Lecture 13

- Partial molar properties for mixtures
  - definition
  - properties: Euler equation, Gibbs-Duhem, chemical potential
    as a partial molar property
  - graphic representation

- Ideal gas mixtures
  - partial pressure
  - U, H. unaffected
  - entropy of mixing, Gibbs free energy of mixing

Read Chs. 9 and 10 Sandler

Objectives

- Definition of mixing properties and partial molar properties
- Gibbs-Duhem equation
- Graphic interpretation of partial molar properties for binary mixtures
- Understand and remember properties for ideal gas mixtures

Mixtures

- Ubiquitous – most systems in nature and in applications involve mixtures

- Mixing materials (especially polymers) is an effective way to tune material properties

- Separation is the inverse process of mixing, a major component in any chemical and pharmaceutical industry.

Mixtures

- Can produce mixtures under any conditions, e.g., having two pure substances at different temperatures or pressures
- Most common mixing occurs at constant T and P
- Mixture property usually not simple addition or average of the pure component properties

Volume: $\qquad V \neq n_A v_A(T, P) + n_B v_B(T, P) \qquad$ e.g. water+ethanol

Enthalpy: $\qquad H \neq n_A h_A(T, P) + n_B h_B(T, P) \qquad$ e.g. water+H_2SO_4

Dielectric constant: $\quad \epsilon \neq x_A \epsilon_A(T, P) + x_B \epsilon_B(T, P) \qquad$ e.g. water+ethanol

Mixing Properties

For an extensive property

$$B^{mix} = B(n_1, n_2, \ldots n_k, T, P) - \sum_i n_i \, b_i(T, P)$$

Same T and P!

Partial Molar Properties

At constant T, P:

$$\bar{B}_i = \left(\frac{\partial B}{\partial n_i}\right)_{T,P,n_{j\neq i}} \qquad \text{(intensive property)}$$

change in B upon adding one mole of i, in a <u>very large</u> system

$$B(n_1, n_2, \ldots n_i + 1, \ldots n_m) = B(n_1, n_2, \ldots n_i, \ldots n_m) + \left(\frac{\partial B}{\partial n_i}\right)_{T,P,n_{j\neq i}} (n_i + 1 - n_i)$$

$$+ \frac{1}{2}\left(\frac{\partial^2 B}{\partial n_i^2}\right)_{T,P,n_{j\neq i}} (n_i + 1 - n_i)^2 \qquad\qquad \left(\frac{\partial^2 B}{\partial n_i^2}\right)_{T,P,n_{j\neq i}} \sim \frac{\bar{B}_i}{n_i}$$

e.g., add 1 mole of water into ocean

Euler Equation

Extensivity of B and the mole number of species

$$B = B(T, P, \{n_i\})$$

$$\lambda B = B(T, P, \{\lambda n_i\}) \qquad \text{First order homogeneous function}$$

Taking derivative with respect to λ and setting $\lambda = 1$

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

Euler equation (summability):

$$B(n_1, n_2, \dots n_k, T, P) = \sum_i n_i \bar{B}_i(x_1, x_2, \dots x_k, T, P)$$

Generalized Gibbs-Duhem

From summability:
$$B(n_1, n_2, \ldots n_k, T, P) = \sum_i n_i \bar{B}_i(x_1, x_2, \ldots x_k, T, P)$$

$$dB(n_1, n_2, \ldots n_k, T, P) = \left(\frac{\partial B}{\partial T}\right)_{P,\{n\}} dT + \left(\frac{\partial B}{\partial T}\right)_{P,\{n\}} dT + \sum_i \bar{B}_i \, dn_i$$

$$dB(n_1, n_2, \ldots n_k, T, P) = \sum_i n_i d\bar{B}_i + \sum_i \bar{B}_i \, dn_i$$

$$\left(\frac{\partial B}{\partial T}\right)_{P,\{n\}} dT + \left(\frac{\partial B}{\partial T}\right)_{P,\{n\}} dT - \sum_i n_i dB_i = 0$$

At fixed T, P
$$\sum_i n_i d\bar{B}_i = 0$$
Partial molar properties of different species are not independent

Chemical Potential as a Partial Molar Property
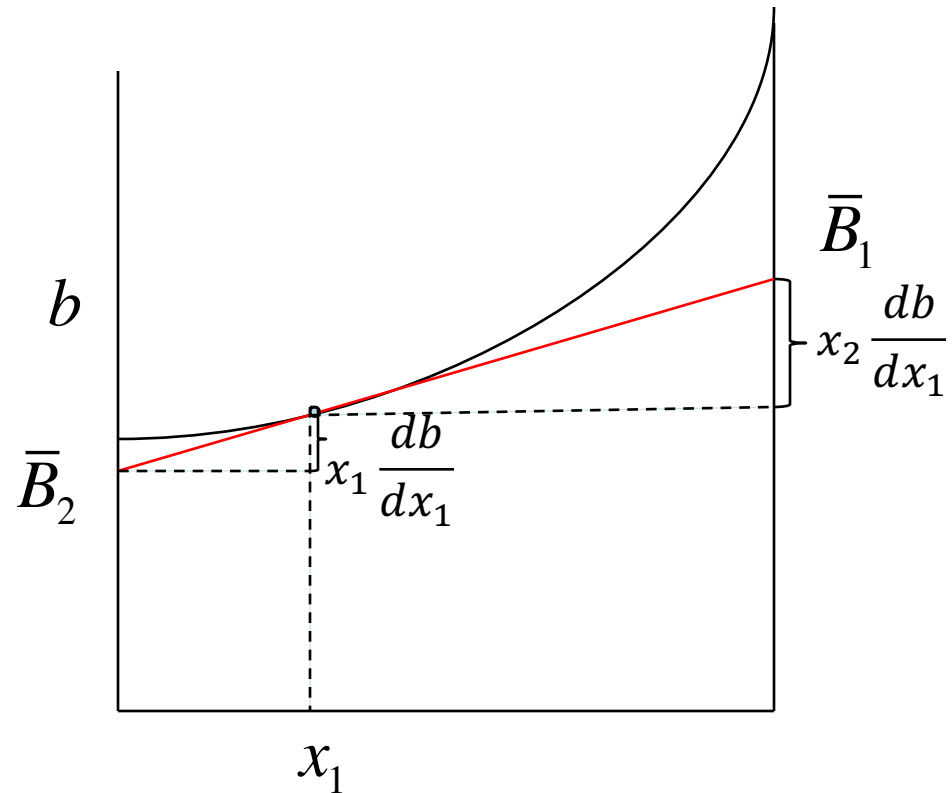
Take $B = G$

$$G(n_1, n_2, \ldots n_k, T, P) = \sum_i n_i \mu_i(x_1, x_2, \ldots x_k, T, P)$$

Graphic Representation (Binary Mixture)

Euler equation (summability):

$$\bar{B}_1 = b + x_2 \frac{db}{dx_1}$$

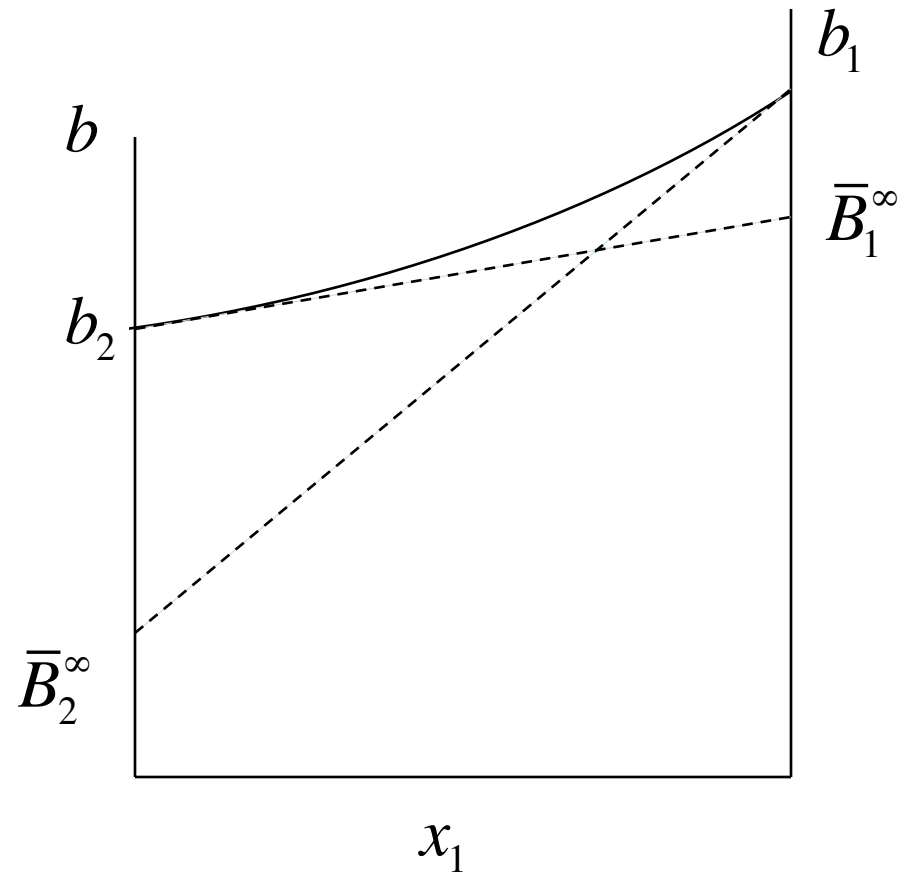$$\bar{B}_2 = b - x_1 \frac{db}{dx_1}$$

Special Cases

$$\lim_{x_i \to 1} \bar{B}_i = b_i$$

     pure component

$$\lim_{x_i \to 0} \bar{B}_i = \bar{B}_i^{\infty}$$

     infinite dilution
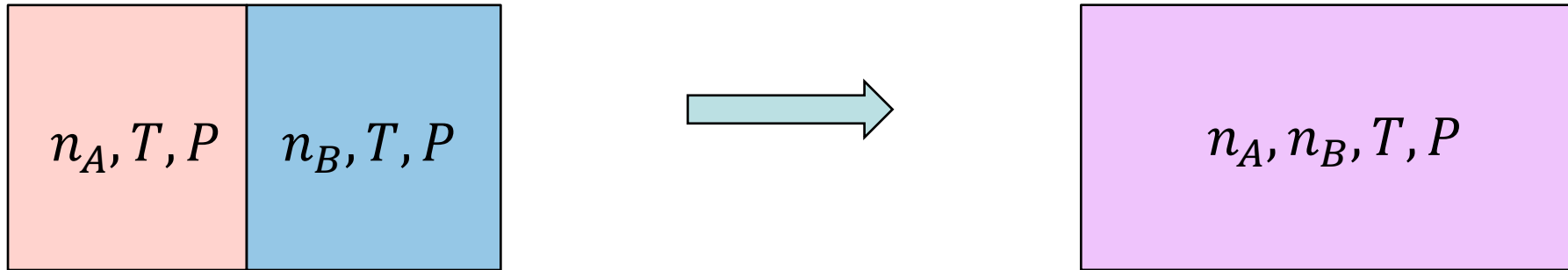
Ideal Gas Mixture

Partial Pressure: pressure of a multicomponent ideal gas is the sum of pressure from each component

$$P = \frac{n_{tot}RT}{V} = \sum_i \frac{n_i RT}{V} \equiv \sum_i P_i \qquad \text{Dalton's law (1802)}$$

Partial Molar Volume: $\qquad$ from $\qquad V = \frac{n_{tot}RT}{P} = \frac{RT}{P}\sum_i n_i$

$$\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P} = v_i = \frac{RT}{P}$$
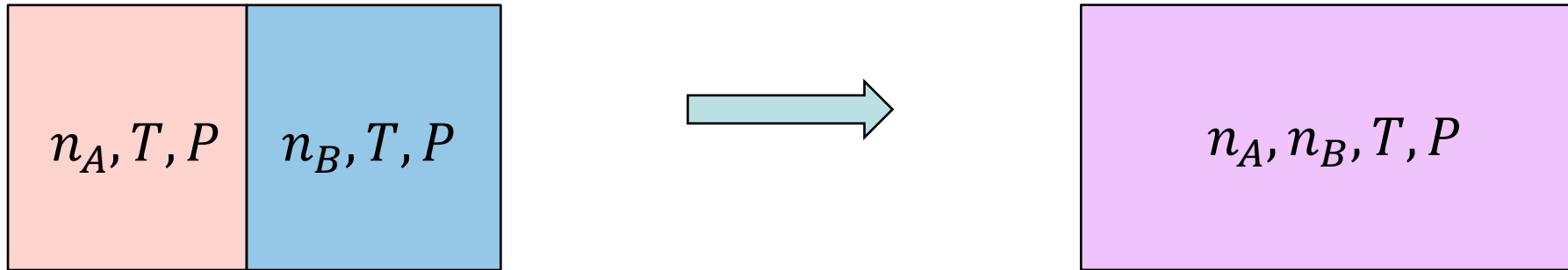
Mixing Ideal Gases

$$V_A = \frac{n_A RT}{P} = n_A v_A \qquad V_B = \frac{n_B RT}{P} = n_B v_B \qquad\qquad V = \frac{(n_A + n_B)RT}{P}$$

$$V = V_A + V_B = n_A v_A + n_B v_B$$

$$V^{mix} = 0$$

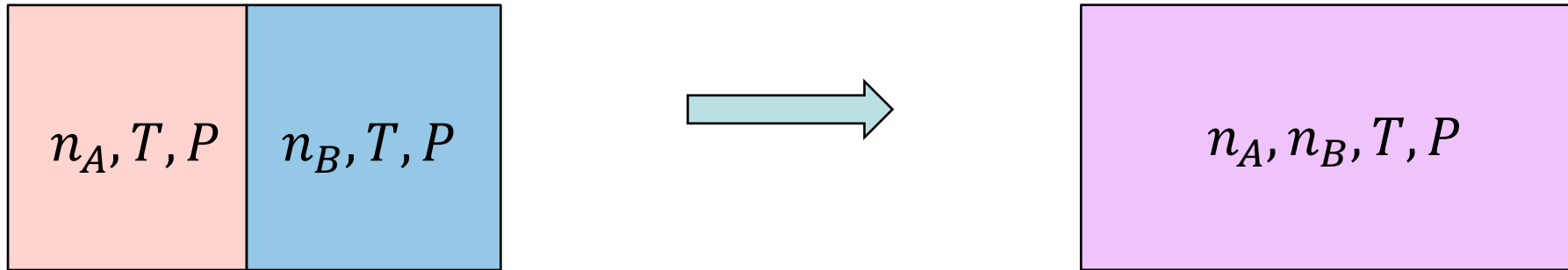# Mixing Ideal Gases

$$U_A = n_A u_A(T) \qquad U_B = n_B u_B(T) \qquad U = n_A u_A(T) + n_B u_B(T)$$

$$H_A = n_A h_A(T) \qquad H_B = n_B h_B(T) \qquad H = n_A h_A(T) + n_B h_B(T)$$

$$U^{mix} = H^{mix} = 0$$

Entropy of Mixing

$$S_A = n_A s_A(T, V_A) \quad S_B = n_B s_B(T, V_B)$$

$$S = n_A s_A(T, V) + n_B s_B(T, V)$$

$$S^{mix} = n_A[s_A(T, V) - s_A(T, V_A)] - n_B[s_B(T, V) - s_B(T, V_B)]$$

$$S^{mix} = n_A RT \ln \frac{V}{V_A} + n_B RT \ln \frac{V}{V_B}$$

$$V_A = \frac{n_A}{n_A + n_B}$$

Entropy of Mixing

$$S^{mix} = n_A RT \ln \frac{V}{V_A} + n_B RT \ln \frac{V}{V_B}$$

$$V_A = \frac{n_A}{n_A + n_B} = x_A \qquad\qquad V_B = \frac{n_B}{n_A + n_B} = x_B$$

$$S^{mix} = -n_A RT \ln x_A - n_B RT \ln x_B$$

Generalize to multicomponent:

$$S^{mix} = -R \sum_i n_i \ln x_i \ \ (> 0)$$

Ideal Gas Mixture

Entropy of mixing

$$S^{mix} = -R \sum_i n_i \ln x_i \ \ (> 0)$$

Free energy of mixing

$$G^{mix} = F^{mix} = RT \sum_i n_i \ln x_i \ \ (< 0)$$

Work of separation

$$W = -G^{mix} = -RT \sum_i n_i \ln x_i \ \ (> 0)$$

Chemical Potential of Ideal Gas in Mixtures

$$G = \sum_i n_i \mu_i(T,P) + G^{mix} = \sum_i n_i \mu_i(T,P) + \sum_i n_i RT \ln x_i = \sum_i n_i \mu_i(T,P,x_i)$$

Recall for pure ideal gas

$$\mu_i(T,P) = \mu_i^{\Theta}(T) + RT \ln \frac{P}{P^{\Theta}}$$

$$\mu_i(T,P,x_i) = \mu_i^{\Theta}(T) + RT \ln \left(\frac{x_i P}{P^{\Theta}}\right) = \mu_i^{\Theta}(T) + RT \ln \left(\frac{P_i}{P^{\Theta}}\right)$$

Questions to Think about

- Why are partial molar properties defined at isothermal and isobaric condition?

- Can partial molar volume be negative?

Lecture 14

- Nonideal mixtures – fugacity in gas mixtures
- Lewis-Randall rule

- Go over midterm exam

Read Chs. 9 and 10 Sandler

Objectives

- Know the concept of fugacity and fugacity coefficients for non-ideal gas mixtures
- Know Lewis Randall rule

Nonideal Gase Mixtures

In general,

$$V^{mix} \neq 0$$

$$U^{mix} \neq 0$$

$$H^{mix} \neq 0$$

$$S^{mix} \neq -R \sum_i n_i \ln x_i$$

So need to use partial molar properties

Chemical Potential and Fugacity

Want an expression for chemical potential that has similar form to I.G.

Recall:

$$\mu_i(T, P, x_i) = \mu_i^{\Theta}(T) + RT \ln\left(\frac{x_i P}{P^{\Theta}}\right) = \mu_i^{\Theta}(T) + RT \ln\left(\frac{P_i}{P^{\Theta}}\right)$$

Define fugacity and fugacity coefficient:

$$\mu_i(T, P, x_i) = \mu_i^{\Theta}(T) + RT \ln\left(\frac{x_i P \phi_i}{P^{\Theta}}\right) = \mu_i^{\Theta}(T) + RT \ln\left(\frac{\phi_i P_i}{P^{\Theta}}\right) = \mu_i^{\Theta}(T) + RT \ln\left(\frac{f_i}{P^{\Theta}}\right)$$

Fugacity for Non-Ideal Gas in Mixture

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,\{n\}} = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{i\neq j}}\right]_{T,\{n\}} = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,\{n\}}\right]_{T,P,n_{i\neq j}} = \left(\frac{\partial V}{\partial n_i}\right) = \bar{V}_i$$

$$\left(\frac{\partial \mu_i^{I.G.}}{\partial P}\right)_{T,\{n\}} = \bar{V}_i^{I.G.} = \frac{RT}{P}$$

$$\mu_i(T,P,x_i) - \mu_i^{I.G.}(T,P,x_i) = \underbrace{\mu_i(T,0,x_i) - \mu_i^{I.G.}(T,0,x_i)}_{0} + \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right)dP$$

Fugacity for Non-Ideal Gas in Mixture

$$\mu_i(T, P, x_i) = \mu_i^\Theta(T, P) + RT \ln\left(\frac{x_i P}{P^\Theta}\right) + \int_0^P \left(\bar{V}_i - \frac{RT}{P}\right) dP$$

$$\ln\left(\frac{f_i}{x_i P}\right) = \ln\phi_i = \frac{1}{RT}\int_0^P \left(\bar{V}_i - \bar{V}_i^{I.G}\right) dP$$

Lewis-Randall Rule

$$f_i = x_i f_i^{(0)}(T,P)$$

$f_i^{(0)}(T,P)$ Fugacity of pure component i at same T and same total P as mixture

Reasonable approximation for P up to 100atm

Basis for formal definition of ideal solution (in the Raoult's law sense)