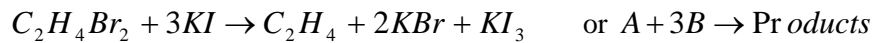


**PROBLEM SET – 2-2**  
**(CHEMICAL KINETICS)**

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,



- a) Derive an equation for calculating the second-order rate constant k.  
b) At 60°C in one set of experiments, for which  $C_{A0} = 0.0266$  and  $C_{B0} = 0.2237$  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  $A \rightarrow B$  is carried out in a constant-volume batch reactor ( $k=0.23 \text{ min}^{-1}$ ).

- 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;

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

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                       $k=4.852 \times 10^8 \text{ s}^{-1}$  at 190°C and  
    $k=2.203 \times 10^4 \text{ s}^{-1}$  at 103°C

for rxn. 2                       $k=4.852 \times 10^8 \text{ s}^{-1}$  at 190°C and  
    $k=8.886 \times 10^6 \text{ s}^{-1}$  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/lit 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  $A \rightarrow B + C$  is to be carried out isothermally in a 20 dm<sup>3</sup> 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  $k = 0.865 \text{ min}^{-1}$

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  $k = 2 \text{ dm}^3/\text{mol}\cdot\text{min}^{-1}$ .

Calculate the time necessary to consume 19.0 mol of A.

c) If the temperature is  $127^\circ\text{C}$ , 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.  $A \rightleftharpoons R$ ,  $C_{A0} = 0.5 \text{ mol/liter}$ ,  $C_{R0} = 0$  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.

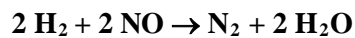
8) Aqueous A at a concentration of  $C_{A0} = 1 \text{ mol/L}$  is introduced into a batch reactor where it reacts away to form product R according to stoichiometry  $A \rightarrow R$ . The concentration of A in the reactor is monitored at various times, as shown below:

**Table**

|                        |      |     |     |     |     |
|------------------------|------|-----|-----|-----|-----|
| t, min                 | 0    | 100 | 200 | 300 | 400 |
| $C_A, \text{ mol/m}^3$ | 1000 | 500 | 333 | 250 | 200 |

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

9) Find the overall order of the irreversible reaction

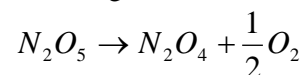


From the following constant-volume data using equimolar amounts of hydrogen and nitric oxide :

**Table**

|                              |     |     |     |     |     |
|------------------------------|-----|-----|-----|-----|-----|
| <b>Total Pressure, mm Hg</b> | 200 | 240 | 280 | 320 | 360 |
| <b>Half-life, sec</b>        | 265 | 186 | 115 | 104 | 67  |

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



|                      |                       |                       |                       |                       |                       |
|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| T, °K                | 288.1                 | 298.1                 | 313.1                 | 323.1                 | 338.1                 |
| k, sec <sup>-1</sup> | $1.04 \times 10^{-5}$ | $3.38 \times 10^{-5}$ | $2.47 \times 10^{-4}$ | $7.59 \times 10^{-4}$ | $4.87 \times 10^{-3}$ |

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