Chem 231 Problem Set 1

1. The half-life of ^{14}C is 5730 years. What is the rate coefficient governing the radioactive decay pathway, and what is the decay pathway? Calculate the time for fractions of 0.5, 0.75, 0.95 and 0.99 of the original ^{14}C in a sample to decay. What in your opinion is the effective span of time over which ^{14}C dating of archeological samples are valid. State any assumptions made.

2. For the reaction A + B → C + D the following data were obtained:

Time (sec)	0	178	275	530	860	1500
[A] x 10^3 (mol dm^{-3})	9.8	8.9	8.6	8.0	7.3	6.5
[B] x 10^3 (mol dm^{-3})	4.8	4.0	3.7	3.0	2.3	1.5

Calculate the rate coefficient and confirm the order of the reaction. How can the rate constant be obtained graphically?

3. The following data were obtained for a reaction:

T (°C)	k x 10^4 (sec^{-1})
35	3.81
40	5.11
45	7.67
50	12.70

Graphically extract the energy of activation for the reaction.

4. For a first-order parallel reaction where A can decompose into B or C, the Arrhenius (A) or pre-exponential factors for formation of B and C, respectively, are 10^{10} sec^{-1} and 10^8 sec^{-1}. The corresponding activation energies E_a are 150 and 75 kJ mol^{-1}, respectively. At what temperature are the two products formed at the same rate?

5. The Rice-Herzfeld mechanism for the decomposition of ethane to ethylene and hydrogen involves two initiation steps (1 and 2), two propagation steps (3 and 4) and a termination step as follows:

(1)	C_2H_6	→	$2\ CH_3$	k_1
(2)	$CH_3 + C_2H_6$	→	$CH_4 + C_2H_5$	k_2
(3)	C_2H_5	→	$C_2H_4 + H$	k_3
(4)	$H + C_2H_6$	→	$C_2H_5 + H_2$	k_4
(5)	$H + C_2H_5$	→	C_2H_6	k_5

Applying the steady state approximation to the radical intermediates CH_3, C_2H_5 and H, show that

$$-d[C_2H_6]/dt = [\ (3/2)k_1 + (k_1^2/4 + (k_1k_3k_4)/k_5)^{1/2}][C_2H_6]$$

6. The formation of gaseous phosgene $COCl_2(g)$ from $CO(g)$ and $Cl_2(g)$ and its decomposition into $CO(g)$ and $Cl_2(g)$ have been explained by two alternative mechanisms:

I.

$$Cl_2 \leftrightarrow 2Cl \quad \text{(rapid equilibrium, } K_1\text{)}$$

$$Cl + CO \leftrightarrow COCl \quad \text{(rapid equilibrium, } K_2\text{)}$$

$$COCl + Cl_2 \rightarrow COCl_2 + Cl$$

II.

$$Cl_2 \leftrightarrow 2Cl \quad \text{(rapid equilibrium, } K_1\text{)}$$

$$Cl + Cl_2 \leftrightarrow Cl_3 \quad \text{(rapid equilibrium, } K_2\text{)}$$

$$Cl_3 + CO \rightarrow COCl_2 + Cl$$

Derive the expression for $d(COCl_2)/dt$ in terms of the reactants CO, Cl_2 and the product $COCl_2$ for both mechanisms. Indicate whether or not kinetic measurements can determine which mechanism is correct.

7. A general way to discuss branched chain reactions is in terms of the following mechanism:

$$nA \rightarrow R \quad k_1$$
$$R + A \rightarrow P + \alpha R \quad k_2$$
$$R \rightarrow nA \quad k_3$$

In these equations, A is a substance decomposing to give product, P, and R is a reactive chain carrier. Step two is a branching step if $\alpha > 1$, *i.e.*, if more radicals are produced than consumed.

i) Assuming the concentration of radicals R to be in steady state, what is the rate law for the production of P?

ii) From your answer to part (i) determine the condition on α which predicts explosion, i.e., which predicts $dP/dt \rightarrow \infty$.