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

Advanced Thermodynamics

Lecture 24

Dr. M. H. Saidi

2011

- These models may be used for solid mixtures and solutions as well.
- Models:
  - Ideal gas mixtures
    - Amagat model, $\frac{V_A}{V_T} = \frac{n_A}{n_T} = y_A$
    - Dalton model, $\frac{P_A}{P_T} = \frac{n_A}{n_T} = y_A$
  - Real mixtures model
    - Ideal solution model
    - General real mixture model
  - Dilute mixtures model
  - Special cases

- Partial Molal Properties:

$$X = f(P,\ T,\ n_A,\ n_B,...)$$

X is an extensive property of the mixtures (like H, U, S,...)

- For a mixture contains two components A and B:

$$dX_{T,\ P} = \left(\frac{\partial X}{\partial n_A}\right)_{T,\ P,\ n_B} dn_A + \left(\frac{\partial X}{\partial n_B}\right)_{T,\ P,\ n_A} dn_B$$

$$X_{T,\ P} = \bar{X}_A n_A + \bar{X}_B n_B$$

$$\text{Partial Molal Properties}\begin{cases} \bar{X}_A = \left(\dfrac{\partial X}{\partial n_A}\right)_{T,\ P,\ n_B} \\ \bar{X}_B = \left(\dfrac{\partial X}{\partial n_B}\right)_{T,\ P,\ n_A} \end{cases}$$

Partial Molal Specific Volumes $\begin{cases} \bar{V}_A = \left(\dfrac{\partial V}{\partial n_A}\right)_{T,\ P,\ n_B} \\ \bar{V}_B = \left(\dfrac{\partial V}{\partial n_B}\right)_{T,\ P,\ n_A} \end{cases}$

- If there is only *A*: $V = \bar{V}_A n,\ \bar{V}_A = \left(\dfrac{\partial V}{\partial n_A}\right)_{T,\ P}$

- Ideal gas mixtures:

$$P(V_A + V_B) = (n_A + n_B)\bar{R}T$$

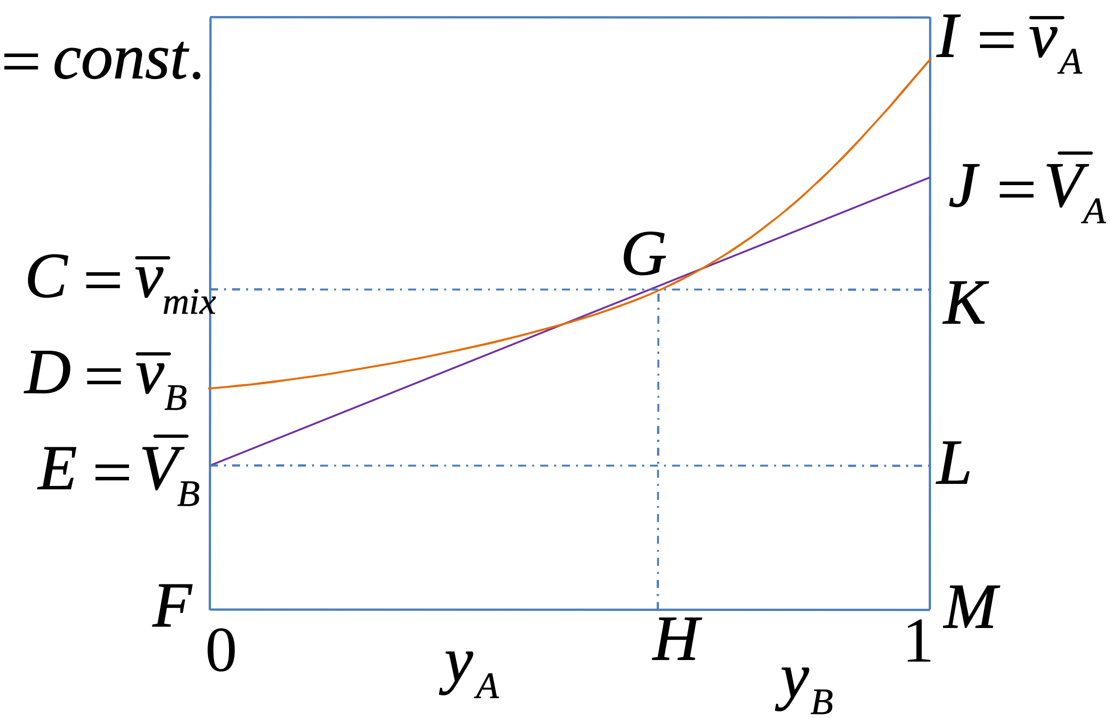
$$\bar{V}_A = \left(\frac{\partial v}{\partial n_A}\right)_{T,\ P,\ n_B} = \frac{\bar{R}T}{P} = \bar{v}$$

$$\bar{V}_B = \left(\frac{\partial v}{\partial n_B}\right)_{T,\ P,\ n_A} = \frac{\bar{R}T}{P} = \bar{v}$$

$$V = \bar{v}_A n_A + \bar{v}_B n_B = V_A + V_B$$

- This is the Amagat model (adding the volumes at constant pressure).

T and $P = const.$



$\bar{V}_A$ and $\bar{V}_B$ Partial Molal Specific Volumes

$\bar{v}_A$ and $\bar{v}_B$ Molal Specific Volumes of Pure A &B

$$CF = GH = KM = \bar{v}_{mix} \qquad DF = \bar{v}_B \qquad IM = \bar{v}_A$$

$$CG = FH = y_A \qquad GK = HM = y_B = (1 - y_A)$$

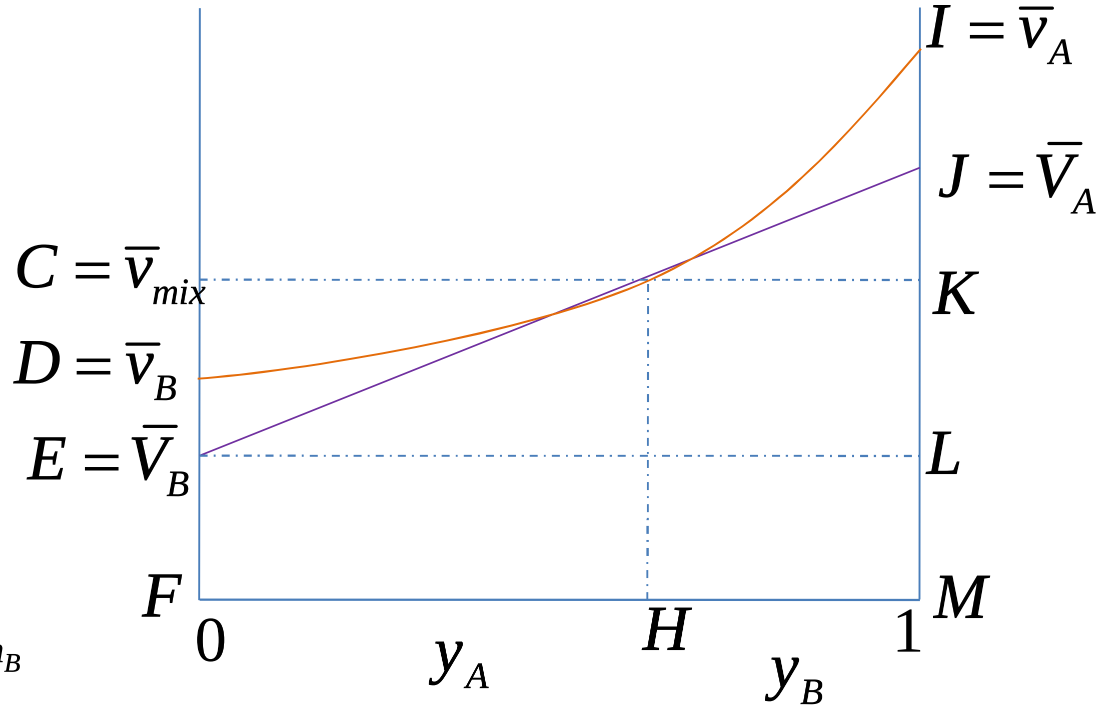
$$\bar{V}_A = JM \qquad \bar{V}_B = EF$$

$$V = n\bar{v} = (n_A + n_B)\bar{v} \rightarrow \bar{V}_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,\ P,\ n_B} = \bar{v} + (n_A + n_B)\left(\frac{\partial \bar{v}}{\partial n_A}\right)_{T,\ P,\ n_B}$$

$$y_A = \frac{n_A}{n_A + n_B} \rightarrow$$

$$\frac{dy_A}{dn_A} = \frac{n_B}{(n_A + n_B)^2}$$

$$\rightarrow \bar{V}_A = \bar{v} + (1 - y_A)\left(\frac{\partial \bar{v}}{\partial y_A}\right)_{T,\ P,\ n_B}$$



- Change in Properties upon mixing:

$$\Delta V_{\text{mixing}} = V_{\text{mixture}} - V_{\text{components before mixing}}$$

$$\rightarrow \Delta V_{\text{mixing}} = (\bar{V}_A n_A + \bar{V}_B n_B) - (\bar{v}_A n_A + \bar{v}_B n_B)$$

$$\boxed{\Delta V_{\text{mixing}} = \left(\bar{V}_A - \bar{v}_A\right) n_A + \left(\bar{V}_B - \bar{v}_B\right) n_B}$$

$$\Delta H_{\text{mixing}} = \left(\bar{H}_A - \bar{h}_A\right) n_A + \left(\bar{H}_B - \bar{h}_B\right) n_B$$

$$\Delta S_{\text{mixing}} = \left(\bar{S}_A - \bar{s}_A\right) n_A + \left(\bar{S}_B - \bar{s}_B\right) n_B$$

- For ideal gas:

$$\begin{cases} \bar{V}_A - \bar{v}_A = 0 \text{ and } \bar{V}_B - \bar{v}_B = 0 \rightarrow \Delta V_{\text{mixing}} = 0 \\ \bar{H}_A - \bar{h}_A = 0 \text{ and } \bar{H}_B - \bar{h}_B = 0 \rightarrow \Delta H_{\text{mixing}} = 0 \\ \left(\bar{S}_A - \bar{s}_A\right) = -\bar{R} \ln y_A \text{ and } \left(\bar{S}_B - \bar{s}_B\right) = -\bar{R} \ln y_B \\ \rightarrow \Delta S_{\text{mixing}} = -\bar{R}\left(n_A \ln y_A + n_B \ln y_B\right) \end{cases}$$

- Real mixtures model
  - Ideal solution model: Lewis Randall Model.
    - Real mixture is a function of component properties and partial molal properties.
  - General real mixture model: General mixtures in terms of pseudo substance constants and pseudo critical constants.
    - Real mixture is a function of pseudo pure substance, equation of state, pseudo critical constants in view of generalized charts.
  - Dilute mixtures model