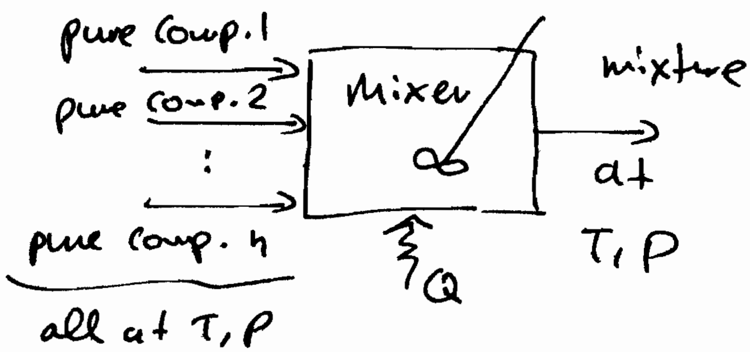
Mixing functions

* Number of direct measurements needed for mixture properties increases exponentially w/ n
* Need simple ways to describe mixture differences from their pure component constituents

E.g.



Do we need to add or remove heat?

Consider a general property (e.g. U, V, S, A, H)

$B = B(T, P, \{N\})$ where $\{N\} \equiv (N_1, N_2, \ldots N_n)$

or $\underline{B} = \underline{B}(T, P, \{x\})$ where $\{x\} \equiv (x_1, x_2, \ldots x_{n-1})$

unless $B \equiv G$, this is <u>not</u> a fundamental eqn.

<u>Mixing function</u> $\Delta B_{mix} \equiv B - \sum_{i=1}^{n} N_i \underline{B}_i(\text{pure comp.})$

$$\Delta \underline{B}_{mix} \equiv \underline{B} - \sum_{i=1}^{n} x_i \underline{B}_i(\text{pure})$$

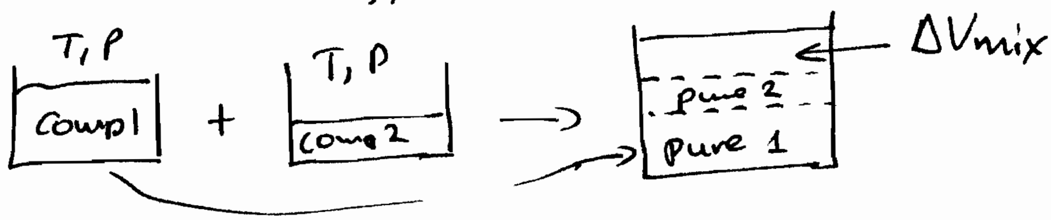
- Mixing functions are defined at a given T, P
- They depend on composition
- represent difference between mixture + pure component contributions

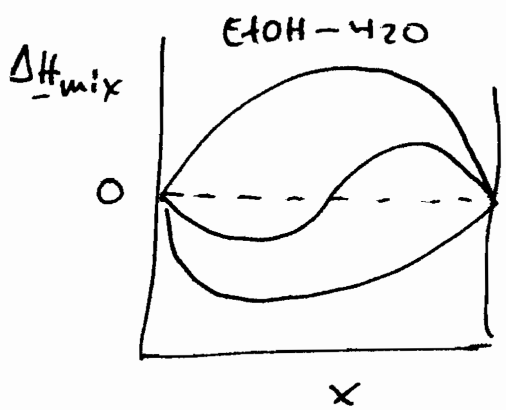
Steady-state open system 1st Law balance on mixer of previous page

$$\Delta U = 0 = Q + \cancel{W} + \sum_{\text{entering}} \underline{H}_{in} N_{in} - N_{out} \underline{H}_{out}$$

$$\Rightarrow Q = H(\text{mixture}) - \sum_{i=1}^{n} N_i \underline{H}_i(\text{pure}) = \Delta H_{mix}$$

In a similar way,





complex behavior possible with composition + temperature

see book web site for expanded color version of fig. 8.2

Partial Molar Properties

We would like to be able to write mixture properties as simple sums of component contributions.

E.g. $dG = -SdT + VdP + \sum_{i=1}^{n} \mu_i dN_i \xrightarrow[\text{integration}]{\text{Euler}}$

$$\boxed{G = \sum_{i=1}^{n} \mu_i N_i}$$

The Gibbs free energy is the sum of the comp. μ's <u>in the mixture</u>

In a similar way,

$$dB = \left.\frac{\partial B}{\partial T}\right)_{P,\{N\}} dT + \left.\frac{\partial B}{\partial P}\right)_{T,\{N\}} dP + \sum_{i=1}^{n} \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_{j\neq i}} dN_i$$

$\rightarrow$ Euler integrate $\rightarrow$ $B = \sum_{i=1}^{n} \overline{B}_i N_i$

where $\overline{B}_i = \left.\frac{\partial B}{\partial N_i}\right)_{T,P,N_{j\neq i}}$ Definition of partial molar property

Example 8.2

If $\Delta \underline{H}_{mix} = C x_1 x_2 RT$ C : constant, ind. of T, P, x

$\left(x_1 = N_1/(N_1+N_2) \quad x_2 = N_2/(N_1+N_2) \right)$

obtain $\overline{H}_1, \overline{H}_2$

$$H = N_1 \underline{H}_1 + N_2 \underline{H}_2 + CRT \frac{N_1 N_2}{N_1 + N_2}$$

pure comp.

$$\overline{H}_1 = \left.\frac{\partial H}{\partial N_1}\right)_{T,P,N_2} = \underline{H}_1 + CRT \frac{N_2(N_1+N_2) - N_1 N_2}{(N_1+N_2)^2}$$

$$= \underline{H}_1 + \frac{CRTN_2^2}{(N_1+N_2)^2} \Rightarrow \overline{H}_1 = \underline{H}_1 + CRTx_2^2$$

Similarly, $\overline{H}_2 = \underline{H}_2 + CRT x_1^2$

Check: $N_1 \overline{H}_1 + N_2 \overline{H}_2 = N_1 \underline{H}_1 + N_2 \underline{H}_2 + CRT \frac{N_1 N_2^2 + N_2 N_1^2}{(N_1+N_2)^2}$

$$= N_1 \underline{H}_1 + N_2 \underline{H}_2 + CRT x_1 x_2 \quad \checkmark$$

Relationships involving $\bar{B}_i$, ΔB_{mix}

$$\Delta B_{mix} = \sum_{i=1}^{n} N_i \bar{B}_i - \sum_{i=1}^{n} N_i \underline{B}_i = \sum_{i=1}^{n} N_i (\bar{B}_i - \underline{B}_i)$$

mixture prop.   pure comp. property

$$\Delta \underline{B}_{mix} = \sum_{i=1}^{n} x_i (\bar{B}_i - \underline{B}_i)$$

All integral relationships, e.g. $H = U + PV \Rightarrow$

$$\Delta H_{mix} = \Delta U_{mix} + P \Delta V_{mix} \;;\; \bar{H}_i = \bar{U}_i + P \bar{V}_i$$

$$G = H - TS \Rightarrow \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \;;\; \bar{G}_i = \bar{H}_i - T \bar{S}_i$$

Differential relationships:

$$\left.\frac{\partial G}{\partial P}\right)_{T,\{N\}} = V \Rightarrow \left.\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\{N\}} = \left.\frac{\partial \mu_i}{\partial P}\right)_{T,\{N\}} = \bar{V}_i$$

$$\left.\frac{\partial (G/T)}{\partial T}\right)_{P,\{N\}} = \frac{S}{T} - \frac{G}{T^2} = -\frac{H}{T^2} \Rightarrow \left.\frac{\partial (\mu_i/T)}{\partial T}\right)_{P,\{N\}} = -\frac{\bar{H}_i}{T^2}$$

Also:

$$\left.\frac{\partial \Delta G_{mix}}{\partial N_i}\right)_{T,P,N_{j\neq i}} = \frac{\partial}{\partial N_i}\left(G - \sum N_i \mu_i(\text{pure})\right) =$$

$$= \mu_i(T,P,\{x\}) - \mu_i(T,P,\text{pure } i)$$