1) (5 points)

a) Write the equilibrium constant expression (K_c) for the following ~~reaction~~ reaction:

$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

$K_c = \frac{[PCl_3]^4 \to 1}{[P_4][Cl_2]^6}$

$K_c = \frac{1}{[Cl_2]^6}$

b) If the equilibrium concentrations of the reactants and products are 14.5 M, 0.250 M, and 11.4 M for P_4, Cl_2, and PCl_3, respectively, what is the value of K_c at 25 °C.

$K_c = \frac{1}{(0.250)^6} = 4096 = 4.10 \times 10^3$

c) Are products or reactants favored based on your value of K_c? products

2) (3 points) Which of the following would NOT have an effect on the rate of a reaction?

a) pressure, if the reaction involved gaseous reactants at a constant temperature $P \propto M$
b) concentration of products
c) mass of reactants → another way to talk about concentration or amounts
d) the order of a reactant concentration
(e) the energy of the bonds broken minus the energy of the bonds formed

Briefly explain your answer.

Statement (e) is equivalent to $\Delta H°$. The beginning and ending bond energies do not indicate what and how collisions take place to form products from reactants.

3) (10 points, 5 extra credit points if all correct)
Data for the reaction A + B + 3C ------> D are given below.

a) Which of the following experimental rate laws (a-j) is correct?

Trial	[A], M	[B], M	[C], M	Initial Rate, M/s
1	0.030	0.060	0.030	4.0×10^{-5}
2	0.030	0.030	0.030	2.0×10^{-5}
3	0.060	0.060	0.030	4.0×10^{-5}
4	0.030	0.060	0.015	4.0×10^{-5}

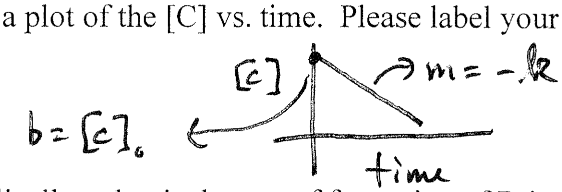
a) k[A][B][C]
b) $k[A]^2[C]$
c) $k[A]^2[B]^2$
(d) k[B]
e) $k[A]^2$
f) $k[B][C]^2$
g) $k[A]^2[B]$
h) k[A][C]
i) $k[A][B]^2[C]$
j) $k[C]^4$

answer: D

b) What is the overall order of the reaction? 1

c) What are the units of the rate constant, k? s^{-1}

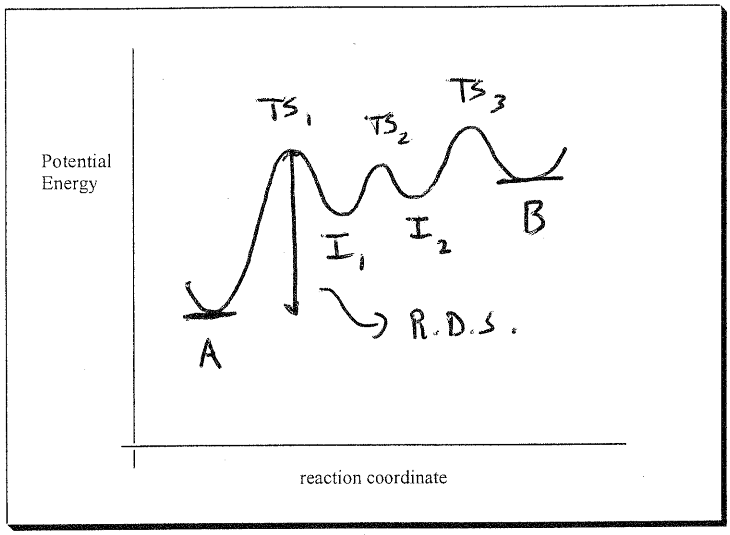
d) Sketch a plot of the [C] vs. time. Please label your axis and identify the slope and the intercept.



e) Symbolically, what is the rate of formation of D in terms of C?

rate of rxn $= -\frac{1}{3}\frac{\Delta[C]}{\Delta t} = \frac{\Delta[D]}{\Delta t}$ = rate of formation of D

) (10 points) **Using the blank reaction coordinate shown below, draw the reaction coordinate for an endothermic reaction (A -----> B) with 2 intermediates whose first step is rate determining. Clearly identify the intermediates, transition states and relative energies of all species.**



5) (10 points) **The reaction and experimental rate law for the gas phase reaction of nitric oxide with chlorine to produce nitrosyl chloride (used to bleach flour):**

$2\ NO(g) + Cl_2(g)$ ----------> $2\ NOCl(g)$ and rate = $k_{observed}[NO]^2[Cl_2]$

a) One proposed mechanism begins with the following elementary step, $NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)$. If this step is a fast step, propose a second rate limiting step that is consistent with the overall stoichiometry. Show that the two step mechanism is consistent with the overall stoichiometry.

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2 \quad \text{fast}$$

$$NOCl_2 + NO \xrightarrow{k_2} 2NOCl \quad \text{slow}$$

$$2NO + Cl_2 \rightarrow 2NOCl \quad ✓$$

b) Determine explicitly the rate law predicted by the mechanism in part a. Discuss its relevance to the experimental rate law.

$$rate_2 = k_2[NOCl_2][NO]$$

$$rate_1 = rate_{-1} \rightarrow k_1[NO][Cl_2] = k_{-1}[NOCl_2]$$

$$[NOCl_2] = \frac{k_1}{k_{-1}}[NO][Cl_2] \qquad rate_2 = \frac{k_2 k_1}{k_{-1}}[NO]^2[Cl_2]$$

mechanistic rate law is consistent w/ exp. rate law

) Now propose a mechanism that is consistent with the overall stoichiometry and experimental rate law that would have the **fewest** elementary steps.

$$2NO + Cl_2 \xrightarrow{k_1} 2NOCl_2 \qquad rate = k_1 [NO]^2 [Cl_2]$$

d) How could one distinguish, experimentally, between the mechanism in part a and part c? Be sure to consider transition state theory in your response.

Part a: step 1 generates an intermediate that may be observable, thus additional exp. evidence to favor Mech A over Mech. C.

e) Is it possible to discuss the reasonableness of each mechanism based on the molecularity of each elementary step? If so, discuss this explicitly.

Yes, Mech. C is a termolecular elementary step which is rare - the probability that 3 particles will collide with the correct energy + orientation to produce products is low. Mech A is more reasonable in that each step is a more likely bimolecular collision.

f) (*extra credit*, 2 points) Propose one mechanism that is consistent with the stoichiometry of the overall reaction but **not** with the experimental rate law (regardless of slow and fast steps).

A) $Cl_2 \rightleftharpoons 2Cl$

$Cl + NO \rightarrow NOCl$

$Cl + NO \rightarrow NOCl$

B) $NO + Cl_2 \rightarrow NOCl + Cl$

$Cl + NO \rightarrow NOCl$

) (12 points) The following data is obtained for the reaction $2C_4H_{6\,(g)}$ --------> $C_8H_{12\,(g)}$ at a given temperature.

t = 0 s	$[C_4H_6]_0$ = 0.01000 M
1000	0.00625
1800	0.00476
2800	0.00370
3600	0.00313
4400	0.00270
5200	0.00241
6200	0.00208

1st t½ (bracket: 0.01000 M to 0.00476)

2nd t½ (bracket: 0.00476 to 0.00241)

a) Determine the order of this reaction and calculate the rate constant value (with units)?

b) What is the rate of reaction when $[C_4H_6]$ = 0.00100 M?

c) Calculate the half-life of this reaction if the $[C_4H_6]_0$ is 10.0 M. Calculate the half-life of this reaction if the $[C_4H_6]_0$ is 5.0 M. Compare your results and explain any similarities or differences.

d) What factors will change the value of the rate constant k?

catalyst and temperature (and mechanism)

e) What factors will change the energy of activation, E_a?

catalyst

(a) The first $t_{1/2}$ is at ~ 1800s

The second $t_{1/2}$ is at ~ 5200s

By process of elimination, the order of C_4H_6 is not 1st since the $t_{1/2}$ is not constant, and it is not 0th since $\frac{-\Delta[C_4H_6]}{\Delta t}$ is not constant, thus the likely order is 2nd.

Constant k method

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$k = \left(\frac{1}{[A]_t} - \frac{1}{0.01000}\right) / t$$

$k_{1000\,s} = 0.0600\ M^{-1} \cdot s^{-1}$

$k_{3600\,s} = 0.0610\ M^{-1} \cdot s^{-1}$

$k_{6200\,s} = 0.0614\ M^{-1} \cdot s^{-1}$

$k_{avg} = 0.0608\ M^{-1} \cdot s^{-1}$

(c) $t_{1/2} = \frac{1}{k[A]_0}$

$t_{1/2\ 10.0\,M} = 1.64$ s

$t_{1/2\ 5.0\,M} = 3.3$ s

As the conc. decreases the $t_{1/2}$ increases. This makes sense for a 2nd order rxn since two molecules of C_4H_6 are required to collide and form a transition state. Less reactant, less collisions, more time to react

b) $rate = (0.0608\ M^{-1} \cdot s^{-1})([C_4H_6]^2) = (0.0608\ M^{-1} \cdot s^{-1})(0.00100\ M)^2$

$= 6.08 \times 10^{-8}\ \frac{M}{s}$