



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

# **Advanced Thermodynamics**

## **Lecture 27**

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∅ Binary phase equilibrium models:

∅ Ideal Solution Model  $\bar{f}_A = y_A f_A$

$$\text{At T and P} \rightarrow \begin{cases} x_A f_A^L = y_A f_A^V \\ x_B f_B^L = y_B f_B^V \\ x_A + x_B = 1 \\ y_A + y_B = 1 \end{cases}$$

∅ All of these fugacities are for pure substances *A* and *B*.

∅ At given *T* and *P*, there is only one physical fugacity (for liquid or vapor) and the other one will be obtained hypothetically.

∅ Raoult's Rule- Ideal Gas Mixture:

∅ This a special case of ISM and used only at low *P* and *T*.

∅ For liquids:

$$\ln \left( \frac{f_A^{\text{liq.}}}{f_A^{\text{sat.}}} \right) \approx \frac{v_A^{\text{liq.}} (P - P_A^{\text{sat.}})}{RT} \approx 0 \rightarrow f_A^{\text{liq.}} \approx f_A^{\text{sat.}} \quad (1)$$

∅ Ideal gas assumptions:

$$\text{Sat. vap. A} \approx \text{I.G.} \rightarrow f_A^{\text{sat.}} \approx P_A^{\text{sat.}} \quad (2)$$

$$f_A^{\text{v}} \approx P \quad (3)$$

∅ Assumption (3) may be a serious assumption.

∅ Simplified equations:

$$\text{At T and P} \rightarrow \begin{cases} x_A P_A^{\text{sat.}} = y_A P \\ (1 - x_A) P_B^{\text{sat.}} = (1 - y_A) P_A^{\text{sat.}} \end{cases}$$

If  $T_{mix} \gg T_{C.A.}$

$\rightarrow x_B \approx 1$  and  $x_A \approx 0$

$$\left. \begin{array}{l} x_A f_A^L = y_A f_A^V \\ x_B f_B^L = y_B f_B^V \end{array} \right\} \rightarrow f_B^L = y_B f_B^V$$

$f_B^L$  is real at T, P but  $f_B^V$  is hypothetical vapor at T, P

Ø If the Raoult's Rule- Ideal Gas Mixture is applied:

$$f_B^l = f_B^{\text{sat.}}$$

$$f_B^{\text{sat.}} \approx P_B^{\text{sat.}}$$

$$f_B^v \approx P$$

$$x_B = 1 \rightarrow P_B^{\text{sat.}} = y_B P$$

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- ∅ Phase: the part of a substance has the same intensive properties
  - ∅ Components: minimum combination of substances which determines all states of the system or determines the combination of each phase.
  - ∅ Chemical Elements: like  $O_2, N_2, H_2, \dots$
  - ∅ Molecular Species: like  $H_2O, H_2SO_4, \dots$
  - ∅ If there is a C.V. without any chemical reaction:

$$n = R - h$$

$n$  : Components No.

$R$  : Substances No.= chemical elements+ molecular species

$h$  : No. of independent reaction between  
chemical elements+molecular species

- ∅ If there is an open simple system which  $P$  and  $T$  determine it and some molecular species enter in and go out of the system, number of independent parameters in the system (the minimum combination of substances which determines all states of the system) is equal to  $n+2$ . If  $F$  denotes the number of intensive independent parameters and  $r$  is equal to phase numbers (which determine the extensive states):

$$n + 2 = F + r$$

- ∅  $F$  denotes for the system degrees of freedom as well.

- ∅ Example:

$H_2O$  at one phase (liq. vap. or solid)  $r = 1$  and  $n = 1 \rightarrow F = 2$

$H_2O$  at 2 phases  $\rightarrow F = 1$

$H_2O$  at 3 phases  $\rightarrow F = 0$