Chemical Kinetics

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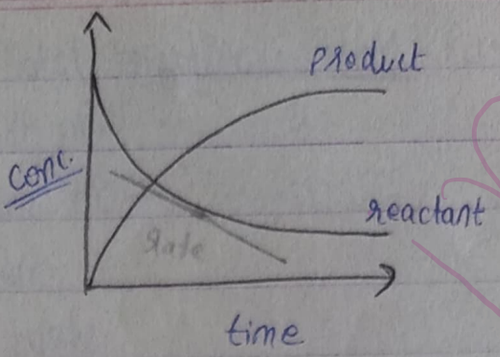
1. Rate of reaction ($\mathcal{R}$) $= \frac{\Delta c}{\Delta t}$

Instantaneous rate $= \frac{dc}{dt}$.



2. For - $aA + bB \longrightarrow cC + dD$

$$\mathcal{R} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}.$$

Rate of appearance $= \frac{d[C]}{dt} = \frac{d[D]}{dt}$.

Rate of disappearance $= \frac{d[A]}{dt} = \frac{d[B]}{dt}$.

3. Rate law / law of mass action -

$aA + bB \longrightarrow$ product

Law of mass action $\Rightarrow \mathcal{R} \propto [A]^a [B]^b$ — for elementary reactions only.

Rate law $\Rightarrow \mathcal{R} = k[A]^x[B]^y$

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

$[A]$ = conc. of A or p_A.

- k = rate constant / velocity constant
- x = order w.r.t to A
- y = order w.r.t to B
- k = specific rate of reaction.

4. Unit of rate = mol L^{-1} s^{-1} = M s^{-1} = atm s^{-1}.

unit of rate constant = $(\text{mol lit}^{-1})^{1-n}$ sec^{-1}.

In a question, look at the given units of k and decide the order of the reaction.

Q. type (1) Table of | rate | [A] | [B] | given. Find order of reaction.

Q. type (2) Mechanism of reaction is given -

elementary - coefficient of reactant = order of reaction

complex - slowest step determines the order.

↳ order should be written only in terms of the given reactants and not in terms of the intermediates. (∵ convert)

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basic (alkaline) hydrolysis = 2nd order

5. Molecularity = total no. of atom/molecules/ions taking part in the elementary reaction.
↓
1/2/3/...
= In complex reaction, molecularity for complete reaction is not defined. It can be calculated for individual steps.

On multiplying the equation, molecularity and order do not change.

For elementary reactions, Molecularity = Order.

6. Pseudo first order reaction -
- Hydrolysis of ester (acidic)
- Inversion of sugar.

→ 1 reactant is present in excess
→ Molecularity > 1 (=2)
order = 1.

7. 0th Order $r \propto [a]^0$

$A \longrightarrow$ product

$t = 0$: A_0 ; 0
$t = t$: A_t ; x

→ $x = kt$; $A_0 - A_t = kt$ • $A_0 - A_t = x$

→ $t_{100\%} = \frac{a}{k}$ $\quad t_{1/2} = \frac{a}{2k} = t_{50\%}$

- Catalyst (metal surface) (Reverse Haber's process)
- enzymatic reactions
- photochemical ($h\nu$).

8. 1st Order $r \propto [a]^1$

→ $k = \frac{2.303}{t} \log_{10}\left(\frac{a}{a-x}\right)$ or $\frac{A_0}{A_t} = kt$

→ $A_t = A_0 e^{-kt}$

$A_t = a - x$ $\quad A_0 = a$

→ $t_{1/2} = \frac{0.693}{k} = \frac{2.303 \times \log 2}{k} = \frac{2.303 \times 0.3010}{k}$

A → product
a 0
a − x x

↳ independent of initial conc.

- $N_2O_5 \xrightarrow{\Delta} NO_2 + O_2$
- radioactive decay
- acidic hydrolysis of ester
- hydrogenation of ethene

9. **nth Order** $r \propto [a]^n$

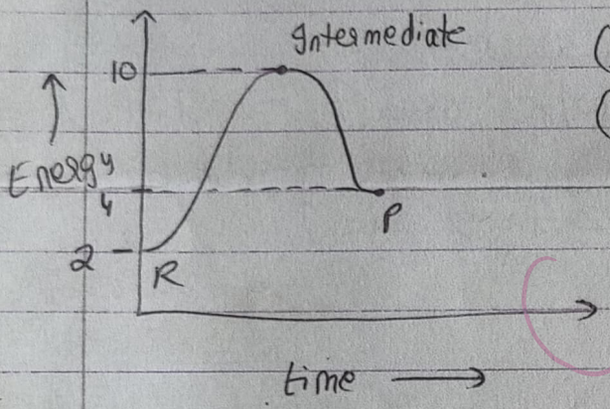
$$\rightarrow kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right] \quad n = 0, 2, 3, \ldots$$

(Where $n = 1 \Rightarrow$ not applicable

$$\rightarrow t_{y_2} = \frac{1}{n-1}\left[\frac{2^{n-1} - 1}{a^{n-1}}\right] \qquad \left[t_{y_2} \propto \frac{1}{a^{n-1}}\right]$$

10. z = collision frequency = $\frac{\text{Total no. of collisions}}{\text{vol.} \times \text{time}}$

($z = 10^{25}$ to 10^{28} s^{-1} ml^{-1}).



$(E_a)_f = 8$

$(E_a)_b = 6$

$\Delta H = (E_a)_f - (E_a)_b = 8 - 6 = 2.$

(ΔH = +ve = endothermic reaction)

threshold energy
TE = 10.

11. Factors affecting E_a – (i) nature of reactant (solid/liquid/gas)
(ii) temp. (iii) catalyst
(iv) orientation.

12. μ = coefficient of temp. = $\frac{K_{T+10}}{K_T}$ = 2 or 3

For a reaction, consider $\mu = 2$ (by default).

$$\rightarrow \frac{K_2}{K_1} = \mu^{\Delta T/10}.$$

13. $K = A\, e^{-E_a/RT}$ Arrhenius equation

For a given reaction, E_a and A = arrhenius constant, both are constant. ∴ K depends only on T.

→ $\frac{K_2}{K_1} = \frac{A e^{-E_a/RT_2}}{A e^{-E_a/RT_1}}$

A = arrhenius constant
= frequency factor
= pre exponential constant.

$\Rightarrow \frac{K_2}{K_1} = e^{-\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]}$

$\therefore \log \frac{K_2}{K_1} = -\frac{E_a}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$.

→ other factors affecting rate of reaction,

(i) gas ↑, volatility ↑ ⇒ surface area ↑ ⇒ rate ↑
(ii) conc. ↑ ⇒ rate ↑ (for +ve order reactions)
(iii) pressure ↑ ⇒ Vol ↓ ⇒ Z ↑ ⇒ Rate ↑.
(iv) catalyst — +ve ⇒ rate ↑
— -ve ⇒ rate ↓
(v) temp. ↑ ⇒ rate ↑ (either exo or endo).

NCERT Points

1. Types of reactions

very fast	Moderate	very slow
- Instantaneously or within few seconds - their rate of rxn cannot be calculated Eg - precipitation rxn	- Few minutes to few hours - their rate of rxn can be significantly determined. - hydrolysis of esters - decomposition reaction	- Months or years - rate of reaction does not have any significance - rusting of iron.

Factors affecting rate of reaction -

(a) Concentration of reactant - conc. of reactant ↑ ⇒ no. of reactant molecules ↑ ⇒ Z ↑ ⇒ rate ↑

(b) Temp. of reaction - temp ↑ ⇒ KE of particles ↑ ⇒ collision ↑ ⇒ Z ↑ ⇒ rate ↑.

(c) Nature of reactants - Reactants having similar chemical nature have higher ROR as compared to reactants with dissimilar nature.

(d) Surface Area - surface area ↑ ⇒ area of contact between reactant molecules ↑ ⇒ Z ↑ ⇒ ROR ↑.
∴ Zn plate < Zn granules < Zn powder.

(e) Catalyst - +ve catalyst increases the ROR by taking the process to an alternate path having lower Ea.

(f) Presence of light - In photochemical reactions, light acts as an activator of reactants.

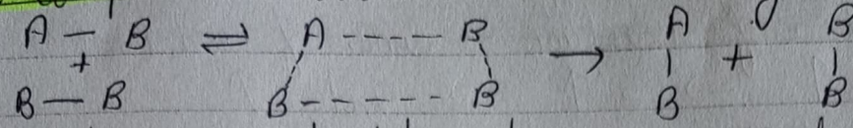
3. The time period in which half of the reactants get converted into products or the time in which concentration of reactants reduces to half its initial value is called half-life.

4. Those reactions which get completed in a single step are called elementary reactions.
Those reactions which get completed in more than one step or series of steps are called as complex reaction.

5. The series of steps in which a complex reaction takes place is called as mechanism of reaction. Each step of a complex reaction is an elementary reaction.

6. The minimum energy which the colliding molecules must have so that their collision becomes effective, that is, they cross the energy barrier and get converted to products is called threshold energy.
→ The minimum amount of extra energy absorbed by the reactant molecules so that their energy becomes equal to threshold energy, i.e., they cross the energy barrier and get converted to products is called activation energy.

7. Activated Complex or Transition State Theory



Reactant activated complex product.

(a) In order that the reactants get converted to products, they have to cross the energy barrier.

(b) When reactant molecule absorbs energy, their bonds start breaking and new bonds start forming in between them. Thus, an intermediate is formed which is called as activated complex or transition state.

(c) It is highly unstable and it immediately dissociates to form stable products.

8. Catalyst is a substance that increases the rxn without itself undergoing any chemical change. It provides an alternate path for the rxn having lower Ea. Thus, catalyst decreases Ea required. Catalyst does not alter ΔG, value of equilibrium constant, ΔH.

9. All collisions taking place between reactants do not result in formation of products, only which are effective resuet in products formation.
The no. of effective collisions depends on –
(i) Energy factor (ii) Orientation factor.

→ Energy factor – the colliding reactant molecules must have threshold energy so that they can cross the energ barrier and get converted to products.

→ Orientation factor – the colliding reactant molecules must have proper orientation at the time of collision so that old bonds are broken and new bonds are formed.

Z = collision frequency f = fraction of molecules having effective collision
r = rxn

$r = zf$ $f = e^{-Ea/RT}$

$\therefore r = Ze^{-Ea/RT}$