1. Partial Molar Enthalpy (continued)

Example 6.8 (p. 347) Isothermal process (how to obtain $\Delta_{mix}h$)

Energy balance: $\frac{dh}{dt} = \sum \dot{n}_{in} h_{in} - \sum \dot{n}_{out} h_{out} + \dot{Q}_{in} - W_{s,by}$

Conditions:
- steady state
- no shaft work
- $Q_{in}$ used to obtain isothermal process
- Multiple feeds are pure substance
- One output flow

$$0 = (\dot{n}_A h_A + \dot{n}_B h_B) - ((\dot{n}_A + \dot{n}_B) h_{soln}) + \dot{Q}_{in}$$

Divide by $(\dot{n}_A + \dot{n}_B)$,

$$0 = (x_A h_A + x_B h_B) - (h_{soln}) + q_{in}$$

where $q_{in} = Q_{in}/(\dot{n}_A + \dot{n}_B)$.

$$q_{in} = h_{soln} - (x_A h_A + x_B h_B) = \Delta_{mix}h$$

$\rightarrow$ see Figure E6.8B for example plot using data in Table E6.8B.
Example 6.9 (p. 349) Effects of temperature changes

Remarks:
- Perform the mixing at the temperature and pressure where the data for $\Delta_{\text{mix}}h$ were obtained.
- If feed (or initial conditions) are not pure, then unmixing process can be performed first. Afterwards the final mixing of all components are performed.
- The temperature changes (i.e. sensible heat) will be based on heat capacity data.

For us, we will assume that

$$c_{P,\text{mix}} = x_1c_{P,1} + \cdots + x_Nc_{P,N}$$

Q: What is $\Delta_{\text{mix}}h$ for ideal gases?

A: Since ideal gases will have no intermolecular forces,

$$h = \sum x_i h_i \rightarrow \Delta_{\text{mix}}h_{\text{ideal gas}} = h - \sum x_i h_i = 0$$

2. Partial Molar Entropy

$S = \text{total entropy of the mixture}$

$$s = \frac{S}{n_1 + \cdots + n_N} = \text{molar entropy of the mixture}$$

$$s_i = s|_{n_1=\cdots=n_N=0} = \text{molar entropy of pure } i$$

$$\bar{s}_i = \left(\frac{\partial s}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \text{partial molar entropy of } i \text{ in the mixture}$$

$$S_{T,P} = \sum_{i=1}^{N} n_i \bar{s}_i \quad ; \quad s_{T,P} = \sum_{i=1}^{N} x_i \bar{s}_i$$

$$dS_{T,P} = \sum_{i=1}^{N} \bar{s}_i \, dn_i \quad ; \quad 0 = \sum_{i=1}^{N} n_i d\bar{s}_i = \sum_{i=1}^{N} x_i d\bar{s}_i$$

$$\Delta_{\text{mix}}S = s - \sum_{i=1}^{N} x_i s_i = \sum_{i=1}^{N} x_i (\bar{s}_i - s_i)$$

$$\Delta_{\text{mix}}S = s - \sum_{i=1}^{N} n_i s_i = \sum_{i=1}^{N} n_i (\bar{s}_i - s_i)$$

$\rightarrow$ same as in the case of partial molar volume and partial molar enthalpy

Main Difference : $\Delta_{\text{mix}}S_{\text{ideal}} \neq 0$
\[ \Delta_{mix}S^{\text{Ideal gas}} = -R \sum x_i \ln x_i \]

For an alternative to derivation given in book, recall supplementary notes:

http://www.chem.mtu.edu/~tbco/cm3230/entropy_of_mixing_supplement.pdf

Note: for any mixtures, including liquid mixtures, for which the following is true:

\[ \Delta_{mix}S = -R \sum x_i \ln x_i \]

Then mixture is termed as “Regular Solution”