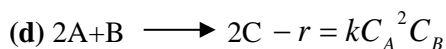


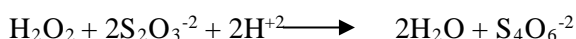
PROBLEM SET 2-1

1) Discuss the following overall reactions with respect to order



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 $[A]_0 = 0.05$ mol/L, $[B]_0 = 0.1$ mol/L

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



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

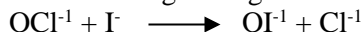
(c) Derive an expression for the half life $t_{1/2}$ interms of k and C_0

(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 $[P] = a + bt + ct^2 + \dots$ and express a, b, c, interms of $[R]_0$ and k.

7) The following table gives kinetic data for the following reaction at 25 °C.



$[OCl^-]$ (mol/L)	$[I^-]$ (mol/L)	$[OH^-]$ (mol/L)	$d[OI^-]/dt(10^{-4} \text{mol/Ls})$
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; $\text{cyclo-C}_5\text{H}_8 \longrightarrow \text{H}_2 + \text{cyclo-C}_5\text{H}_6$
 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_0

- 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 $A + B \longrightarrow C + D$ $[A]_0=400$ mmol/L, $[B]_0=0.4$ 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 $[A]_0=0.4$ mmol/L, $[B]_0=1000$ 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 $OCI^{-1} + I^{-1} \longrightarrow OI^{-1} + CI^{-1}$ in aqueous solutions at 25 °C initial rates r_0 as a function of initial concentrations

$10^3 [OCI^{-1}]$ (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
$10^3 r_0$ (mol/Ls)	0.48	0.5	0.24	0.94

Find the rate constant.

- 12) The decompositions of benzenediazonium chloride in water is given by



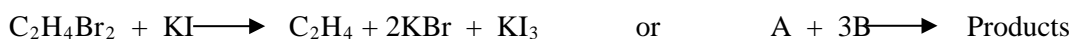
Since the concentration of water is nearly fixed we can determine the pseudo order with respect to benzenediazonium chloride as with a reaction having a single reactant. Moelwyn-Hughes and Johnson followed the reaction at 40°C by monitoring the pressure of nitrogen evolved by the reaction. The following data were taken with the pressure in arbitrary units.

Time (s)	0	120	360	600	1200	2400	3600
$P^\infty - P$	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,



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