

Chapter -4- CHEMICAL KINETICS**LEVEL-1**

1. Express rate of reaction and order of reaction in relative terms.

Ans. Rate = $k[A]^x[B]^y$

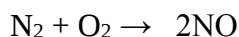
Order of reaction = $x + y$

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.

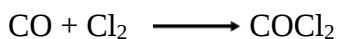
3. What is an elementary reaction?

Ans- The reaction taking place in single step is an elementary reaction.



4. Write one reaction of fractional order.

Ans -The reaction with fractional order is :-



$$\text{Rate} = k [CO]^2 [Cl_2]^{1/2}$$

5. For the reaction



the concentration of NO_2 increases by 3×10^3 mol/ litre in 8 seconds. What is the rate of the reaction?

$$\begin{aligned} \text{Ans- Rate of reaction} &= \frac{1}{4} \frac{d[NO_2]}{dt} \\ &= \frac{1}{4} \times \frac{3.0 \times 10^{-3}}{8} \text{ mol l}^{-1} \text{ s}^{-1} \\ &= 9.37 \times 10^{-5} \text{ mol l}^{-1} \text{ s}^{-1} \end{aligned}$$

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. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ in presence of $\text{H}^+ \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$

10. For a reaction: $\text{A} + \text{B} \rightarrow \text{Products}$.

The rate law expression is, $\text{rate} = k [\text{A}]^{1/3} . [\text{B}]^2$

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 $0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$. 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,

$$k = \frac{1}{t} [[\text{A}]_0 - [\text{A}]_t]$$

$$\therefore t = \frac{1}{k} [[\text{A}]_0 - [\text{A}]_t]$$

Given $k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$

$A_0 = 0.10 \text{ M}$

$A_t = 0.075 \text{ M}$

Substituting values

$$t = \frac{1}{0.0030} [0.10 - 0.075]$$

$$= 8.33 \text{ s}$$

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, $2\text{NH}_3(\text{g}) \xrightarrow{\text{Pt}} \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is a zero order reaction with $k = 2.5 \times 10^{-4} \text{ M s}^{-1}$. What are the rates of production of N_2 and H_2 ?

Ans. Rate for the given reaction is given by

$$k = 2.5 \times 10^{-4} \text{ M s}^{-1}$$

Therefore, for the given reaction, rate is given by

$$-\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k = 2.5 \times 10^{-4} \text{ M s}^{-1}$$

Hence, the rate of production of N_2 is

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

And, the rate of production of H_2 is

$$\begin{aligned}\frac{d[H_2]}{dt} &= 3 \times 2.5 \times 10^{-4} \text{ M s}^{-1} \\ &= 7.5 \times 10^{-4} \text{ M s}^{-1}\end{aligned}$$

3. Write the rate law and order for the following reaction:-



Ans: The rate law for the reaction is:-

$$R = k [AB_2] [C_2]$$

$$\text{order} = 1+1 = 2$$

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 .

$$\text{Slope} = -E_a / 2.303 R$$

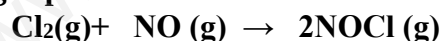
5. Time required to decompose SO_2Cl_2 to half of its initial concentration is 60 min. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans- For the first order reaction:-

$$\begin{aligned}\text{Rate constant (k)} &= 0.693 / t_{1/2} \\ &= 0.693 / 60 \times 60 \text{ sec} \\ &= 1.924 \times 10^{-4} \text{ s}^{-1}\end{aligned}$$

LEVEL-3

1. The following experimental data was collected for the reaction:



Trial	Initial conc. [Cl ₂] mol L ⁻¹	Initial conc [NO] mol L ⁻¹	Initial rate mol L ⁻¹ s ⁻¹
1	0.010	0.010	1.20 x 10 ⁻⁴
2	0.010	0.030	10.8 x 10 ⁻⁴
3	0.020	0.030	21.6 x 10 ⁻⁴

Construct the rate equation for the reaction.

Ans – Let the rate law is $r = k[Cl_2]^x [NO]^y$

$$\text{From trial 1,} \quad 1.20 \times 10^{-4} = k[0.010]^x [0.010]^y$$

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

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

$$\text{Dividing (2) by (1), } 9 = 3^y \quad y=2$$

$$\text{Dividing (3) by (2), } 2 = 2^x \quad x=1$$

$$\text{So the rate equation is } r = k[\text{Cl}_2]^1 [\text{NO}]^2$$

Order of the reaction is 3

2. Prove that $t_{99.9\%} = 10t_{1/2}$ in first order reaction .

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

$$= 2.303/k \log 1000$$

$$= 2.303 (3)/k$$

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

$$t_{1/2} = 0.693/k$$

$$\text{therefore :-} \quad t_{1/2} = 10 t_{99.9\%}$$

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 $(1/16)^{\text{th}}$ value ?

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

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

$$t = 2.303/60 \log 16$$

$$= 2.303/60 (1.2041)$$

$$= 2.773/60$$

$$= 0.0462 \text{ sec}^{-1}$$

4. The decomposition of Cl_2O_7 AT 400K In the gas phase to Cl_2 and O_2 is 1st order reaction

After 55secs at 400k the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant. Calculate the pressure of Cl_2O_7 after 100 secs of decomposition at this temp.

$$\text{Solution: } k = 2.303/t \log a/a-x = 2.303/55 \log 0.62 / 0.44$$

$$= 6.24 \times 10^{-3} \text{ sec}^{-1}$$

$$\text{When } t = 100 \text{ sec,}$$

$$6.24 \times 10^{-3} = 2.303/100 \log 0.62/a-x$$

$$\log 0.62/a-x = 6.24 \times 10^{-3} \times 100/2.303$$

$$= 0.2709$$

$$a-x = 0.033 \text{ atm}$$

5. The rate constant for the first order reaction of certain reaction is described by the equation:- $\log k(s^{-1}) = 14.34 - (1.25 \times 10^4 K)/T$

What is the activation energy for this reaction?

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

Ans: HERE, $\log k = 14.34 - (1.25 \times 10^4)/T$ (1)

By Arrhenius equation,

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

$$\ln = K/A = -E_a/RT \text{ or } \log k$$

$$= \log A - E_a/2.303RT$$
(2)

Comparing eqns (1) and (2),

$$E_a/2.303RT = 1.25 \times 10^4/T \text{ or } E_a$$

$$= 1.25 \times 10^4 \times 2.303 \times R$$

$$= 1.25 \times 10^4 \times 2.303 \times 8.314 \text{ J/mol}$$

$$= 239.3 \text{ KJ/mol}$$

Now,

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

Substituting in equation (1),

$$\log(0.693/256) = 14.34 - 1.25 \times 10^4/T$$

$$-2.56 = 14.34 - 1.25 \times 10^4/T$$

$$\text{or } T = 739.6 \text{ K.}$$

6. Find the two-third life, $t_{2/3}$, of a first order reaction in which $k = 5.4 \times 10^{-14} \text{ s}^{-1}$.

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,

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

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

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

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

Two-third life of the given first order reaction is $2.035 \times 10^{13} \text{ s}$

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

$$a-x = a - 20\% \text{ of } a = 80\% \text{ of } a$$

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

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

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{a}{a-x} \\ &= \frac{2.303}{t} \log \frac{a}{0.8a} \\ &= \frac{2.303}{t} \log \frac{5}{4} \\ &= \frac{2.303}{t} (\log 5 - \log 4) \\ &= \frac{2.303}{10} (0.6990 - 0.6021) \\ &= 0.02232 \text{ min}^{-1} \end{aligned}$$

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

$$\begin{aligned} k &= \frac{2.303}{t} \log \frac{a}{a-x} \\ a-x &= a - 75\% \text{ of } a = a/4 \quad t = t_{75\%} \\ t_{75\%} &= \frac{2.303}{0.02232} \log \frac{a}{a/4} \\ &= \frac{2.303}{0.02232} \log 4 \end{aligned}$$

$$= 62.125 \text{ min.}$$

8. At 380°C, 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°C.

Soln:-

$$K_1 = 0.693/360$$

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

$$\text{Log} k_2/k_1 = (E_a/2.303R) [(T_2 - T_1)/T_1 T_2]$$

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

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

$$= 1.5487$$

$$K_2/k_1 = \text{Antilog} (1.5487)$$

$$= 35.38$$

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

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

Rate at 450,

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

$$= (2.303)/(6.792 \times 10^{-2}) \log(100/25)$$

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

$$= 20.415 \text{ minutes.}$$