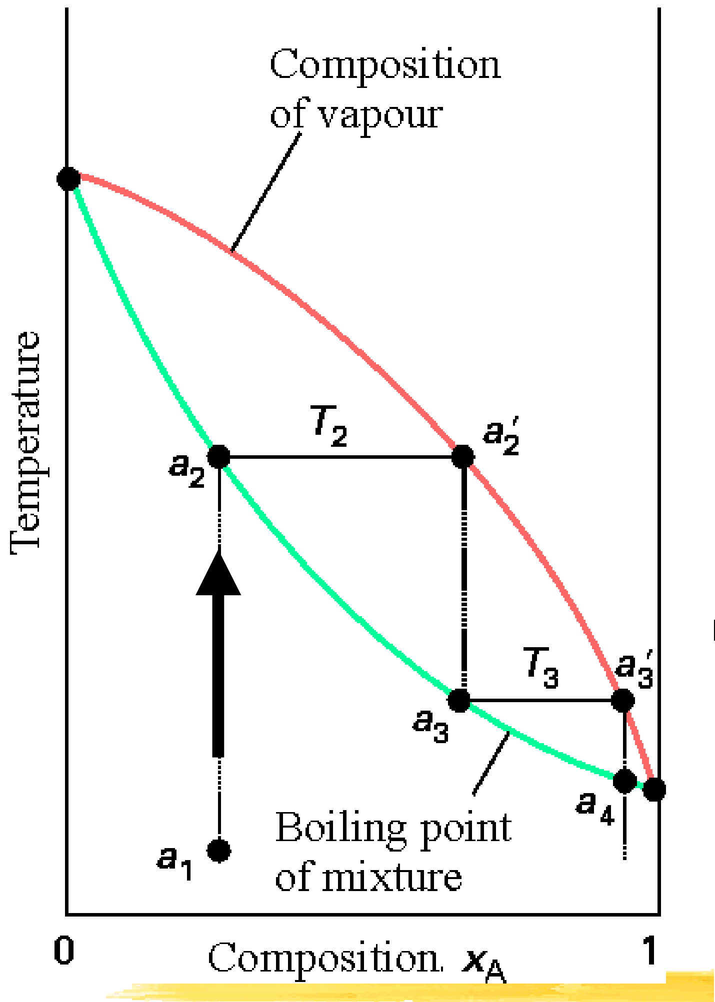
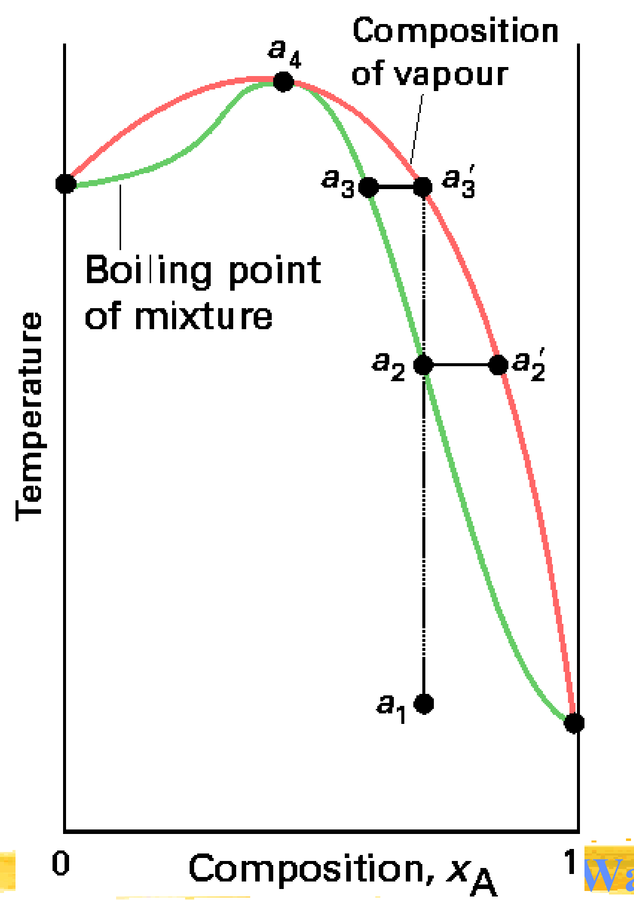
Finally, as promised: Whisky distillery

Fractional distillation:

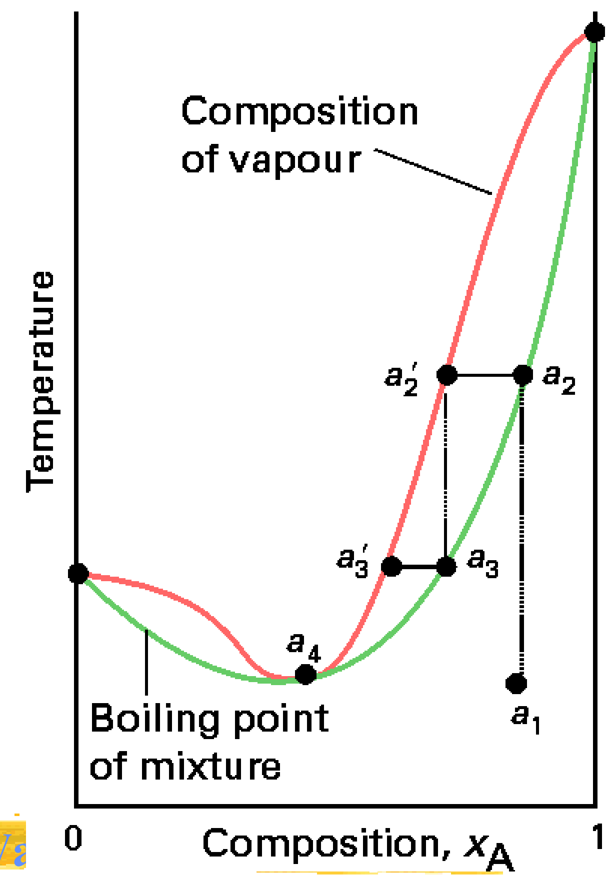


Non-ideal mixtures

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

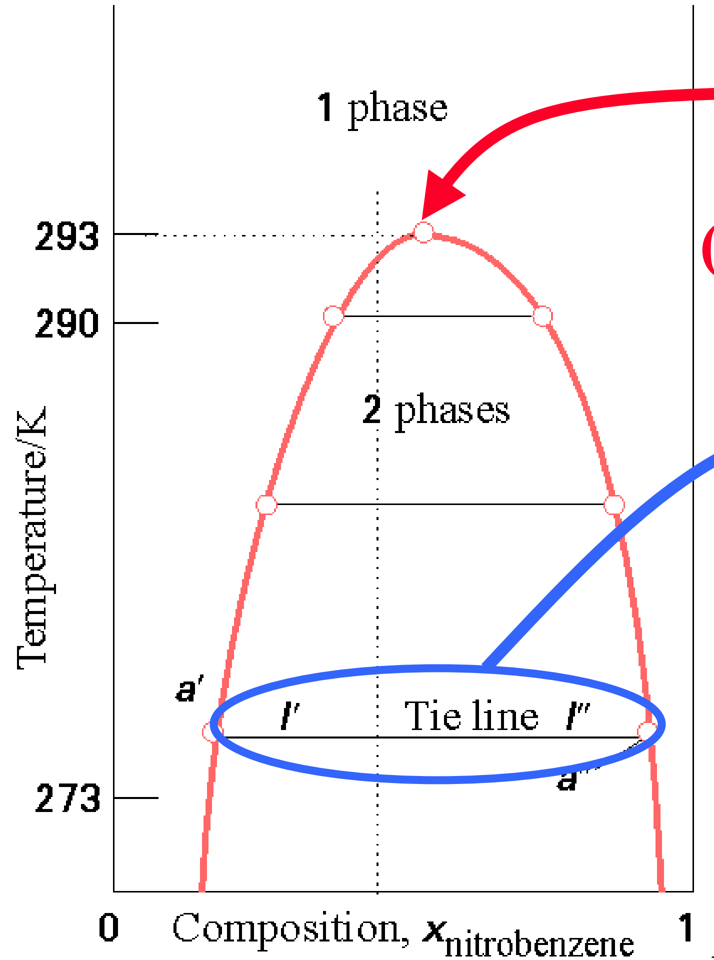


Low-boiling azeotrope, e.g., ethanol/water



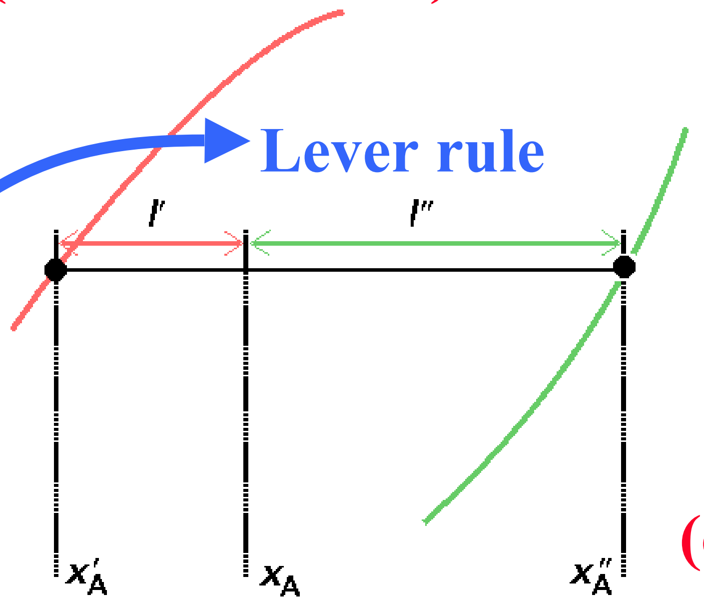
Liquid-liquid phase diagrams of partially miscible liquids

E.g., hexane/nitrobenzene:

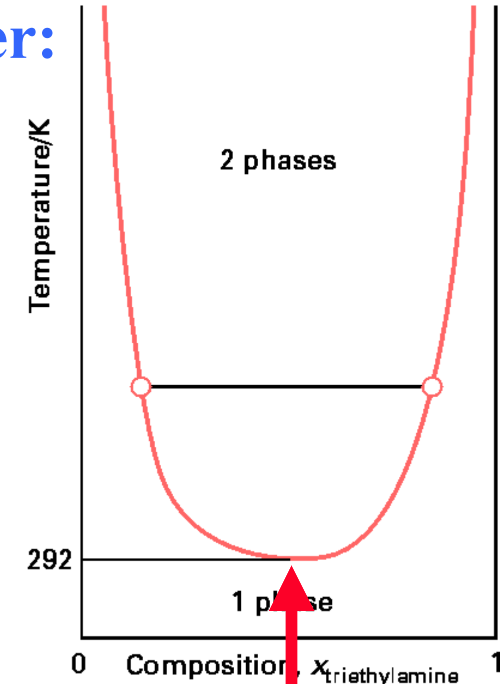


Upper critical solution temperature (thermal motion)

Lever rule



E.g., triethylamine /water:



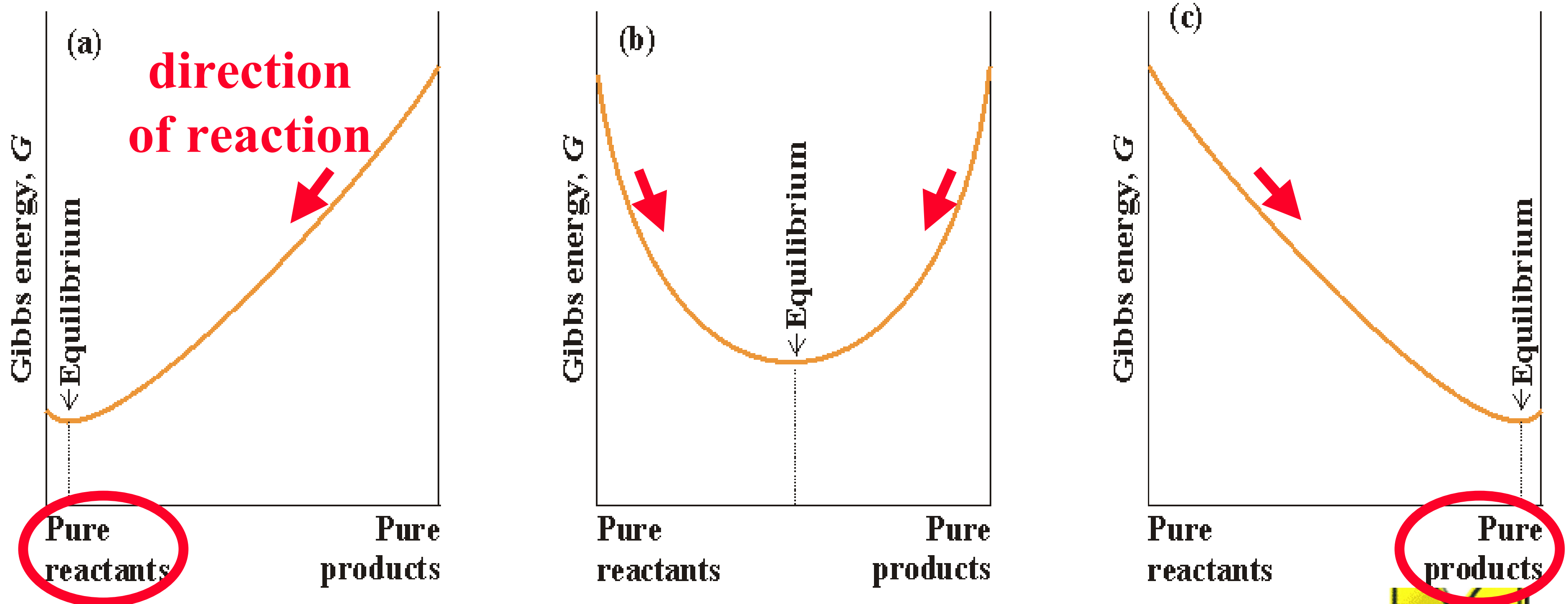
Lower T_{crit} (complex formed)

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

Principles of chemical equilibrium

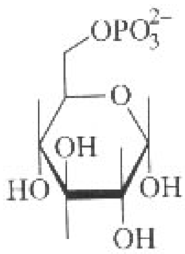
Atkins, Chapter 7

At constant T and p a reaction mixture tends to adjust its composition until its Gibbs energy is at a minimum

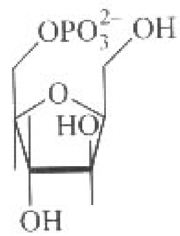


Describing equilibrium quantitatively: The reaction Gibbs energy

Example 1



Glucose-6-phosphate



Fructose-6-phosphate

G6P(aq) $\rightarrow$ F6P(aq); change by Δn

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

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

Example 2

$N_2(g) + 3\, H_2(g) \rightarrow 2\, NH_3(g)$

change by Δn

$\Rightarrow \Delta G = \mu_{NH3} \times 2\Delta n - \mu_{N2} \times \Delta n - \mu_{H2} \times 3\Delta n$

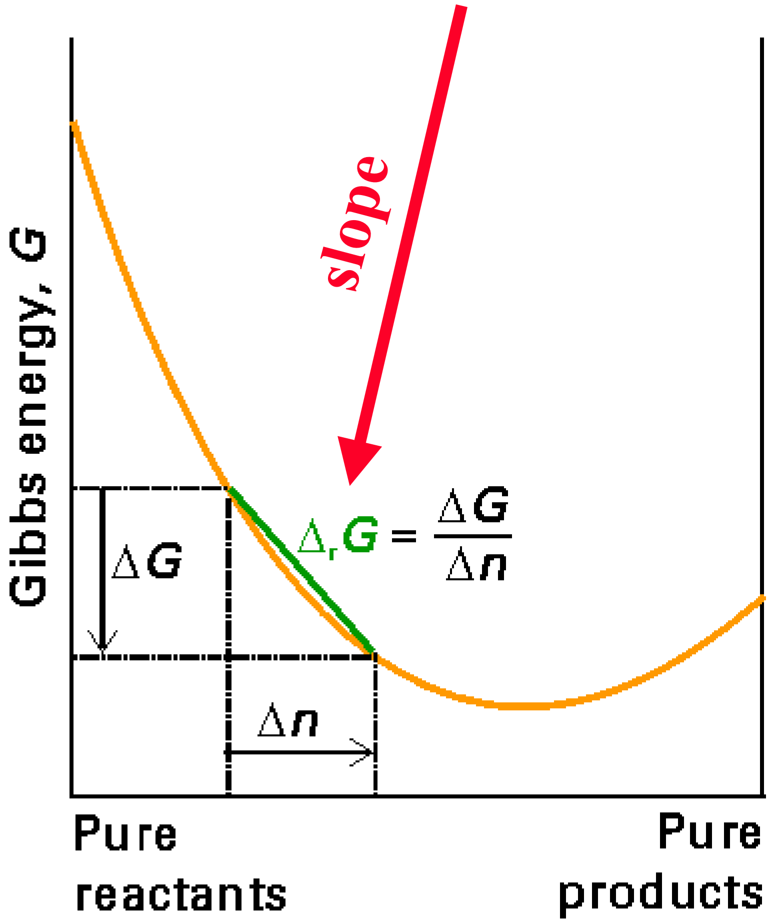
$$\frac{\Delta G}{\Delta n} = 2\mu_{NH_3} - (\mu_{N_2} + 3\mu_{H_2})$$

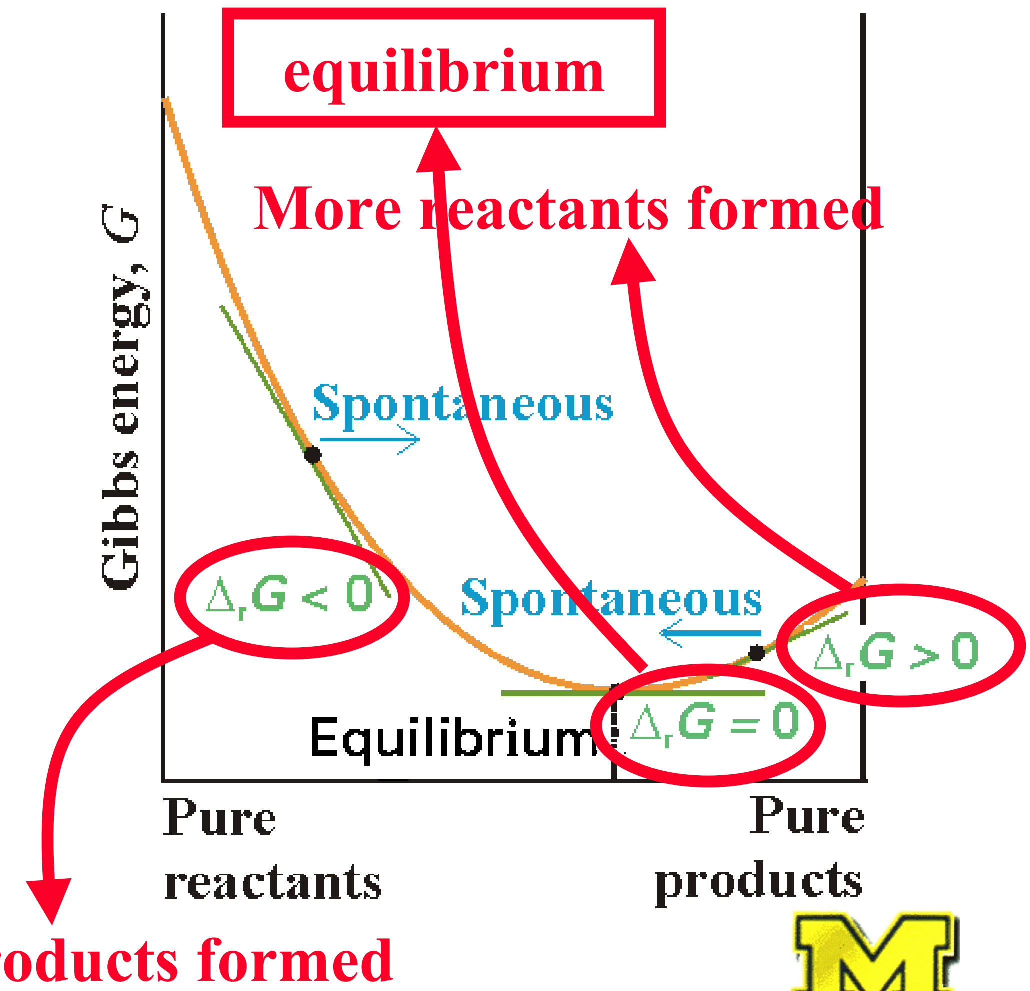
$$= \Delta_r G$$

general: aA + bB $\rightarrow$ cC + dD $\Rightarrow$ $\boxed{\Delta_r G = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)}$

What is the reaction Gibbs energy?

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





Variation of $\Delta_r G$ with composition

Composition dependence of chemical potential: $\mu_J = \mu_J^{\ominus} + RT \ln a_J$

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

$$\boxed{\Delta_r G^{\ominus}}$$

Standard reaction Gibbs energy (standard state of pure materials)

$$\Rightarrow \Delta_r G = \Delta_r G^{\ominus} + RT\ln \underbrace{\frac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b}}$$

reaction quotient Q: products/reactants

$$\Rightarrow \boxed{\Delta_r G = \Delta_r G^{\ominus} + RT\ln Q}$$