



**Sharif University of Technology
School of Mechanical Engineering
Center of Excellence in Energy Conversion**

Advanced Thermodynamics

Lecture 26

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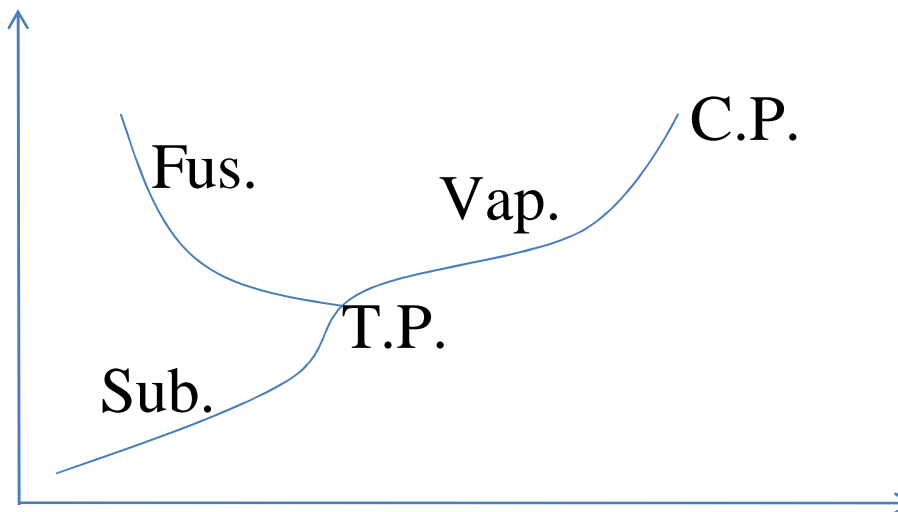
∅ In a pure substance

∅ If there is thermal equilibrium $\rightarrow dT = 0 \rightarrow T = \text{const.}$

∅ If there is mechanical equilibrium $\rightarrow dP = 0 \rightarrow P = \text{const.}$

$$dg = -s \cancel{dT}_0 + v \cancel{dP}_0 + \sum_{i=1}^N g_i dn_i = 0$$

$$\Rightarrow \sum_{i=1}^N g_i dn_i = 0 \rightarrow \bar{g}_{liq} = \bar{g}_{vap} \text{ Phase Equilibrium}$$



∅ According to the 2nd law of thermodynamics:

$$G = U - T S + P V \rightarrow dG = dU - T dS - S dT + V dP + P dV$$

$$dW_{rev} = -dU + T_0 dS - P_0 dV \rightarrow dW = -dG - S dT + V dP \leq 0$$

∅ The criterion to put the system out of stable condition

$$dG + S dT - V dP \geq 0$$

$$\text{For constant } T \text{ and } P \rightarrow dG \geq 0$$

$$G = G(T, P, n_1, \dots, n_r) \rightarrow$$

$$dG = \left(\frac{\partial G}{\partial P} \right)_{T, n_1, \dots, n_r} dP + \left(\frac{\partial G}{\partial T} \right)_{P, n_1, \dots, n_r} dT + \sum_{i=1}^N \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} dn_i$$

$$dG_{T, P} = V dP - S dT + \sum_{i=1}^N m_i dn_i$$

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

Equilibrium Criterion (T and P are constant) $\rightarrow \sum_{i=1}^N m_i dn_i \geq 0$

Ø For two components:

$$m_1 dn_1 + m_2 dn_2 = 0 \rightarrow m_1 = m_2$$

Ø If a system is in equilibrium, the chemical potential of each component at all phases must be the same, $g' = g'' = g'''$

Ø It is possible to use fugacity instead of Gibbs function.

$$dG_T = RT d \ln f_T = v dP_T$$
$$\rightarrow f^{\text{sat. liq.}} = f^{\text{sat. vap.}} = f^{\text{sat.}}$$

- ∅ The fugacity of a compressed liquid (or solid) at high pressure may be calculated by using the fugacity of saturated condition:

$$dg_T = RT d \ln f_T = v dP_T$$

$$\rightarrow \int_{f^{sat.}}^f RT d \ln f = \int_{P^{sat.}}^P v dP_T \rightarrow RT d \ln \left(\frac{f}{f^{sat.}} \right) = \int_{P^{sat.}}^P v dP_T$$

$$\Rightarrow RT d \ln \left(\frac{f}{f^{sat.}} \right) \approx v (P - P^{sat.})$$

- ∅ This equation may be used to obtain the compressed liquid fugacity through the generalized charts.
- ∅ Since for the solids and liquids at moderate pressure, v is very low

$$\rightarrow f^{liq.} \approx f^{sat.} \text{ and } f^{solid} \approx f^{sat.}$$

∅ Binary phase equilibrium:

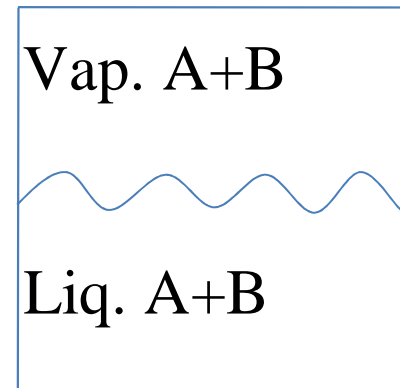
x_A and x_B : mole fraction in liquid phase T, P

y_A and y_B : mole fraction in gas phase

$$\bar{G}_A^{liq.} = \bar{G}_A^{vap.} \rightarrow \bar{f}_A^{liq.} = \bar{f}_A^{vap.}$$

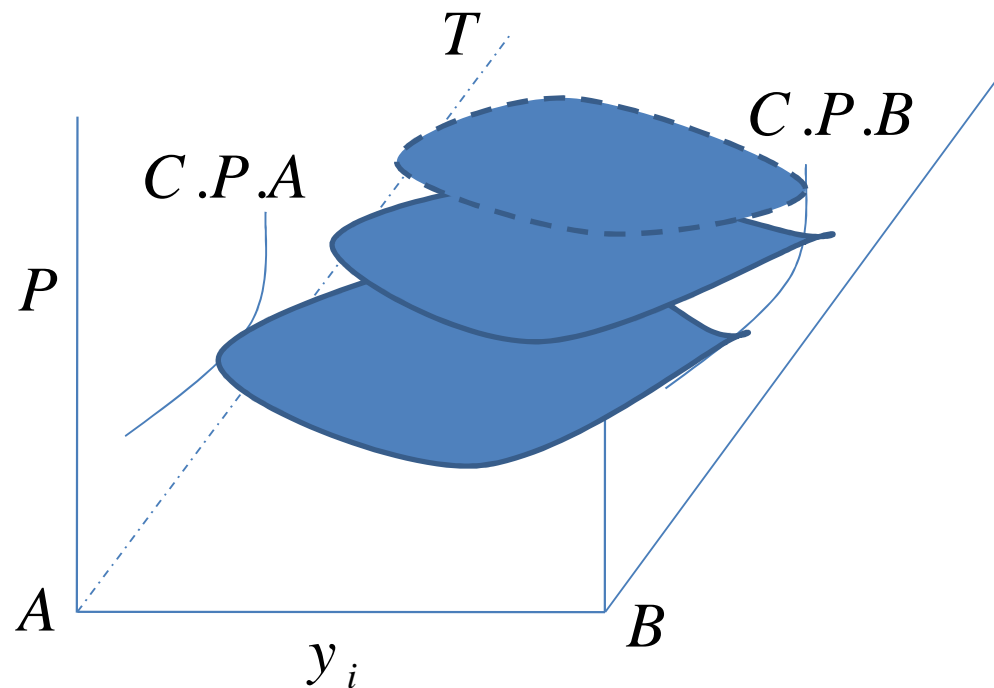
$$\bar{G}_B^{liq.} = \bar{G}_B^{vap.} \rightarrow \bar{f}_B^{liq.} = \bar{f}_B^{vap.}$$

Each $f = f(T, P, \text{comp. phase})$

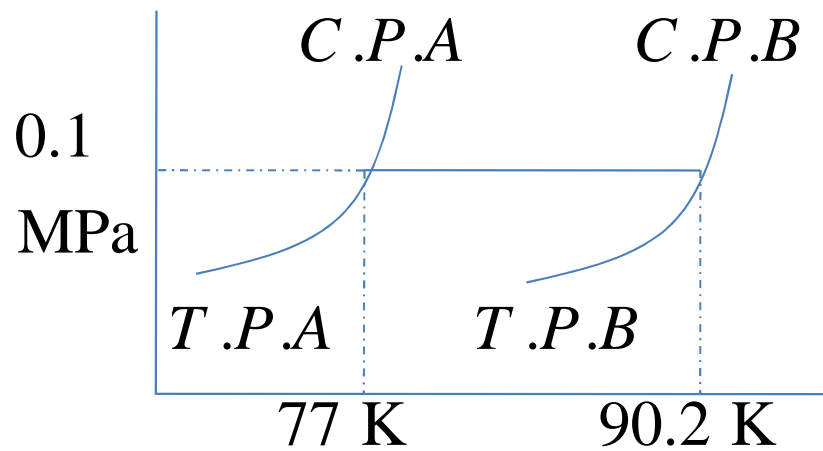


$$y_B = 1 - y_A$$

$$x_B = 1 - x_A$$



$P = 0.1 \text{ MPa}$



y_{N_2} and y_{O_2}

Gas N_2, O_2

x_{N_2} and x_{O_2}

Liq. N_2, O_2

