = v dP$$

For ideal liquid

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

For real liquid

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

$$(2) - (1)$$

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

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

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

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

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

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

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

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

$$a_i = \gamma_i x_i$$

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^{sat})

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

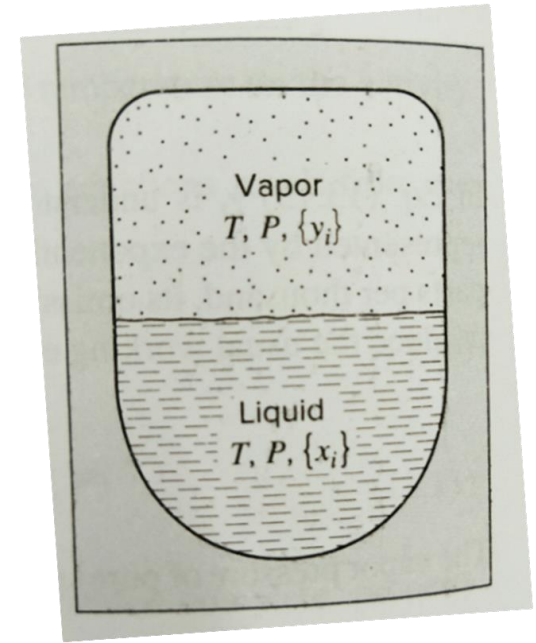
$$x_i \gamma_i^l f_i^l = y_i \Phi_i^v P$$

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

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

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

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



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:

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

λ = 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:

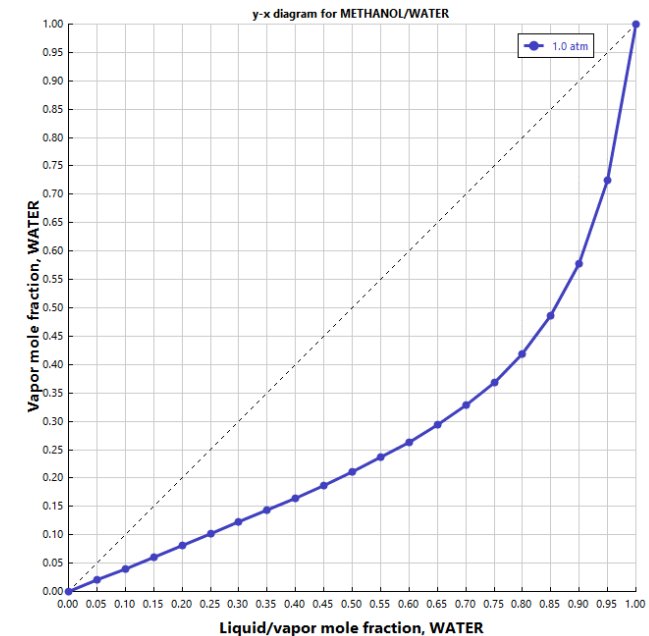
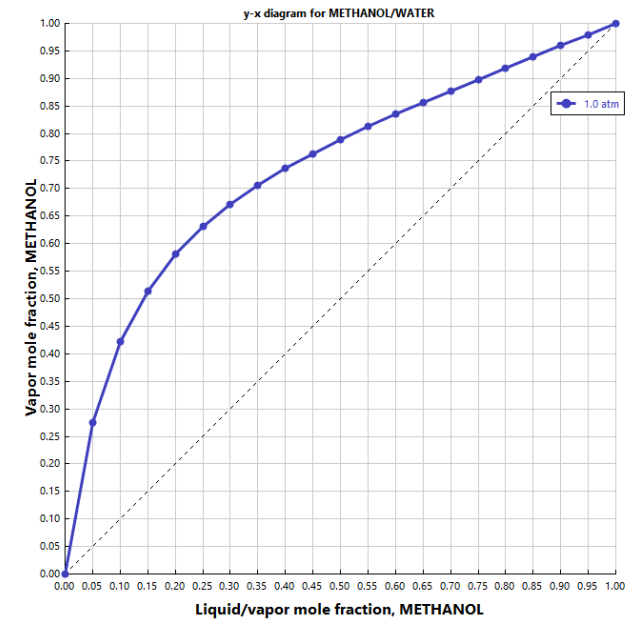
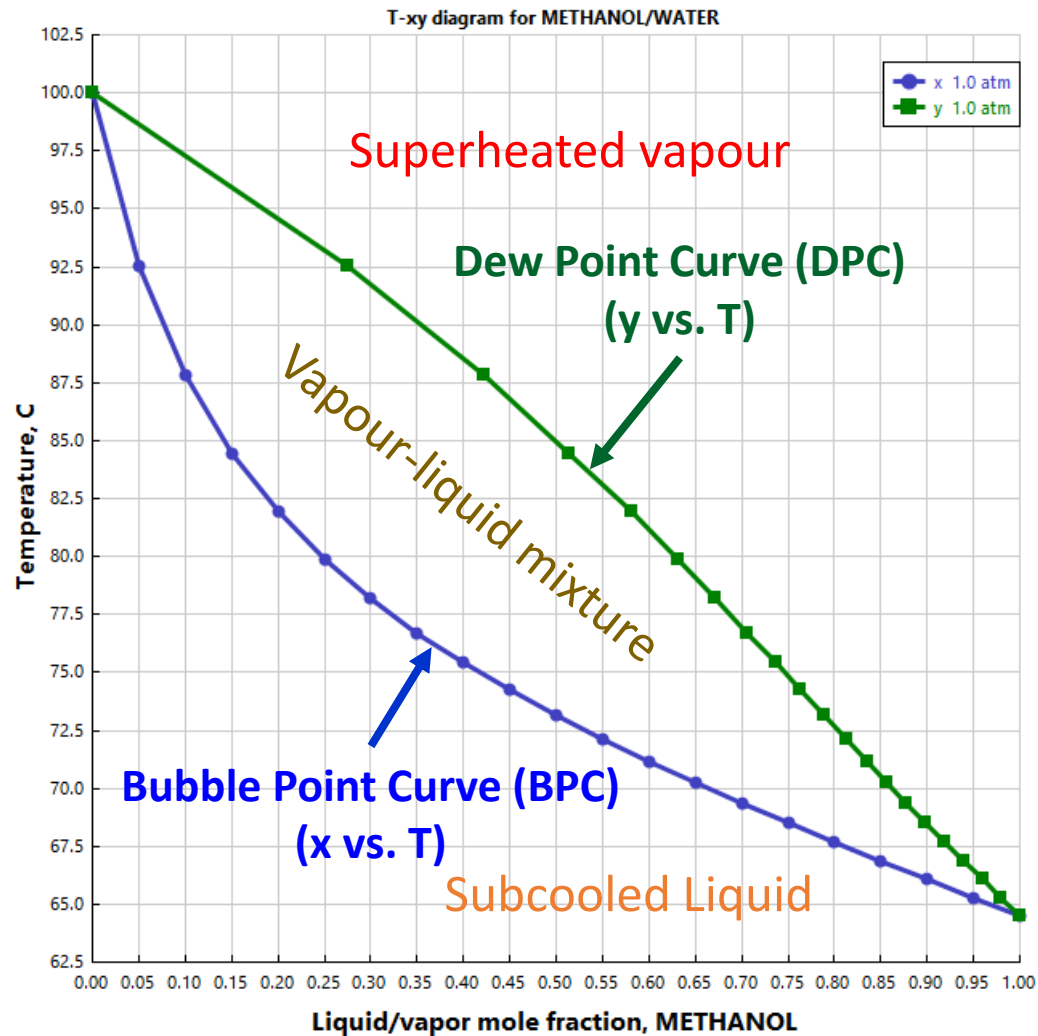
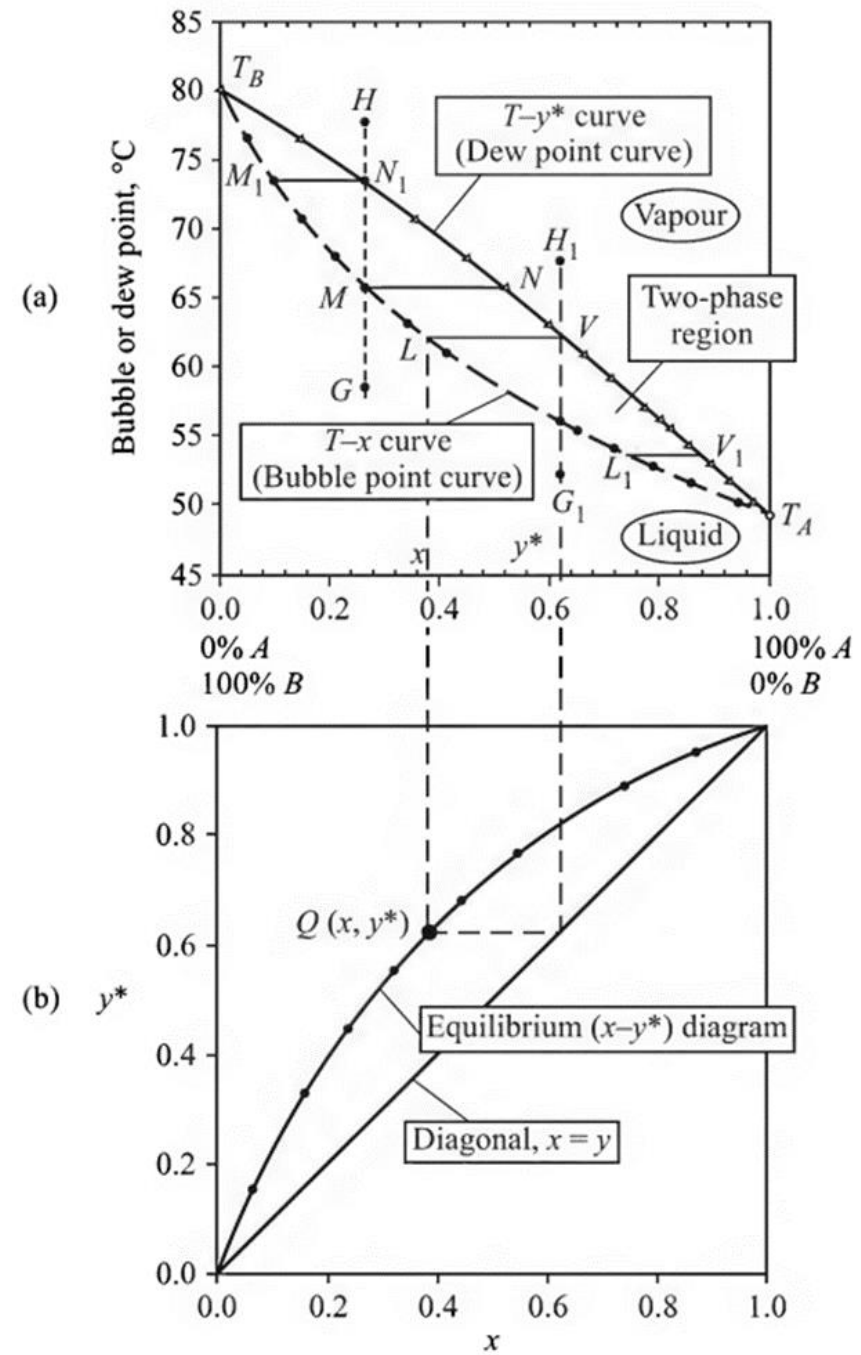


Fig. Constant pressure vapor liquid equilibria

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



➤ Vapor-liquid equilibria at increased pressures

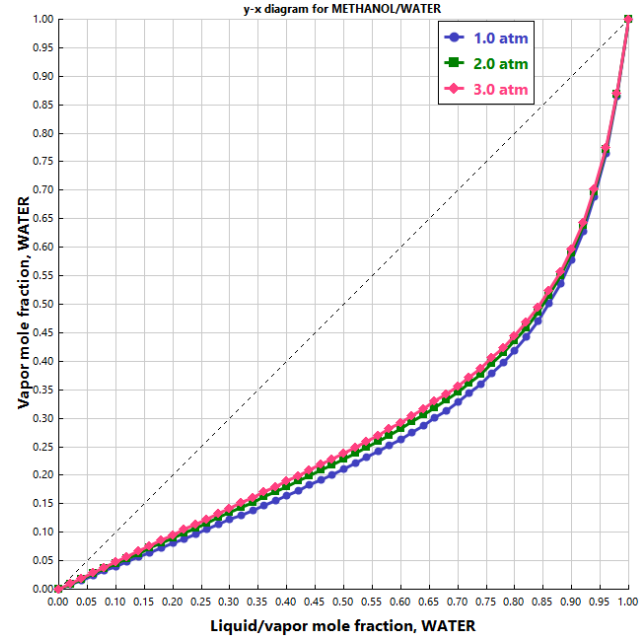
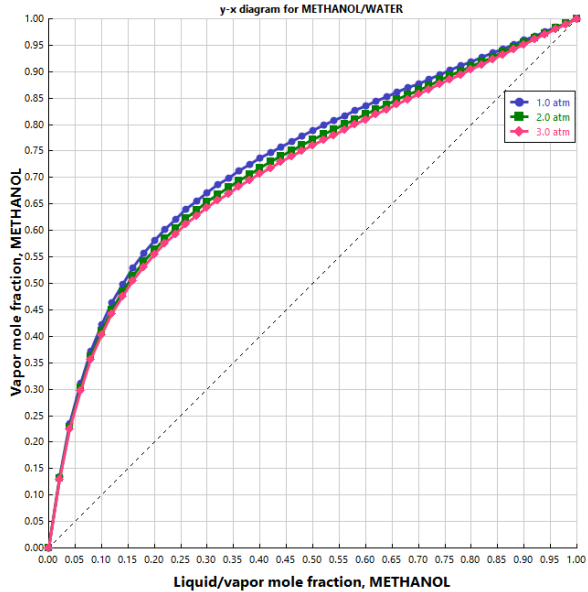
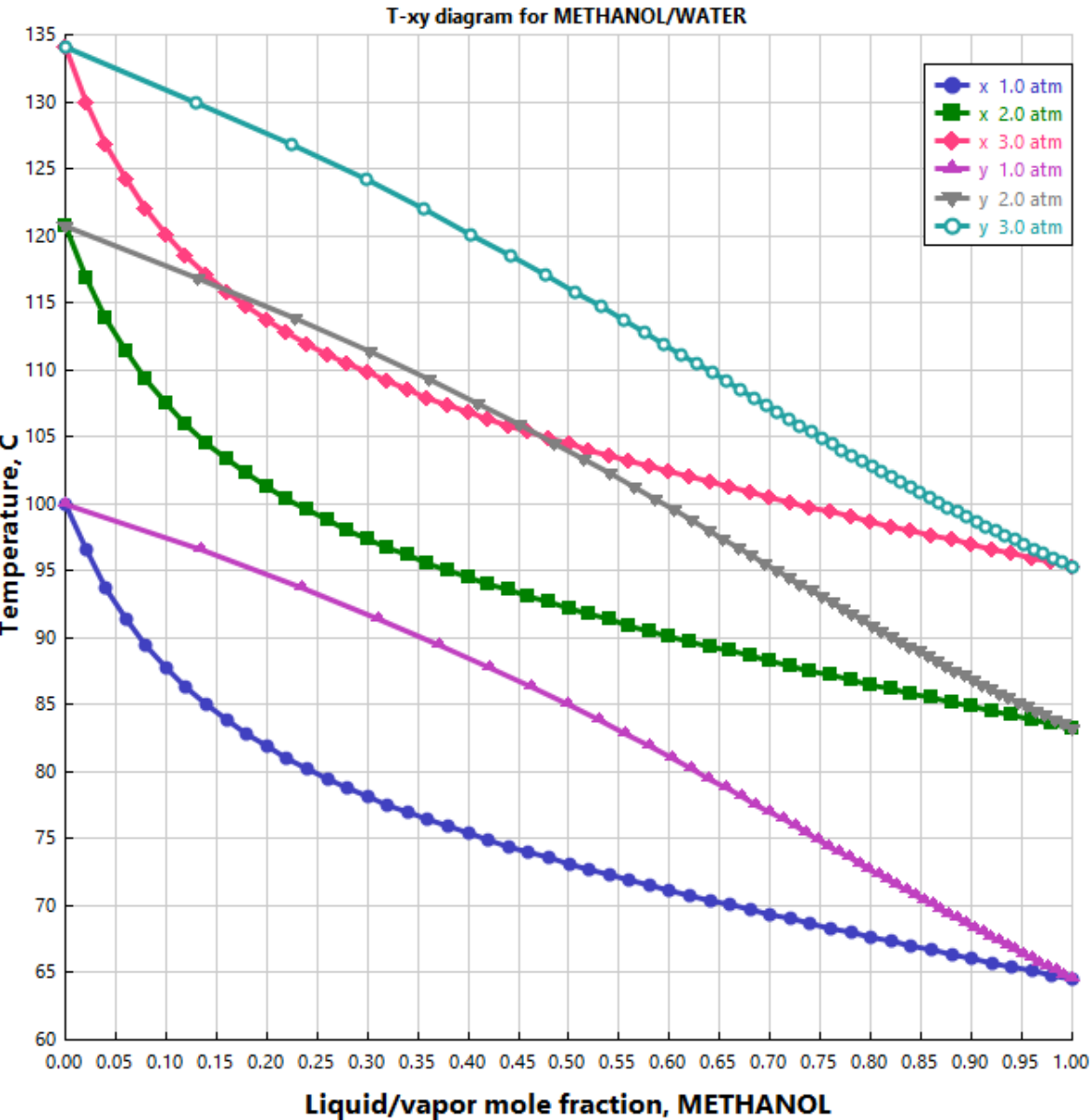


Fig. Vapor liquid equilibria at increased pressures

Relative volatility (α)

- 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 α 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 α above unity, the greater the degree of separability.

➤ P-x-y diagram for methanol-water

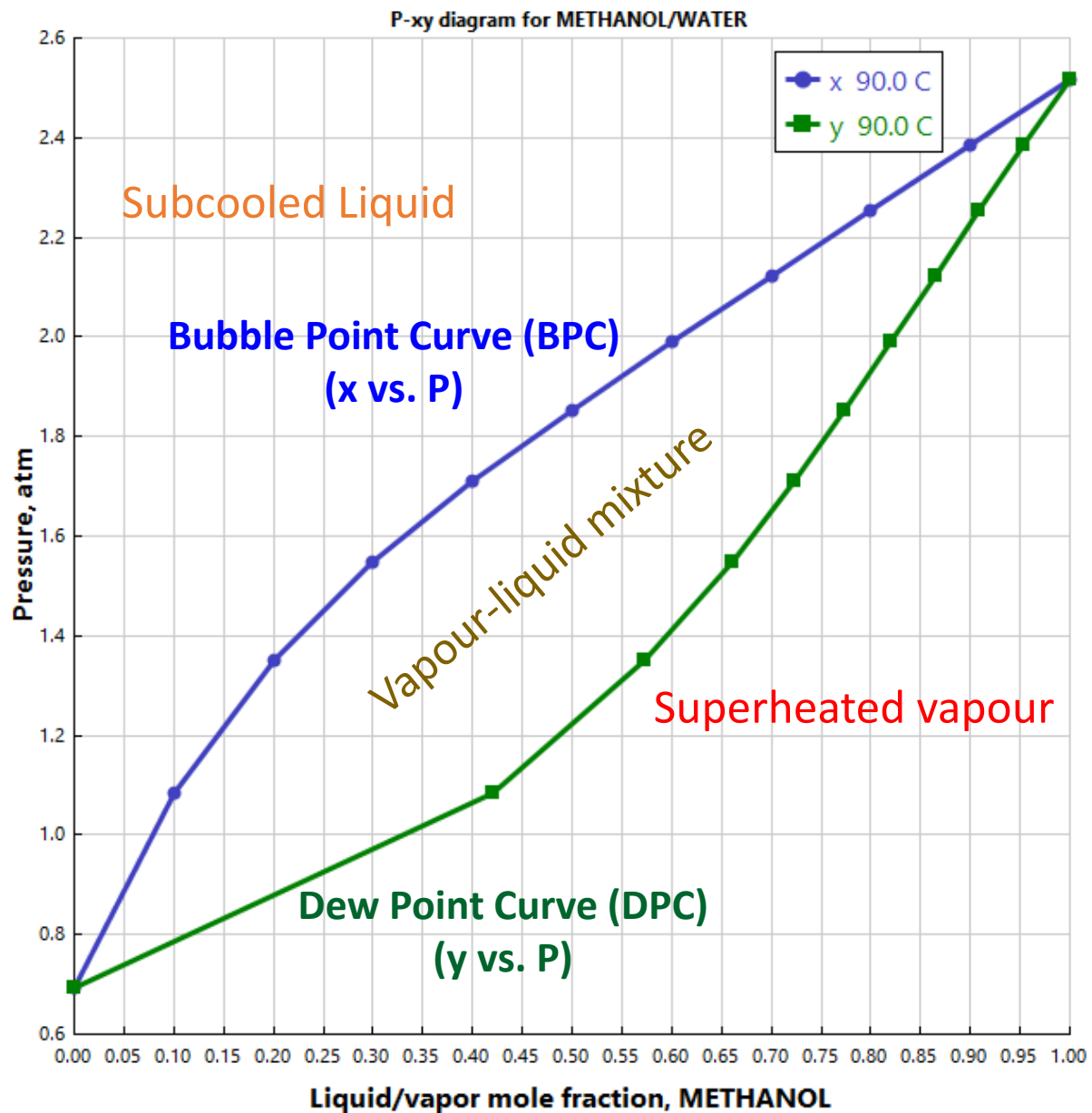
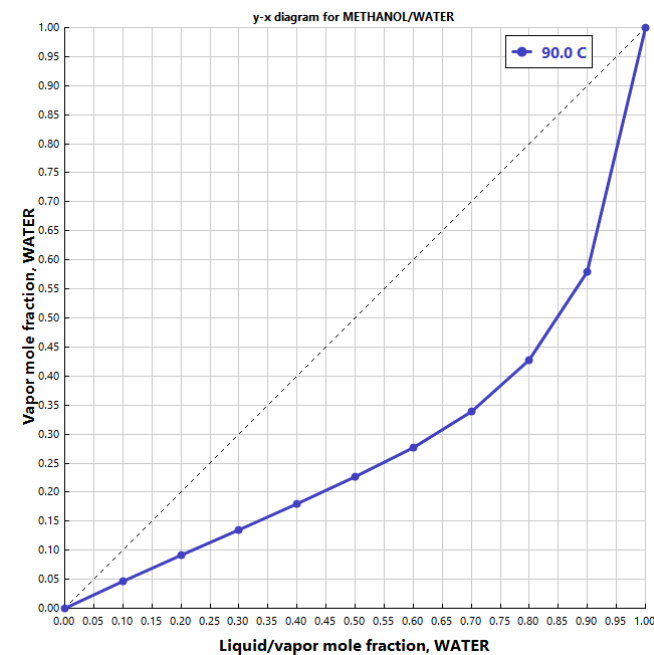
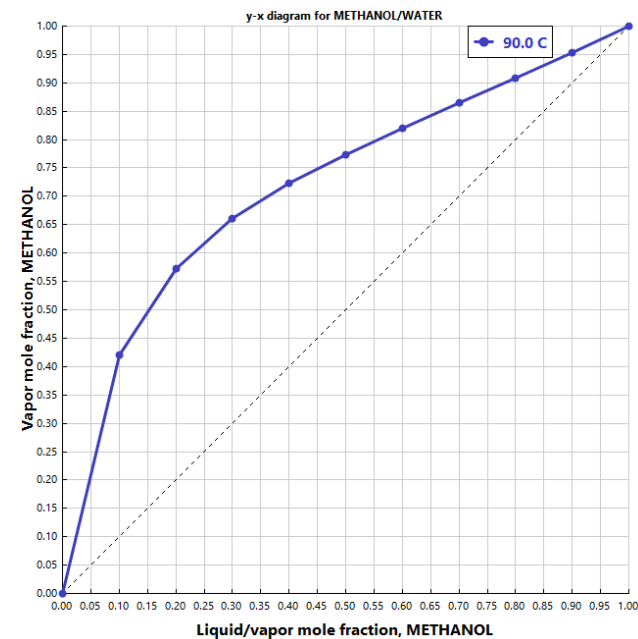


Fig. Constant temperature vapor liquid equilibria



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

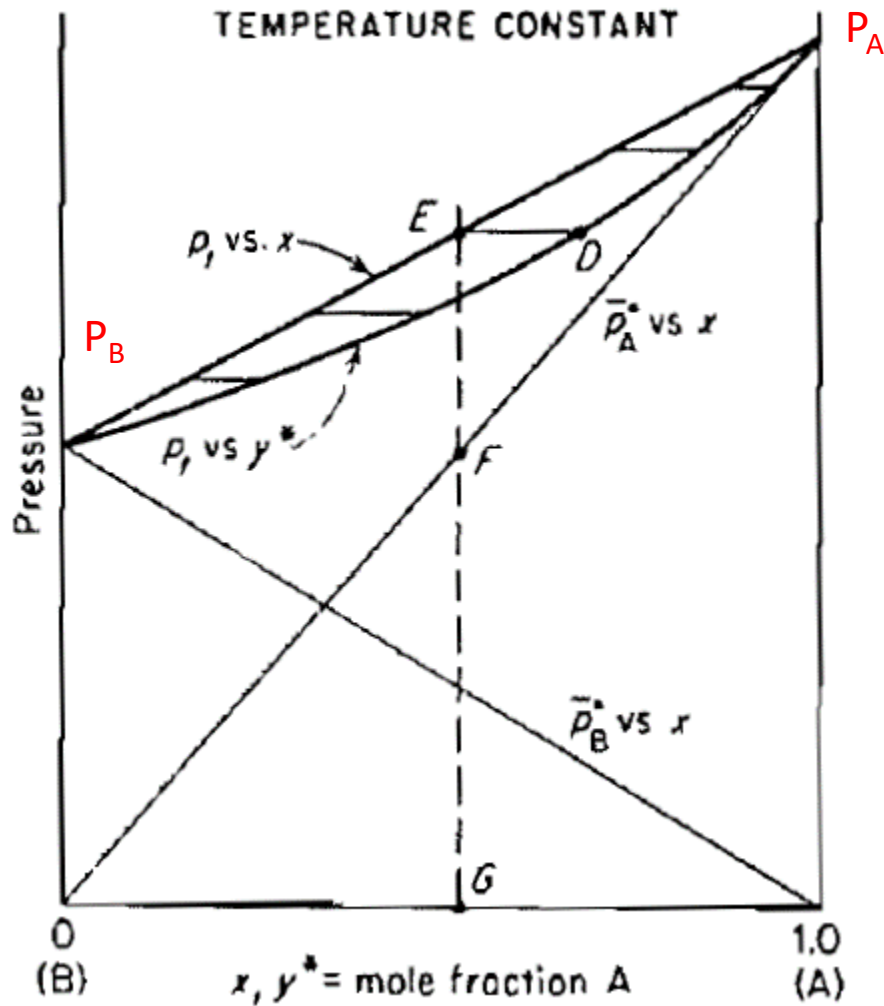


Fig. Ideal solutions

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

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

The relative volatility α 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.

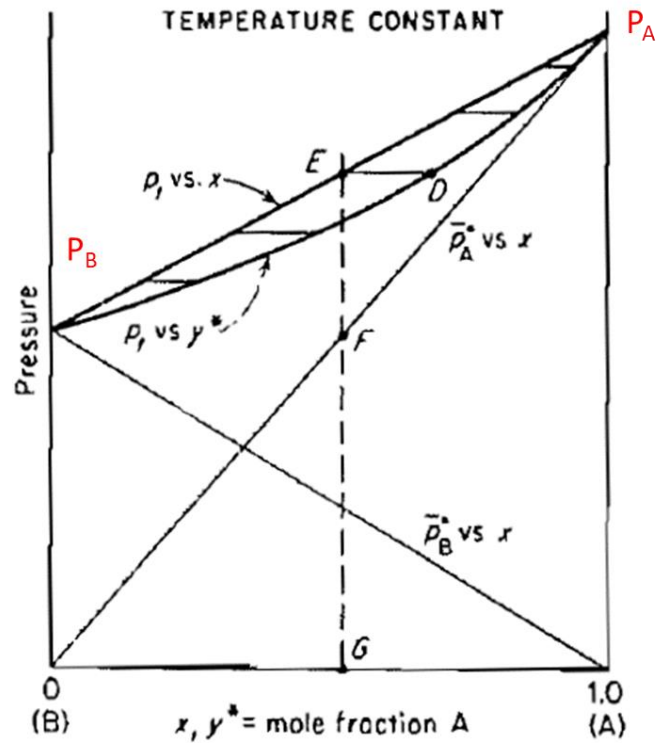
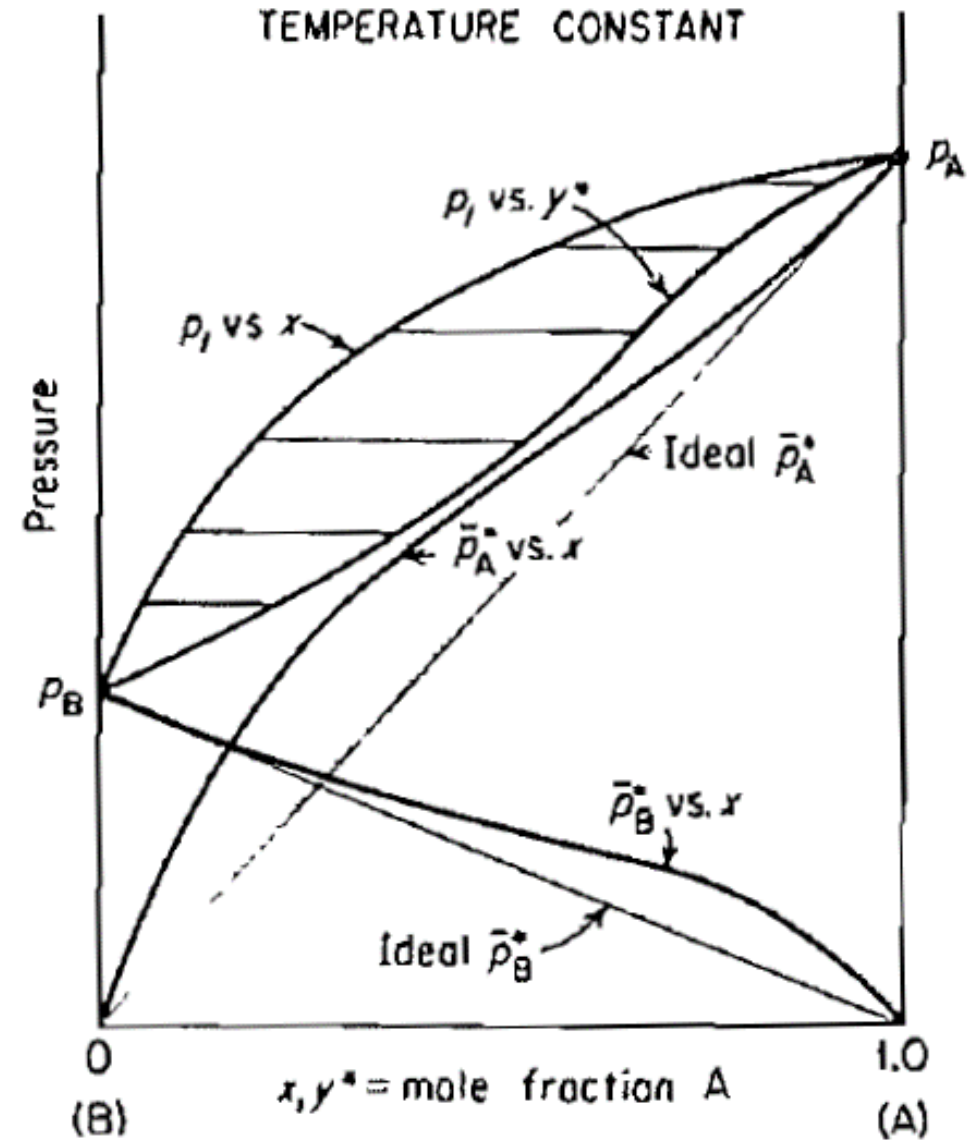
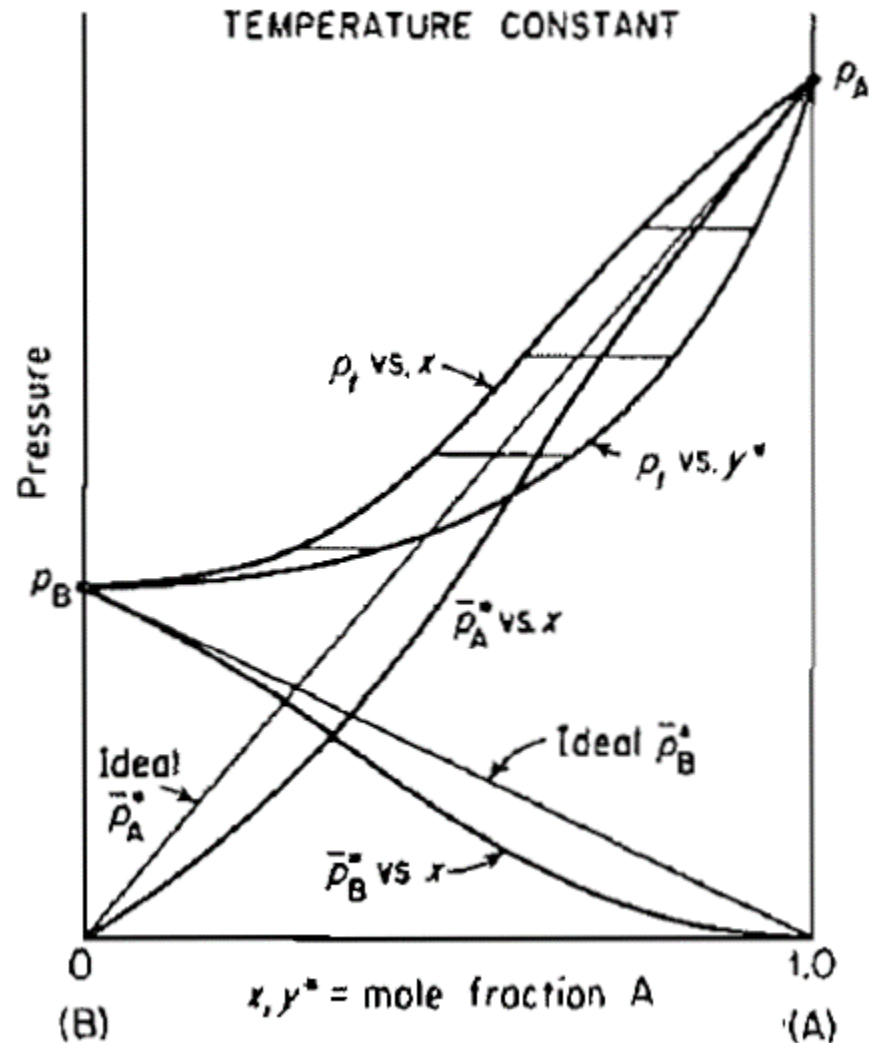


Fig. Ideal solutions

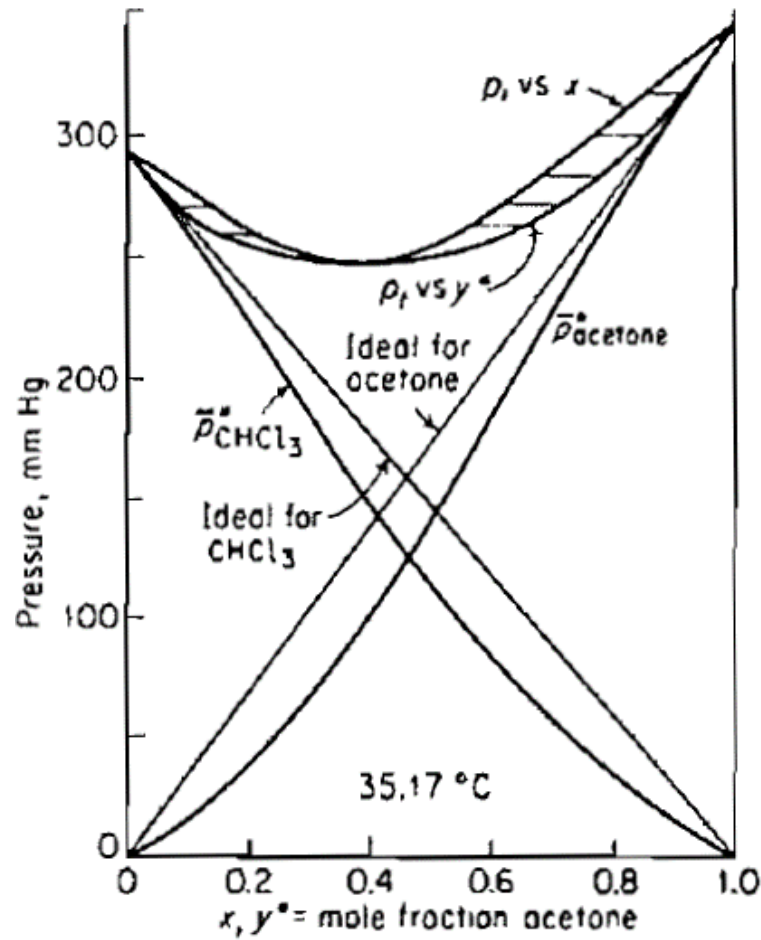


➤ Negative deviations from Ideality

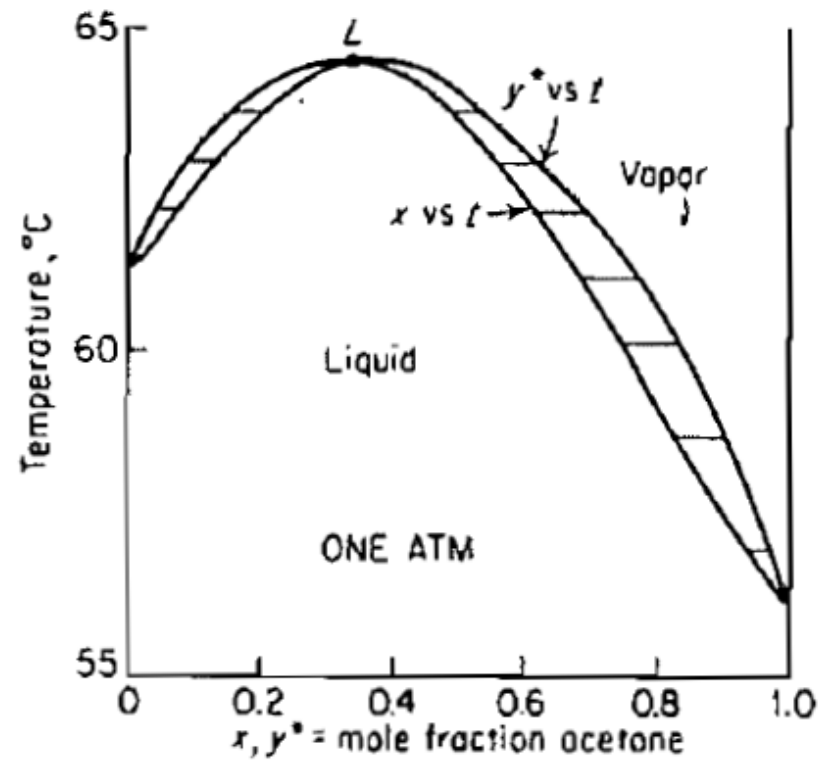
- When the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from Raoult's law.



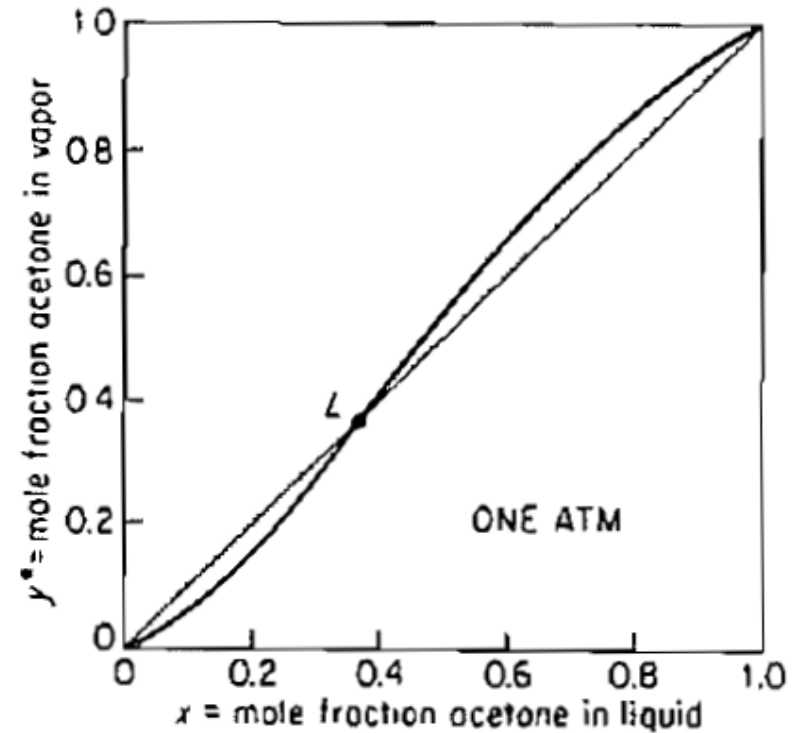
➤ Maximum boiling mixtures - azeotropes



(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

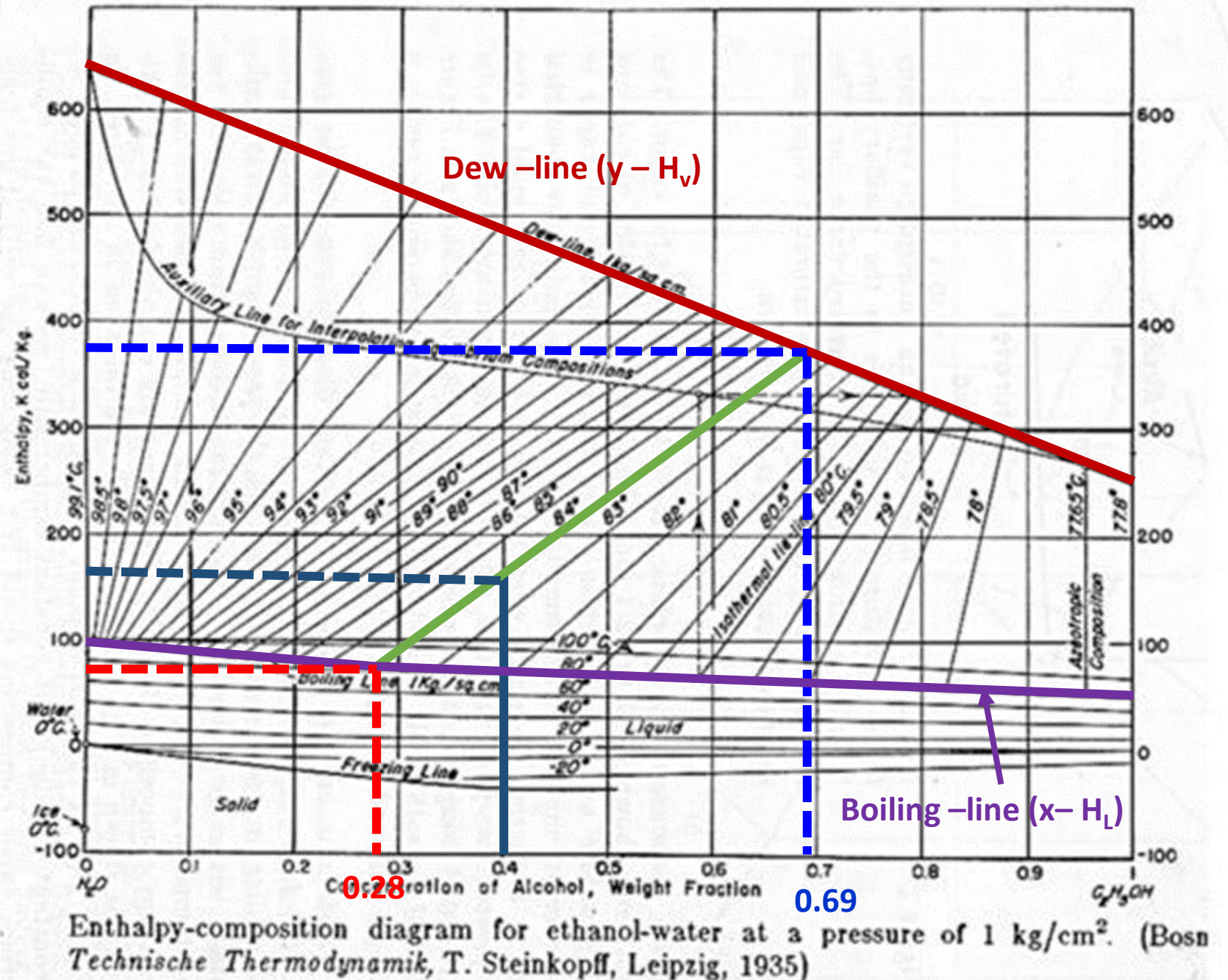
✓ $x_{\text{ethanol}} = 0.28$

✓ $y_{\text{ethanol}} = 0.69$

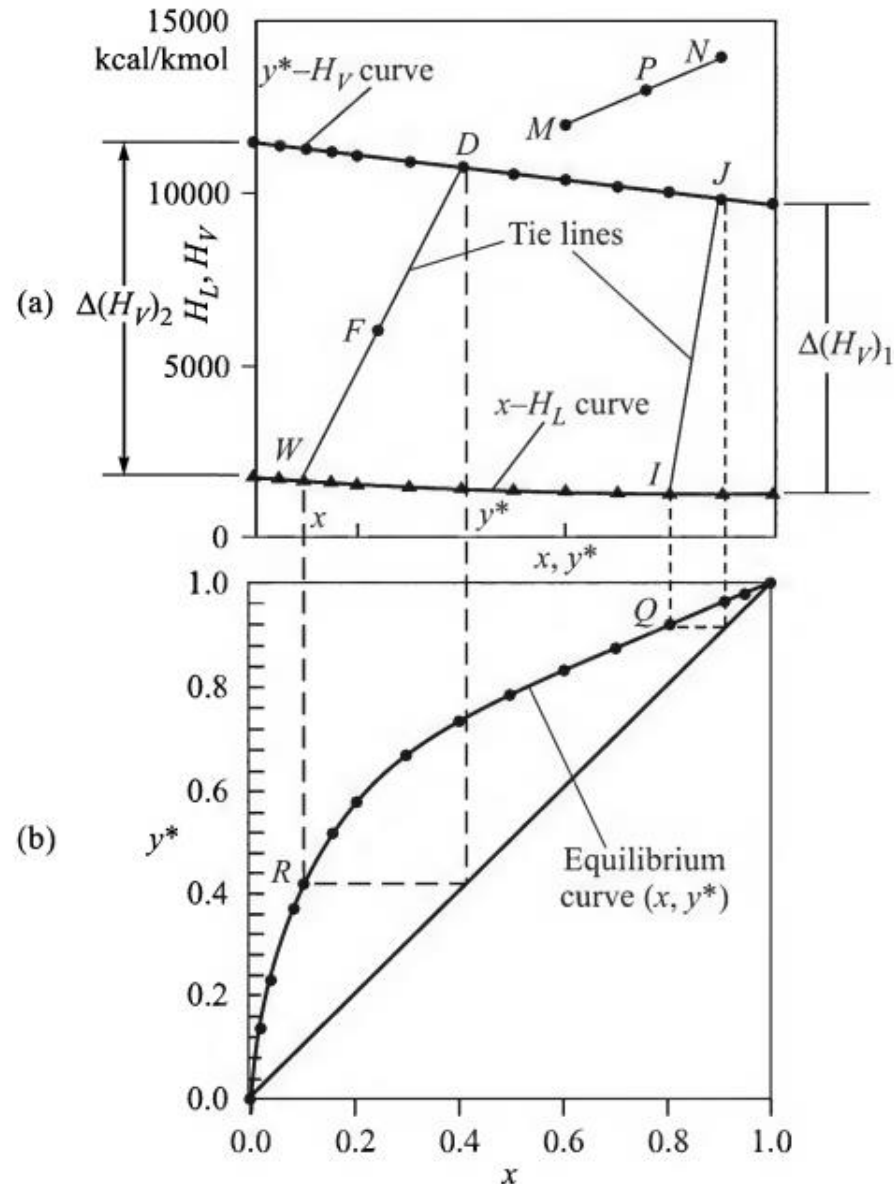
✓ $H_F = 165 \text{ Kcal/kg}$

✓ $H_v = 380 \text{ Kcal/kg}$

✓ $H_L = 70 \text{ Kcal/kg}$



Enthalpy Concentration Diagram to Equilibrium Diagram



Total material balance:

$$M + N = P$$

Component A balance:

$$Mz_M + Nz_N = Pz_P$$

Enthalpy balance:

$$MH_M + NH_N = PH_P$$

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

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

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

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, γ 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

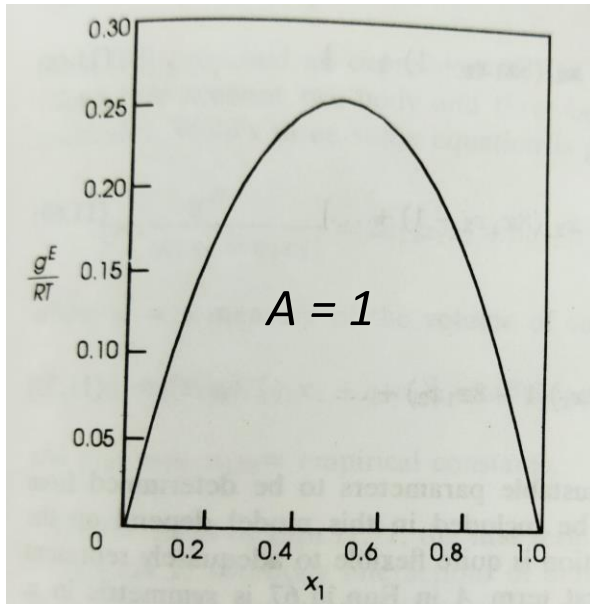
a. Two suffix Margules Equation

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

A = adjustable parameter

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

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

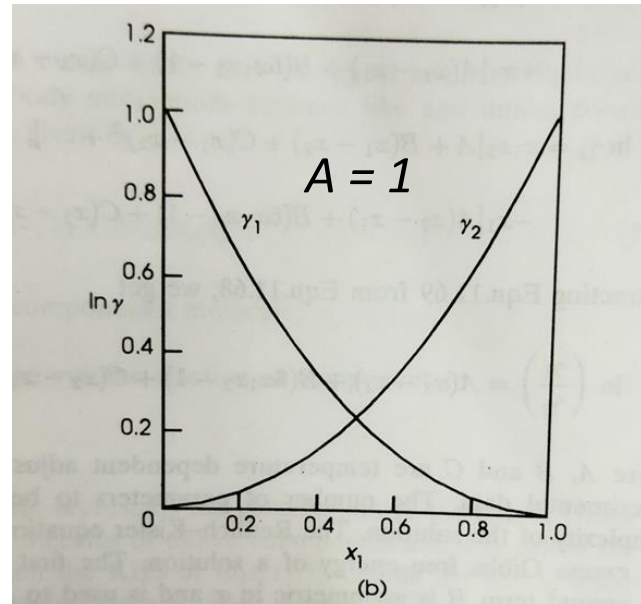


b. Three suffix Margules Equation

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

$$\ln \gamma_1 = x_2^2 [A_1 - 2(A_2 - A_1)]x_1$$

$$\ln \gamma_2 = x_1^2 [A_2 - 2(A_1 - A_2)]x_2$$



➤ **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

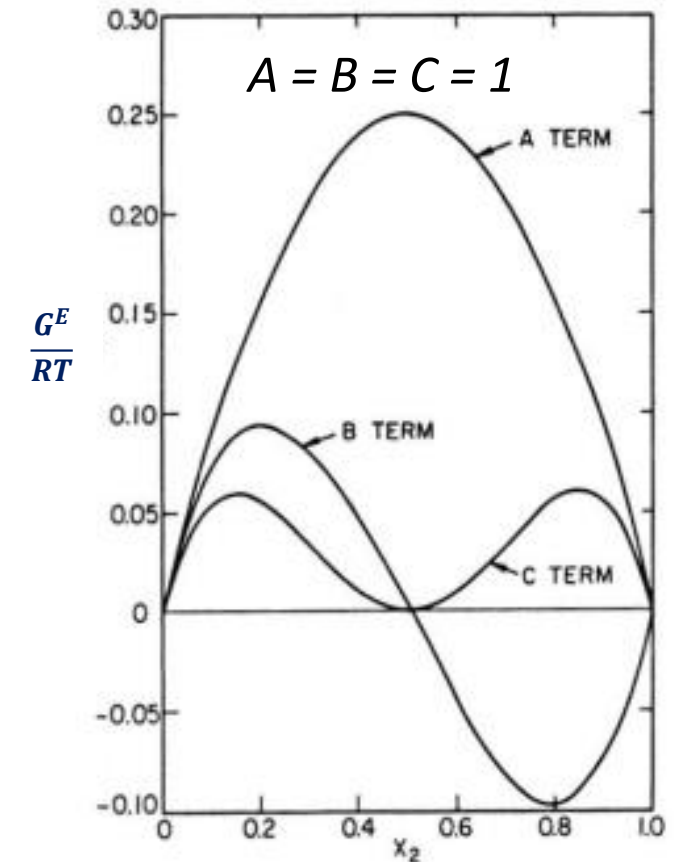
$$\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots]$$

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

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

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

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



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 γ_1 is liquid phase activity coefficient, where $\ln \gamma_1 = 0.09$. then find out the value of γ_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

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

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

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

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

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

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

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

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

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

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 Λ_{12} and Λ_{21} are two adjustable parameter which related to pure component molar volume and characteristic energy differences. λ

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

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

v_i = molar volume of pure component 'i'

λ_{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 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 Λ_{12} and Λ_{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

- α_{12} is a parameter specific to a particular pair of species.
- α_{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:

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

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

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

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

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

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

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

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

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

Thermodynamics Consistency Test of VLE Data

➤ *It obeys Gibbs Duhem equation*

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

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

$$\frac{h^E}{RT^2} dT + \frac{v^E}{RT} dP - \sum x_i d\ln\gamma_i = 0$$

$$\sum x_i d\ln\gamma_i = 0 \quad \text{(at constant T \& P)}$$

For binary mixture

$$x_1 \frac{d\ln\gamma_1}{dx_1} = x_2 \frac{d\ln\gamma_2}{dx_2}$$

Integral Method

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} = 0$$

Thermodynamics Consistency Test of VLE Data

Problem:

From the isobaric VLE data for acetone – carbon tetrachloride at 450 Torr calculate T and y₁ at x₁ = 0.447, 0.6525 and 0.8955 using van Laar and three suffix Margules equation. Compare with experimental data

T (°C)	x ₁	y ₁	T (°C)	x ₁	y ₁
55.29	0.049	0.189	42.42	0.6525	0.728
49.50	0.1625	0.393	41.92	0.741	0.784
46.26	0.297	0.515	41.54	0.8955	0.9015
44.06	0.447	0.61	41.53	0.926	0.927
43.05	0.565	0.667	41.16	0.945	0.945

Antoine constants

	A	B	C
Acetone	7.11714	1210.595	229.664
Carbon tetrachloride	6.84083	1117.91	220.576

Test for thermodynamics consistency of VLE data mentioned above.

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

Thermodynamics Consistency Test of VLE Data

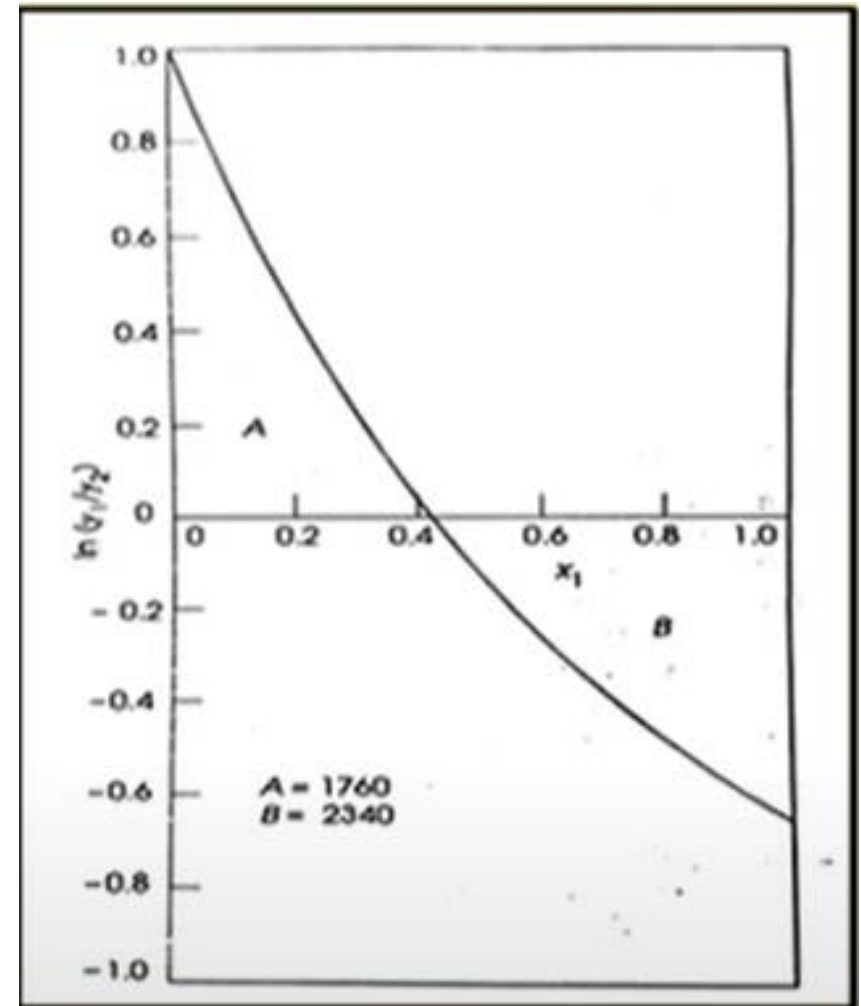
Three suffix Margules Equation

$$\frac{G^E}{RT} = x_1 x_2 (A_2 x_1 + A_1 x_2)$$

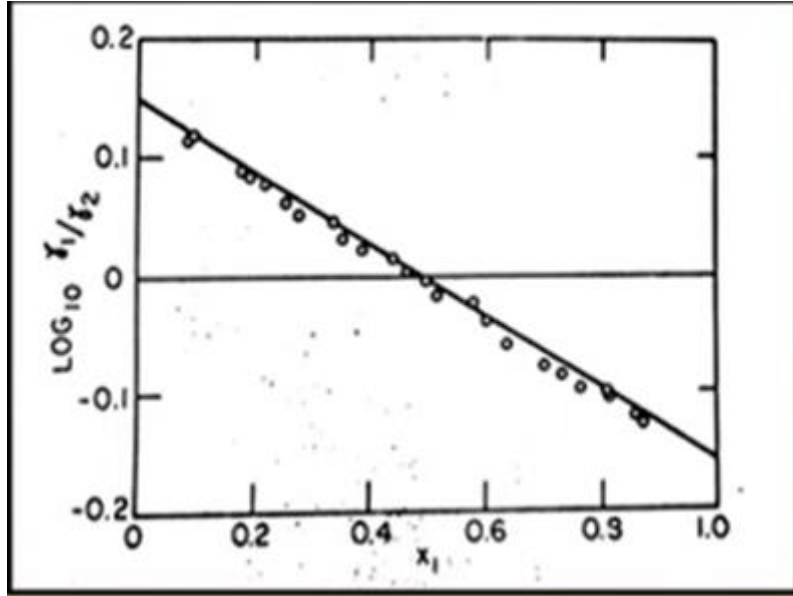
$$\ln \gamma_1 = x_2^2 [A_1 - 2(A_2 - A_1)X_1]$$

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

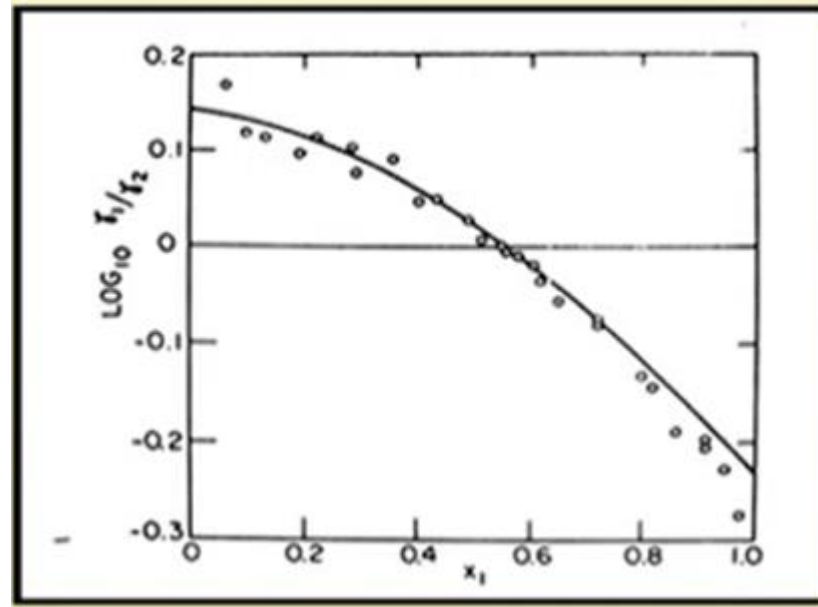
x_1	$\ln(\frac{\gamma_1}{\gamma_2})$	x_1	$\ln(\frac{\gamma_1}{\gamma_2})$
0.049	0.8235	0.6525	- 0.3496
0.1625	0.8115	0.741	- 0.4668
0.297	0.2234	0.8955	- 0.6396
0.447	- 0.415	0.926	- 0.6908
0.565	- 0.2245	0.945	- 0.7056



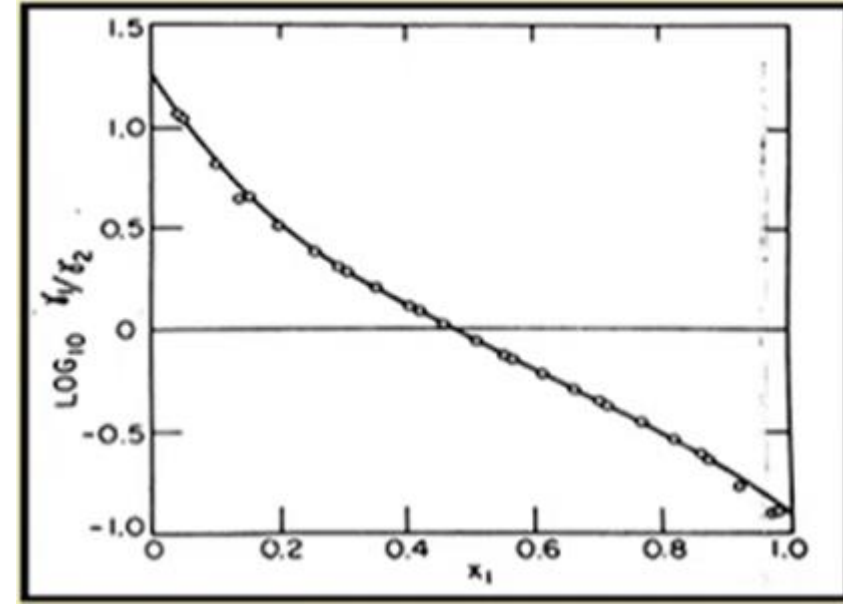
Thermodynamics Consistency Test of VLE Data



(a)



(b)



(c)

Activity coefficient ratio of (a) simple mixture [hexane (1) – toluene (2) at 1.013 bar, (b) mixture of intermediate complexity [benzene (1) – isooctane (2)] at total pressure ranging from 0.981 to 1.013 bar, © highly complex mixture [ethanol (1) – methylcyclohexane (2) in the region 30 – 35 °C.

Thermodynamics Consistency Test of VLE Data

○ Redlich –Kister equation

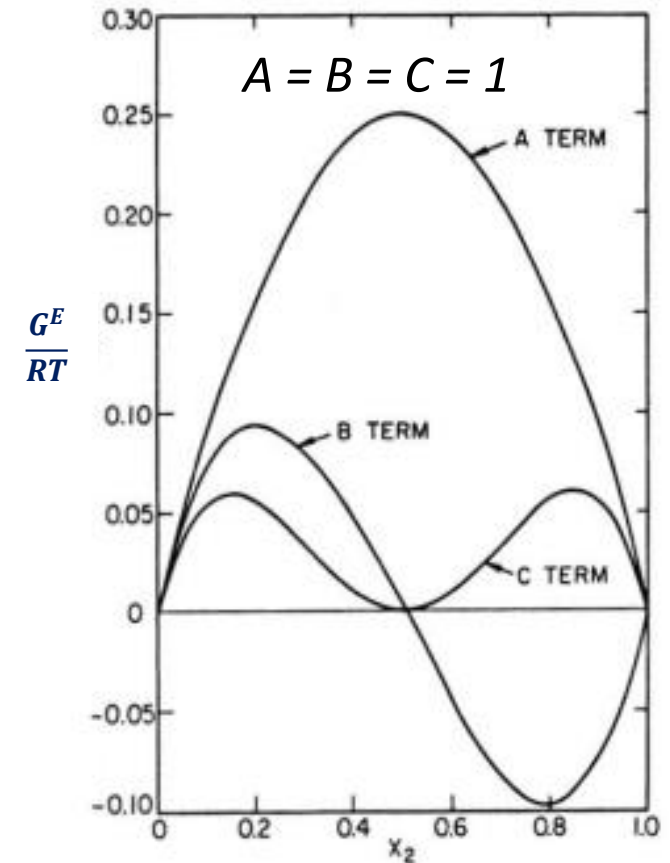
$$\frac{G^E}{RT} = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots]$$

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

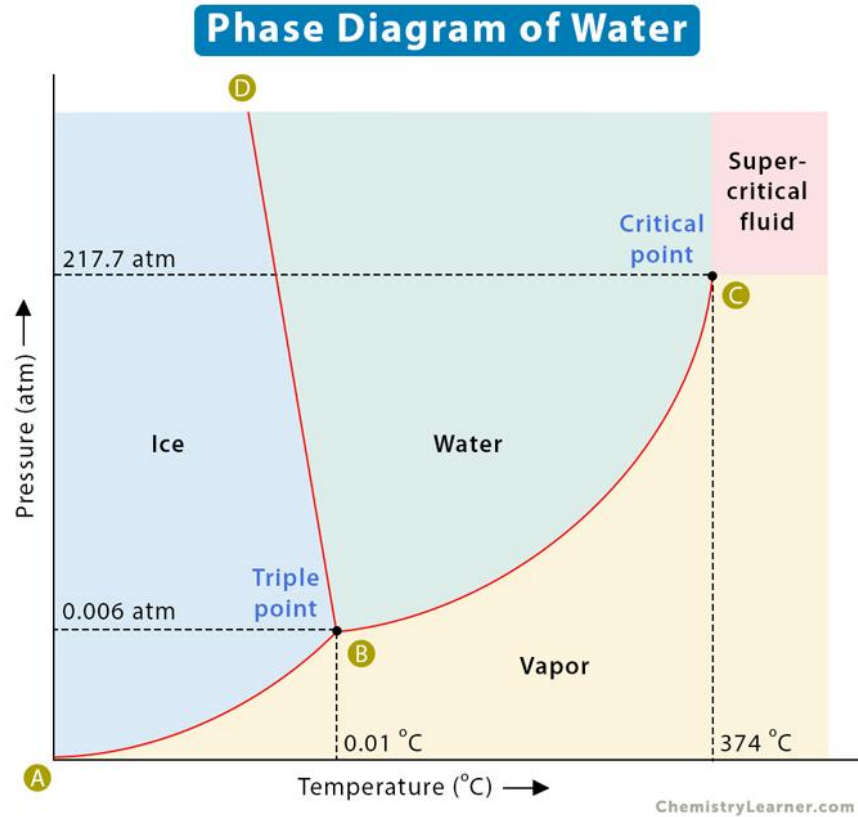
$$\ln \gamma_1 = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] + x_2 [A(x_2 - x_1) + B(6x_1 x_2 - 1) + C(x_1 - x_2)(8x_1 x_2 - 1) + \dots]$$

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

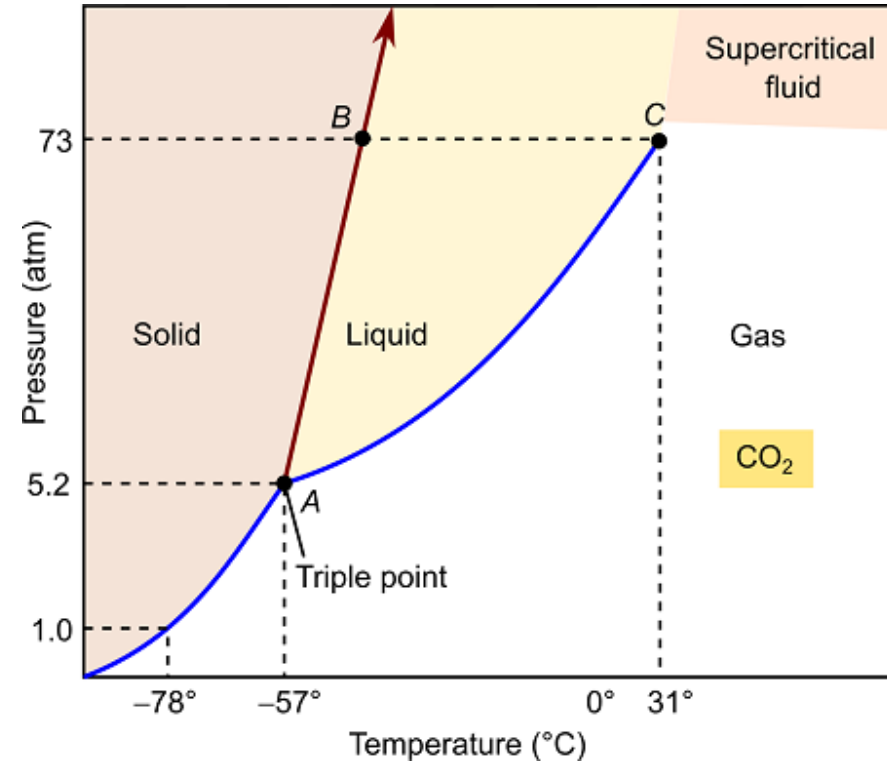
$$\ln \frac{\gamma_1}{\gamma_2} = A(x_1 - x_2) + B(6x_1 x_2 - 1) + C(x_2 - x_1)(8x_1 x_2 - 1) + \dots]$$



Phase Diagram of Pure Substance

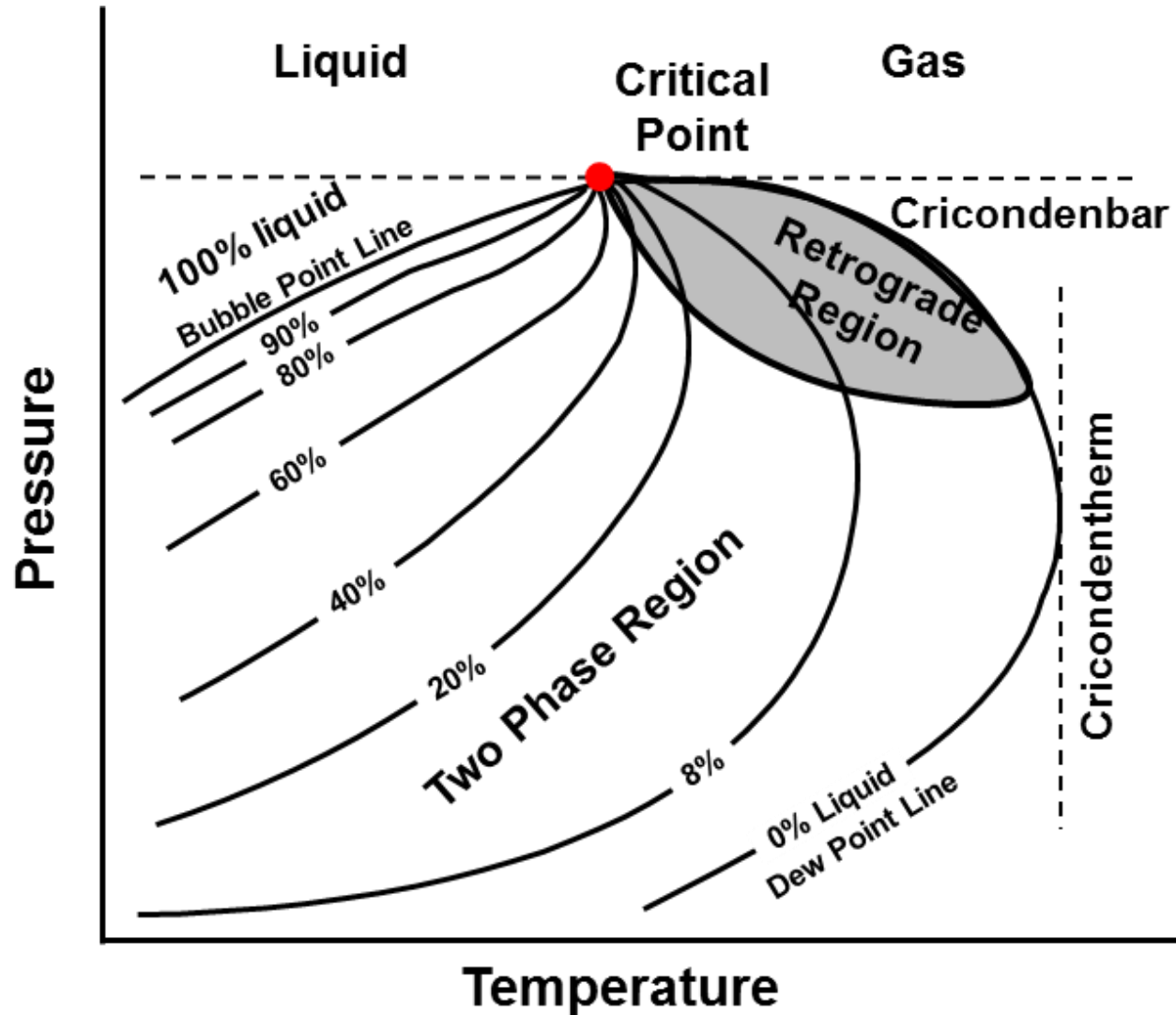


Phase diagram of Water (P-T diagram)



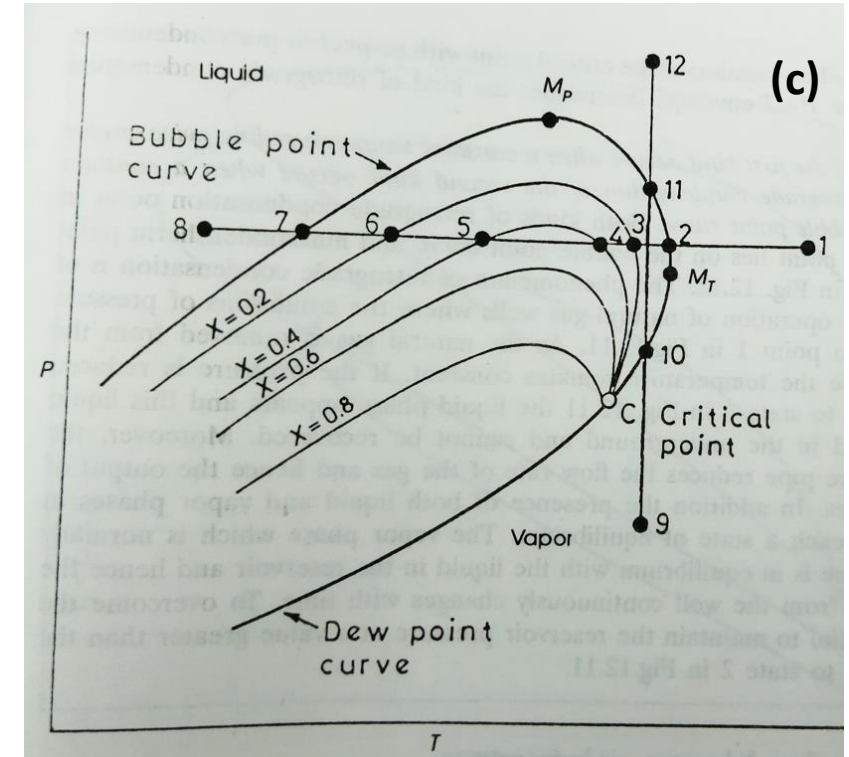
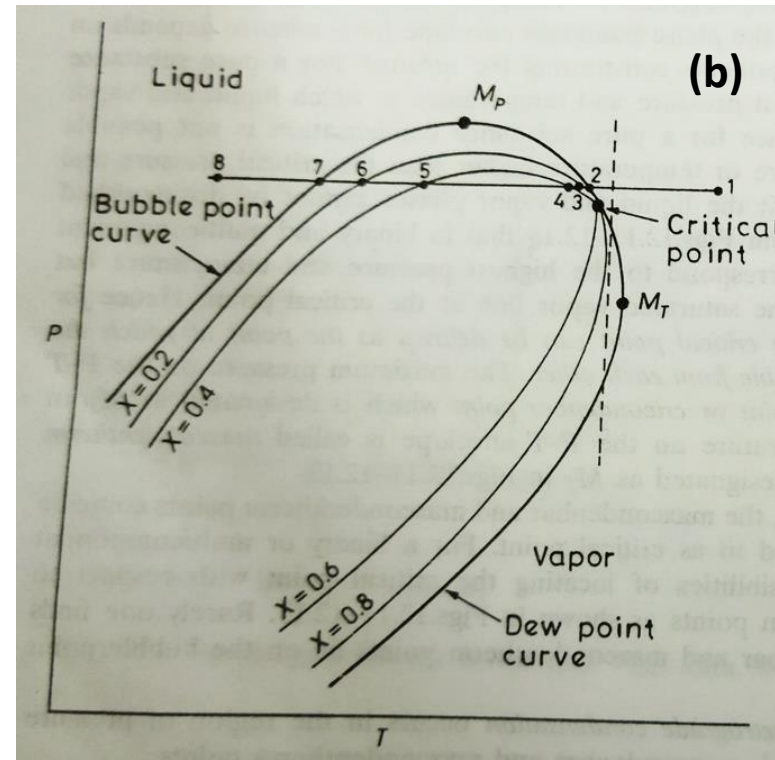
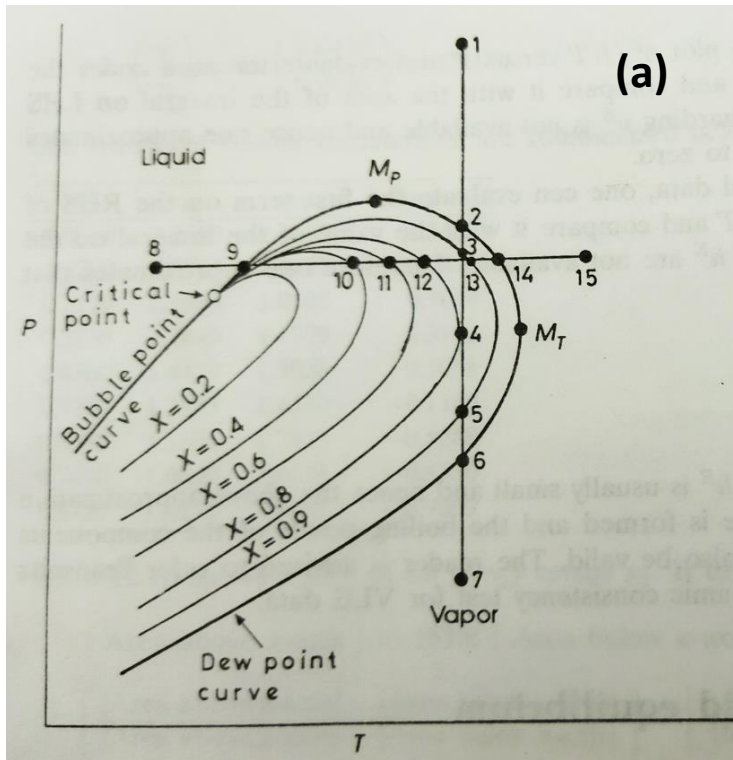
Phase diagram of CO_2 (P-T diagram)

Retrograde Condensation



- The critical point can be defined as the point at which the liquid and vapour phase are indistinguishable.
- The maximum pressure on the P-T curve is called the **maxcondenbar point** or **criconderbar point (M_p)**
- The maximum temperature on the P-T curve is called the **maxcondentherm point** or **cricondertherm point (M_T)**

Retrograde Condensation



Typical pressure –temperature diagram for a binary component mixture in which (a) both the maxcondenbar and maxcondentharm points lies on the dew point curve (b) the maxcondenbar point lies on the bubble point curve and maxcondentharm points lies on the dew point curve (c) both the maxcondenbar and maxcondentharm points lies on the bubble point curve.

Retrograde Condensation

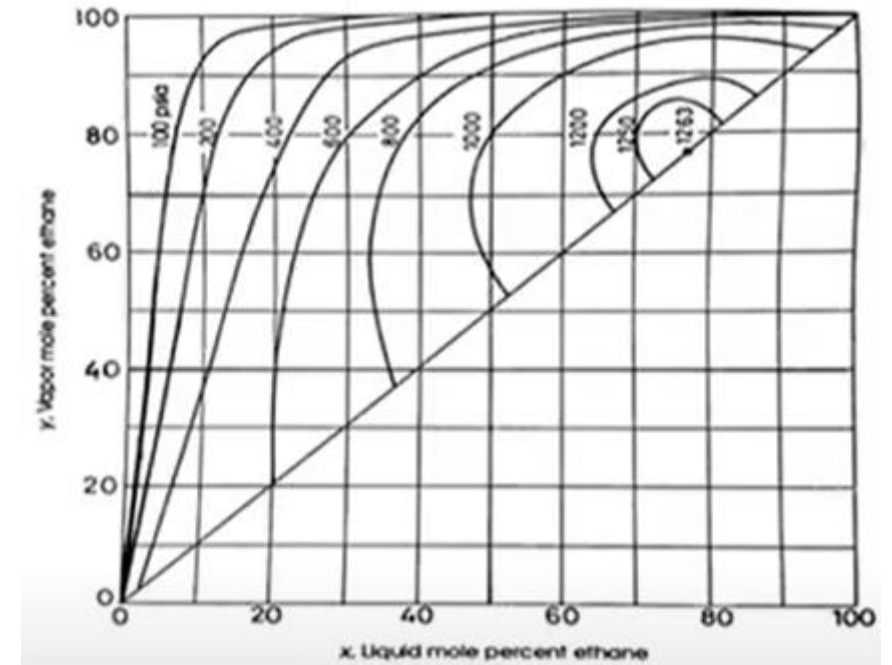
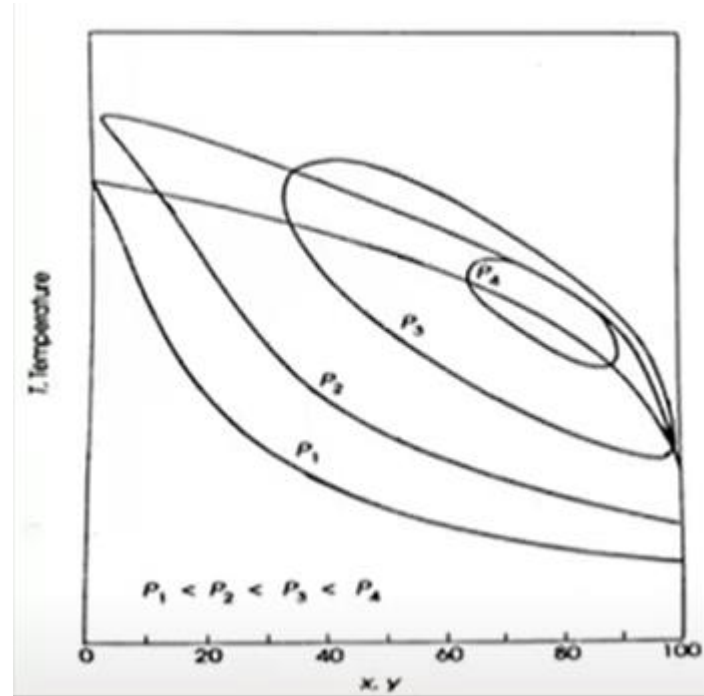
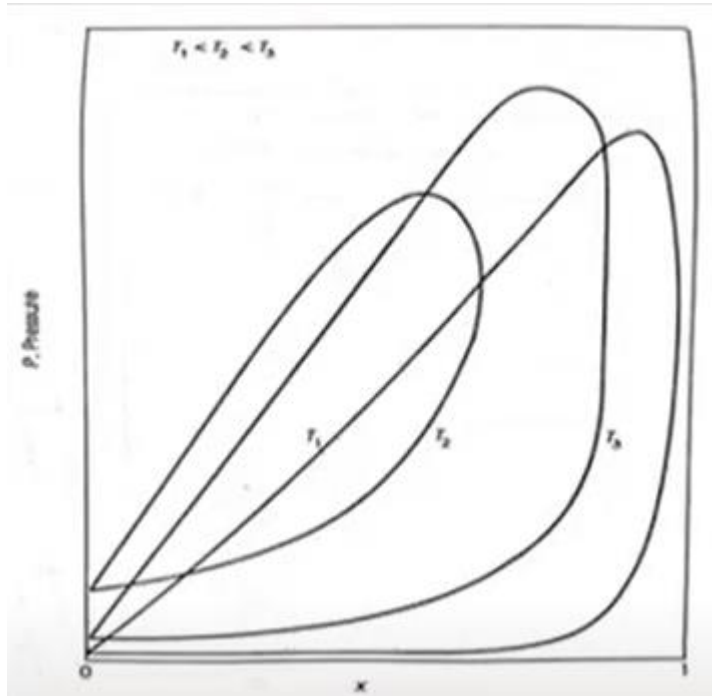
Retrograde condensation of 1st kind:

- *Constant temperature line twice cross the dew point curve*
- *Retrograde dew formation at constant temperature: phenomena of liquid formation when pressure is reduced at constant temperature*
- *Retrograde dew formation at constant pressure: phenomena of liquid formation when temperature is raised at constant pressure*

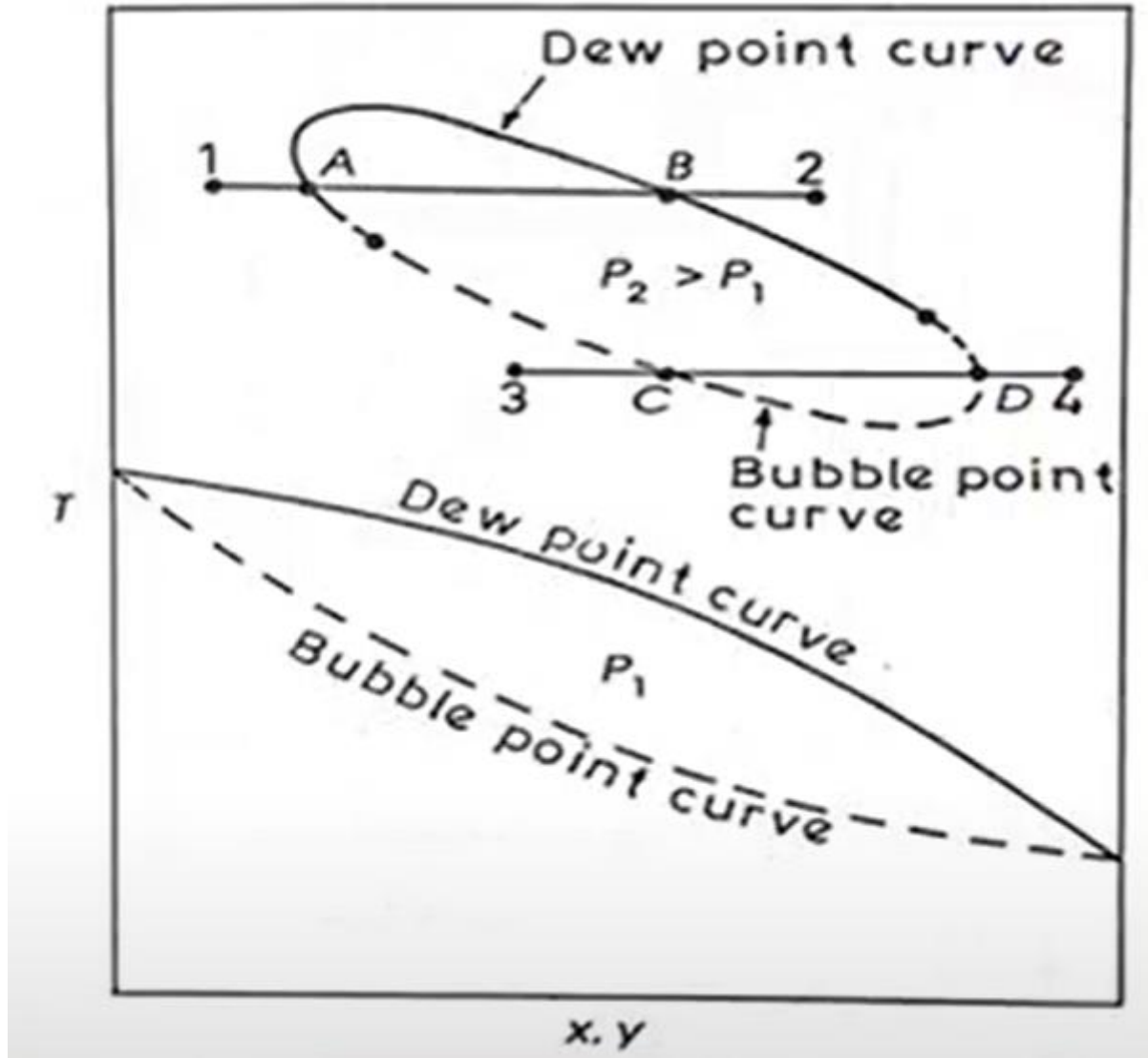
Retrograde condensation of 2nd kind:

- *Constant pressure line twice cross the bubble point curve*
- *Retrograde bubble formation at constant temperature: phenomena of vapour phase formation when pressure is increased at constant temperature*

Retrograde Condensation



Retrograde Condensation



Retrograde condensation at constant temperature and pressure with different composition

Partial and complete immiscibility

- *If the system is miscible then Δg_{mix} of the system will decrease*
- *Δg_{mix} is increase then the system will preferred to stay separated*

$$\left(\frac{\partial G_{mix}}{\partial P}\right)_{T,x} = v_{mix}$$

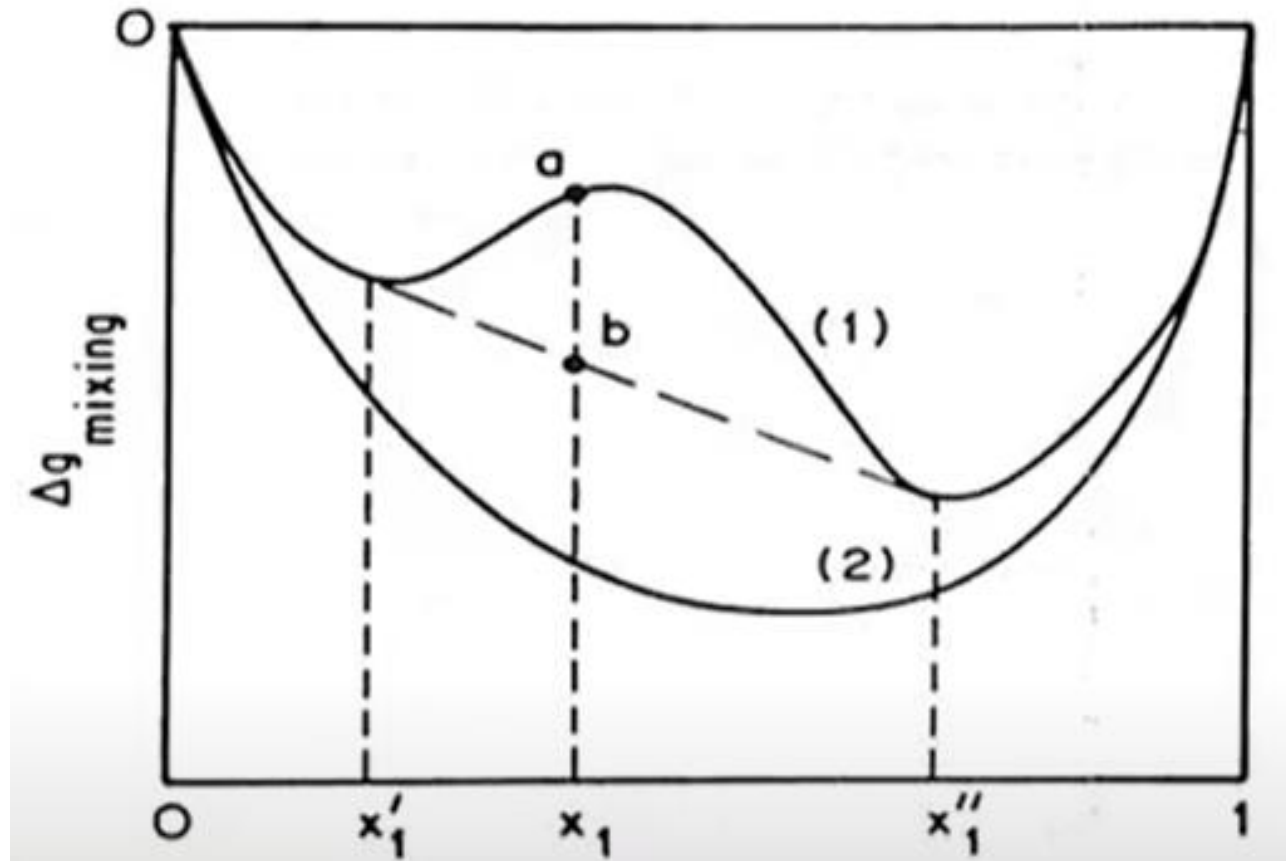
$$\Delta G_{mix} < 0$$

$$\frac{\partial^2 G_{mix}}{\partial x^2} > 0 \text{ for all } x$$

$$\Delta v_{mix} = f(T, P)$$

$$\Delta G_{mix} = f(x)$$

Partially Miscible System



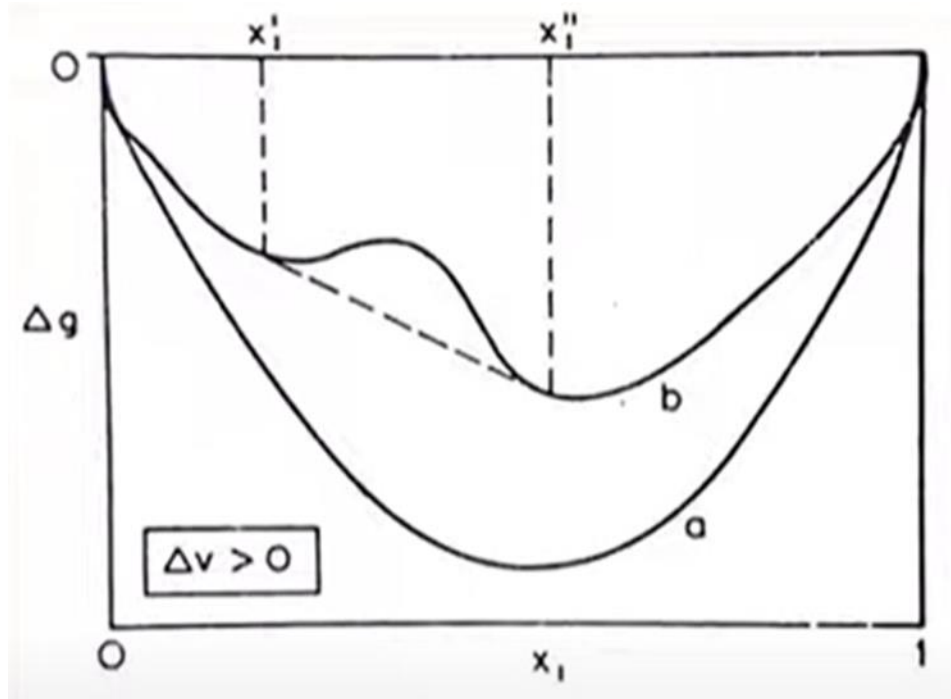
$$F = C - P + 2$$

$$F = 2 - 3 + 2$$

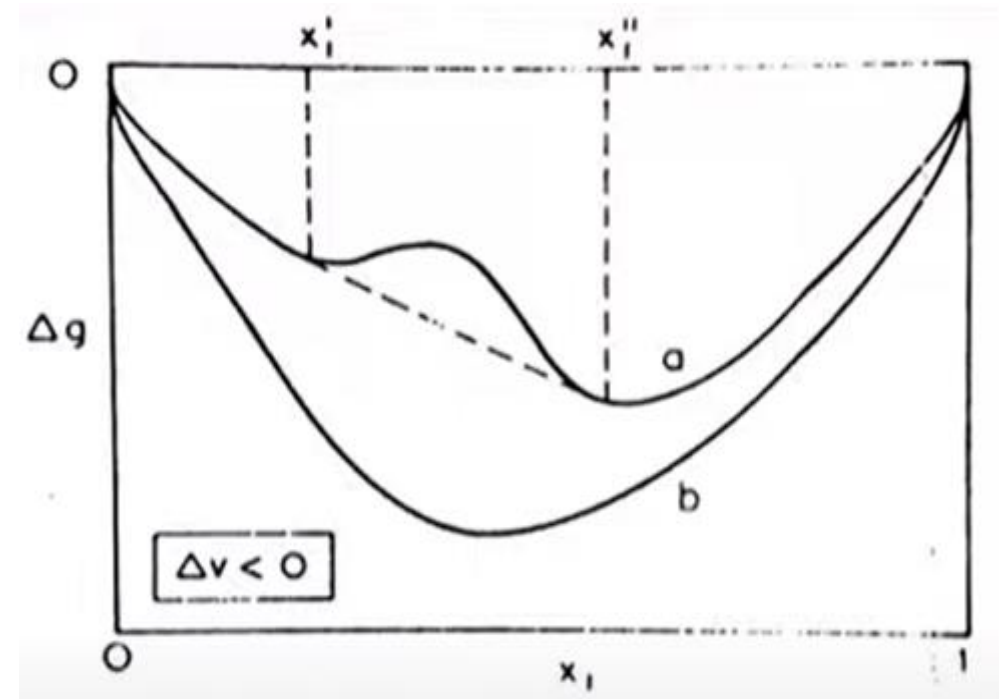
$$F = 1$$

Molar Gibbs energy of mixing at constant temperature and pressure of a binary mixture, 1) partially miscible and 2) totally miscible

Partially Miscible System

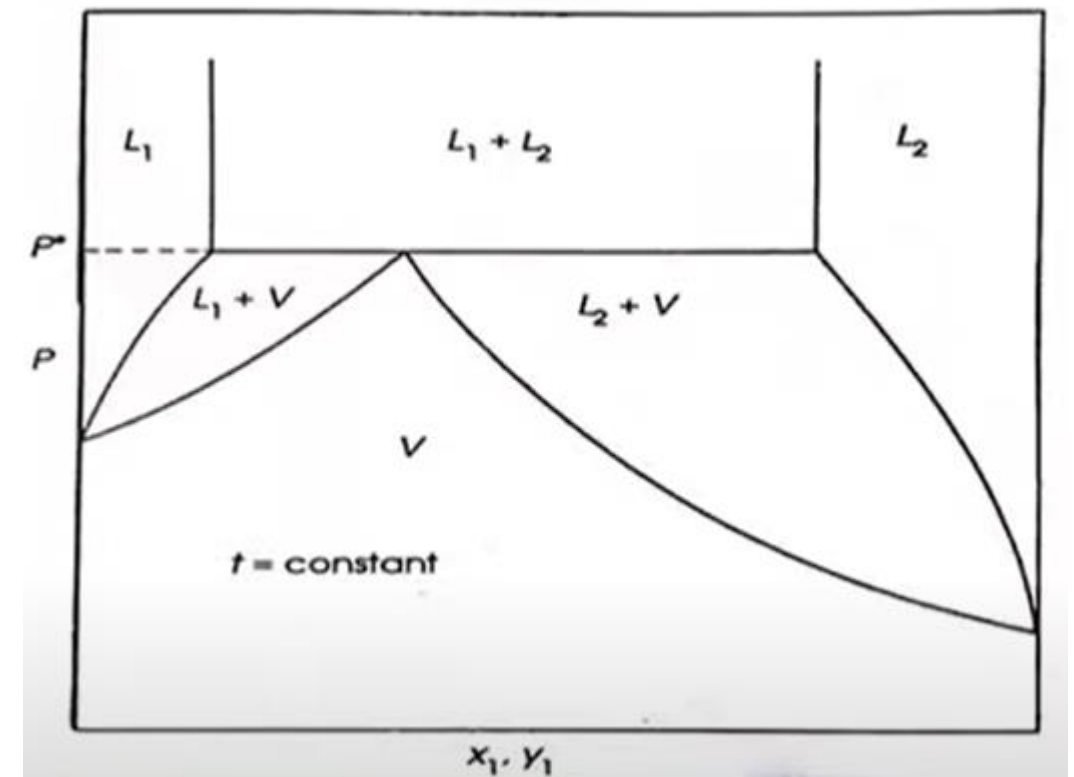
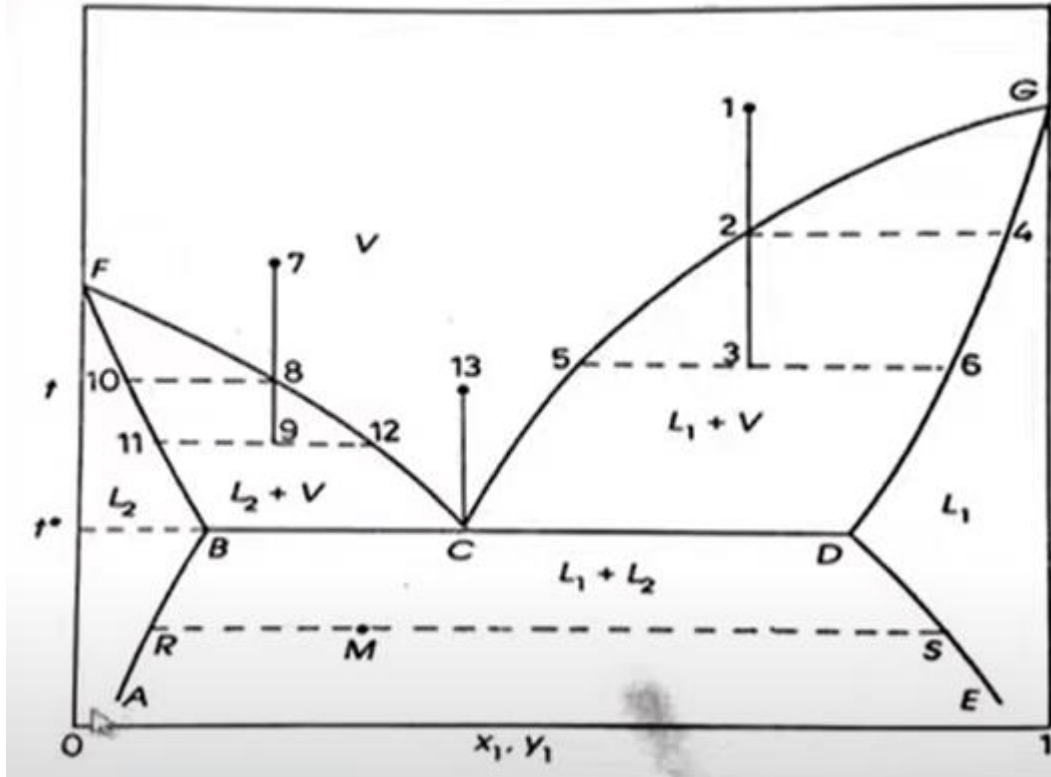


Effect of pressure on miscibility: a) low pressure, no immiscibility; b) high pressure, immiscible for $x_1' < x_1 < x_1''$



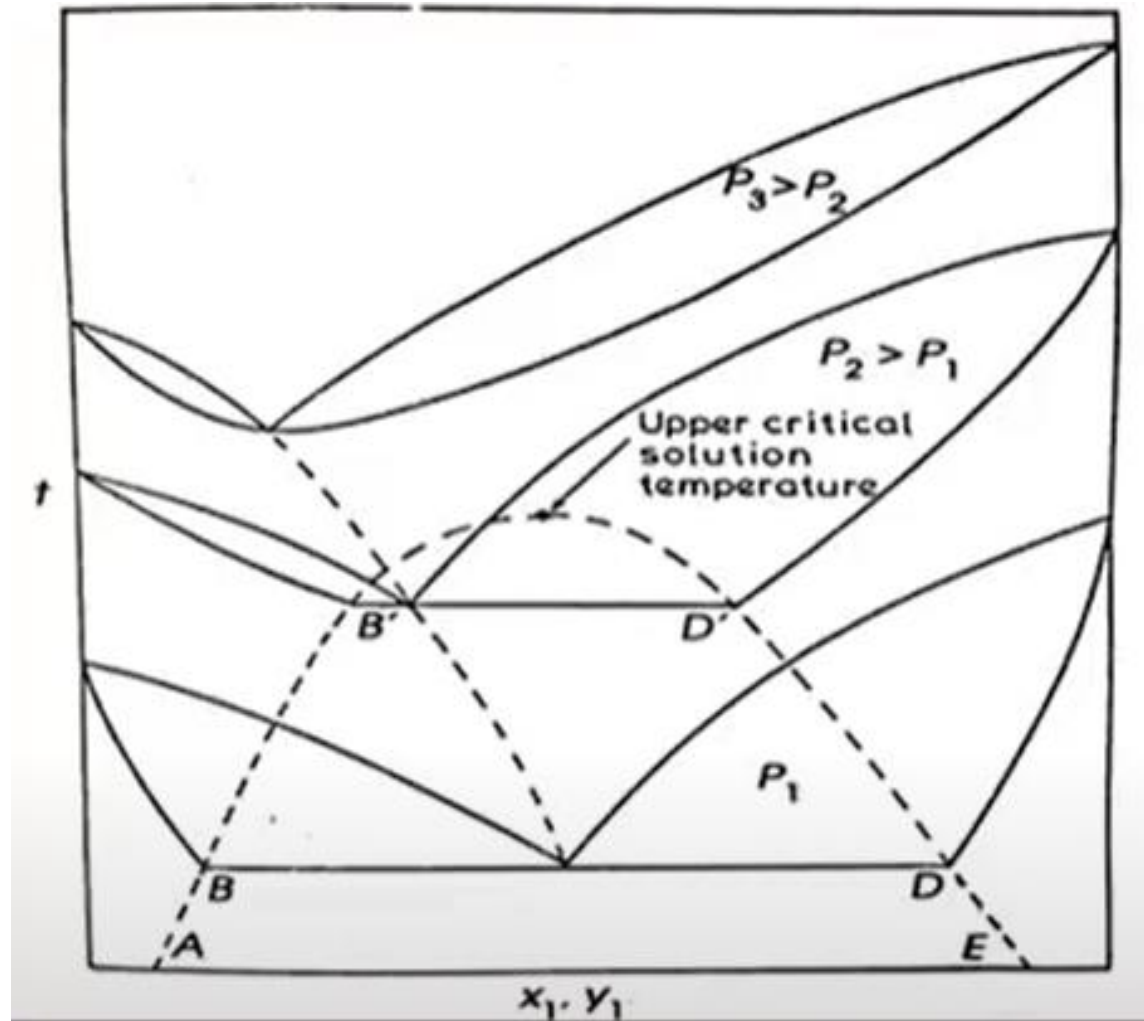
Effect of pressure on miscibility: a) low pressure, immiscible for $x_1' < x_1 < x_1''$; b) high pressure, no immiscibility.

Partially Miscible System



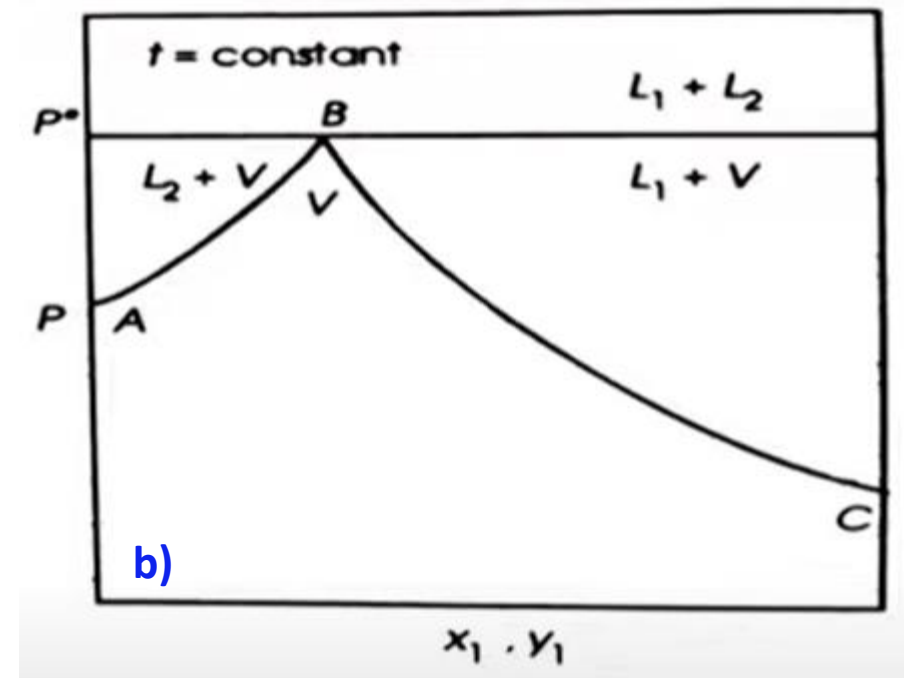
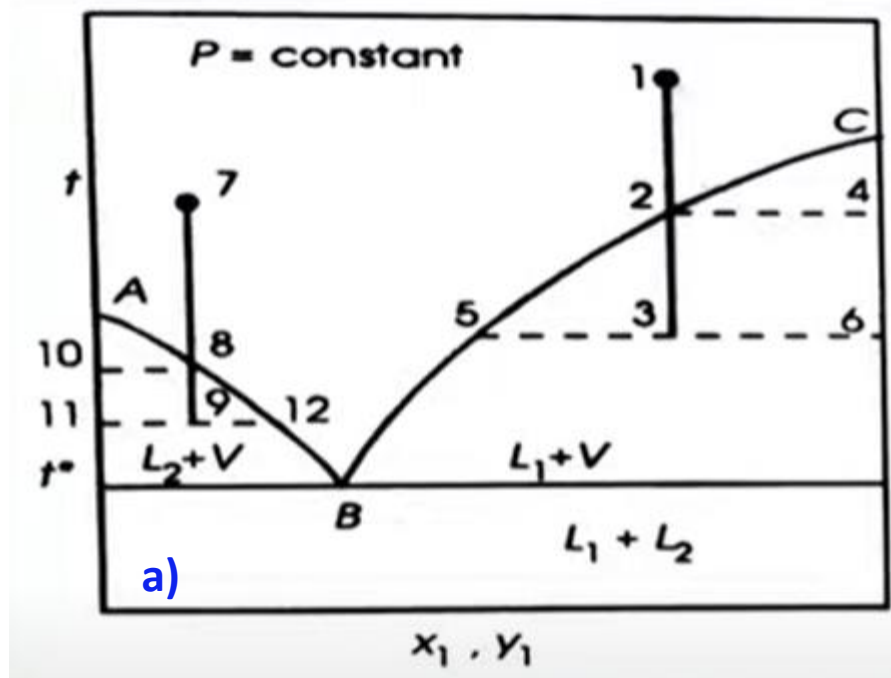
a) T-x-y diagram and b) P-x-y diagram for a partially miscible system

Partially Miscible System



Temperature-composition diagram at different pressure

Completely Immiscible System



a) T-x-y diagram and b) P-x-y diagram for a completely immiscible system

Problem:

Assuming that benzene and water form a completely immiscible system, prepare a temperature-composition (T-x-y) diagram for benzene (1) water (2) system at a pressure 760 Torr.

Antione constant are as follows:

	A	B	C
Benzene (1)	6.87987	1196.760	219.161
Water (2)	16.3872	3885.700	230.170

Chemical Reaction Equilibrium:



ν_i = stoichiometric coefficient/number

= positive (+) for product

= negative (-) for reactant



$$\nu_{N_2} = -1; \nu_{H_2} = -3; \nu_{NH_3} = 2$$

The changes in the number of moles of species present are directly proportional to stoichiometric number

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = \dots = d\varepsilon$$

ε = reaction coordinate/extend of reaction

❖ It characterizes the extend or degree to which a reaction has taken place

$$dn_i = \nu_i d\varepsilon$$

$\frac{\varepsilon}{n_i}$ = Fractional mole conversion

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^{\varepsilon} \nu_i d\varepsilon \quad n_i = n_{i0} + \nu_i \varepsilon$$

Summation over all species yields

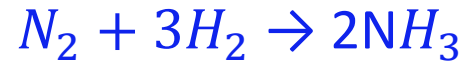
$$n = \sum_i n_{i0} + \varepsilon \sum_i \nu_i \quad n = n_0 + \nu \varepsilon$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon}$$

Chemical Reaction Equilibrium:

Problem 1:

The following reaction occurs in a system initially consist of 3 moles nitrogen and one mole hydrogen.



Find out the expression for he mole fraction as a function of reaction coordinate.

Problem 2:

Consider a vessel that initially contain only n_0 mol of water vapor. If decomposition occurs according to the reaction



Find out the expression that relate the number of moles and mole fraction of each chemical species to the reaction coordinate.

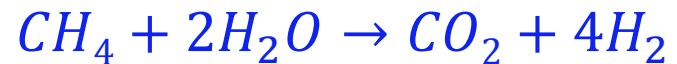
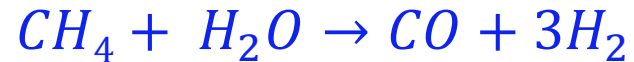
Chemical Reaction Equilibrium:

For Multi-reaction stoichiometry:

$$y_i = \frac{n_{i0} + \sum_j v_{i,j} \varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j}$$

Problem 3:

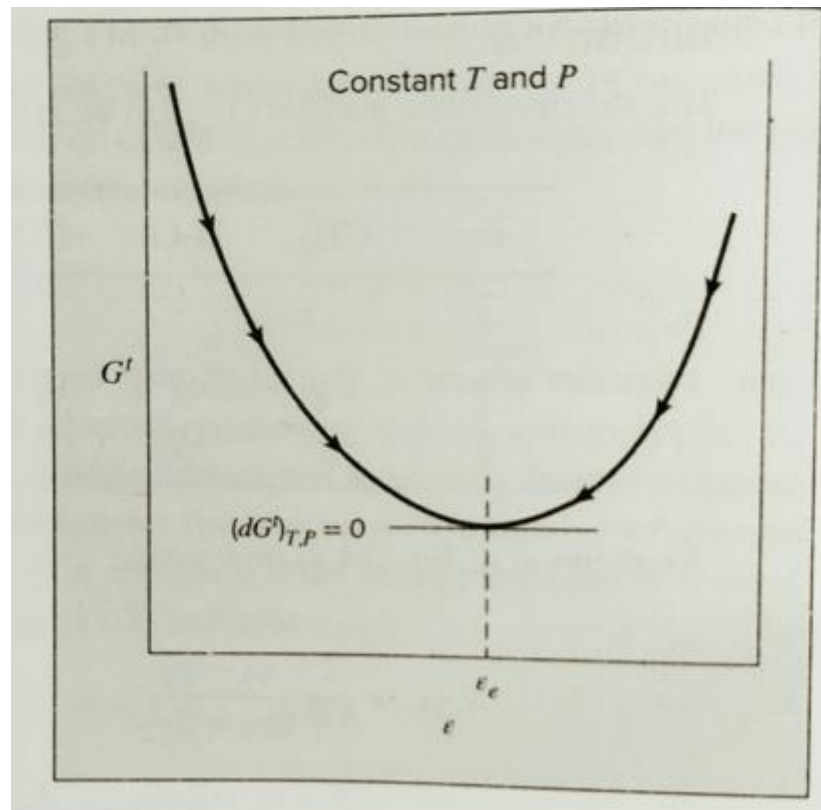
Consider a system in which following reactions occurs



Where the number 1 and 2 indicate the value of j , the reaction index. If 2 mol of CH_4 and 3 mol of H_2O are initially present, determine expression of y_i as a function of ε_1 and ε_2 .

Chemical Reaction Equilibrium:

- For a closed system at constant T and P , total Gibbs free energy must decrease of a reversible process.
- For minimum total Gibbs free energy $(dG^t)_{T,P} = 0$



The Standard Gibbs Energy Changes and Equilibrium Constant

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

$$n_i = n_{i0} + \nu_i \varepsilon$$

$$dn_i = \nu_i d\varepsilon$$

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

$$\sum_i \mu_i \nu_i = \left[\frac{\partial (nG)}{\partial \varepsilon} \right]_{T,P} = \left[\frac{\partial G^t}{\partial \varepsilon} \right]_{T,P} = 0$$

$$\sum_i \mu_i \nu_i = 0$$

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

$$G_i^0 = \Gamma_i(T) + RT \ln f_i^0$$

$$\mu_i - G_i^0 = RT \ln \frac{\hat{f}_i}{f_i^0}$$

$$\nu_i (\mu_i - G_i^0) = \nu_i RT \ln \frac{\hat{f}_i}{f_i^0}$$

$$\sum_i [\nu_i G_i^0 + RT \ln \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i}] = 0$$

$$\ln \prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = \frac{-\sum_i \nu_i G_i^0}{RT}$$

$$\prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = K_{eq}$$

$$\ln K_{eq} = \frac{-\sum_i \nu_i G_i^0}{RT} = \frac{-\Delta G^0}{RT}$$

$$\Delta G^0 = -RT \ln K_{eq}$$

Equilibrium Constant with Composition

$$\prod_i \left(\frac{\hat{f}_i}{f_i^0} \right)^{\nu_i} = K_{eq}$$

(at standard state for a gas is a ideal gas, $P^0 = f^0$)

$$\prod_i \left(\frac{\hat{f}_i}{P^0} \right)^{\nu_i} = K_{eq}$$

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

$$\prod_i \left(\frac{\hat{\phi}_i y_i P}{P^0} \right)^{\nu_i} = K_{eq}$$

$$\prod_i \left[(\hat{\phi}_i y_i)^{\nu_i} \left(\frac{P}{P^0} \right)^{\nu_i} \right] = K_{eq} \quad \sum_i \nu_i = \nu$$

$$\prod_i [(\hat{\phi}_i y_i)^{\nu_i}] \left(\frac{P}{P^0} \right)^{\nu} = K_{eq}$$

$$K_{eq} = K_y K_{\phi} \left(\frac{P}{P^0} \right)^{\nu}$$

$$K_y = \prod_i (y_i)^{\nu_i}; \quad K_{\phi} = \prod_i (\hat{\phi}_i)^{\nu_i}$$

$K_{\phi} = 1$ for ideal gas

$$K_{eq} = K_y \left(\frac{P}{P^0} \right)^{\nu}$$

Calculation of K_y :



$$K_y = \frac{(y_c)^c \cdot (y_d)^d}{(y_a)^a \cdot (y_b)^b}$$

$$K_{eq} = K_y \left(\frac{P}{P^0} \right)^{\nu}$$

$$\Delta G^0 = -RT \ln K_{eq}$$

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \nu \varepsilon}$$

Effect of Temperature on Equilibrium Constant

$$\Delta G^0 = \sum_i \nu_i G_i^0 \quad \Delta H^0 = \sum_i \nu_i H_i^0$$

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

$$dG = v dP - S dT; \quad G = H - TS$$

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT} (v dP - S dT) - \frac{H - TS}{RT^2} dT$$

$$d\left(\frac{G}{RT}\right) = \frac{v}{RT} dP - \frac{S}{RT} dT - \frac{H}{RT^2} dT + \frac{S}{RT} dT$$

$$d\left(\frac{G}{RT}\right) = \frac{v}{RT} dP - \frac{H}{RT^2} dT$$

If Gibbs energy is only function of T, then

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

For standard Gibbs energy and enthalpy

$$d\left(\frac{G_i^0}{RT}\right) = - \frac{H_i^0}{RT^2} dT$$

$$d\left(\frac{\sum_i \nu_i G_i^0}{RT}\right) = - \frac{\sum_i \nu_i H_i^0}{RT^2} dT$$

$$\frac{d\left(\frac{\Delta G^0}{RT}\right)}{dT} = - \frac{\Delta H^0}{RT^2}$$

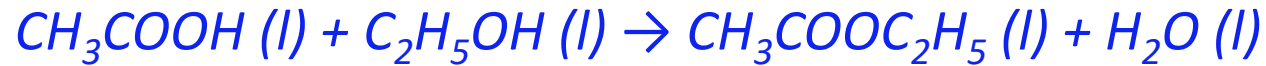
$$\frac{d(\ln K_{eq})}{dT} = \frac{\Delta H^0}{RT^2}$$

van't Hoff Equation

$$\ln \frac{K_{eq}}{K'_{eq}} = - \frac{\Delta H^0}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

Problem:

Acetic acid is esterified in the liquid phase with ethanol at 90 °C and atmospheric pressure to produce ethyl acetate and water according to the reaction:



If initially there is one mole of acetic acid and two mol of ethanol present, estimate the mole fraction of acetic acid, ethyl acetate, ethanol, and water in the reacting mixture at equilibrium.

	CH ₃ COOH (l)	C ₂ H ₅ OH (l)	CH ₃ COOC ₂ H ₅ (l)	H ₂ O (l)
ΔH_{f298}° (J)	- 484500	- 227690	- 480000	- 285830
ΔG_{f298}° (J)	- 389900	- 174780	- 332200	- 237129

Degree of freedom with reaction:

- To define the number of independent variable
- To control the system degree of freedom should be zero

$$\text{DOF} = C - P + 2 - r - s$$

C = No. of component

P = no. of phase

2 = Temperature and pressure

r = no of independent chemical reaction

s = special constraint

Problem 3:

Determine degree of freedom, F for each of the following system

- A system of two miscible nonreacting species that exists as an azeotropes in vapour/liquid equilibrium
- A system prepared by decomposing CaCO_3 into an evacuate space
- A system prepare by partially decomposition NH_4Cl into an evacuate space



- A system consisting of the gases CO , CO_2 , H_2 , H_2O , and CH_4 in chemical equilibrium

WISH YOU ALL THE BEST

AND

A VERY HAPPY DIWALI