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

3. Entropy of Mixing, Free Energy of mixing
   i. \( \Delta G_{mix} = n R T (x_A \ln x_A + x_B \ln x_B) \) Purely entropic, as in gas mixture.
   ii. \( \Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix} = 0 \) No enthalpy change, \( \Delta G \) is due to entropy of mixing
   iii. \( \Delta V_{mix} = \left( \frac{\partial \Delta G_{mix}}{\partial p} \right)_T = 0 \) No volume change, just like ideal gas

4. 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

iii. Can make same argument for negative deviation.

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

3. Colligative Properties
   a. These are properties of solutions in the dilute limit, where there is a solvent “A” and a solute “B” where \( n_A \gg n_B \).
   b. These properties are a direct result of \( \mu_A^{\text{mix}} (\ell, T, p) < \mu_A^{\text{pure}} (\ell, T, p) \)
   c. Use two measures of concentration:
      i. Mole Fraction: \( x_B = n_B/(n_A+n_B) \sim n_B/n_A \)
      ii. Molality: \( m_B = \text{(moles solute)/(kg solvent)} = n_B/(M_A) \)
         Where \( M_A \) is the mass in kg of one mole solvent.
   d. There are FOUR Colligative Properties
      i. Vapor pressure lowering
      ii. Boiling point elevation (You should be able to derive the boiling point elevation of freezing point depression; look in lecture notes)
      iii. Freezing point depression
      iv. Osmotic pressure (Be able to derive)
4. Statistical Mechanics
   a. Boltmann probability distribution
      For two states i and j with energies $\epsilon_i$ and $\epsilon_j$, 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. \( q_{\text{conf}} = \sum_{i} g_i e^{-\epsilon_i/kT} \)
      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: \( aA + bB \rightarrow cC + dD \)
         \[ \text{Rate of reaction: Rate} = \frac{1}{a} \frac{d[\text{A}]}{dt} = \frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt} \]
      ii. Zero order reactions (rare)
         1. Reaction: \( A \rightarrow \text{products} \)
         2. Rate: \( [A] = -kt + [A]_0 \)
         3. Half life: \( t_{1/2} = \frac{[A]_0}{2k} \)
      iii. First order reactions
         1. Reaction: \( A \rightarrow \text{products} \)
         2. Rate: \( [A] = [A]_0 e^{-kt} \quad \ln[A] = -kt + \ln[A]_0 \)
         3. Half life: \( t_{1/2} = (\ln 2) / k = 0.693/k \)
         \[ \text{so} \quad k = (0.693)/(t_{1/2}) \]
iv. Second order reactions
   1. Reaction: \( A \rightarrow \text{products} \)
   2. Rate: \( \frac{1}{[A]} = \frac{1}{[A]_0} + kt \)
   3. Half life: \( t_{1/2} = \frac{1}{(k[A]_0)} \)

b. Steady State and Equilibrium Approximations
   i. Steady state approximation
      1. \( \frac{k_1}{k_2} \)
      2. Assume \([B]\) is small and slowly varying: \([B]\) reaches a steady state concentration \([B]_{SS}\) and remains there
      3. \( \frac{d[C]}{dt} = k_2[B]_{SS} = \frac{k_1k_2[A]}{k_1+k_2} = \frac{d[A]}{dt} \)
   ii. Equilibrium approximation
      1. \( \frac{k_1}{k_2} \)
      2. Assume \( k_2 << k_1 \) 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. \( \frac{d[C]}{dt} = k_2[B] = k_2K_{eq}[A] = \frac{k_1k_2[A]}{k_{-1}} \)

c. Chain Reactions
d. Temp Dependence
   i. Arrhenius Law: \( k = Ae^{-E_a/RT} \)
      1. where \( E_a = \) Activation Energy
      2. where \( A = \) Pre-Exponential Factor

ii. 

iii. 

e. Catalysis
   i. Review Enzyme catalysis