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Course 565/665 Lecture Number _____ Date 9/17/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Falmer

Change of Problem:

~~13.6~~ → 13.5

Correction to 4/15/03's lecture:

$$\mu_i = \mu_i^\circ + kT \ln \gamma_i x_i$$

$$\mu_A = \mu_A^\circ + \underline{kT} \ln \gamma_i x_i$$

The kT is essential.

Defining μ° 's

Given A and B,

$$\mu_B = \mu_B^\circ + kT \ln \gamma_B x_B$$

- μ_B when B is the solvent: ($|B| \gg |A|$)

$$\gamma_B x_B \rightarrow 1 \quad \text{since} \quad \begin{array}{l} x_B \rightarrow 1 \\ \gamma_B \rightarrow 1 \end{array}$$

for these cases, $\mu_B = \mu_B^\circ$

- μ_B when B is the solute: ($|B| \ll |A|$)

$$\gamma_B x_B \rightarrow 0 \quad \text{since} \quad \begin{array}{l} x_B \rightarrow 0 \\ \gamma_B \rightarrow 1 \end{array}$$

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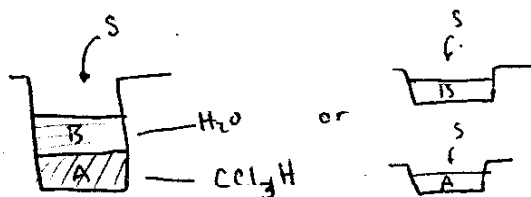
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Lecturer Lavagnoro Note Taker Fulmer

Somehow by some convention, $\gamma_B x_B \rightarrow 1$ even though $x_B \rightarrow 0$. This is quoted from the book. I don't know why nor do I understand its motivation.

Solute Partitioning

- * Solvents A and B
- * 1 Solute S



Partition Coefficient $\equiv K_A^B = \frac{x_{SB}}{x_{SA}}$ at equilibrium

$$\ln K_A^B = \frac{x_{SB}}{x_{SA}} = \chi_{SA} (1 - x_{SA})^2 - \chi_{SB} (1 - x_{SB})^2$$

$$\frac{\mu_{SA}}{kT} = \frac{z_{WS}}{kT} + \ln x_{SA} + \chi_{SA} (1 - x_{SA})^2$$

$$\frac{\mu_{SB}}{kT} = \dots$$

$$k K_A^B = \frac{-(\mu_{SB}^{\circ} - \mu_{SA}^{\circ})}{kT} - \ln \left(\frac{\gamma_{SB}}{\gamma_{SA}} \right)$$

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At infinite dilution ...

$$x_{SA}, x_{SB} \rightarrow 0$$

$$\gamma_{SA} \rightarrow 1; \gamma_{SB} \rightarrow 1$$

$$\ln K_A^B = \frac{\mu_{SA}^{\circ} - \mu_{SB}^{\circ}}{kT} = \chi_{SA} - \chi_{SB} = \ln K_A^B$$

Example | $\Delta\mu^{\circ} = \mu_{H_2O}^{\circ} - \mu_{butane}^{\circ} = +6 \text{ kcal/mol}$

Butane transfer
into water:

$$K_{hc}^w = e^{-\Delta\mu^{\circ}/kT} = \exp\left(\frac{-6000}{(1.987)(300)}\right) = 4.3 \times 10^{-5}$$

A Special Case

Disolving S into a single solvent A

$$\ln K_{SA} = +\chi_{SA} = \frac{\mu_{SA}^{\circ}}{kT}$$

[Sign Error?]

$$\mu_{SA}^{\circ} = -kT \chi_{SA}$$

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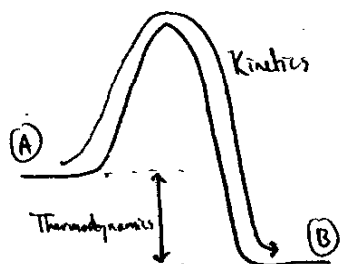
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Kinetics vs. Thermodynamics:



Thermodynamics relates the relative position of given states or energy levels. It tells us if the transition from A to B is energetically favorable. Kinetics, however, tells us the rate at which this transition occurs. Generally, we think in terms of reactants surmounting some reaction barrier to get to products. If the barrier is small compared to thermal energy, the rate will be large. Conversely, if the barrier is large, then the rate will be small.

See Math Review Handout for summary of Vector Calculus.