CHEMICAL KINETICS

These notes have been verified by CBSE Science Toppers & reputed faculties

COMPLETE NCERT
- No syllabus removed

We have integrated Previous Year Q's in the notes

APNI KAKSHA

#Jad Ab Phod!
HOW TO STUDY THE NOTES?

Apni Kaksha

- Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme
Flow Chart of Complete Chapter (NCERT)

**Chemical Kinetics**

- Rate of Reaction
  - Average Rate
  - Instantaneous Rate

**Factors Affecting Rate**

- Order and molecularity of a reaction
- Half life of a reaction
- Temperature dependence of rate of a reaction

- Arrhenius Equation

- Introduction
  - Need of Kinetics

**Integrated Rate Equation**

- Zero order reaction
- First order reaction
- Pseudo first order reaction
- Effect of catalyst

**Collision Theory**
For a chemical reaction $R \rightarrow P$:

1. Reaction will happen or not? : Thermodynamics: Reaction is feasible only if $\Delta G < 0$.
2. To which extent reaction will happen? : Chemical equilibrium
3. What is the speed of chemical reaction? : Chemical kinetics: Concept of rate of a reaction.

Rate of reaction - [Velocity of reaction]

The rate of change of concentration of any species taking part in a chemical reaction with time is known as rate of reaction.

\[ \text{Rate} = \frac{\text{Change in Concentration}}{\text{time}} = \frac{\Delta C}{\Delta t} \]

\[ \text{Unit: } \frac{(\text{mol/L})}{\text{s}} \text{ or } \frac{(\text{atm})}{\text{s}} \text{ for gaseous reactant or product.} \]

Types of rate -

(i) Average Rate -:

\[ R_{\text{av}} = \frac{\text{Total change in conc}}{\text{Total time taken}} \]

\[ \text{Rate} = \frac{\Delta [\text{Reactant}]}{\Delta t} = \frac{\Delta [\text{Product}]}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta C}{\Delta t} \]

\[ R \rightarrow P \]

at time $t_1$: $C_1$ [Concentration of product after time $t_1$]

at time $t_2$: $C_2$

(ii) Instantaneous Rate -:

\[ R_{\text{inst}} = \lim_{\Delta t \to 0} R_{\text{av}} = \lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt} \]

= Slope of concentration and time graph.

Rate of appearance and rate of disappearance:

Let us consider a reaction $R \rightarrow P$

At time $t_1$: $R_1 \rightarrow P_1$

At time $t_2$: $R_2 \rightarrow P_2$

\[ \Delta R = R_2 - R_1 \]

\[ \Delta P = P_2 - P_1 \]

\[ \Delta t = t_2 - t_1 \]
Rate of disappearance of \( R \) = \( \frac{\text{Decrease in } [R]}{\text{Time taken}} = -\frac{\Delta [R]}{\Delta t} \)

Rate of appearance of \( P \) = \( \frac{\text{Increase in } [P]}{\text{Time taken}} = \frac{\Delta [P]}{\Delta t} \)

**Example:** \( \text{Hg} (l) + \text{Cl}_2 (g) \rightarrow \text{HgCl}_2 (s) \)

→ Rate of reaction = Rate of disappearance of \( \text{Hg} \ | \text{HgCl}_2 \)

\[
= -\frac{\Delta [\text{Hg}]}{\Delta t} = -\frac{\Delta [\text{HgCl}_2]}{\Delta t} = \frac{\Delta [\text{Cl}_2]}{\Delta t}
\]

**Note:** If stoichiometric coefficients of reactants or products are not equal to one, then rate of disappearance of any of the reactants or rate of appearance of products is divided by their respective stoichiometric coefficients.

→ \( a \ A + b \ B \rightarrow \ c \ C + d \ D \)

Rate of reaction = \( -\frac{1}{a} \ \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \ \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \ \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \ \frac{\Delta [D]}{\Delta t} \)

**Example:**

(i) \( 2 \ \text{HI} (g) \rightarrow \text{H}_2 (g) + \text{I}_2 (g) \)

→ Rate of disappearance of \( \text{HI} \) = \( 2 \times \) Rate of appearance of \( \text{H}_2 \ | \text{I}_2 \)

→ Rate of reaction = Rate of appearance of \( \text{H}_2 \ | \text{I}_2 \) = \( \frac{1}{2} \) Rate of disappearance of \( \text{HI} \)

\[
= \frac{\Delta [\text{H}_2]}{\Delta t} = \frac{\Delta [\text{I}_2]}{\Delta t} = -\frac{1}{2} \ \frac{\Delta [\text{HI}]}{\Delta t}
\]

(ii) \( 5 \ \text{Br}^- (aq.) + \text{BrO}_3^- (aq.) + 6 \ \text{H}^+ (aq.) \rightarrow 3 \ \text{Br}_2 (aq.) + 3 \ \text{H}_2 \text{O} (l) \)

Rate of reaction = \( -\frac{1}{5} \ \frac{\Delta [\text{Br}^-]}{\Delta t} = -\frac{\Delta [\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \ \frac{\Delta [\text{H}^+]}{\Delta t} \)

**Question:** For the reaction \( 2 \ \text{Na}_2 \text{O}_5 (s) \rightarrow 4 \ \text{NO}_2 (g) + \text{O}_2 (g) \), the rate of formation of \( \text{NO}_2 (g) \) is \( 2.8 \times 10^{-3} \) \( \text{M s}^{-1} \). Calculate the rate of disappearance of \( \text{Na}_2 \text{O}_5 (s) \)!

**Answer:**

\[
2 \ \text{Na}_2 \text{O}_5 (s) \rightarrow 4 \ \text{NO}_2 (g) + \text{O}_2 (g)
\]

Rate of Reaction = \( -\frac{1}{2} \ \frac{\Delta [\text{Na}_2 \text{O}_5]}{\Delta t} = \frac{1}{4} \ \frac{\Delta [\text{NO}_2]}{\Delta t} \)
The rate of disappearance of $\text{N}_2\text{O}_5$ is given by:

$$\frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t} = 2 \times \frac{1}{4} \times \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{1}{2} \times 2.8 \times 10^{-3} \text{ Ms}^{-1} = 1.4 \times 10^{-3} \text{ Ms}^{-1}$$

Given that the rate of formation of $\text{NO}_3$ is $2.8 \times 10^{-3}$ Ms$^{-1}$.

**Question:** The decomposition of $\text{N}_2\text{O}_5$ in $\text{CCl}_4$ at 310 K has been studied by monitoring the concentration of $\text{N}_2\text{O}_5$ in the solution. Initially, the concentration of $\text{N}_2\text{O}_5$ is 2.33 mol L$^{-1}$ and after 184 minutes, it is reduced to 2.08 mol L$^{-1}$. Calculate the average rate of this reaction and what is the rate of production of $\text{NO}_3$ during this period?

**Answer:**

Average Rate $= \frac{1}{2} \frac{\Delta [\text{N}_2\text{O}_5]}{\Delta t} = \frac{-1}{2} \left( \frac{(2.08 - 2.33) \text{ mol L}^{-1}}{184 \text{ min}} \right)$

$= 6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1} = 6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 1.13 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$

Rate $= \frac{1}{4} \left[ \frac{\Delta [\text{NO}_2]}{\Delta t} \right] = 6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

Rate of production of $\text{NO}_3$ $= 4 \times 6.79 \times 10^{-4} = 2.79 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

**Factors influencing rate of a reaction:**

1. **Concentration:** Rate of reaction increases with concentration of reactant.
   - Liquid | Aqueous medium

2. **Temperature:** Rate of a reaction increases with increase of temperature.

3. **Nature of reactants:** Different reactant require different amount of energies for breaking of old bonds and for formation of new bonds.

4. **Catalyst:** It changes the rate of reaction, without being used (consumed) in the reaction.

**Rate Law | Rate Equation | Rate Expression:**

[Dependence of rate on conc$^n$]

- Rate law is expression in which reaction rate is given in terms of mol of reactants with each term raised to some power.

[CBSE 2011 | Delhi 2011]
The power raised on concentration terms in rate expression may or may not be same as stoichiometric coefficient of the reacting species in a balanced chemical equation.

Consider a general reaction: \( aA + bB \rightarrow cC + dD \)

Rate equation: \( \text{Rate} = k[A]^x[B]^y \)

The equation which relate rate of a reaction to concentration of the reactants is called rate equation or rate expression.

Order of a reaction: The sum of powers of the concentration of the reactants in rate law expression is called order of that chemical reaction.

For a reaction: \( aA + bB \rightarrow cC + dD \)

\( \text{Rate} = k[A]^x[B]^y \)

Then order of reaction = \( x + y \)

Order of a reaction can be determined only by experiment. We can not predict theoretically.

Order of a reaction can be 0, 1, 2 and even a fraction.

### Reaction

1. \( \text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl} \)
   
   \[ \text{Rate} = k [\text{CHCl}_3]^1 [\text{Cl}_2]^{1/2} \]
   
   \( 1 + \frac{1}{2} = 1.5 \)

2. \( \text{CH}_3\text{-CH} = \text{CH}_2 + \text{H}_2\text{O} \downarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \)
   
   \[ \text{Rate} = k [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]^1 \]
   
   \( 1 + 0 = 1 \)

### Units of rate constant:

\[ k = \frac{\text{Rate}}{[A]^x[B]^y} \]

\( \text{unit of } k = \frac{\text{Conc} \times \text{time}}{(\text{Conc}^a)^x (\text{Conc}^b)^y} = \text{Conc}^n \times \frac{1}{\text{time}} [\text{Conc}^{x+y}] \)

From above: \( \text{Rate} = k[A]^x[B]^y \)

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CASE 2011/2010/DECEMBER 2011/2010

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Unit of $k = \frac{(\text{mol L}^{-1})}{s} \times \frac{1}{(\text{mol L}^{-1})^n}$

$n =$ order of reaction $= x + y$

For zero order reaction: $n = 0$ then unit of $k = \text{mol L}^{-1} \text{ s}^{-1}$

For first order reaction: $n = 1$ : unit of $k = \text{s}^{-1}$

For second order reaction: $n = 2$ : unit of $k = \text{mol}^{-1} \text{ L s}^{-1}$

**Question:** Identify order of following reaction: 

(i) $k = 2.3 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$

(ii) $3 \times 10^{-4} \text{ s}^{-1}$

**Answer:**

(i) $\text{L mol}^{-1} \text{ s}^{-1}$ : Unit of second order

So, this represent second order reaction.

(ii) $\text{s}^{-1}$ : Unit of first order reaction.

**Question:** Write the rate equation for reaction $2 \text{NO}_2(g) + \text{O}_2(g) \rightarrow \text{NO}_2(g)$ by using following experimental data table?

**Solution:** Let us write rate expression for reaction: $\text{Rate} = k [\text{NO}_2]^x [\text{O}_2]^y$.

Put the data of experiment (i) in equation (i):

$0.096 \text{ mol L}^{-1} \text{ s}^{-1} = k [0.30]^x [0.30]^y$ — (iii)

Similarly, experiment (ii) and equation (i) —:

$0.334 \text{ mol L}^{-1} \text{ s}^{-1} = k [0.60]^x [0.30]^y$ — (iv)

Experiment (iii) and equation (i) —:

$0.192 \text{ mol L}^{-1} \text{ s}^{-1} = k [0.30]^x [0.60]^y$ — (v)

Divide equation (ii) by (iii) —:

$\frac{0.096}{0.334} = \left[ \frac{0.30}{0.60} \right]^x \left[ \frac{0.30}{0.30} \right]^y$

$\Rightarrow \frac{1}{4} = \frac{1}{2^x}$  Then $x = 2$

Divide (iv) by (i) —:

$\frac{0.192}{0.096} = \left[ \frac{0.30}{0.30} \right]^x \left[ \frac{0.60}{0.30} \right]^y \Rightarrow 2 = 2^y$  Then $y = 1$

Put the value of $x$ and $y$ in equation (i) —:

$\text{Rate} = k [\text{NO}_2]^2 [\text{O}_2]^1$ — (v)

**Order of reaction:** $2 + 1 = 3$

**Value of rate constant:** Put the value of rate, $[\text{NO}]$, $[\text{O}_2]$ in equation (v) from any experiment.
Question: For the reaction $2 \text{NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{NOCl}(g)$, the following data were collected. All the measurements were taken at 263K.

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its unit.

(iii) What is the initial rate of disappearance of $\text{Cl}_2$ in experiment 4? [Delhi 2012] 3M

Answer:

Rate law: $\text{Rate} = k [\text{NO}]^x [\text{Cl}_2]^y$

→ Initial rate becomes $(\text{Rate})_0 = k [\text{NO}]^x [\text{Cl}_2]^y$

→ Comparing experiment 1 and 2: $(\text{Rate})_1 = k [0.15]^x [0.15]^y = 0.60$  

$(\text{Rate})_2 = k [0.15]^x [0.30]^y = 1.20$

→ Dividing equation (ii) by equation (i) → \[
\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{1.20}{0.60} = \frac{k [0.15]^x [0.30]^y}{k [0.15]^x [0.15]^y} \quad \text{Then, } 2^y = 2^1 \quad \Rightarrow y = 1
\]

→ Comparing experiments 1 and 3:

$(\text{Rate})_1 = k [0.15]^x [0.15]^y = 0.60$

$(\text{Rate})_3 = k [0.30]^x [0.15]^y = 2.40$

→ Dividing equation (iv) by equation (iii): \[
\frac{(\text{Rate})_3}{(\text{Rate})_1} = \frac{k [0.30]^x [0.15]^y}{k [0.15]^x [0.15]^y} = \frac{2.40}{0.60}
\]

→ $2^x = 4 \quad \text{then } x = 2$

# Rate law: $\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2]$

# Rate constant $k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{0.60}{(0.15)^2 (0.15)} = 177.51 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$

# Initial rate of disappearance of $\text{Cl}_2$ in experiment 4 in $\text{v}_4$:

$v_4 = k [\text{NO}]^2 [\text{Cl}_2] = 177.51 \times (0.25)^2 (0.25)$

$v_4 = 2.77 \text{ M} \text{ min}^{-1}$
Molecularity of a reaction:

- The no. of reacting species [atoms, ions or molecules] taking part in a one step reaction [an elementary reaction], which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

  [CASE 2010/2011/2014] 

Molecularity

- Unimolecular Reaction → When one reacting species is involved.

- Bimolecular Reaction → Reaction via simultaneous collision between two species.

Example:

i) \( \text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O} \) : Unimolecular.

ii) \( 2\text{HI} \rightarrow \text{H}_2 + \text{I}_2 \) : Bimolecular.

Note: Generally molecularity greater than 2 is not observed, because simultaneous collisions of more than 2 molecules are not possible.

Difference between Order and Molecularity

Molecularity

- It is defined as the no. of molecules of reactant taking part in a reaction.

ii) Example: \( \text{NH}_4\text{NO}_2 \xrightarrow{\Delta} \text{N}_2 + 2\text{H}_2\text{O} \)

  Molecularity = 1

- It is a theoretical value.

- It is always a whole no. It can neither be zero nor fractional.

- It is derived from rate determining step in the mechanism of a reaction.

Note: Let us consider a reaction \( 2\text{H}_2\text{O}_2 \xrightarrow{\text{Alkaline medium}} \text{H}_2\text{O} + \text{O}_2 \).

Evidences suggest that this reaction takes place in two step:

i) \( \text{H}_2\text{O}_2 + I^- \rightarrow \text{H}_2\text{O} + I^0 \) [slow]

ii) \( \text{H}_2\text{O}_2 + I^0 \rightarrow \text{H}_2\text{O} + I^+ + \text{O}_2 \) [fast]
Slow step [first step] is the rate determining step [RDS].

Rate equation for reaction can be written on the basis of RDS.

\[
\text{Rate} = -\frac{d[C_{H_2O_2}]}{dt} = k [C_{H_2O_2}]^1 [I^-]^1
\]

\[\rightarrow \text{Overall order of reaction} = 1 + 1 = 2\]

**Integrated Rate Equations**

**Zero Order Reaction:**
Let us consider a zero order reaction \( R \rightarrow P \)

Then rate = \(-\frac{d[R]}{dt} = k [R]^0 = k\)

\[\Rightarrow \frac{d[R]}{dt} = -k \]

\[\Rightarrow [R] = -kt + I - (i)\]

At \( t = 0 \), the concentration of reactant \( R = [R]_0\).

By equation (i) \[ [R]_0 = -k \times 0 + I \]

\[\Rightarrow \text{integrated rate equation} - [R] = -kt + [R]_0\]

\[\Rightarrow \text{Straight line graph between } [R] \text{ and } t\]

\[\Rightarrow \text{slope} = -k\]

Example of zero order reaction:

(i) Enzyme catalysed reactions.

(ii) Decomposition of \( \text{NH}_3\) on a hot platinum surface at high pressure.

\[2 \text{NH}_3 (g) \xrightleftharpoons{1130 K}^{\text{Pt Catalyst}} \xrightarrow{1130 K} \text{N}_2 (g) + 3 \text{H}_2 (g)\]

\[\text{[Delhi 2016]}\]

\[\Rightarrow \text{Rate} = k [\text{NH}_3]^0\]

Explanation: At high pressure the metal surface gets saturated with gas molecules, so a further change in reaction condition is unable to change the amount of ammonia on the surface of the catalyst, making the rate of reaction independent of its concentration.

(iii) \( 2 \text{HI} (g) \xrightarrow{Au} \text{H}_2 (g) + \text{I}_2 (g)\)

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Integrated rate equation of first order reactions:

Consider a first order reaction: \( R \rightarrow P \)

\[ \text{Rate} = -\frac{\text{d}[R]}{\text{dt}} = k[R] \Rightarrow \frac{\text{d}[R]}{[R]} = -k \, \text{dt} \]

\( \Rightarrow \text{When } t=0 \text{ then } [R] = [R]_0 \)

- Put this value in equation(i): \( \ln [R] = -k \cdot t + \ln [R]_0 \)

\( \ln [R] = -k \cdot t + \ln [R]_0 \)

\( \ln [R] = -k \cdot t + I \)

\[ I = \ln [R]_0 \] — (ii)

By equation (i) and (ii) — :

\[ \ln [R] = -k \cdot t + \ln [R]_0 \]

\[ \ln [R] = -k \cdot t + \ln [R]_0 \]

\[ \ln [R] = \ln [R]_0 - k \cdot t \]

\[ \ln [R] = \ln [R]_0 - \text{slope} \cdot t \]

\[ \ln [R] = \ln [R]_0 - \frac{\text{slope}}{2.303} \cdot t \]

\[ \ln [R] = \ln [R]_0 - \frac{k}{2.303} \cdot t \]

On rearranging equation (iii) : \( \ln [R] - \ln [R]_0 = -k \cdot t \)

\[ \ln \frac{[R]}{[R]_0} = -k \cdot t \]

\[ \ln \frac{[R]}{[R]_0} = -k \cdot t \]

\[ [R] = e^{-k \cdot t} \text{ then } [R] = [R]_0 e^{-k \cdot t} \]

\[ R \rightarrow P \]

At \( t_1, [R]_1 \) then by equation (iii)

\[ \ln [R]_1 = -k \cdot t_1 + \ln [R]_0 \]

\[ \ln [R]_1 = -k \cdot t_1 + \ln [R]_0 \]

\[ \ln [R]_2 = -k \cdot t_2 + \ln [R]_0 \]

\[ \ln [R]_2 = -k \cdot t_2 + \ln [R]_0 \]

\[ k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2} \]

Graph between \([R]_1\) and time \( t \) →

First Order

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Example: (i) All natural and artificial radioactive decay of unstable nuclei take place by 1st order kinetics.

\[ _{88}^{226} \text{Ra} \rightarrow _{2}^{4} \text{He} + _{86}^{222} \text{Rn} \]

(ii) Hydrogenation of ethene

\[ \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{P}} \text{C}_2\text{H}_6(\text{g}) \quad \text{Rate} = k \left[ \text{C}_2\text{H}_4 \right] \]

**Question:** The initial concentration of \( \text{N}_2\text{O}_5 \) in the following 1st order reaction

\[ \text{N}_2\text{O}_5(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \]

was \( 1.24 \times 10^{-2} \text{ mol L}^{-1} \) at 318 K. The concentration of \( \text{N}_2\text{O}_5 \) after 60 minutes was \( 0.20 \times 10^{-2} \text{ mol L}^{-1} \). Calculate the rate constant of the reaction at 318 K?

**Answer:** For 1st order reaction:

\[ k = \frac{2.303}{(60 \text{ min} - 0 \text{ min})} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}} = \frac{2.303}{60} \log 6.0 \text{ min}^{-1} \]

\[ k = 0.0304 \text{ min}^{-1} \]

**First order gas phase reaction:**

Let us consider a 1st order reaction:

\[ A(\text{g}) \rightarrow B(\text{g}) + C(\text{g}) \]

At \( t = 0 \):

\[ p_A \text{ atm} \quad 0 \quad 0 \]

At time \( t \):

\[ (p_i - x) \quad x \quad x \]

\( p_i, p_A, p_C \) : Partial pressure of \( A, B, C \) respectively.

\( x \) : Decrease in pressure after time \( t \).

\[ \text{Total pressure at time } t \]

\[ p_t = p_A + p_B + p_C \]

\[ p_t = (p_i - x) + x + x \]

Then \( x = p_t - p_i \)

**Partial pressure** at time \( t \)

\[ p_A = p_i - x = p_i - (p_t - p_i) \]

\[ p_A = 2p_i - p_t \]
Question: Experimental data for the first order thermal decomposition of \( \text{SO}_3 \text{U}_2 \) at constant volume.

\[ \text{SO}_3 \text{U}_2 \xrightarrow{A} \text{SO}_2 + \text{U}_2 \]

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Time</th>
<th>Total Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 s</td>
<td>( P_i = 0.4 )</td>
</tr>
<tr>
<td>2</td>
<td>100 s</td>
<td>( P_f = 0.1 )</td>
</tr>
</tbody>
</table>

\[
\log \left( \frac{P_i}{P_f} \right) = \frac{2.303}{100 \text{ s}} \log \left( \frac{0.4}{0.1} \right) = \frac{2.303}{100} (2 \log 2) = 1.307 \times 10^{-2}
\]

**Half life of a reaction:** "The time in which the concentration of a reactant is reduced to one half of its initial concentration." [Delhi 2015 C]

For reaction \( R \rightarrow P \),

At \( t = 0 \) \( [R]_0 \),

At \( t = \frac{1}{2} t_y \) \( \frac{[R]_0}{2} \)

→ **Half life for zero order reaction**

\[
\text{Rate constant} \ k = \frac{[R]_0 - [R]}{t}
\]

At \( t = \frac{1}{2} t_y \) (Half life) \( [R] = \frac{[R]_0}{2} \)

\[
k = \frac{[R]_0 - \frac{[R]_0}{2}}{\frac{1}{2} t_y} = \frac{[R]_0}{2 \frac{1}{2} t_y} = \frac{[R]_0}{t_y} \]

\[
dt_y = \frac{[R]_0}{2k}
\]

→ **Half life of zero order reaction**

depends on initial concentration of reactant.

a) \( \frac{1}{2} t_y < [R]_0 \)

b) \( \frac{1}{2} t_y < \frac{1}{k} \)

→ **Half life (\( t_y \)) is independent of initial concentration.** [Delhi 2017 C]

Apni Kaksha 😊
A → Products

Reactant Concentration versus Time

Rate versus Reactant Concentration

<table>
<thead>
<tr>
<th>Order</th>
<th>Reaction type</th>
<th>Differential rate law</th>
<th>Integrated rate law</th>
<th>Straight line plot</th>
<th>Half-life</th>
<th>Units of k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>R → P</td>
<td>d[R]/dt = -k</td>
<td>kt = [R]₀ - [R]</td>
<td>[R] vs t</td>
<td>[R]₀/2k</td>
<td>conc time⁻¹ or mol L⁻¹ s⁻¹</td>
</tr>
<tr>
<td>1</td>
<td>R → P</td>
<td>d[R]/dt = -k[R]</td>
<td>[R] = [R]₀e⁻ᵏᵗ or kt = ln([R]₀/[R])</td>
<td>ln[R] vs t</td>
<td>ln 2/k</td>
<td>time⁻¹ or s⁻¹</td>
</tr>
</tbody>
</table>

[A] vs time for a 0 order reaction

Half life decreases with decreasing concentration.

[A] vs time for a 1st order reaction

Length of half life is constant.
A first order reaction is found to have a rate constant \( k = 5.5 \times 10^{-14} \). Find the half-life of the reaction.

**Answer:** For first order, half-life \( t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}} \)

\[ t_{1/2} = 1.26 \times 10^{14} \text{ s} \]

**Question:** A first order reaction takes place in 30 min for 50% completion. Calculate the time required for 90% completion of this reaction. Given \( \log 2 = 0.3010 \)

**Answer:** 90% completion time = \( t_{y_2} = 30 \text{ min} \)

\[ k = \frac{0.693}{30 \text{ min}} = \frac{0.693}{30 \text{ min}} = 0.023 \text{ min}^{-1} \]

For the same reaction, time required for 90% completion:

\[ k = 0.023 \text{ min}^{-1}; [R]_0 = 100 \quad [R] = 100 - 90 = 10 \]

\[ t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{0.023 \text{ min}^{-1}} \log \frac{100}{10} = 100.13 \text{ min} \]

**Pseudo first order reaction:** A chemical reaction between two substances when one reactant is present in excess quantity.

**Hydrolysis of ethyl acetate:** \( \text{CH}_3-C-O-C_2H_5 + H_2O \overset{H^+}{\rightarrow} \text{CH}_3-C-OH + C_2H_5OH \)

If, at time \( t = 0 \):

- \( 0.01 \text{ mol} \) ethyl acetate
- \( 0 \text{ mol} \) water
- \( 0 \text{ mol} \) water
- \( 0 \text{ mol} \) water

and, at time \( t \):

- \( 0 \text{ mol} \) ethyl acetate
- \( 9.99 \text{ mol} \) water
- \( 0.01 \text{ mol} \) water
- \( 0 \text{ mol} \) water

\([H_2O]_{t=0} = [H_2O]_t\) means that concentration of H2O does not change. So it can not change the rate. \([H_2O] = \text{constant}\)

Rate of reaction = \( k' [H_2O] [\text{CH}_3\text{COO}C_2H_5] \)

\[ \text{Rate of reaction} = k [\text{CH}_3\text{COO}C_2H_5] \rightarrow \text{It indicates 1st order kinetics}. \]

**Hydrolysis of cane sugar:**

\[ \text{C}_{12}H_{22}O_{11} + H_2O \overset{H^+}{\rightarrow} \text{C}_6H_{12}O_6 + \text{C}_6H_{12}O_6 \]

Glucose Fructose

\[ \text{Rate} = k [\text{C}_{12}H_{22}O_{11}] \]

Abni Kaksha ☺
Question: For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained.

(i) If concentration of water remains constant then show that it follows pseudo first order reaction.

(ii) Calculate average rate of reaction between time interval 10 to 20 second.

\[
\begin{array}{|c|c|c|}
\hline
\text{Time (second)} & 0 & 10 & 20 \\
\text{[CH}_3\text{C}^\text{OCH}_3]\text{[mol l}^{-1}\text{]} & 0.10 & 0.05 & 0.025 \\
\hline
\end{array}
\]

Answer:

(i) \[ [\text{H}_2\text{O}] = \text{Constant (During reaction)} \]

So, rate = \( k \left[ \text{methyl acetate} \right] \)

\[ \text{CH}_3\text{C}^\text{OCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C}^\text{OH} + \text{CH}_3\text{OH} \]

First order, then

\[ k = \frac{2.303}{t} \log \left( \frac{[\text{CH}_3\text{C}^\text{OCH}_3]}{[\text{CH}_3\text{C}^\text{OCH}_3]} \right) \]

At time \( t_1 = 10 \text{ second} \)

\[ k_1 = \frac{2.303}{10} \log \frac{0.10}{0.05} = 6.93 \times 10^{-2} \text{ s}^{-1} \]

At time \( t_2 = 20 \text{ second} \)

\[ k_2 = \frac{2.303}{20} \log \frac{0.10}{0.025} = 6.93 \times 10^{-2} \text{ s}^{-1} \]

Rate constant for the reaction has a constant value under any given time interval. Hence the given reaction follows pseudo first order kinetics.

(ii) Average rate = \( \frac{-\Delta [\text{CH}_3\text{C}^\text{OCH}_3]}{\Delta t} \)

\[ \Delta t = 20 - 10 \]

\[ \text{Average rate} = \frac{-0.025 - 0.05}{10} = 0.003 \text{ mol l}^{-1} \text{ s}^{-1} \]

Important Previous Year Questions

1. For a first order reaction \( \text{H}_2\text{O}_2 (aq) \rightarrow \text{H}_2\text{O} (l) + \text{O}_2 (g) \), rate constant \( k = 1.06 \times \text{10}^{-3} \text{ min}^{-1} \).

2. How long will it take for 15 l of a sample of \( \text{H}_2\text{O}_2 \) to decompose?

Answer: Let us consider \( [\text{H}_2\text{O}_2]_0 = 1.00 \text{ mol l}^{-1} \), then \( [\text{H}_2\text{O}_2]_t = \frac{100}{15} \text{ mol l}^{-1} \)

\[ k = \frac{2.303}{t} \log \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]} \Rightarrow t = \frac{2.303}{1.06 \times \text{10}^{-3}} \log \frac{100}{0.67} = 153.3 \text{ min}. \]
6. How long time it will take for 0.5% of the sample to decompose?

Now: \([H_2O_2]_0 = 100 \text{ mol/L} \quad [H_2O_2]_t = 100 - 0.5 = 15 \text{ mol/L}\)

\[t = \frac{2.303}{k} \log \frac{[H_2O_2]_0}{[H_2O_2]_t} = \frac{2.303}{1.06 \times 10^{-3}} \log 6.67 = 1780.05 \text{ min}\]

[2.7] The rate constant for a zero order reaction is 0.0030 mol L\(^{-1}\) s\(^{-1}\). How long will it take for the initial concentration to fall from 0.10 M to 0.075 M?

**Answer**: For zero order reaction, \[k = \frac{[R]_0 - [R]}{t}\]

\([R]_0 = 0.10 \text{ M}\]
\([R] = 0.075 \text{ M}\]

\[k = 0.0030 \text{ mol L}^{-1} \text{s}^{-1}\]

\[t = 0.33 \text{ second}\]

3. For a reaction \(Na_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2\)

i) Show that it follows first order reaction?

ii) Calculate the half-life?

**Answer**: For first order reaction, \[k = \frac{2.303}{t} \log \left( \frac{[Na_2O_5]_0}{[Na_2O_5]} \right)\]

\(t = 300 \text{ second}\), \([Na_2O_5]_0 = 1.6 \times 10^{-2} \text{ mol L}^{-1}\) and \([Na_2O_5] = 0.8 \times 10^{-2} \text{ mol L}^{-1}\)

\[k = \frac{2.303}{300} \log \left( \frac{1.6 \times 10^{-2}}{0.8 \times 10^{-2}} \right) = 2.31 \times 10^{-3} \text{s}^{-1}\]

At \(t = 600\), \([Na_2O_5] = 0.4 \times 10^{-2}\)

\[k = \frac{2.303}{600} \log \left( \frac{1.6 \times 10^{-2}}{0.4 \times 10^{-2}} \right) = 2.31 \times 10^{-3} \text{s}^{-1}\]

Rate constant remains same in both condition (a & b), so we can say above reaction is first order.

**Apni Kaksha**
$ii) \quad k = 2.303 \times 10^{-3} \ \text{s}^{-1} \ \text{then} \ \frac{1}{y_2} = \frac{0.693}{k} = \frac{0.63}{2.303 \times 10^{-3}} = 300 \text{s}^{-1}$

$[4] \text{first order reaction} \quad 2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \ \text{at 400} \text{c, data is given below}$

$\text{(i)} \quad \text{Calculate the rate constant (with its unit).}$

$\text{At time } t = 20 \text{ min, } [\text{N}_2\text{O}_5] = 0.283 \text{ mol} \text{L}^{-1}$

$\text{& } [\text{N}_2\text{O}_5]_0 = 0.4 \text{ mol} \text{L}^{-1}$

$K = \frac{2.303 \log \frac{0.4}{0.283}}{20} = \frac{2.303 \log 1.391}{20}$

$K = \frac{0.01625 \text{ min}^{-1}}{1.62 \times 10^{-2} \text{ min}^{-1}} = 0.01625 \text{ min}^{-1}$

$\text{(ii)} \quad \text{What will be concentration of } \text{N}_2\text{O}_5 \text{ after 100 min?}$

$K = \frac{2.303 \log \frac{0.4}{[\text{N}_2\text{O}_5]}}{100}$

$\text{then } \log \frac{0.4}{[\text{N}_2\text{O}_5]} = 0.070$  \hspace{1cm} 

$\log 0.705 = 0.807$  \hspace{1cm} 

$[\text{N}_2\text{O}_5] = \frac{0.4}{0.807} = 0.498 \text{ mol} \text{L}^{-1}$

$\text{(iii)} \quad \text{Initial rate of reaction?}$

$\text{Initial rate} = k [\text{N}_2\text{O}_5] = 0.4 \times 1.62 \times 10^{-2} = 6.4 \times 10^{-3} \text{ mol} \text{L}^{-1} \text{min}^{-1}$

$[5] \quad \text{For a reaction } A + B \rightarrow P \text{ the rate is given by}$

$\text{Rate} = k[A][B]^2$

$[\text{CBSE 2015 Delhi 2015}]$

$\text{(a)} \quad \text{How is the rate affected if } [B] \text{ is doubled?}$

$\text{Rate of reaction} = k [A] [2B]^2 = 4 [A] [B]^2 = 4 \times \text{original rate}$

$[b) \quad \text{What is overall order of reaction if } A \text{ is present in large excess?}$

$\text{If } A \text{ is present in large excess, then the reaction will be independent of the concentration of } A. \ \text{Rate} = k [A]^m [B]^n$

$\text{Then order of reaction } = 2$
The rate of the reaction is dependent on temperature. This is expressed in terms of temperature coefficient. Rate of reaction increases with temperature.

**Temperature Coefficient**: It is the ratio of rate constant at temperature $300K$ [$298 + 10$] to the rate constant at temperature $298K$.

It is observed that for a chemical reaction with rise in temperature by $10^\circ$, the rate constant is nearly doubled. [CBSE 2014C | Delhi 2015C] 2M

**Arrhenius Theory**:

Arrhenius theory states that products are formed through intermediates or activated complexes.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

When a molecule of $H_2$ and a molecule of $I_2$ collide to form an unstable intermediate. Unstable intermediate [activated complex] exist for a very short time and then breaks up to form a molecule of HI. [Delhi 2013C] 2M

**Activation Energy** [$E_a$] := Minimum energy required to convert a reactant into activated complex is known as activation energy.

$$E_a = \text{Energy difference between activated complex and reactant molecules.}$$ [CBSE 2010 | 2011 | 2012] 1M

**Arrhenius Equation** := The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation.

$$K = A \cdot e^{-\frac{E_a}{RT}}$$

- $A$ := Frequency Factor
- $E_a$ := Activation Energy
- $T$ := Temperature
- $R$ := Gas Constant
Taking log of both side of Arrhenius equation:

\[
\log k = \log A - \frac{E_a}{2.303 RT}
\]

**Graph:** \( \log k \) vs \( \frac{1}{T} \) gives slope \( = -\frac{E_a}{2.303 R} \)

**Intercept:** \( = \log A \)

If \( k_1 \) is the rate constant at temperature \( T_1 \)

\[ \log k_1 = \log A - \frac{E_a}{2.303 R T_1} \]

At \( T_2 \) \( \Rightarrow \) rate constant \( k_2 \)

\[ \log k_2 = \log A - \frac{E_a}{2.303 R T_2} \]

\[
\frac{\log k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right]
\]

**Question:** The rate of most reactions become double when their temperature is raised from 298 K to 308 K. Calculate their activation energy.

*Given, \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \)*

**Answer:** \( T_1 = 298 \text{ K}, \ T_2 = 308 \text{ K}, \ \frac{k_2}{k_1} = 2 \)

\[
\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right] \Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{308 - 298}{298 \times 308} \right]
\]

\( E_a = \frac{52903.05}{R} \text{ J mol}^{-1} \)

**Question:** The rate constant for the first order decomposition of \( H_2O_2 \) is given by the following equation

\[ \log k = 14.2 - \frac{1 \times 10^4}{T} \]

Calculate \( E_a \) for this reaction and rate constant \( k \), if its half life period be 200 min. *[Given \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)]*

**Answer:** \( \log k = 14.2 - \frac{1 \times 10^4}{T} \)

Arrhenius Equation: \( \log k = \log A - \frac{E_a}{2.303 RT} \)

On comparing equation (i) \( \Rightarrow \) (ii):

\[
\frac{E_a}{2.303 R} = 1 \times 10^4 \text{ K}
\]

\( \Rightarrow E_a = 2.303 \times 8.314 \times 10^4 = 191.4 \text{ K J mol}^{-1} \)
Calculation of rate constant $k$:

Given $t_{1/2} = 200 \text{ min} = 200 \times 60 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200 \times 60} = 5.77 \times 10^{-5} \text{ s}^{-1}$$

**Question:** For a decomposition reaction, the values of $k$ at two different temperatures are given below:

$$k_1 = 2.15 \times 10^{-6} \text{ L/(mol.s)} \text{ at 650 K}$$

$$k_2 = 2.33 \times 10^{-7} \text{ L/(mol.s)} \text{ at 700 K}$$

Calculate the value of $E_a$ for the reaction.

[Given $\log 11.11 = 1.046$, $R = 0.314 \text{ J.K}^{-1} \text{ mol}^{-1}$]

**Answer:**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 \cdot T_2} \right)$$

$$\log \frac{2.33 \times 10^{-7}}{2.15 \times 10^{-8}} = \frac{E_a}{2.303 \times 0.314} \left[ \frac{700 - 650}{700 \times 650} \right]$$

$$\log 11.11 = 1.046 = \frac{E_a}{2.303 \times 0.314} \left[ \frac{50}{4.55 \times 10^5} \right]$$

$$E_a = 182.25 \text{ KJ/mol}$$

**Question:** The decomposition of A into products has a value of $k$ as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 KJ mol$^{-1}$. At what temperature would $k$ be $1.5 \times 10^4 \text{ s}^{-1}$?

**Answer:**

$$T_1 = 10 + 273 = 283 \text{ K}$$

$$k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$E_a = 60 \text{ KJ mol}^{-1}$$

At $T_2 = ?$ \Rightarrow $k_2 = 1.5 \times 10^4 \text{ s}^{-1}$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60}{2.303 \times 0.314} \left[ \frac{T_2 - 283}{283 \cdot T_2} \right]$$

$$0.523 = 31.33 \cdot 63 \left[ \frac{T_2 - 283}{283 \cdot T_2} \right]$$

$$0.953 \cdot T_2 = 283$$

$$T_2 = 297 \text{ K}$$

**Maxwell Boltzmann Distribution Curve:**

According to Maxwell and Boltzmann, the distribution of kinetic energy may be described by plotting the fraction of molecules with a given kinetic energy.
The peak of the curve corresponds to the most probable kinetic energy. The most probable kinetic energy is the kinetic energy of maximum fraction of molecules. When the temperature is raised, the maximum of the curve moves to the higher energy value and curve broadens out and proportion of molecules with higher energy increases.

Increasing the temperature of the substance increases the fraction of molecules, which collide with energy greater than E_a.

**Effect of Catalyst:**

→ The rate of a chemical reaction changes by the presence of catalyst. It alters the rate by providing alternative path of lower greater activation energy to the reactants.

→ The catalyst [which increases rate of a reaction] reduces the activation energy.

→ A catalyst does not change the enthalpy [ΔH], Gibbs energy of reaction [ΔG] and equilibrium constant [K] of a reaction.

(IM) [Delhi 2017]
**Collision Theory**: This theory is based on kinetic theory of gases. According to this theory - the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other perfectly.

**Collision Frequency**: The no. of collisions per second per unit volume of reaction mixture is known as collision frequency.

For a biomolecular elementary reaction \( A + B \rightarrow \text{Products} \)

\[
\text{Rate of this reaction} = Z_{AB} e^{-E_a/RT}
\]

\( Z_{AB} \): Collision frequency of reactant A and B.

\( e^{-E_a/RT} \): Represents the fraction of molecules with energies equal to or greater than \( E_a \).

The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed.

\[
\text{CH}_3\text{Br} + \text{OH} \rightarrow \text{CH}_3\text{OH} + \text{Br}
\]

Diagram showing molecules having proper and improper orientation.

To account for effective collisions, another factor \( P \), called the probability or etonic factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented.

\[
\text{Rate} = P Z_{AB} e^{-E_a/RT}
\]

In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.