Finally, as promised: Whisky distillery

Fractional distillation:

Non-ideal mixtures

High-boiling azeotrope, e.g., nitric acid/water

Low-boiling azeotrope, e.g., ethanol/water
Liquid-liquid phase diagrams of partially miscible liquids

E.g., hexane/nitrobenzene:

- Upper critical solution temperature (thermal motion)
- Lever rule

E.g., triethylamine/water:

- Lower $T_{\text{crit}}$ (complex formed)

Amount of phase of composition $a'' = \frac{l'}{l''}$

Amount of phase of composition $a' = \frac{l''}{l''}$
At constant $T$ and $p$ a reaction mixture tends to adjust its composition until its Gibbs energy is at a minimum.
Describing equilibrium quantitatively: The reaction Gibbs energy

**Example 1**

Glucose-6-phosphate $\rightarrow$ Fructose-6-phosphate

$\text{G6P(aq)} \rightarrow \text{F6P(aq)}$; change by $\Delta n$

$\Rightarrow \Delta G = \mu_{\text{F6P}} \times \Delta n - \mu_{\text{G6P}} \times \Delta n$

$\Rightarrow \frac{\Delta G}{\Delta n} = \mu_{\text{F6P}} - \mu_{\text{G6P}} = \Delta_r G$

general: $aA + bB \rightarrow cC + dD$

**Example 2**

$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$

change by $\Delta n$

$\Rightarrow \Delta G = \mu_{\text{NH}_3} \times 2\Delta n - \mu_{\text{N}_2} \times \Delta n$

$\phantom{=} - \mu_{\text{H}_2} \times 3\Delta n$

$\frac{\Delta G}{\Delta n} = 2\mu_{\text{NH}_3} - (\mu_{\text{N}_2} + 3\mu_{\text{H}_2})$

$= \Delta_r G$

$\Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$
What is the reaction Gibbs energy?

\[ \Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \]

More products formed

More reactants formed

\[ \Delta_r G = \frac{\Delta G}{\Delta n} \]

Nils Walter: Chem 260
Variation of $\Delta_r G$ with composition

Composition dependence of chemical potential: $\mu_j = \mu_j^\Theta + RT \ln a_j$

\[ \Rightarrow \quad \Delta_r G = \{c(\mu_C^\Theta + RT \ln a_C) + d(\mu_D^\Theta + RT \ln a_D)\} \]
\[\quad - \{a(\mu_A^\Theta + RT \ln a_A) + b(\mu_B^\Theta + RT \ln a_B)\} \]
\[= \{(c\mu_C^\Theta + d\mu_D^\Theta) - (a\mu_A^\Theta + b\mu_B^\Theta)\} \]
\[+ RT\{c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B\} \]

\[\Rightarrow \quad \Delta_r G = \Delta_r G^\Theta + RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \]

Standard reaction Gibbs energy (standard state of pure materials)

reaction quotient $Q$: products/reactants

\[\Rightarrow \quad \Delta_r G = \Delta_r G^\Theta + RT \ln Q \]