Chapter -4- CHEMICAL KINETICS

LEVEL-1

1. **Express rate of reaction and order of reaction in relative terms.**
   Ans**.** Rate = $k[A]^x[B]^y$
   Order of reaction = $x + y$

2. **Slow reactions require less activation energy as compared to fast reactions. Do you agree with the statement?**
   Ans No, the statement is not correct. The rate of a reaction is inversely proportional to the activation energy. This means that the slow reactions will need more activation energy than the fast reactions**.**

3. **What is an elementary reaction?**
   Ans- The reaction taking place in single step is an elementary reaction.
   $N_2 + O_2 \rightarrow 2NO$

4. **Write one reaction of fractional order.**
   Ans -The reaction with fractional order is :-
   $CO + Cl_2 \longrightarrow COCl_2$
   Rate = $k\,[CO]^2\,[Cl_2]^{1/2}$

5. **For the reaction**
   $2N_2O_5$ (g) → $4NO_2$ (g) + O_2 (g)
   the concentration of NO_2 increases by 3 x 10^3 mol/ litre in 8 seconds. What is the rate of the reaction?
   Ans- Rate of reaction = ¼ $d[NO_2]/dt$
   = ¼ x 3.0 x 10^{-3}/8 mol l^{-1} s^{-1}
   = 9.37 x 10^{-5} mol l^{-1} s^{-1}

6. **One gram of pulverized wood burns faster than a gram piece of wood. Explain.**
   Ans. One gram of pulverized wood has more surface area and therefore, it burns faster than 1 gram of wood.

7. **What is meant by effective collision ?**
   Ans- -The collision that leads to the formation of product molecule is called effective collision

8. **Explain the term activated complex .**

Ans - It is defined as intermediate compound between reactants and products which is highly unstable ,has the highest energy and readily changes into product

9. **Define pseudo unimolecular reaction . Give two examples .**
Ans - The reaction which is bimolecular but its order is one is called pseudo unimolecular reaction ,
e.g. $CH_3COOC_2H_5+H_2O$ in presence of H^+ → $CH_3COOH+C_2H_5OH$

10. **For a reaction: A + B → Products.**
The rate law expression is, rate = k $[A]^{1/3}$.$[B]^2$
What is the order of the reaction?
Ans: Order of the reaction = 1/3 + 2 = 7/2

LEVEL -2

1. **The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?**
Ans. For a first order reaction,

$$k = \frac{1}{t}[[A_0] - [A]_t]$$

$$\therefore t = \frac{1}{k}[[A_0] - [A]_t]$$

Given k = 0.0030 mol $L^{-1}S^{-1}$
A_0 = 0.10 M
A_t = 0.075 M
Substituting values

$$t = \frac{1}{0.0030}[0.10 - 1.0075]$$

$$= 8.33 \text{ s}$$

Hence, the concentration of A will fall from 0.10 M to 0.075 M in 8.33 seconds.

2. **The decomposition of NH_3 on platinum surface, $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ is a zero order reaction with k = 2.5 × 10^{-4} M s^{-1}. What are the rates of production of N_2 and H_2?**
Ans. Rate for the given reaction is given by
k = 2.5 × 10^{-4} M s^{-1}
Therefore, for the given reaction, rate is given by

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k = 2.5 \times 10^{-4} \text{ M s}^{-1}$$

Hence, the rate of production of N_2 is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4}\ M\ s^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4}\ M\ s^{-1}$$

$$= 7.5 \times 10^{-4}\ M\ s^{-1}$$

3. **Write the rate law and order for the following reaction:-**
$AB_2 + \rightarrow AB_2C + C$ (slow)
$AB_2 + C \rightarrow AB_2C$ (fast)
Ans: The rate law for the reaction is:-
$R = k [AB_2] [C_2]$
order = 1+1 = 2

4. **What is shape of graph between log k vs. 1/t ? What is the relationship between its slope and activation energy E_a ?**

Ans :- The shape of graph is straight line .

Slope = $-E_a/ 2.303\ R$

5. **Time required to decompose SO_2Cl_2 to half of its initial concentration is 60 min. If the decomposition is a first order reaction, calculate the rate constant of the reaction.**
Ans- For the first order reaction:-
Rate constant (k) = $0.693 / t_{1/2}$
= 0.693/ 60 x 60 sec
= $1.924 \times 10^{4}\ s^{-1}$

LEVEL-3

1. **The following experimental data was collected for the reaction:**
$Cl_2(g) + NO\ (g) \rightarrow 2NOCl\ (g)$

Trial	Intial conc. $[Cl_2]$ mol L^{-1}	Intial conc [NO] mol L^{-1}	Intial rate mol $L^{-1}\ s^{-1}$
1	0.010	0.010	1.20×10^{-4}
2	0.010	0.030	10.8×10^{-4}
3	0.020	0.030	21.6×10^{-4}

Construct the rate equation for the reaction.

Ans – Let the rate law is $r = k[Cl_2]^x [NO]^y$
From trial 1. $1.20 \times 10^{-4} = k[0.010]^x[0.0010]^y$

From trial 2. $10.8 \times 10^{-4} = k[[0.010]^x [0.0030]^y$

From trial 3. $1.20 \times 10^{-4} = k[0.020]^x[0.0030]^y$

Dividing (2) by (1), $9 = 3^y$ y=2

Dividing (3) by (2), $2 = 2^x$ x=1

So the rate equation is $r = k[Cl_2]^1 [NO]^2$

Order of the reaction is 3

2. **Prove that $t_{99.9\%} = 10t_{½}$ in first order reaction .**

Ans :- $t_{99.9\%} = 2.303/k \log [A_0] /0.001[A_0]$

$=2.303/k \log 1000$

$=2.303 (3)/k$

$t_{99.9\%} = 6.93/k$

$t_{½} = 0.693/k$

therefore :- $t_{½} = 10\ t_{99.9\%}$

3. **The rate constant for a first order reaction is $60s^{-1}$ .How much time will it take to reduce initial concentration of the reactant to $(1/16)^{th}$ value ?**

Ans :- $k = (1/16)^{th}\ sec^{-1}$

$t = 2.303/k \log [A_0] /1/16[A_0]$

$t = 2.303/60 \log 16$

$= 2.303/60 (1.2041)$

$= 2.773/60$

$= 0.0462\ sec^{-1}$

4. **The decomposition of CI_2O_7 AT 400K In the gas phase to CI_2 and 0_2 is Ist order reaction**

After 55secs at 400k the pressure of CI_2o_7 falls from 0.062 to 0.044 atm. Calculate the rate constant. Calculate the pressure of CI_2O_7 after 100 secs of decomposition at this temp.

***Solution*: k**=2.303/t log a/a-x=2.303/55 log o.62 0.44

$=6.24x10^{-3}sec^{-1}$

When t = 100sec,

$6.24x10^{-3} = 2.303/100 \log 0.62/a-x$

log 0.62/a-x =$6.24x10^{-3}$ x100/2.303

=0.2709

a-x=0.033 atm

5. **The rate constant for the first order reaction of certain reaction is described by the equation:- $\log k(s^{-1})=14.34-(1.25x10^4K)/T$**

What is the activation energy for this reaction?

At what temperature, will the half-life period be 256 minutes?

Ans: HERE, $\log k=14.34-(1.25x10^4)/T$ ……(1)

By Arhenius equation,

$K=Ae^{-Ea/RT}$

ln=K/A=-Ea/RT or logk

=logA-Ea/2.303RT ……..(2)

Comparing eqns (1) and(2),

$Ea/2.303RT=1.25x10^4/T$ or Ea

$=1.25x10^4x2.303xR$

$=1.25x10^4x2.303x8.314J/mol$

=239.3KJ/mol

Now,

$K=0.693/t_{1/2}=0.693/256$

Substituting in equation (1),

$\log(0.693/256)=14.34-1.25x10^4/T$

$-2.56=14.34-1.25x10^4/T$

or T=739.6K.

6. **Find the two-third life , $t_{2/3}$, of a first order reaction in which k= $5.4x10^{-14}$ s^{-1} .**
Solution:-

The rate constant k for the first order reaction is expressed by the relation,

$k = 2.303/t \log(a/(a-x))$

$t = 2.303/k \log(a/(a-x))$

Substitute,

$t = t_{2/3}$, $k = 5.4 \times 10^{-14}\ s^{-1}$ $x = 2a/3$

$t_{2/3} = 2.303/5.4 \times 10^{-14}\ s^{-1} \log(a/(a-2a/3))$

$= 2.303/5.4 \times 10^{-14}\ s^{-1} \log 3$

$= 2.035 \times 10^{13}$ s

Two-third life of the given first order reaction is 2.035×10^{13} s

7. **A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.**

Solution: Let initial conc. of reactant be 'a', then conc. after 10 minutes will be

a-x= a- 20% of a= 80% of a

$a = \frac{80}{100} \times a = 4a/5 = 0.8a$

For the first order reaction, rate constant k can be expressed as,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t} \log \frac{a}{0.8a}$$

$$= \frac{2.303}{t} \log \frac{5}{4}$$

$$= \frac{2.303}{t} (\log 5 - \log 4)$$

$$= \frac{2.303}{10} (0.6990 - 0.6021)$$

$= 0.02232\ min^{-1}$

Knowing the rate constant k we can find time for 75% completion of reaction by using the relation:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

a-x = a- 75% of a= a/4 $t = t_{75\%}$

$$t_{75\%} = \frac{2.303}{0.02232} \log \frac{a}{a/4}$$

$$= \frac{2.303}{0.02232} \log 4$$

= 62.125 min.

8. **At 380^0C, the half life period for the first order decomposition of H_2O_2 is 360 minutes. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450^0C.**

Soln:-

$K_1 = 0.693/360$

$= 1.92 \times 10^{-3}$ min^{-1}

$\log k_2/k_1 = (Ea/2.303R)\,[(T_2-T_1)/T_1T_2]$

$= (200 \times 10^3) / (2.303 \times 8.314)\,[(723 - 653)/(653 \times 723)]$

$= (200 \times 10^3 \times 70)/(2.303 \times 8.314 \times 653 \times 723)$

$= 1.5487$

K_2/k_1 = Antilog (1.5487)

= 35.38

$K_2 = 35.38 \times 1.92 \times 10^{-3}$

$= 6.792 \times 10^{-2}$ min^{-1}

Rate at 450,

$t = (2.303/k_2) \log (100)/(100-75)$

$= (2.303)/(6.792 \times 10^{-3}) \log(100/25)$

$= (2.303 \times 0.6021)/(6.792 \times 10^2)$

= 20.415 minutes.