PROBLEM SET – 2-2
(CHEMICAL KINETICS)

1) 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,

$$C_2H_4Br_2 + 3KI \rightarrow C_2H_4 + 2KBr + KI_3 \qquad \text{or} \quad A + 3B \rightarrow \text{Products}$$

a) Derive an equation for calculating the second-order rate constant k.

b) At 60°C in one set of experiments, for which C_{Ao} = 0.0266 and C_{Bo} = 0.2237 mol/L, the bromide (A) was 59.1 % reacted at the end of 15h. Calculate the value of the rate constant, k, and specify the units.

2) The first order reaction **A→B** is carried out in a constant-volume batch reactor (k=0.23 min^{-1}).

a) Derive the equation for time as a function of reactant concentration.

b) Calculate the time necessary to reduce the number of moles of A to 1 % of its initial value.

3) For a gas reaction at 400 K the rate is reported as;

$$-r_A = -\frac{1}{V}\frac{dn_A}{dt} = kC_A^2, \quad mol/m^3.s$$

What is the value of the rate constant for this reaction if the rate equation is expressed as;

4) The rate constants for two different reactions are given:

for rxn. 1 — k=4.852x10^8 s^{-1} at 190°C and
k=2.203x10^4 s^{-1} at 103°C

for rxn. 2 — k=4.852x10^8 s^{-1} at 190°C and
k=8.886x10^6 s^{-1} at 103°C

a) Calculate the activation energy for the two reactions.

b) Find out the temperature rises needed to double the reaction rate, at 103°C for each reaction.

c) Comment on the results of part a and b.

5) Liquid A decomposes in a batch reactor. Initially there is 1 mole/lt A. 50% of A is converted in a 5 minute run. How much longer would it take to reach 75% conversion?

a) For first order kinetics. **b)** For second order kinetics.

6) The gas phase reaction **A→B+C** is to be carried out isothermally in a 20 dm^3 constant-volume batch reactor. Twenty moles of pure A is initially placed in the reactor. The reactor is well mixed.

a) If the reaction is first order : $-r_A = k\,C_A$ with k= 0.865 min^{-1}
Calculate the time necessary to reduce the number of moles of A in the reactor to 0.2 mole.

b) If the reaction is second order : $-r_A = k\,C_A^2$ with k= 2 $dm^3/mol.min^{-1}$.
Calculate the time necessary to consume 19.0 mol of A.

c) If the temperature is 127°C, what is the initial total pressure? What is the final total pressure assuming the reaction goes to completion ?

7) The first order reversible liquid reaction. **A** $\rightleftarrows$ **R**, C_{Ao} = 0.5 mol/liter, C_{Ro} =0
takes place in a batch reactor. After 8 minutes, conversion of a is 33.3 % while equilibrium conversion is 66. 7 %. Find the rate equation for this reaction.

8) Aqueous A at a concentration of C_{A0}= 1 mol/L is introduced into a batch reactor where it reacts away to form product R according to stoichiometry **A→R.** The concentration of A in the reactor is monitored at various times, as shown below:

Table

t, min	0	100	200	300	400
C_A, mol/m^3	1000	500	333	250	200

For C_{A0}= 500 mol/m^3, find the conversion of reactant after 5 hours in the batch reactor.

9) Find the overall order of the irreversible reaction

$$2\,H_2 + 2\,NO \rightarrow N_2 + 2\,H_2O$$

From the following constant-volume data using equimolar amounts of hydrogen and nitric oxide :

Table

Total Pressure, mm Hg	200	240	280	320	360
Half-life, sec	265	186	115	104	67

10) Moelwn-Hughes has tabulated the following values of the rate constant for the reaction:

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$$

T, °K	288.1	298.1	313.1	323.1	338.1
k, sec^{-1}	$1.04x10^{-5}$	$3.38x10^{-5}$	$2.47x10^{-4}$	$7.59x10^{-4}$	$4.87x10^{-3}$

If the rate constant obeys Arrhenius law, determine the pre-exponential factor and activation energy.