CHEMICAL ENGINEERING THERMODYNAMICS II (0905323)
06 -THERMODYNAMICS OF MULTICOMPONENT MIXTURES

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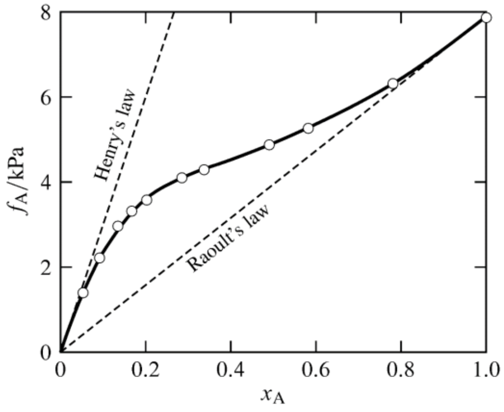
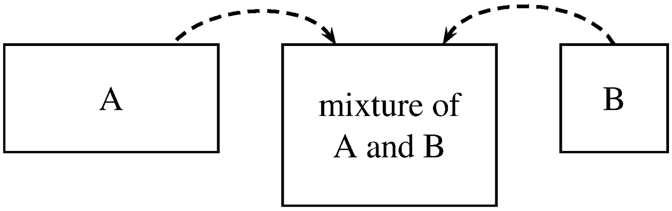
- Property Changes on Mixing
- Partial Molar Properties
- Mixture Properties & Partial Molar Quantities





A

mixture of
A and B

B

Scope

- This lecture is concerned with the relationship between thermodynamic properties and the temperature, pressure, and composition of a mixture.
- The difference between pure component and mixture description is due to the **added composition dependence**.

Differences Between Pure Component & Mixtures

- For a pure component we can write the thermal EOS as

$$U = U(T,P) \Rightarrow u = u(T,P)$$
$$V = V(T,P) \Rightarrow v = v(T,P)$$

- For a mixture containing C components

$$U = U(T,P,N_1,\cdots,N_C) = U(T,P,\mathbf{N})$$
$$u = u(T,P,x_1,\cdots,x_{C-1}) = u(T,P,\mathbf{x})$$
$$V = V(T,P,N_1,\cdots,N_C) = V(T,P,\mathbf{N})$$
$$v = v(T,P,x_1,\cdots,x_{C-1}) = v(T,P,\mathbf{x})$$

- Notice the use of **boldface** notation to indicate a vector of variables (**N** & **x**).

Definitions

- The mole fraction is defined as

$$x_i = \frac{N_i}{N}, \quad i = 1,2,\cdots,C$$
$$\sum_{i=1}^{C} x_i = 1$$

- *C* is the number of components, and subscript *i* indicates *i*th component in the mixture.
- We prefer to deal with the number of moles rather than mole fraction.
  - Mathematically, the number of moles of a component can be changed while fixing the number of moles of other components.
  - This is not the case for mole fractions. Changing one mole fraction will change the rest of mole fractions.

Naïve Approach to Composition Dependence

- We want to know the concentration dependence of the mixture.
- The naïve approach is to postulate that each thermodynamic mixture property is the sum of the analogous properties for the pure component at the same (T,P) weighted with their fractional compositions e.g.

$$u(T,P,\mathbf{x})=\sum_{i=1}^{C}x_i u_i(T,P)$$

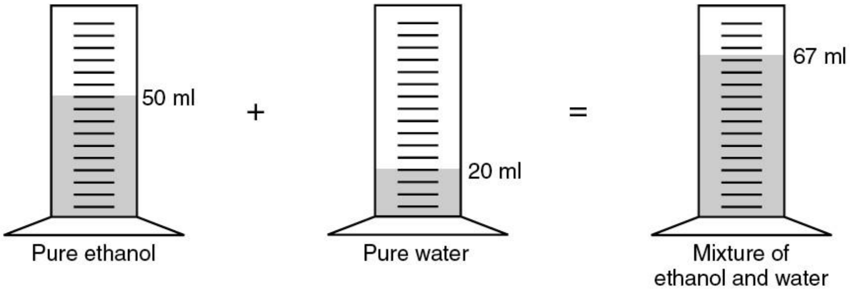
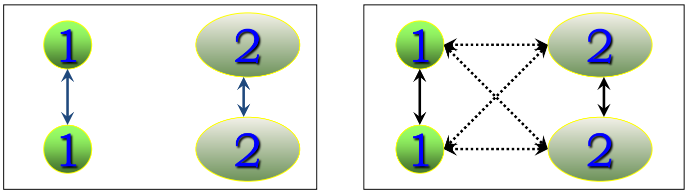


Figure 6.5 Mixing of ethanol and water.

Why the Naïve Approach Fails?

- Unfortunately, this is not an accurate representation of the mixture properties.
- Mixtures deviate from this naïve description due to the cross term interactions not accounted for by this approach.



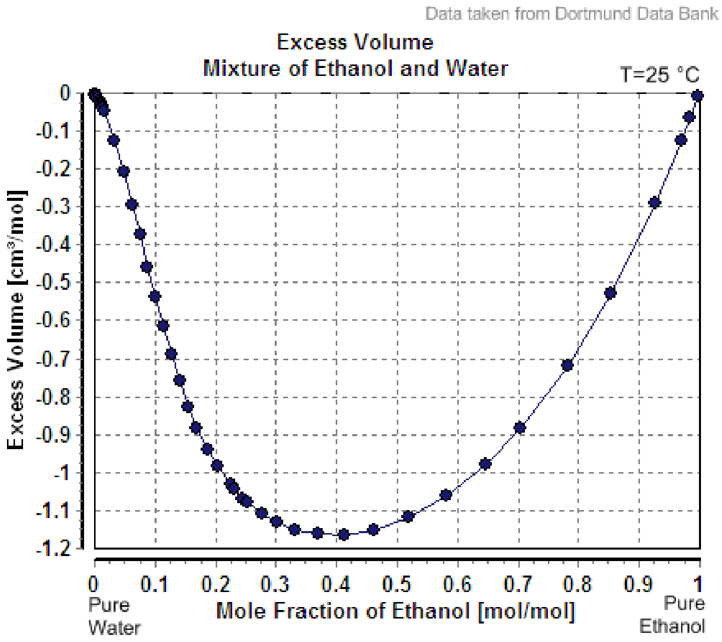
Property Changes on Mixing

- Evidently, there is a property change on mixing. Property changes on mixing are defined as

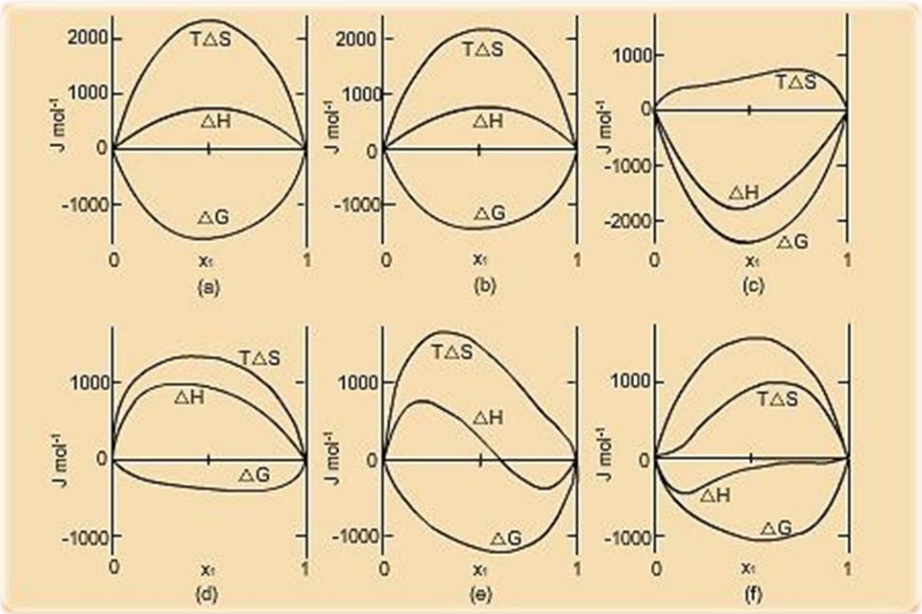
$$\begin{pmatrix}\text{Property change}\\ \text{on mixing}\end{pmatrix} = \begin{pmatrix}\text{Actual mixture}\\ \text{property}\end{pmatrix} - \begin{pmatrix}\text{Naive approach}\\ \text{value}\end{pmatrix}$$

$$\Delta h_{\text{mix}} = h(T,P,\mathbf{x}) - \sum_{i=1}^{C} x_i h_i(T,P)$$

$$\Delta v_{\text{mix}} = v(T,P,\mathbf{x}) - \sum_{i=1}^{C} x_i v_i(T,P)$$


Data taken from Dortmund Data Bank

Excess Volume
Mixture of Ethanol and Water



Partial Molar Properties

- Define any partial molar property as

$$\bar{\theta}_i = \bar{\theta}_i(T,P,\mathbf{x}) = \left.\frac{\partial(N\theta)}{\partial N_i}\right|_{T,P,N_{j\neq i}}$$

- This leads to defining mixture properties in terms of partial molar quantities as

$$\theta = \sum_{i=1}^{C} x_i \bar{\theta}_i(T,P,\mathbf{x})$$

Mixture Properties & Partial Molar Quantities

- The mixture property expression is similar in form to the naïve approach form.
- The major difference is that the partial molar quantities are mixture properties that needs to be known/obtained, while the naïve approach is based solely on pure component properties.
- The partial molar property is generally not equal to the pure component molar property

$$\theta_i(T,P) \neq \bar{\theta}_i(T,P,\mathbf{x})$$

Notation for Partial Molar Quantities

Name	Symbol	Derivative	Mixture Property
Partial molar internal energy	$\bar{u}_i$	$\left(\frac{\partial(Nu)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$u=\sum_{i=1}^{C} x_i\bar{u}_i$
Partial molar volume	$\bar{v}_i$	$\left(\frac{\partial(Nv)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$v=\sum_{i=1}^{C} x_i\bar{v}_i$
Partial molar enthalpy	$\bar{h}_i$	$\left(\frac{\partial(Nh)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$h=\sum_{i=1}^{C} x_i\bar{h}_i$
Partial molar entropy	$\bar{s}_i$	$\left(\frac{\partial(Ns)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$s=\sum_{i=1}^{C} x_i\bar{s}_i$
Partial molar Gibbs energy	$\bar{g}_i$	$\left(\frac{\partial(Ng)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$g=\sum_{i=1}^{C} x_i\bar{g}_i$
Partial molar Helmholtz energy	$\bar{a}_i$	$\left(\frac{\partial(Na)}{\partial N_i}\right)_{T,P,N_{j\neq i}}$	$a=\sum_{i=1}^{C} x_i\bar{a}_i$

Property Changes on Mixing

- We can make use of the definition of partial molar properties to obtain an expression for the "property changes on mixing"

$$\begin{pmatrix}\text{Property Change}\\ \text{on mixing}\end{pmatrix}=\begin{pmatrix}\text{Actual Mixture}\\ \text{Property}\end{pmatrix}-\begin{pmatrix}\text{Mixture Property}\\ \text{via the naive approach}\end{pmatrix}$$

$$\Delta\theta_{\text{mix}}(T,P,N_1,\cdots,N_C)=\theta(T,P,N_1,\cdots,N_C)-\sum_{i=1}^{C}N_i\theta_i(T,P)$$

- The mixture property is obtainable from the partial molar property as

$$\theta=\sum_{i=1}^{C}x_i\bar{\theta}_i(T,P,\mathbf{N})$$

Enthalpy & Volume Changes on Mixing

- Volume change on mixing

$$\Delta V_{\text{mix}}(T,P,\mathbf{N}) = V(T,P,\mathbf{N}) - \sum_{i=1}^{C} N_i v_i(T,P)$$

$$= \sum_{i=1}^{C} N_i\left[\overline{v}_i(T,P,\mathbf{N}) - v_i(T,P)\right]$$

- Enthalpy change on mixing

$$\Delta H_{\text{mix}}(T,P,\mathbf{N}) = H(T,P,\mathbf{N}) - \sum_{i=1}^{C} N_i h_i(T,P)$$

$$= \sum_{i=1}^{C} N_i\left[\overline{h}_i(T,P,\mathbf{N}) - h_i(T,P)\right]$$

Other Properties

- Similar expressions can be obtained for other properties. The equivalent of pure component properties are obtained by using partial molar properties in a mixture
- Consider the Helmholtz free energy
  - Pure Component
  - Mixture $a = u - Ts$

$$\frac{\partial}{\partial N_i}(Na)\Big|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}(Nu)\Big|_{T,P,N_{j\neq i}} - T\frac{\partial}{\partial N_i}(Ns)\Big|_{T,P,N_{j\neq i}}$$

$$\overline{a}_i = \overline{u}_i - T\overline{s}_i$$

- Consider the partial molar heat capacity at a constant pressure for a mixture

$$\bar{c}_{P,i} = \frac{\partial}{\partial N_i}(Nc_P)\Big|_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\Big|_{T,P,N_{j\neq i}} \frac{\partial}{\partial T}(Nh)\Big|_{P,N_j}$$

$$= \frac{\partial}{\partial T}\Big|_{P,N_j} \frac{\partial (Nh)}{\partial N_i}\Big|_{T,P,N_{j\neq i}} = \left(\frac{\partial \bar{h}_i}{\partial T}\right)\Big|_{P,N_j}$$

- Shows that the partial molar heat capacity for a mixture is defined in a manner similar to that for a pure component.

For each relationship among the thermodynamic variables in a pure fluid, there exists an identical relationship for the partial molar thermodynamic properties in a mixture!

Ex: The enthalpy of a binary liquid system of species (1) & (2) at fixed T and P is represented by the eqn.:

$$H = 400\,x_1 + 600\,x_2 + 500\,x_1 x_2 \qquad H \text{ in } KJ/Kg.$$

a. Find an expression for $\bar{H}_1$ and $\bar{H}_2$ as a function of mole fraction x_1, x_2

b. Determine the values $\bar{H}_1^{\infty}$, $\bar{H}_2^{\infty}$

c. Determine the values H_1, H_2

soln.

a. $H = 400x_1 + 600x_2 + 500\,x_1 x_2$

$$H = 400\,\frac{n_1}{n_T} + 600\,\frac{n_2}{n_T} + 500\,\frac{n_1}{n_T}\cdot\frac{n_2}{n_T}$$

$$n_T H = 400n_1 + 600n_2 + 500\,\frac{n_1 n_2}{n_T^{\cancel{2}}}$$

$$n_T H = 400n_1 + 600n_2 + 500\,\frac{n_1 n_2}{(n_1+n_2)}$$

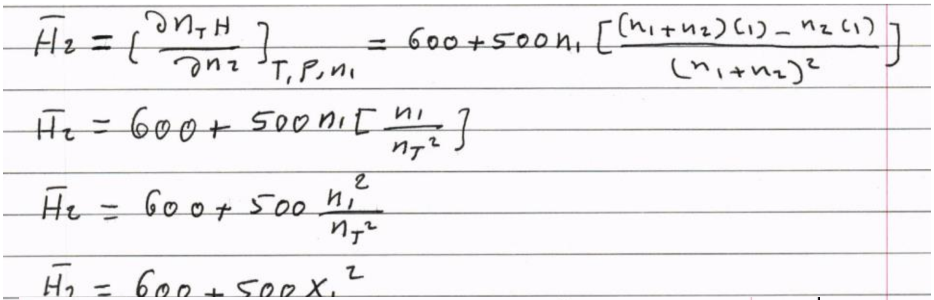
$$\bar{H}_1 = \left[\frac{\partial n_T H}{\partial\ }\right]_{T,P,n_2}$$

$$\bar{H}_1 = 400 + 500\,n_2\left[\frac{(n_1+n_2)(1) - n_1}{(n_1+n_2)^2}\right]$$

$$\bar{H}_1 = 400 + 500\,n_2\left[\frac{n_2}{(n_1+n_2)^2}\right]$$

$$\bar{H}_1 = 400 + 500\,\frac{n_2^2}{n_T^2}$$

$$\bar{H}_1 = 400 + 500x_2^2$$

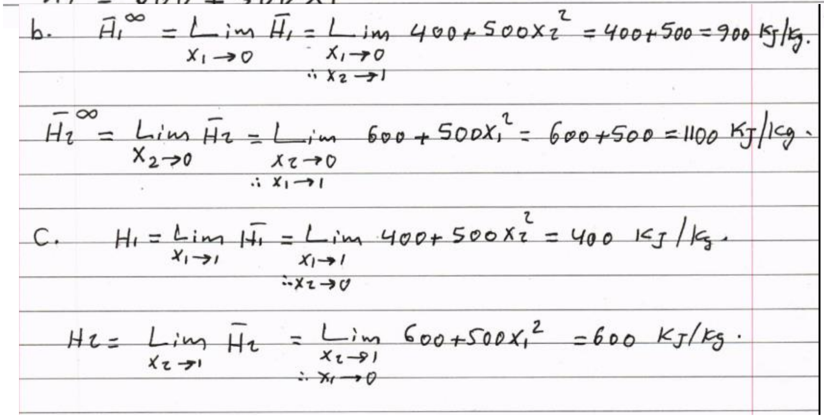


$$\bar{H}_2 = \left[\frac{\partial n_T H}{\partial n_2}\right]_{T,P,n_1} = 600 + 500 n_1 \left[\frac{(n_1+n_2)(1) - n_2(1)}{(n_1+n_2)^2}\right]$$

$$\bar{H}_2 = 600 + 500 n_1 \left[\frac{n_1}{n_T^2}\right]$$

$$\bar{H}_2 = 600 + 500 \frac{n_1^2}{n_T^2}$$

$$\bar{H}_2 = 600 + 500 x_1^2$$

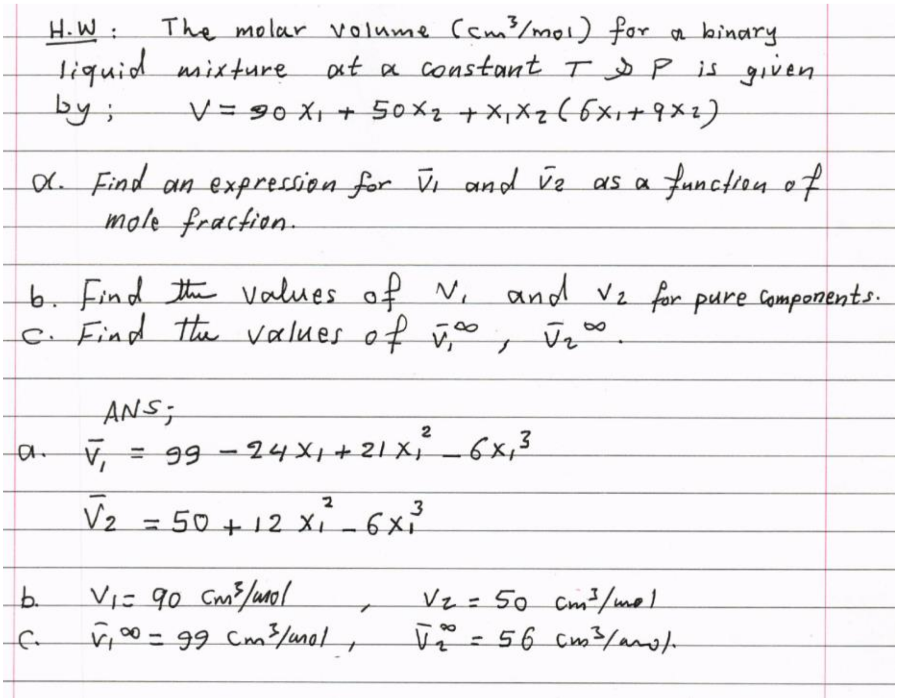


b. $\bar{H}_1^{\infty} = \lim\limits_{x_1 \to 0} \bar{H}_1 = \lim\limits_{\substack{x_1 \to 0 \\ \therefore x_2 \to 1}} 400 + 500 x_2^2 = 400 + 500 = 900$ KJ/Kg.

$\bar{H}_2^{\infty} = \lim\limits_{x_2 \to 0} \bar{H}_2 = \lim\limits_{\substack{x_2 \to 0 \\ \therefore x_1 \to 1}} 600 + 500 x_1^2 = 600 + 500 = 1100$ KJ/Kg.

c. $H_1 = \lim\limits_{x_1 \to 1} \bar{H}_1 = \lim\limits_{\substack{x_1 \to 1 \\ \therefore x_2 \to 0}} 400 + 500 x_2^2 = 400$ KJ/Kg.

$H_2 = \lim\limits_{x_2 \to 1} \bar{H}_2 = \lim\limits_{\substack{x_2 \to 1 \\ \therefore x_1 \to 0}} 600 + 500 x_1^2 = 600$ KJ/Kg.



H.W : The molar volume (cm³/mol) for a binary liquid mixture at a constant T & P is given by; $V = 90 x_1 + 50 x_2 + x_1 x_2 (6 x_1 + 9 x_2)$

a. Find an expression for $\bar{V}_1$ and $\bar{V}_2$ as a function of mole fraction.

b. Find the values of V_1 and V_2 for pure components.
c. Find the values of $\bar{V}_1^{\infty}$, $\bar{V}_2^{\infty}$.

ANS;

a. $\bar{V}_1 = 99 - 24 x_1 + 21 x_1^2 - 6 x_1^3$

$\bar{V}_2 = 50 + 12 x_1^2 - 6 x_1^3$

b. $V_1 = 90$ cm³/mol , $V_2 = 50$ cm³/mol
c. $\bar{V}_1^{\infty} = 99$ cm³/mol , $\bar{V}_2^{\infty} = 56$ cm³/mol.

شكرا لحسن ألاستماع