



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

Advanced Thermodynamics

Lecture 25

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2011

- ∅ Ideal solutions: $\bar{V}_A - \bar{v}_A = 0$, at P, T and same phase as the mixture.
- ∅ Ideal gas is a special case of ideal solutions.

$$\text{ISM} \rightarrow V = \bar{V}_A n_A + \bar{V}_B n_B = \bar{v}_A n_A + \bar{v}_B n_B$$

- ∅ It is similar to Amagat model (but $\bar{V}_A - \bar{v}_A = 0$ at P, T and same phase as the mixture!)

m_i : electrochemical potential of ith component =
 driving force which causes mass transfer=
 partial molal Gibbs function

$$m_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}} = \left(\frac{\partial H}{\partial N_i} \right)_{S, P, N_{j \neq i}} = \left(\frac{\partial A}{\partial N_i} \right)_{T, V, N_{j \neq i}} = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}$$

∅ For a pure substance ($T = \text{const.}$)

$$d\bar{g}_A = \bar{v}_A dP = \bar{R}T d \ln f_A \quad \text{and} \quad \lim_{P \rightarrow 0} \left(\frac{f_A}{P} \right) = 1$$

∅ For a component in a mixture ($T = \text{const.}$)

$$d\bar{G}_A = \bar{V}_A dP = \bar{R}T d \ln \bar{f}_A \quad \text{and} \quad \lim_{P \rightarrow 0} \left(\frac{\bar{f}_A}{y_A P} \right) = 1$$

\bar{f}_A = The fugacity of a component at the mixture conditions

f_A = The fugacity of a pure A, $\bar{f}_A = y_A f_A$

$$\Rightarrow \bar{R}T d \int_{\ln \left(\frac{\bar{f}_A}{f_A} \right)^* = \ln y_A}^{\ln \left(\frac{\bar{f}_A}{f_A} \right)} \ln \left(\frac{\bar{f}_A}{f_A} \right) \ln = \int_{P^* \rightarrow 0}^P (\bar{V}_A - \bar{v}_A) dP$$

$$T \text{ and composition} = \text{const.} \rightarrow \bar{R}T \ln \left(\frac{\bar{f}_A}{y_A f_A} \right) = \int_0^P (\bar{V}_A - \bar{v}_A) dP$$

∅ There is a mixture containing 75% CH_4 and 25% C_2H_4
at $T = 25^{\circ}C$ & $P = 8.25 MPa$. Find gas mass

∅ I.G. assumption:

$PV = mRT$, using Dalton model \rightarrow

$$P_{CH_4} = y_{CH_4} P = 0.75 \times 8.25 = 6.188 MPa \quad \& \quad P_{C_2H_4} = 2.063 MPa$$

$$m_{CH_4} = \frac{P_{CH_4} V}{R_{CH_4} T} = 20.02 Kg \quad \& \quad m_{C_2H_4} = \frac{P_{C_2H_4} V}{R_{C_2H_4} T} = 11.07 Kg$$

$$\rightarrow m = m_{CH_4} + m_{C_2H_4} = 31.09 Kg$$

∅ Using I.S.M. assumption:

$$V = \bar{V}_A n_A + \bar{V}_B n_B \rightarrow \frac{V}{n_t} = (y\bar{v})_{CH_4} + (y\bar{v})_{C_2H_4}$$

$$\bar{V}_A - \bar{v}_A = 0$$

∅ Using I.S.M. assumption:

no chart for \bar{v}_{CH_4} and $\bar{v}_{C_2H_4}$ → use the generalized charts →

$$T_{r,CH_4} = \frac{T}{T_{CH_4}} = 1.56, P_{r,CH_4} = \frac{8.25}{4.04} = 1.78, T_{r,C_2H_4} = 1.06, P_{r,C_2H_4} = 1.61$$

Generalized compressibility factor chart → $Z_{CH_4} = 0.88$ & $Z_{C_2H_4} = 0.35$

$$\bar{v}_{CH_4} = \frac{Z\bar{R}T}{P} = \frac{0.88 \times 8.31434 \times 298.2}{8250} = 0.26457 \text{ m}^3/\text{Kmole}$$

$$\bar{v}_{C_2H_4} = \frac{Z\bar{R}T}{P} = \frac{0.35 \times 8.31434 \times 298.2}{8250} = 0.1052 \text{ m}^3/\text{Kmole}$$

$$\rightarrow \bar{v} = 0.75(0.26457) + 0.25(0.1052) = 0.2247 \text{ m}^3/\text{Kmole}$$

$$M = \sum y_i M_i = 0.75 \times 16 + 0.25 \times 28 = 19$$

$$\rightarrow v = \frac{\bar{v}}{M} = 0.011825 \text{ m}^3/\text{Kg} \rightarrow m = \frac{V}{v} = \frac{0.5}{0.011825} = 42.3 \text{ Kg}$$

- ∅ Example: Dilute non-electrolyte liquid solutions:
 - ∅ Water as solvent and salt as a solute (low volume fraction)
Index 1 is for solvent and 2 is for solute
- ∅ Henry's Law for dilute liquid solution:
 - ∅ The fugacity of a solute of a dilute liquid solution is proportional to its fraction, $f_2 = K_2 x_2$.
- ∅ This law was presented for partial pressure instead of fugacity at first, $P_2 = K_2 x_2$.

∅ According to Henry's Law :

∅ Gibbs-Duhem relation for const. P and $T \rightarrow \sum_{i=1}^N n_i d m_i = 0$

$$n_1 d m_1 + n_2 d m_2 = 0$$

∅ Since $(d\bar{G}_i)_T = (d m_i)_T = \bar{R}T d \ln f_i$

$$\rightarrow n_1 \bar{R}T d \ln f_1 + n_2 \bar{R}T d \ln f_2 = 0$$

$$\rightarrow x_1 \left[\frac{\partial (\ln f_1)}{\partial x_2} \right]_{T, P} + x_2 \left[\frac{\partial (\ln f_2)}{\partial x_2} \right]_{T, P} = 0$$

$$\underline{x_1 + x_2 = 1} \quad \boxed{\left[\frac{\partial \ln f_1}{\partial \ln x_1} \right]_{T, P} = \left[\frac{\partial \ln f_2}{\partial \ln x_2} \right]_{T, P}}$$

$$f_2 = K_2 x_2 \rightarrow \ln f_2 = \ln K_2 + \ln x_2 \rightarrow \left[\frac{\partial \ln f_2}{\partial \ln x_2} \right]_{T,P} = 1$$

$$\left[\frac{\partial \ln f_1}{\partial \ln x_1} \right]_{T,P} = \left[\frac{\partial \ln f_2}{\partial \ln x_2} \right]_{T,P} \Rightarrow \left[\frac{\partial \ln f_1}{\partial \ln x_1} \right]_{T,P} = 1$$

$$\rightarrow \int_{f_1^0}^{f_1} d \ln f_1 = \int_{x_1=1}^{x_1} d \ln x_1 \rightarrow \boxed{f_1 = f_1^0 x_1}$$

f_1^0 = Fugacity of pure 1 at the same T and P of solution

- ∅ If the vapor in equilibrium with the liquid is assumed to be ideal gas

$$P_1 = P_1^0 x_1$$

- ∅ This law, which is a resultant of Henry's law, is named Rault's law for the solvent.
- ∅ It may be shown that if the Henry's law is valid for a solute in a dilute solution, the Raul law is valid for the solvent of that solution.