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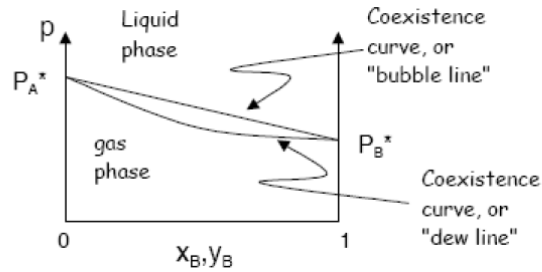
5.60 Thermodynamics & Kinetics
Spring 2008

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5.60 Final Exam Review

1. Phase Equilibria- 2 components

a. Drawing P-x,y and T-x,y diagrams



2. Ideal and Non Ideal Solutions

a. Raoult's Law, Henry's Law, Dalton's Law

- i. Dalton's Law: $p_A = y_A p$
- ii. Raoult's Law: $p_A = x_A p_A^*$ and $p_B = x_B p_B^* = (1-x_A)p_B^*$
- iii. Henry's Law: $p_B = x_B K_B$

b. Chemical potential and Ideal Solutions

$$\mu_A(\ell, T, p) = \mu_A^*(\ell, T, p) + RT \ln x_A$$

↑ Chemical potential "A" in mixture
 ↑ Chemical potential "A" in pure liquid
 ↑ Mole fraction of "A" in mixture

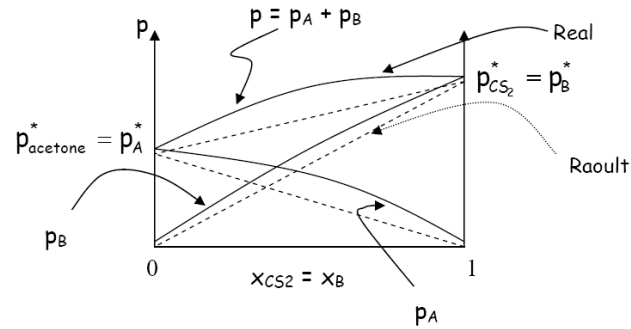
c. Entropy of Mixing, Free Energy of mixing

- i. $\Delta G_{\text{mix}} = nRT(x_A \ln x_A + x_B \ln x_B)$ Purely entropic, as in gas mixture.
- ii. $\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}} = 0$ No enthalpy change, ΔG is due to entropy of mixing
- iii. $\Delta V_{\text{mix}} = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial p} \right)_T = 0$ No volume change, just like ideal gas

d. Non ideal solutions

- i. Positive Deviations: $\Delta u > 0$ (most common)
Mixing is energetically not favorable in liquid phase

ii. Vapor pressure is higher than expected by Raoult's Law

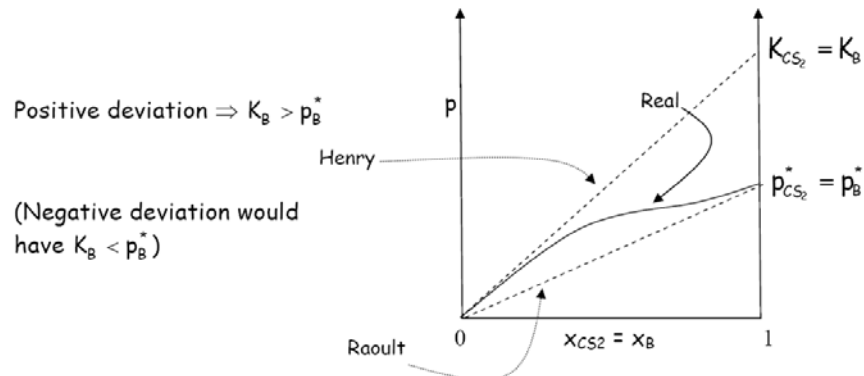


$$p_{CS_2} > x_{CS_2} p_{CS_2}^*$$

$$p_{\text{acetone}} > x_{\text{acetone}} p_{\text{acetone}}^*$$

$$\Rightarrow p_{\text{tot}}(\text{real}) > p_{\text{tot}}(\text{Raoult})$$

iii. Can make same argument for negative deviation.



iv. Don't forget about azeotropes (exam III)

3. Colligative Properties

- These are properties of solutions in the dilute limit, where there is a solvent "A" and a solute "B" where $n_A \gg n_B$.
- These properties are a direct result of $\mu_A^{\text{mix}}(\ell, T, p) < \mu_A^{\text{pure}}(\ell, T, p)$
- Use two measures of concentration:
 - Mole Fraction: $x_B = n/(n_A + n_B) \sim n_B/n_A$
 - Molality: $m_B = (\text{moles solute})/(\text{kg solvent}) = n_B/(n_A M_A)$
Where M_A is the mass in kg of one mole solvent.
- There are FOUR Colligative Properties
 - Vapor pressure lowering
 - Boiling point elevation (You should be able to derive the boiling point elevation of freezing point depression; look in lecture notes)
 - Freezing point depression
 - Osmotic pressure (Be able to derive)

4. Statistical Mechanics

a. Boltzmann probability distribution

For two states i and j with energies ϵ_i and ϵ_j , the relative probability of being in state i is:

$$P_i = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}$$

b. Partition Functions

i. Molecular partition function: $\sum_i e^{-\epsilon_i/kT} \equiv q$

ii. Canonical partition function: $\sum_i e^{-E_i/kT} \equiv Q$

iii. $q_{conf} = \sum_{\substack{\text{energies} \\ \epsilon_i}} g_i e^{-\epsilon_i/kT}$

iv. $S = -\frac{A}{T} + \frac{U}{T} = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$

v. $p = -\left(\frac{\partial A}{\partial V} \right)_{T,N} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{T,N}$

vi. $\mu = -\left(\frac{\partial A}{\partial N} \right)_{T,V} = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{T,V}$

vii. $H = U + pV$

viii. $G = A + pV$

ix. $S = -k \sum_i p_i \ln p_i$

c. Energy Levels

d. Model Systems

e. Applications

5. Reaction Kinetics

a. Complex reactions and mechanisms

i. For reaction: $aA + bB \rightarrow cC + dD$

$$\text{Rate of reaction: Rate} = \frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

ii. Zero order reactions (rare)

1. Reaction: $A \rightarrow \text{products}$

2. Rate: $[A] = -kt + [A]_0$

3. Half life: $t_{1/2} = [A]_0 / (2k)$

iii. First order reactions

1. Reaction: $A \rightarrow \text{products}$

2. Rate: $[A] = [A]_0 e^{-kt}$ $\ln[A] = -kt + \ln[A]_0$

3. Half life: $t_{1/2} = (\ln 2) / k = 0.693/k$

[so $k = (0.693)/(t_{1/2})$]

iv. Second order reactions

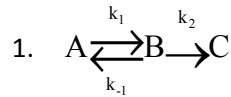
1. Reaction: $A \rightarrow \text{products}$

2. Rate: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$

3. Half life: $t_{1/2} = 1/(k[A]_0)$

b. Steady State and Equilibrium Approximations

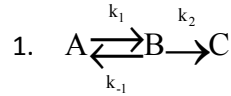
i. Steady state approximation



2. Assume [B] is small and slowly varying: [B] reaches a steady state concentration $[B]_{SS}$ and remains there

3. $\frac{d[C]}{dt} = k_2[B]_{SS} = \frac{k_1 k_2 [A]}{k_{-1} + k_2} = -\frac{d[A]}{dt}$

ii. Equilibrium approximation



2. Assume $k_2 \ll k_{-1}$ and k_1 (so $[B] \rightarrow C$ is the rate limiting step): Then A and B quickly come into equilibrium, while C slowly builds up

3. $K_{eq} = \frac{k_1}{k_{-1}} \approx \frac{[B]}{[A]}$

4. $\frac{d[C]}{dt} = k_2[B] = k_2 K_{eq} [A] = \frac{k_1 k_2}{k_{-1}} [A]$

c. Chain Reactions

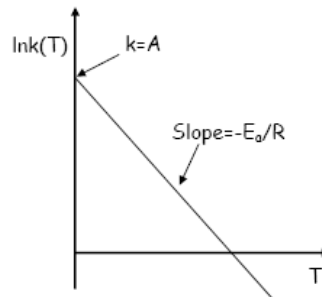
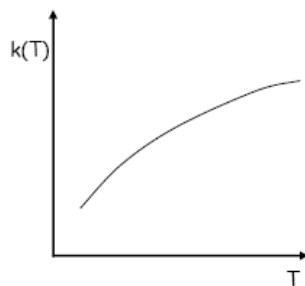
d. Temp Dependence

i. Arrhenius Law: $k = A e^{-E_a/RT}$

1. where E_a = Activation Energy

2. where A = Pre-Exponential Factor

ii.



iii.

e. Catalysis

i. Review Enzyme catalysis