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

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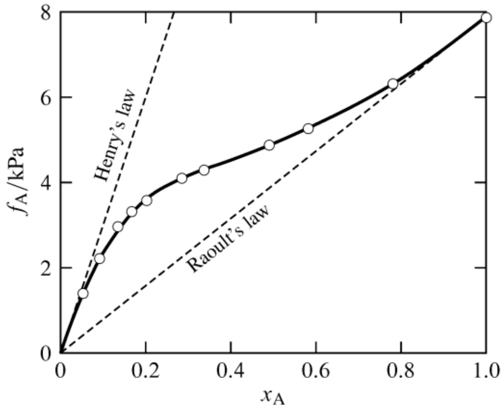
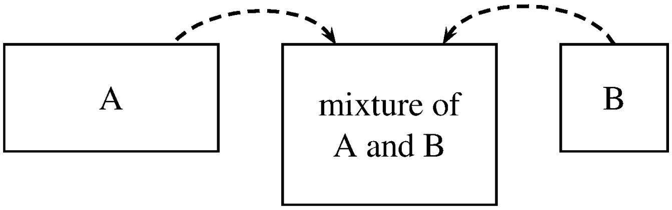




A

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.

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

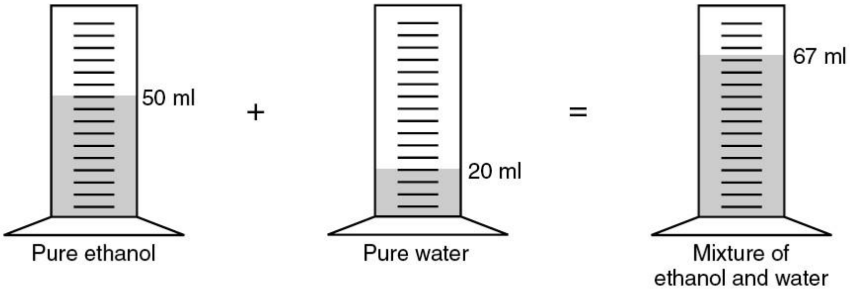
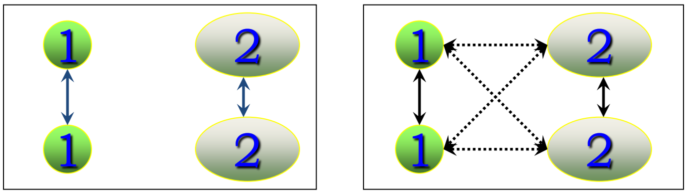


Figure 6.5 Mixing of ethanol and water.

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.



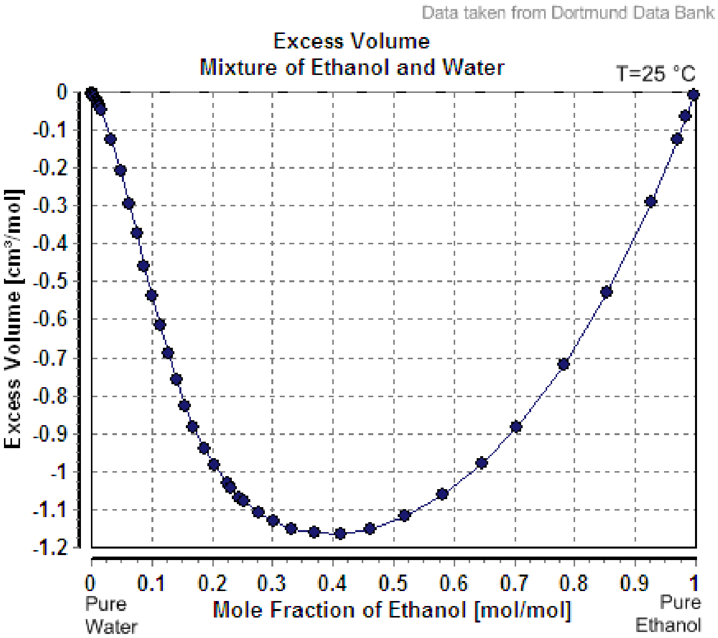
Property Changes on Mixing

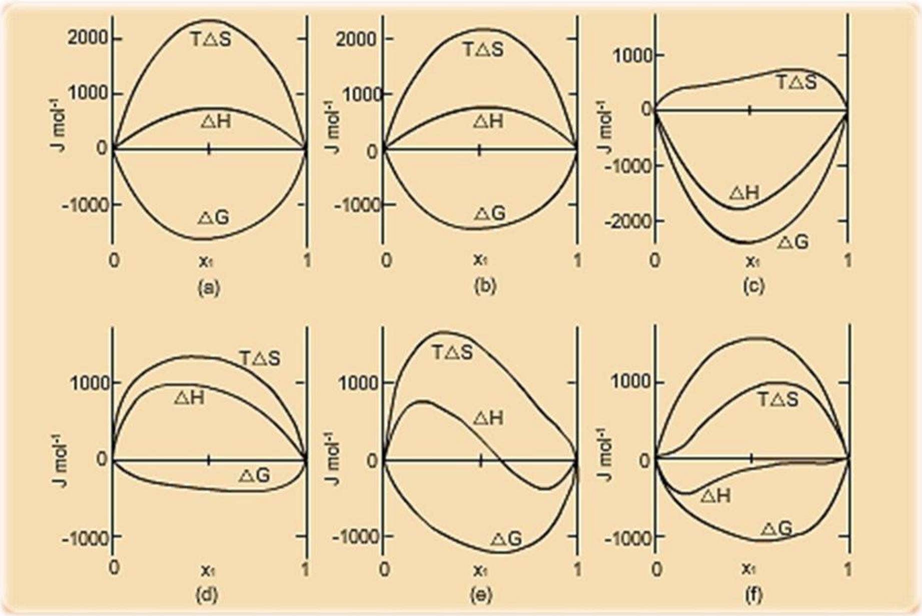
- Evidently, there is a property change on mixing. Property changes on mixing are defined as

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

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

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


Data taken from Dortmund Data Bank
Excess Volume
Mixture of Ethanol and Water
T=25 °C
Excess Volume [cm³/mol]
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1
-1.1
-1.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
Pure Water
Mole Fraction of Ethanol [mol/mol]
Pure Ethanol


2000
1000
0
-1000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(a)
2000
1000
0
-1000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(b)
1000
0
-1000
-2000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(c)
1000
0
-1000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(d)
1000
0
-1000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(e)
1000
0
-1000
J mol⁻¹
TΔS
ΔH
ΔG
0
x₁
1
(f)

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 $a = u - Ts$

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

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

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

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

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

- 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!

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