PROBLEM SET 2-1

1) Discuss the following overall reactions with respect to order

(a) $2A \longrightarrow 4B+C \quad -r = kC_A$

(b) $A+B \longrightarrow C \quad -r = kC_A C_B^{-1}$

(c) $2A+B \longrightarrow 2C \quad -r = kC_A C_C^{-1/2}$

(d) $2A+B \longrightarrow 2C \quad -r = kC_A^{2} C_B$

2) The second order rate constant for the reaction $A + B \longrightarrow C + D$ is 0.11 L/mol.sec. What is the concentration of C after 10 min. when the reactants are mixed with initial concentration of $[A]_o$ = 0.05 mol/L, $[B]_o$ = 0.1 mol/L

3) Hydrogen peroxide reacts with thiosulfate ion slightly acidic solution as follows:

$$H_2O_2 + 2S_2O_3^{-2} + 2H^{+2} \longrightarrow 2H_2O + S_4O_6^{-2}$$

This reaction rate is independent of hydrogen ion concentration in the pH range 4 to 6. The following data were obtained at 25 °C and pH 5. Initial concentrations:
$[H_2O_2]$ = 0.036 mol/L, $[S_2O_3^{-2}]$ = 0.0204 mol/L.

t/min	16	36	43	52
$[S_2O_3^{-2}]/10^{-3}$ mol/L	10.3	5.18	4.16	3.13

(a) What is the order? **(b)** What is the rate constant?

4) (a) Integrate the rate equation

$$-\frac{dC}{dt} = kC^{1/2}$$

(b) How could a group of data be checked graphically to see if they describe a half order
(c) Derive an expression for the half life $t_{1/2}$ interms of k and C_o
(d) What is the unit of k

5) A solution A is mixed with an equal volume of a solution of B containing the same number of moles and the reaction $A + B \longrightarrow C$ occurs. At the end of 1 h, A is 75 % reacted. How much of A will be unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B (b) first order in both A and B (c) zero order in both A and B.

6) Show that for a first order reaction $R \longrightarrow P$ the concentration of the product can be represented as a function of time $[P] = a+bt+ct^2+\ldots\ldots$ and express a, b, c, interms of $[R]_o$ and k.

7) The following table gives kinetic data for the following reaction at 25 °C.
$OCl^{-1} + I^- \longrightarrow OI^{-1} + Cl^{-1}$

$[OCl^-]$ (mol/L)	$[I^-]$ (mol/L)	$[OH^-]$ (mol/L)	$d[OI^{-1}]/dt(10^{-4}$mol/Ls)
0.0017	0.0017	1	1.75
0.0034	0.0017	1	3.5
0.0017	0.0034	1	3.5
0.0017	0.0017	0.5	3.5

What is the rate law for the reaction and what is the value of the rate constant.

8) Consider the gaseous reaction; $\text{cyclo-}C_5H_8 \longrightarrow H_2 + \text{cyclo-}C_5H_6$
If P is the total pressure
(a) How dP/dt related to $-d[C_5H_8]/dt$
(b) If the reaction is first order what are the units of k
(c) Derive the integrated rate equation interms of P and P_o

9) The composition of a liquid reaction $2A \longrightarrow B$ was followed by spectrophotometric method

t(min)	0	10	20	30	40	∞
[B] (mol/L)	0	0.089	0.153	0.2	0.23	0.312

Show the order is first order and find k.

10) For the reaction $A + B \longrightarrow C + D$ $[A]_o$=400 mmol/L, $[B]_o$=0.4 mmol/L gave the following data

t(s)	0	120	240	360	∞
10^4 [C] (mol/L)	0	2	3	3.5	4

And a run $[A]_o$=0.4 mmol/L, $[B]_o$=1000 mmol/L gave the following data

t(s)	0	69	208	485	∞
10^4[C] (mol/L)	0	2	3	3.5	4

Find the rate law and constant if $-r=k[A]^2[B]$

11) For the reaction $OCl^{-1} + I^{-1} \longrightarrow OI^{-1} + Cl^{-1}$ in aqueous solutions at 25 °C initial rates r_o as a function of initial concentrations

10^3 [OCl^{-1}] (mol/L)	4	2	2	2
10^3 [I^{-1}] (mol/L)	2	4	2	2
10^3 [OH^{-1}] (mol/L)	1000	1000	1000	250
10^3 r_o (mol/Ls)	0.48	0.5	0.24	0.94

Find the rate constant.

12) The decompositions of benzendiazonium chloride in water is given by
$C_6H_5N_2^+ + H_2O \longrightarrow C_6H_5OH + N_2 + H_3O^+$
Since the concentration of water is nearly fixed we can determine the pseudo order with respect to benzendiazonium chloride as with a reaction having a single reactant. Moelwyn-Hughes and Johnson followed the reaction at 40°C by monitoring the pressure of nitrogen evolved by the reaction. The following data were taken with the pressure in arbitrary units.

Time (s)	0	120	360	600	1200	2400	3600
P∞ - P	60	21.55	19.45	17.6	13.62	8.15	4.88

a) Determine the pseudo first order rate constant at this temperature.
b) Find the pressure of evolved nitrogen at 1500s.

13) At t=0 butadiene was introduced to an empty vessel at 326°C and dimerization takes place $2C_4H_6 \longrightarrow C_8H_{12}$ followed by monitoring the total pressure. Show that reaction is second order. Find the rate constant.

Time (s)	0	0.731	1.751	2.55	3.652	5.403	7.14
P(torr)	632	584.2	535.4	509.3	482.8	453.3	432.8

14) The reaction between ethylene bromide (A) and potassium iodide (B) in 99% methanol (inert) has been found to be first order with respect to each reactant (second order overall). The reaction can be presented by,

$C_2H_4Br_2 + KI \longrightarrow C_2H_4 + 2KBr + KI_3$ or $A + 3B \longrightarrow$ Products

Derive an equations for calculating the second-order rate constant k.