Multiple-Component Phase Diagrams:

1. There is a mixture of toluene and benzene with $x_{benzene} = 0.33$. At 60C, the vapor pressure of benzene and toluene are 51.3 and 18.5 kPa, respectively.

   a) As the pressure reduced. At what pressure will boiling begin?

   b) What will be the composition of the first bubble of vapor?

   c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

   d) What is the composition of the last trace of liquid?

2. An ethanol (e) and chloroform (c) liquid mixture contains a mole fraction of ethanol $x_e = 0.20$. At $25°C$, the vapor pressures of the pure liquids are 103 Torr for ethanol, and 295 Torr for chloroform. You may assume that gas phase mixtures of ethanol and chloroform vapors behave like ideal gases.

   a. If both components obey Raoult's law, what is the total vapor pressure p_T above the solution?

   b. Calculate ΔG for a solution that is formed at $25°C$ by combining two containers, one containing 0.2 moles of pure liquid ethanol, and the other containing 0.8 moles of pure liquid chloroform.

   c. The actual observed total pressure of the vapor above the solution of part (a) is 304 Torr. Is the Henry's law constant for ethanol K_e mixed with chloroform such that:

      i. $K_e > 103\,Torr$
      ii. $K_e = 103\,Torr$
      iii. $K_e < 103\,Torr$

Colligative Properties:

1. Consider the following data:

$$\Delta H_{vap}\left(H_2O\right) = 40kJ/mol$$
$$\Delta H_{fus}\left(H_2O\right) = 6.0kJ/mol$$

   a. One gram of pure crystalline substance A (ammonium acetate) known to have a molecular weight of $7.7\times10^{-2}kg$ is dissolved in 1.0 kg of pure water. What is the expected freezing point depression in degrees Celsius?

   b. Your answer to the previous question is based on several assumptions. What are those assumptions?

   c. If the observed freezing point depression is larger than your prediction in part A, what is the most likely reason for this departure from the standard model for colligative properties?

2. An unknown non-volatile solid is dissolved in 100g of water. At $26°C$, the vapor pressure of the solution was observed to be 24.75 bar, whereas the vapor pressure of pure water at the same temperature is 25.20 bar. The molecular weight of the unknown compound is 120 g/mole. Calculate the mass of the unknown solid in the solution.

3. There is a $10g\cdot L^{-1}$ solution of polystyrene and benzene. Solution density is $0.88g\cdot cm^{-3}$. The equilibrium height of the column is 11.5 cm at $25°C$. Find the average molecular weight of polystyrene.

4. An aqueous solution of NaCl is separated from a solution of pure water by a membrane permeable only to water. There is a piston above the NaCl solution so that its pressure can be adjusted.

   a. Suppose we add 0.1 moles of NaCl to 2L of water at T = 298 K. What is the osmotic pressure of the solution?

   b. One method of purifying salt water is to apply pressure to such a system. Do you think this process is more efficient at low temperatures or high temperatures?

Kinetics:

1. Consider the recombination reaction: $3A(g)+M(g)=A_3(g)+M(g)$

   The empirical rate law is believed to have the form: $\frac{dP_{A_3}}{dt}=kP_M^{\alpha}P_{A_2}^{\beta}P_A^{\gamma}$,
   where P is pressure (in bar) and α, β, γ are the orders with respect to M, A_2 and A, which are to be determined by initial rate data. . [Note that A_2 is not a typo! The species A_2 is found empirically to be involved in the reaction mechanism.]

   a) The rate of the reaction can be monitored by observing either $\frac{dP_A}{dt}$ or $\frac{dP_{A_3}}{dt}$. What is the relationship between $\frac{dP_A}{dt}$ and $\frac{dP_{A_3}}{dt}$ imposed by the reaction stoichiometry?

   b) What are the units of k for the empirical rate law as written?

   c) The observed initial rates obtained from measurement of P_{A3} at t = τ and at t = 0 initial pressures (designated by P^o) are:

P_A^o, bar	P_{A2}^o, bar	P_M^o, bar	$\frac{P_{A3}(\tau)-P_{A3}^o}{\tau}$, bar/s
0.01	0.01	1.00	1.0
0.02	0.01	1.00	4.0
0.02	0.02	1.00	8.0
0.02	0.01	0.5	2.0

   What are the values of α, β, γ, and k?

2. Consider the following reaction: $A + B \underset{K\text{-}1}{\overset{K1}{\rightleftharpoons}} I \xrightarrow{K2} P$

   a. When is the pre-equilibrium approximation valid?

   b. When is the steady-state approximation valid?

   c. Use the pre-equilibrium approximation to derive the rate law for the reaction.

   d. In 5.12 you studied the S_N1 mechanism for nucleophilic substitution. For this reaction would the steady-state or pre-equilibrium approximation be more appropriate?

3. Consider the reaction: $2A + B \rightarrow D$

Suppose that the mechanism of this reaction is found to consist of the elementary reactions:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \quad .$$

$$A + C \xrightarrow{k_2} D$$

a. Write the equations for:

$$\frac{d[C]}{dt} =$$

$$\frac{d[D]}{dt} =$$

b. For which species in the mechanism is it appropriate to impose the steady-state approximation? For this species, find the steady-state concentration.

c. Use the steady-state approximation to derive the rate law for $\frac{d[D]}{dt}$ in terms of [A], [B], and the rate coefficients k_1, k_{-1}, and k_2.

d. If $k_2[A]_0 >> k_{-1}$, what are the apparent orders of the reaction with respect to [A] and [B]? Also, what is the effective rate coefficient (expressed in terms of k_1, k_{-1}, k_2 and $[A]_0$)?

e. Same as the previous question, except for $k_2[A]_0 << k_{-1}$.

f. Suppose $[A]_0 = [B]_0 = 0$, but $[C]_0 \neq 0$. What would be the initial decay rate of [C]? What would be the final value of [D] (expressed in terms of $[C]_0$) assuming that C is completely consumed in the reaction?

4. **Free radical kinetics**: In lecture #30, we treated the free radical decomposition of acetaldehyde. The mechanism, including side reactions, consists of the following six elementary steps:

a. The ultimate goal of this problem is to find the conditions which enable you to control the relative production rates of CH_4 and H_2. Write the rate equations for the formation of CH_4 and H_2:

$$\frac{d[CH_4]}{dt} =$$

$$\frac{d[H_2]}{dt} =$$

b. There are four free radical species to which the steady state approximation applies: $H\bullet, H\dot{C}O, CH_3\dot{C}O, \bullet CH_3$. Write (but do not yet attempt to solve) the steady-state equation for each free radical.

$$\frac{d[H\bullet]}{dt} = 0 =$$

$$\frac{d\left[H\dot{C}O\right]}{dt} = 0 =$$

$$\frac{d\left[CH_3\overset{\bullet}{C}O\right]}{dt} = 0 =$$

$$\frac{d[\bullet CH_3]}{dt} = 0 =$$

c. Solve for $[H\overset{\bullet}{C}O]_{SS}$:

d. Solve for $[H\bullet]_{SS}$ and use $[H\overset{\bullet}{C}O]_{SS}$ to simplify your expression for $[H\bullet]_{SS}$ so that it contains only rate coefficients and no concentrations (other than $[H\bullet]_{SS}$ itself).

e. Solve for $[CH_3\overset{\bullet}{C}O]_{SS}$ in terms of $[\bullet CH_3]$:

f. Solve for $[\bullet CH_3]_{SS}$ and use the result you obtained for $[CH_3\overset{\bullet}{C}O]_{SS}$ to simplify the expression for $[\bullet CH_3]_{SS}$. (Hint: You will not need to use the quadratic formula if you have done the algebra correctly).

g. Write an equation, employing all relevant steady-state results from the previous parts, that gives the ratio of formation rates for H_2 and CH_4. Your expressions *must not contain any concentrations for the free radicals!*

h. Explain, using the results of part (h), how you would adjust the reaction conditions so that the % yield of H_2 is *minimized.*