3.020 Lecture 17

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1 Solution modeling

- Ideal gas mixtures $\longrightarrow$ ideal solution model
- Non-ideal solution models
  - Activity : activity coefficient
- Dilute solution model
- Regular solution models

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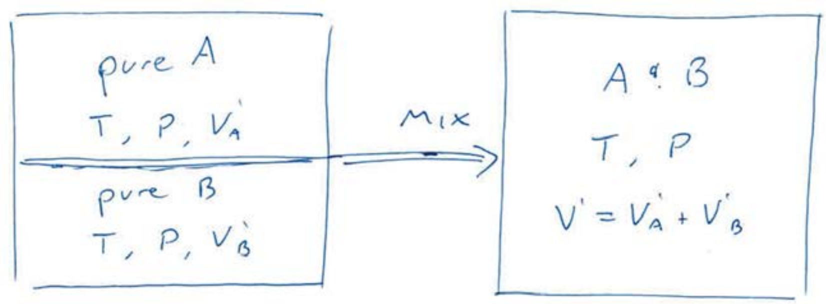
2 Ideal gas mixtures



- model as isothermal expansion of each component

$$d\mu_i\Big|_T = V_i\, dP_i \quad \longrightarrow \quad \Delta\mu_i = \int dP_i V = \int_P^{P_i} dP^* \frac{RT}{P^*} = RT \ln\left(\frac{P_i}{P}\right)$$

$d\mu_i\Big|_T$: This is $\Delta\mu_i$ for isothermal expansion

$d\mu_i\Big|_T$: This is also $\Delta\mu_i$ for the mixing process

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- Gibbs free energy of this mixing process

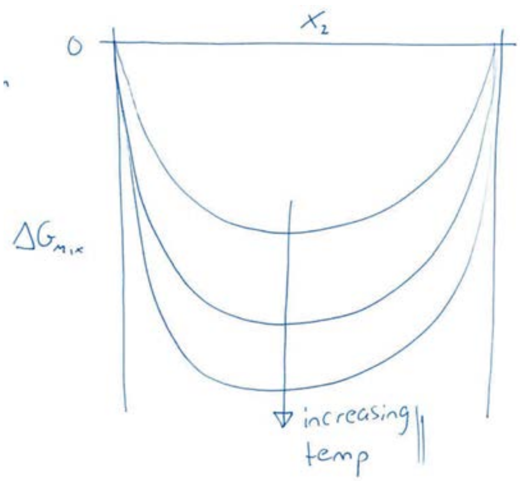
$$
\begin{aligned}
\Delta G_{mix} &= \sum_i X_i \Delta\mu_i \\
&= \sum_i X_i RT \ln \underbrace{(P_i/P)}_{Dalton} \\
&= \sum_i X_i RT \ln X_i
\end{aligned}
$$

- note that

$$\Delta G_{mix} < 0$$

$$\frac{d^2 \Delta G_{mix}}{dX_2^2} > 0$$

everywhere $\implies$ mixing is always spontaneous



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3 The ideal solution model $\Delta\mu_i = RT \ln X_i$

- motivated by ideal gases mixing
- approximates a broader class of real-world systems

$\Delta \overline{S}_i = \left.\frac{\partial \Delta\mu_i}{\partial T}\right|_{P,n_k} = -R \ln X_i > 0$ **process driven by entropy increase**

$\Delta \overline{V}_i = \left.\frac{\partial \Delta\mu_i}{\partial P}\right|_{T,n_k} = 0$ **no volume of mixing** $\implies$ **final volume is sum of pure components**

$\Delta \overline{H}_i = \Delta\mu_i - T\Delta \overline{S}_i = 0$ **no interactions between molecules, no bonds**

$\Delta \overline{U}_i = \Delta \overline{H}_i - P\Delta \overline{V}_i = 0$ **made/broken , no change in enthalpy or energy**

Q. What if molecules interact? What if ideal model doesn't apply ?

A. Capture deviation from ideal model (more bookeeping !!)

$$\text{Let } \Delta\mu_i = RT\ln a_i = RT\ln\gamma_i X_i$$
$$a_i = \text{activity of component i} = \gamma_i\ X_i$$
$$\gamma_i = \text{activity coefficient of component i}$$

$$\Delta G_{mix} = \sum_i X_i\Delta\mu_i = \sum_i X_i RT\ln\gamma_i X_i$$
$$= \underbrace{\sum_i X_i RT\ln X_i}_{\textbf{ideal case}} + \underbrace{\sum_i X_i RT\ln\gamma_i}_{\textbf{derivation from ideal}}$$

- Non-ideal behavior captured by $\gamma_i \neq 1$

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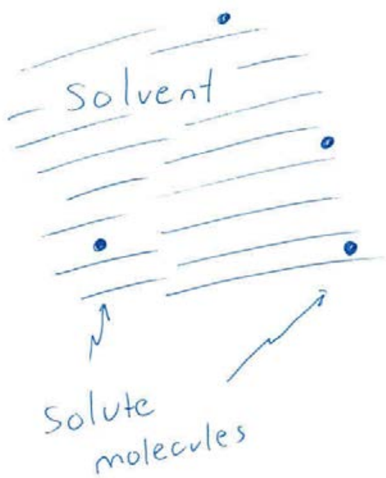
4 Dilute solution model



Assume :

1. Each solute molecule is surrounded by solvent, and solute-solve interactions are negligible
2. Each solvent molecule is, on average, surrounded by other solvent, and therefore "acts" like a pure substance.

Assumption 1 $\longrightarrow$ Henry's law of the solute

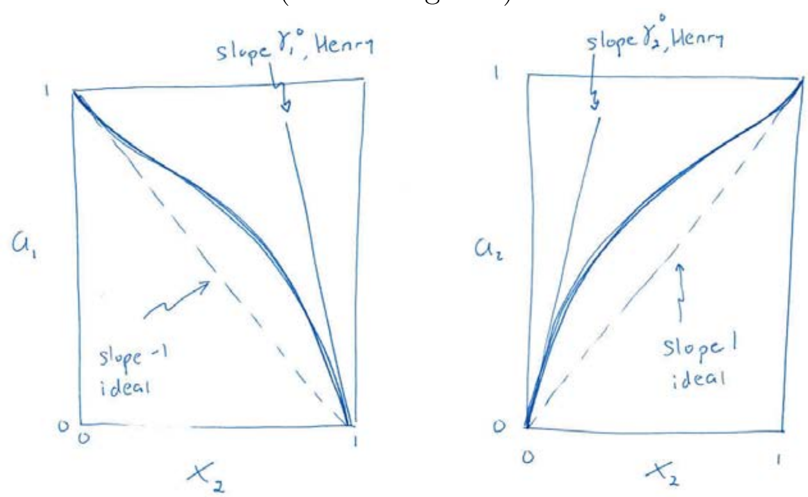
$$\lim_{X_2\to 0} a_2 = \underbrace{\gamma_2^0\ X_2}_{\textbf{Henry's constant}}$$

Assumption 2 $\longrightarrow$ Raoult's law of the solvent

$$\lim_{X_1\to 0} a_1 = X_1$$

Can be derived from Henry via G-D integration. See 8.2.3 and Pset 5

- variation of activity with composition
  Could look like this (DeHoff Fig. 8.4)



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5 Regular solution models

Assume :

1. Entropy of mixing is captured by ideal model, $\Delta S_{mix,ideal}$
   will show later that this is just "configuration entropy "
2. Intermolecular interactions are captured by non-zero $\Delta H_{mix} \neq 0$

$$\begin{aligned}\Delta G_{mix} &= \Delta H_{mix} - T\ \Delta S_{mix,ideal}\\ &= \Delta H_{mix} + RT \sum_i X_i \ln X_i\end{aligned}$$

- the Simple Regular Model is the simplest case of regular solution models for binary systems

$$\Delta H_{mix} = a_0\ X_1\ X_2$$

$a_0 > 0$: **endothermic mixing**; $a_0 < 0$: **exothermic mixing**

$$\Delta G_{mix} = a_0 X_1 X_2 + RT \sum_i X_i \ln X_i$$