

# Module 6

Phase equilibrium of multicomponent systems

# Lecture 6.1

Conditions of Equilibrium

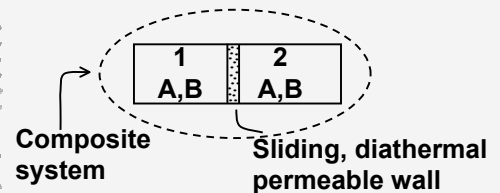
## THERMODYNAMIC EQLBM.

Basic postulate : In isolated systems all spontaneous processes proceed in the direction of increase entropy



At Equilibrium => Entropy Max with respect to any allowed variations

## PHASE EQUILIBRIUM



## PHASE EQUILIBRIUM

Change in entropy due to interaction

$$dS = dS^1 + dS^2$$

$$= \left( \frac{\partial S^1}{\partial V^1} \right) dV^1 + \left( \frac{\partial S^1}{\partial N_A^1} \right) dN_A^1 + \left( \frac{\partial S^1}{\partial N_B^1} \right) dN_B^1 + \left( \frac{\partial S^1}{\partial U^1} \right) dU^1$$

$$+ \left( \frac{\partial S^2}{\partial V^2} \right) dV^2 + \left( \frac{\partial S^2}{\partial N_A^2} \right) dN_A^2 + \left( \frac{\partial S^2}{\partial N_B^2} \right) dN_B^2 + \left( \frac{\partial S^2}{\partial U^2} \right) dU^2$$

## PHASE EQUILIBRIUM

or

$$dS = \left\{ \frac{p^1}{T^1} dV^1 - \frac{\mu_A^1}{T^1} dN_A^1 - \frac{\mu_B^1}{T^1} dN_B^1 + \frac{dU^1}{T^1} \right\} + \left\{ \frac{p^2}{T^2} dV^2 - \frac{\mu_A^2}{T^2} dN_A^2 - \frac{\mu_B^2}{T^2} dN_B^2 + \frac{dU^2}{T^2} \right\}$$

## PHASE EQUILIBRIUM

### Constraints

$$V^1 + V^2 = \text{Const} \Rightarrow dV^1 + dV^2 = 0$$

$$N_A^1 + N_A^2 = \text{Const} \Rightarrow dN_A^1 + dN_A^2 = 0$$

$$N_B^1 + N_B^2 = \text{Const} \Rightarrow dN_B^1 + dN_B^2 = 0$$

$$U^1 + U^2 = \text{Const} \Rightarrow dU^1 + dU^2 = 0$$

## PHASE EQUILIBRIUM

$$dS = \underbrace{\left( \frac{p^1}{T^1} - \frac{p^2}{T^2} \right)}_{F_p} J_w dt + \underbrace{\left( \frac{1}{T^1} - \frac{1}{T^2} \right)}_{F_Q} J_Q dt$$

$$- \underbrace{\left( \frac{\mu_A^1}{T^1} - \frac{\mu_A^2}{T^2} \right)}_{F_{NA}} J_{NA} dt - \underbrace{\left( \frac{\mu_B^1}{T^1} - \frac{\mu_B^2}{T^2} \right)}_{F_{NB}} J_{NB} dt$$

## Affinity-Flux relationship

Since each  $F_i J_i \geq 0$

This implies  
if  $F_i > 0$   $J_i > 0$ ; if  $F_i < 0$   $J_i < 0$

Referring to diffusion of species:

$$dN_A^1 > 0 \quad \text{if} \quad \mu_A^1/T^1 < \mu_A^2/T^2$$

Species diffuse towards a region  
of low chemical Potential

## PHASE EQUILIBRIUM

Generalisation to  $\pi$  phases in eqblm.

$$T^1 = T^2 = T^3 = \dots = T^\pi$$

$$P^1 = P^2 = P^3 = \dots = P^\pi$$

$$\mu_j^1 = \mu_j^2 = \mu_j^3 = \dots = \mu_j^\pi \quad \text{for all } j$$

## ANALYZING PHASE EQUILIBRIUM

Implications of conditions of equilibrium

$$\mu_i^1(T, P, x_1, x_2, \dots, x_r) = \mu_i^2(T, P, y_1, y_2, \dots, y_r)$$

or

$$f_i^1(T, P, x_1, x_2, \dots, x_r) = f_i^2(T, P, y_1, y_2, \dots, y_r)$$

- Difficulty of solving the general problem
- Need for idealisation
- Need for calculating fugacities of liquid & solid solutions

## DETERMINING FUGACITY OF LIQUID & SOLID SOLUTIONS

- Ideal Solution Model (Lewis – Randall rule)

$$f_i = f_i^0 x_i$$

- Concept of Simple Solutions
- Determining  $f_i^0$

$$\text{Phase equilibrium : } f_L^0 = f_V^0 = f_S^0$$

## POYNTING CORRECTION

Effect of Pressure on fugacity of liquids / solids

$$\left( \frac{\partial \ln f^0}{\partial P} \right)_T = \frac{v^0}{RT}$$

$$\ln \left( \frac{f_1^0}{f_{sat}^0} \right)_T = \frac{1}{RT} \int_{P_{sat}}^P v^0 dP$$

## PROBLEM

Calculate the fugacity of liquid water at 25°C and at its equilibrium vapour pressure.

Compare with its fugacity at 25°C and 1 atm and at 25°C and 100 atm.

(Sussman p 300)

## SOLUTION

- a) The vapour pressure of H<sub>2</sub>O at 25°C = 23.76 mm Hg\* = 0.0313 atm

At this low value of P<sub>r</sub>, the vapour is in an ideal state

$$f_{liq}(at P_{H_2O}) = P_{H_2O}(at 25^\circ C) = 0.0313 \text{ atm}$$

which is the fugacity of liquid water and water vapour at 25°C and 0.0313 atm

## SOLUTION

- b) If the total pressure on the system is increased to 1 atm :

$$\ln \frac{f_{1atm}}{0.0313} = \frac{\bar{V}}{RT} (1 - 0.0313)$$

and, assuming  $\bar{V}_{liq}$  to be independent of pressure

$$\bar{V}_{25^\circ C} = 0.001 \text{ m}^3/\text{kg} = .018 \text{ m}^3/\text{kmol}$$

## SOLUTION

Thus we obtain

$$\ln \frac{f_1}{0.0313} = \frac{.018}{(8314.3) \times 298} (0.969 \times 1.013 \times 10^5) \\ = 0.00077$$

Therefore, when we remember that

$\ln(1+x) = x$ , when x is small

$$\frac{f_1}{0.0313} = 1.0007 \Rightarrow f_1 \approx .0313$$

## SOLUTION

- c) At 100 atm total pressure :

$$\ln \frac{f}{0.0313} = 0.08$$

$$\text{and } \frac{f}{0.0313} = 1.08$$

$$\text{Therefore } f_{100} = 0.0338 \text{ atm}$$

## RAOULT'S LAW

Liquid : Ideal Solution;

Vapour : Ideal gas mixture

$$f_i^L = f_i^V$$

$$f_{iL}^0 x_i = P y_i$$

Neglecting Poynting Correction

$$f_{iL}^0 = P_i^{sat} \text{ at mixture temperature}$$

This gives

$$P_i^{sat} x_i = P y_i \text{ (Raoult's Law)}$$

## RAOULT'S LAW

=>Provides  $r$  (=no of components) equations relating properties at VLE

no. of variables;  $T, P, \{y_i\}, \{x_i\} = 2r$

only  $r-1$   
are indep.

∴ Specifying  $r$  of these variables, the remaining variables can be found

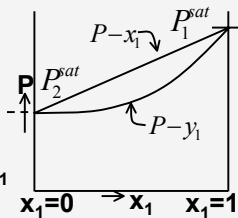
## RAOULT'S LAW

### EX. BINARY SYSTEMS

$$\left. \begin{aligned} y_1 P &= x_1 P_1^{sat} \\ y_2 P &= x_2 P_2^{sat} \end{aligned} \right\} P = x_1 P_1^{sat} + x_2 P_2^{sat}$$

∴ at a given  $T$ ,  
(fixed  $P_1^{sat}, P_2^{sat}$ )

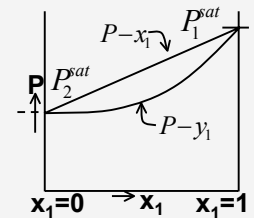
$P$  is a linear fn. of  $x_1$



## RAOULT'S LAW

To find  $y_1$  corresp. to any  $x_1$  =>

$$y_1 = \frac{x_1 P_1^{sat}}{P} = \frac{x_1 P_1^{sat}}{x_1 P_1^{sat} + x_2 P_2^{sat}}$$



## RAOULT'S LAW

**Example** Assuming  $\text{NH}_3 - \text{H}_2\text{O}$   
[C&B, p764] mixture as ideal sol  
determine  $y$ 's for

$$x_{\text{NH}_3} = 0.7 \quad x_{\text{H}_2\text{O}} = .3$$

at  
 $40^\circ\text{C}$

## RAOULT'S LAW

### Solution

At  $40^\circ\text{C}$  sat. properties

$$P_{\text{NH}_3} = 1554.3 \text{ kPa}$$

$$P_{\text{wat}} = 7.384 \text{ kPa}$$

$$\begin{aligned} \therefore y_{\text{NH}_3} P &= x_{\text{NH}_3} P_{\text{NH}_3}^{sat} = 0.7 \times 1554.3 \text{ kPa} \\ &= 1088.03 \text{ kPa} \end{aligned}$$

$$\begin{aligned} y_{\text{H}_2\text{O}} P &= x_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^{sat} = 0.3 \times 7.384 \text{ kPa} \\ &= 2.22 \text{ kPa} \end{aligned}$$

## RAOULT'S LAW

Applying the two

$$P = 1090.25 \text{ kPa}$$

$$\therefore y_{NH_3} = \frac{1088.03}{1090.25} = .998$$

$$y_{H_2O} = \frac{2.22}{1090.25} = .002$$

Note the difference in  $y$  values !

# End of Lecture

## Lecture 6.3

A few applications

### Cor. 1 : GIBB'S PHASE RULE

Let  $C$  : No. of components

If all phases had no interaction with each other, each would require  $C+1$  independent variables of state for its complete specification i.e. we would have  $\pi(C+1)$  independent variables.

### Cor. 1 : GIBB'S PHASE RULE

No. of constraints arising due to phase equilibrium

$$\left. \begin{array}{l} T \rightarrow \pi - 1 \\ P \rightarrow \pi - 1 \\ \mu \rightarrow (\pi - 1)C \end{array} \right\} \sum = \pi(C + 2) - C - 2$$

$\therefore$  No. of degrees of freedom remaining is

$$f = C + 2 - \pi$$

### Cor. 2 : CLASIUS CLAPEYRON EQ.

For pure substance, if two phases 1 & 2 are in eqlbm.

$$\mu_1 = \mu_2 \Rightarrow g_1 = g_2$$

$$h_1 - TS_1 = h_2 - TS_2$$

or  $h_1 - h_2 = T(S_1 - S_2)$

## Cor. 2 : CLASIUS CLAPEYRON EQ.

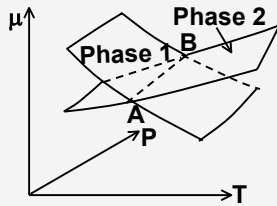
Also

$$\mu = g = f(T, P)$$

For two phases

$$\mu(T, P)$$

are as shown =>



A - B : conditions of eqbm.  
& represents relationship between T & P during eqbm.

## Cor. 2 : CLASIUS CLAPEYRON EQ.

To obtain this relationship, note that along this line

$$d\mu^1 = d\mu^2 \Rightarrow dg^1 = dg^2$$

$$\Rightarrow v^1 dP - S^1 dT = v^2 dP - S^2 dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{S^1 - S^2}{V^1 - V^2} \text{ along eqbm. curve}$$

$$= \frac{(h_1 - h_2)}{T(V^1 - V^2)}$$

Completely general equation

## Cor. 2 : CLASIUS CLAPEYRON EQ.

S-L Eqbm : Change in f.p. with pr.

S-V, L-V Eqbm : Change in b.p. with pr.



assuming further that vap. phase behaves like an ideal gas

## Cor. 2 : CLASIUS CLAPEYRON EQ.

$$\frac{dP}{dT} = \frac{h_V - h_L}{T(v^V - v^L)} \approx \frac{L}{Tv^V} \approx \frac{L}{T} \cdot \frac{P}{RT}$$

$$\frac{dP}{P} \approx \frac{L}{RT^2} dT$$

$$\ln P = C - \frac{L}{RT}$$

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Antoine Eq.  $\ln P = C - \frac{A}{B+T} \leftarrow 0^\circ\text{C}$

## LAW OF BOILING POINT ELEVATION

Raoult's Law  $y_i P = x_i P_i^{sat}$

Consider non-volatile solute (Comp. 2)  
dissolved in a solvent (Comp. 1)

$$P_1^V = x_1 P_1^{sat}$$

pr. of solvent vap. in eqbm. with sol.

$\{P_1^{sat} = \text{vap. pr. of pure solvent at sol } T\}$

## LAW OF BOILING POINT ELEVATION

We wish to find  $\left(\frac{\partial T}{\partial x_2}\right)_{P, V}$

From Raoult's law, written as

$$f(x_1, p_1^V, T) = 0$$

$$\left(\frac{\partial T}{\partial x_1}\right)_{p_1^V} = - \left(\frac{\partial T}{\partial p_1^V}\right)_{x_1} \left(\frac{\partial p_1^V}{\partial x_1}\right)_T$$

From Raoult's law  $\left(\frac{\partial p_1^V}{\partial x_1}\right)_T = P_1^{sat}$

## LAW OF BOILING POINT ELEVATION

$$\therefore \left( \frac{\partial T}{\partial x_1} \right)_{P_1^V} = -P_1^{sat} \left( \frac{\partial T}{\partial P_1^V} \right)_{x_1}$$

For infinitely dilute soln., i.e.  
 $x_2 \rightarrow 0$ ;  $x_1 \rightarrow 1$  so that  $P_1^V \rightarrow P_1^{sat}$

$$\left( \frac{\partial T}{\partial x_1} \right)_{P_1^V \rightarrow P_1^{sat}} = -P_1^{sat} \left( \frac{\partial T}{\partial P_1^{sat}} \right)_{x_1 \rightarrow 1}$$

$$= - \left\{ \frac{dT}{d(\ln P_1^{sat})} \right\}_{x_2 \rightarrow 1}$$

## LAW OF BOILING POINT ELEVATION

Further, since  $x_1 + x_2 = 1$ ,  $dx_1 = -dx_2$

$$\& \therefore \left( \frac{\partial T}{\partial x_2} \right)_{x_2 \rightarrow 0} = \left[ \frac{dT}{d(\ln P_1^{sat})} \right]_{x_2 \rightarrow 0}$$

$$= \frac{T P_1^{sat} \Delta V}{L} \text{ from Clapeyron's eq.}$$

$$\approx \frac{T P_1^{sat} v_g}{h_{fg}}$$

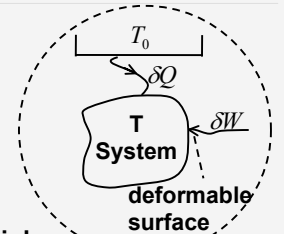
$$\approx \frac{RT^2}{h_{fg}} \left\{ \text{assuming vap} \equiv \text{ideal gas} \right\}$$

## Lecture 6.4

### Extremum Principles

## GENERAL CONDITION OF EQLBM.

For systems having work & heat interaction with surroundings



Entropy Max Principle  
 (for system + surroundings)

Universe  $\equiv$  System + Surroundings

## GENERAL CONDITION OF EQLBM.

$$dS_0 + dS_{\text{sys}} \geq 0$$

Now, 
$$dS_0 = -\frac{\delta Q}{T_0}$$

Work done on system =  $-P_0 dV_{\text{sys}}$

{ $P_0$ , surroundings pr. assumed const.}

## GENERAL CONDITION OF EQLBM.

First Law for system

$$dQ = dU_{\text{sys}} - \text{Work input}$$

$$= dU_{\text{sys}} + P_0 dV_{\text{sys}}$$

$$\therefore dS_0 = -\frac{dQ}{T_0} = -\frac{dU_{\text{sys}} + P_0 dV_{\text{sys}}}{T_0}$$

## GENERAL CONDITION OF EQLBM.

Entropy Max Principle gives

$$dS_{\text{sys}} - \frac{dU_{\text{sys}} + p_0 dV_{\text{sys}}}{T_0} \geq 0$$

or  $dU_{\text{sys}} + p_0 dV_{\text{sys}} - T_0 dS_{\text{sys}} \leq 0$

or for system  $d(U + p_0 V - T_0 S) \leq 0$

Availability

General Equilibrium Condition

Availability will be minimum

## GENERAL CONDITION OF EQLBM.

⇒ In any natural process availability will reduce



Social & Philosophical Implication

⇒ Resource depletion

⇒ Limits to Growth

## OTHER FORMULATIONS OF GEN EQLBM. CONDITION UNDER RESTRICTIONS

I Const. U, V {Isolated Sys}  
above eq. reduces to {∴ dU = 0, dV = 0}

$(dS)_{U,V} \geq 0$  Entropy Max Principle

II Const. V & S

$(dU)_{S,V} \leq 0$  Min Energy Principle

## OTHER FORMULATIONS OF GEN EQLBM. CONDITION UNDER RESTRICTIONS

III Const. S & P

as proved earlier, a necessary condition for eqlbm would be

$P_{\text{sys}} = P = p_0$

∴ G.C. becomes  $dU + PdV \leq 0$

or  $dH \leq 0$

MIN ENTHALPY PRINCIPLE

## OTHER FORMULATIONS OF GEN EQLBM. CONDITION UNDER RESTRICTIONS

IV Const. T & V  
as proved earlier, a necessary condition for eqlbm is

$T = T_{\text{sys}} = T_0$

∴ G.C. ⇒  $d(U - T_0 S) \leq 0$

$d(U - TS) \leq 0$

$dF \leq 0$

MIN HELMHOLTZ FUNCTION PRINCIPLE

## OTHER FORMULATIONS OF GEN EQLBM. CONDITION UNDER RESTRICTIONS

V Const. T & P  
necessary conditions for eqlbm

$T = T_0$

$P = p_0$

G.C. ⇒  $d(U + p_0 V - T_0 S) \leq 0$

$d(U + PV - TS) \leq 0$

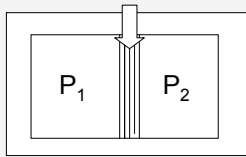
$dG \leq 0$

MIN GIBB'S FUNCTION PRINCIPLE

⇒ U, H, F, G are called thermodynamic potentials ∴ of these results

## Equivalence of various criteria

Consider attainment of equilibrium when the Stop is removed



The final equilibrium state has the Max entropy, as also minimum energy at that state !

## STABILITY OF THERMODYNAMIC SYSTEMS

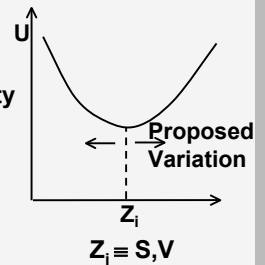
Min U principle

$$U = U(S, V, N_1, N_2, \dots)$$

Consider for simplicity pure substance

$$U = U(S, V)$$

$$= U(Z_i)$$



## STABILITY OF THERMODYNAMIC SYSTEMS

Taylor's Series exp.

$$\Delta U = \delta U + \frac{1}{2!} \delta^2 U + \frac{1}{3!} \delta^3 U + \dots$$

$$\delta U = \sum \left( \frac{\partial U}{\partial Z_i} \right) \delta Z_i = \left( \frac{\partial U}{\partial S} \right) dS + \left( \frac{\partial U}{\partial V} \right) dV$$

## STABILITY OF THERMODYNAMIC SYSTEMS

$$\delta^2 U = \sum_i \sum_j \left( \frac{\partial^2 U}{\partial Z_i \partial Z_j} \right) \delta Z_i \delta Z_j$$

$$= \left( \frac{\partial^2 U}{\partial S^2} \right) dS^2 + 2 \left( \frac{\partial^2 U}{\partial S \partial V} \right) dS dV + \frac{\partial^2 U}{\partial V^2} dV^2$$

$$\delta^3 U = \sum_i \sum_j \sum_k \left( \frac{\partial^3 U}{\partial Z_i \partial Z_j \partial Z_k} \right) \delta Z_i \delta Z_j \delta Z_k$$

## STABILITY OF THERMODYNAMIC SYSTEMS

For U to be a minima

$$\Delta U > 0; \delta U = 0; \delta^m U > 0$$

where

$\delta^m U$  is the lowest order non-vanishing variation of U.

$$\delta^2 U > 0 \Rightarrow U_{SS} dS^2 + 2U_{SV} dS dV + U_{VV} dV^2 > 0$$

$$\text{or } \frac{1}{U_{SS}} \{ U_{SS}^2 dS^2 + 2U_{SS} U_{SV} dS dV + U_{SV}^2 dV^2 - U_{SV}^2 dV^2 \} + U_{VV} dV^2 > 0$$

## STABILITY OF THERMODYNAMIC SYSTEMS

$$\text{or } \frac{(U_{SS} dS + U_{SV} dV)^2}{U_{SS}} + \left( U_{VV} - \frac{U_{SV}^2}{U_{SS}} \right) dV^2 > 0$$

=> {Since dS, dV are arbitrary variations} +ve definiteness of this quadratic form requires

$$U_{SS} > 0; U_{VV} - \frac{U_{SV}^2}{U_{SS}} > 0$$

## STABILITY OF THERMODYNAMIC SYSTEMS

← CONDITIONS OF STABILITY →

$$U_{SS} > 0 \Rightarrow \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial S} \right)_V = \left( \frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V} > 0$$

or  $C_V > 0$

## STABILITY OF THERMODYNAMIC SYSTEMS

$$U_{VV} - \frac{U_{SV}^2}{U_{SS}} > 0 \Rightarrow$$

$$LHS = \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial V} \right)_S - \frac{\left[ \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right)_S \right]^2}{\frac{\partial}{\partial S} \left( \frac{\partial U}{\partial S} \right)_V}$$

$$= - \left( \frac{\partial p}{\partial V} \right)_S - \left( \frac{\partial p}{\partial S} \right)_V \left( \frac{\partial p}{\partial S} \right)_V / \left( \frac{\partial T}{\partial S} \right)_V$$

## STABILITY OF THERMODYNAMIC SYSTEMS

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

$$= - \left\{ \left( \frac{\partial p}{\partial V} \right)_S + \left( \frac{\partial p}{\partial S} \right)_V \left( \frac{\partial S}{\partial V} \right)_T \right\}$$

$$= - \left( \frac{\partial p}{\partial V} \right)_T > 0$$

or  $\frac{1}{\kappa_T V} > 0 \Rightarrow \kappa_T V > 0$

## STABILITY OF THERMODYNAMIC SYSTEMS

∴ FOR STABLE EQ.

$$\delta^2 U > 0 \Rightarrow \begin{cases} C_V > 0 \\ \kappa_T > 0 \end{cases}$$

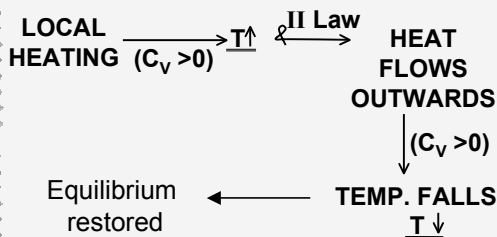
If  $\delta^2 U = 0 \longrightarrow$  Neutral Eqbm.

$\delta^2 U < 0 \longrightarrow$  Unstable Eqbm.

$\delta^2 U > 0 \longrightarrow$  Meta stable Eqbm.

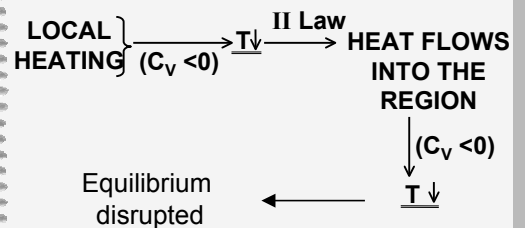
for small changes  
in S, V only

## PHYSICAL INTERPRETATION OF STABILITY CRITERIA



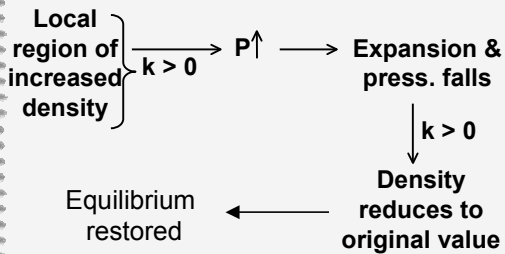
## PHYSICAL INTERPRETATION OF STABILITY CRITERIA

Suppose  $C_V < 0$ , Then



## PHYSICAL INTERPRETATION OF STABILITY CRITERIA

Similarly



## PHYSICAL INTERPRETATION OF STABILITY CRITERIA

Similarly, for multicomponent systems

Min G Principle

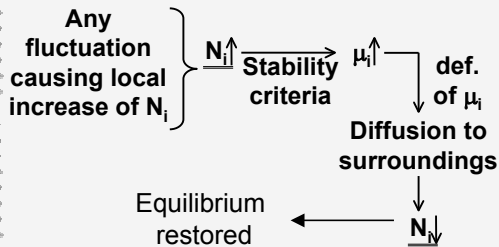
$$\left( \frac{\partial^2 G}{\partial N_i^2} \right)_{T,P,N_j} > 0$$

or

$$\left( \frac{\partial \mu_i}{\partial N_i} \right)_{T,P,N_j} > 0$$

## PHYSICAL INTERPRETATION OF STABILITY CRITERIA

Physical interpretation



## PHYSICAL INTERPRETATION OF STABILITY CRITERIA

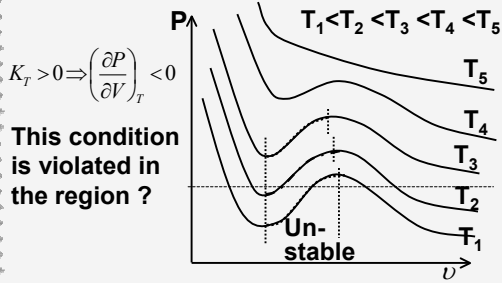
Le - Chatelier's Principle => a system is stable if any in-homogeneity that somehow develops in a system should induce a process that tends to eradicate the in-homogeneity.

End of Lecture

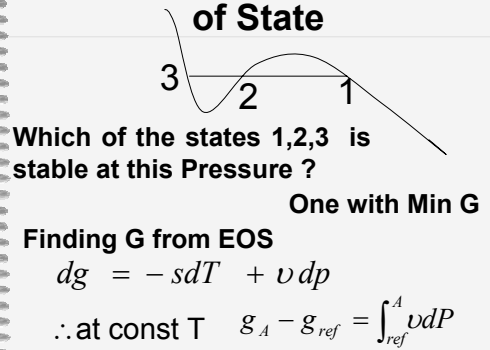
Lecture 6.5

Stability Analysis-  
examples

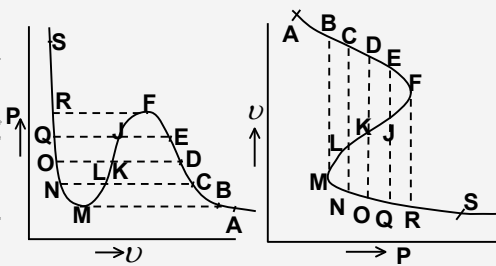
## Analysis of V-W Equation of State



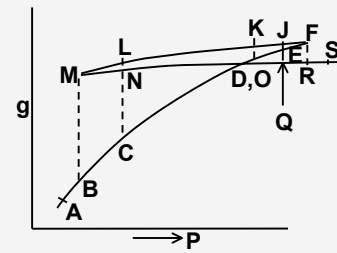
## Analysis of V-W Equation of State



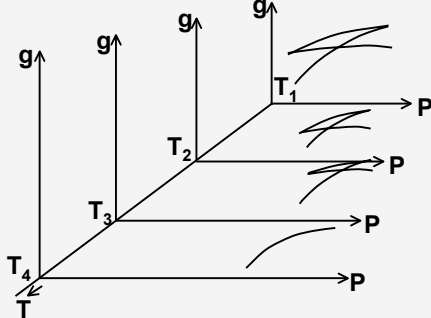
## Analysis of V-W Equation of State



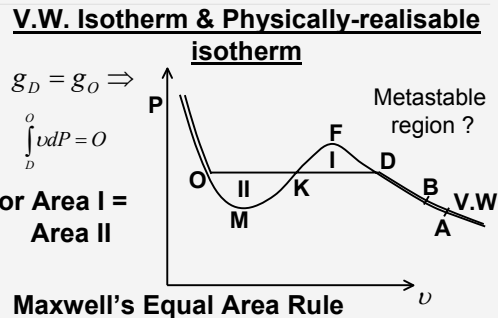
## Analysis of V-W Equation of State



## Analysis of V-W Equation of State



## Analysis of V-W Equation of State



## STABILITY ANALYSIS OF BINARY MIXTURES

⇒ Mixing of two liquids at const p&T to form a binary mixture

⇒ Equilibrium condition – Min Gibbs function

$$g < \sum g_i^0 x_i$$

or  $\Delta G_{mix} = (g - \sum g_i^0 x_i) < 0$

## STABILITY ANALYSIS OF BINARY MIXTURES

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

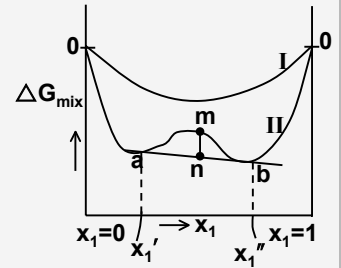
Both curves

I & II have

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

I: Stable Mixture

II: Identify region of instability?



## STABILITY ANALYSIS OF BINARY MIXTURES

condition of stability  $\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2} > 0$

$$\Delta G_{mix} = g - \sum x_i g_i^0 = RT [x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \gamma_1 + x_2 \ln \gamma_2]$$

Prove

$$\frac{\partial \Delta G_{mix}}{\partial x_1} = RT [\ln(\gamma_1 x_1) - \ln(\gamma_2 x_2)] = RT [\ln(f_1/f_1^0) - \ln(f_2/f_2^0)]$$

## STABILITY ANALYSIS OF BINARY MIXTURES

$$\frac{\partial^2 \Delta G_{mix}}{\partial x_1^2} = RT \left\{ \frac{\partial \ln f_1}{\partial x_1} - \frac{\partial \ln f_2}{\partial x_1} \right\}$$

Using Gibbs Duhem equation

$$x_1 \frac{\partial \ln f_1}{\partial x_1} + x_2 \frac{\partial \ln f_2}{\partial x_1} = 0$$

Stability Criteria at Const T, P

$$\frac{\partial \ln f_1}{\partial x_1} > 0 ; \frac{\partial \ln f_2}{\partial x_2} > 0$$

## STABILITY ANALYSIS OF BINARY MIXTURES

For VLE assuming  $f_1 \approx P y_1$  and  $f_2 \approx P y_2$ , we can prove that for stability of equilibrium

$$\frac{dy_1}{dx_1} > 0$$

$\frac{dP}{dx_1}$ ,  $\frac{dP}{dy_1}$  and  $(y_1 - x_1)$  have the same sign

End of Lecture