1. Which of the following is a valid rate law if [A] is of order 2? (10 points)
   A) $k [A]^2 [B]$
   B) $k [A]^3 / [B]$
   C) $k [A] [C] / (1 - [A]^2)$
   D) $k [A] [B]$
   E) $k [B] / [A]$

2. If two reactions have $E_A = 100 \text{ kJ/mol}$ and $50 \text{ kJ/mol}$ respectively and have the same rate under identical conditions at 300K, which is faster under the same conditions at 400 K? (10 points)
   A) cannot be determined
   B) rates remain identical
   C) the first is faster
   D) the second is faster
   E) depends on concentrations present

3. If the concentration of A is doubled the rate of a given reaction increases by a factor of 8. What order is the reaction with respect to A? (10 points)
   A) 0
   B) 1
   C) 2
   D) 3
   E) 8

Do either three problems from 4 through 7

4. The reaction of a hydrogen halide, A, with an olefin, B, to give product P according to the stoichiometric relation $A + B \rightarrow P$ is proposed to occur by the following mechanism:

   $2 A \rightarrow A_2$ (fast equilibrium $K_1$)
   $A + B \rightarrow C$ (fast equilibrium $K_2$)
   $A_2 + C \rightarrow P + 2 A$ (slow, $k_3$)

   Based on this mechanism, derive an expression for the rate law in terms of [A], [B] and [P] only. If equal concentrations of A and B are mixed, the initial rate is $v_0$. What will be the effect on $v_0$ if [A] and [B] are doubled? What will be the effect on $v_0$ if [A] is unchanged and [B] is quadrupled? (20 points)

5. A reacts to form P. A plot of the reciprocal of the concentration of A versus time is a straight line. When the initial concentration of A is $1.0 \times 10^{-2}$ M, its half-life is found to be 20 minutes. What is the order of the reaction? Write a one-line mechanism which is consistent with the kinetics. What is the value of the rate constant for your mechanism? When the initial concentration of A is $3.0 \times 10^{-3}$ M, what will be the half-life? (20 points)

6. Suppose you have a reaction $A \rightarrow B$ which has an equilibrium constant $K_{eq}$. Derive an expression which relates the forward reaction rate constant $k_f$ to the reverse rate constant, $k_r$. Assuming you start with only A with concentration [A] = [A$_0$] and [B] = 0, write down the expression for d[A]/dt as a function of only [A], $K_{eq}$ and $k_f$. Write a solution to this equation for [A] as a function of only [A], $K_{eq}$ and $k_f$ (given that dy/dt + ay = c has the solution $y = (c/a) + c' \exp(-at)$ where $c'$ is determined by initial conditions). Draw a sketch of the concentrations of A and B as a function of time, indicating initial and equilibrium values. (20 points)

7. A unimolecular elementary reaction (A $\rightarrow$ B) has $\Delta H^\ddagger = 100 \text{ kJ/mol}$ and $\Delta S^\ddagger = -25 \text{ J/mol K}$. Calculate the rate constant for this reaction at 300K using the transition state theory approximations. Calculate the instantaneous reaction rate if [A] = [B] = $10^{-3}$ M solutions. Describe in your own words how a catalyst might modify the transition state model and increase the reaction rate. ($k_B = 1.3807 \times 10^{-23} \text{ J K}^{-1}, R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1}, h = 6.626 \times 10^{-34} \text{ J s}$) (20 points)