* Chapter 03

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CHEMICAL KINETICS

- branch of physical chemistry which deals with study of rate of reactions, mechanism by which reactions proceed and factors affecting rate of reactions.

* Types of chemical reactions:

Theory

- On the basis of rate of reaction:

(1.) Instant (fast) rxn:
- type of chemical reaction involving ionic species (ionic rxn) and are carried out in few seconds i.e. 10-14 seconds. (almost impossible to determine rate of rxn)

(2.) Slow rxn: (moderate)
- type of chemical reaction preceeding with measurable rate at normal temperature
- generally, molecular reactions.

(3.) Very slow rxn:
- type of chemical reaction preceeding very slowly i.e taking days and months for completion at room temperature.
- Corroision; Rancidity.

* Rate of reaction:

- change in concentration of reactant or product per unit time.
- Always a positive quantity; negative signs represents decrease in concentration of reactant.
- unit: mole / Ltr·sec.

$$\text{Rate of RXn} = \frac{\text{change in conc}^n \text{ of react / prod.}}{\text{time taken in change.}}$$

- for general reaction $R \longrightarrow P$, can be expressed as

$$\text{Rate of disappearance of } R = -\frac{d[R]}{dt}$$

$$\text{Rate of appearance of } P = \frac{d[P]}{dt}$$

here;

$d[R]$ = small conc^n change of P.
$d[P]$ = small conc^n change of R.
dt = small interval of time

→ * Representation of rate of reaction:

(A.) Average rate of rxn:

- rate of reaction measured over a long time interval.
- for general reaction $R \longrightarrow P$

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

[Δt is large int. of time]
interval

(B.) Instantaneous rate of reaction:

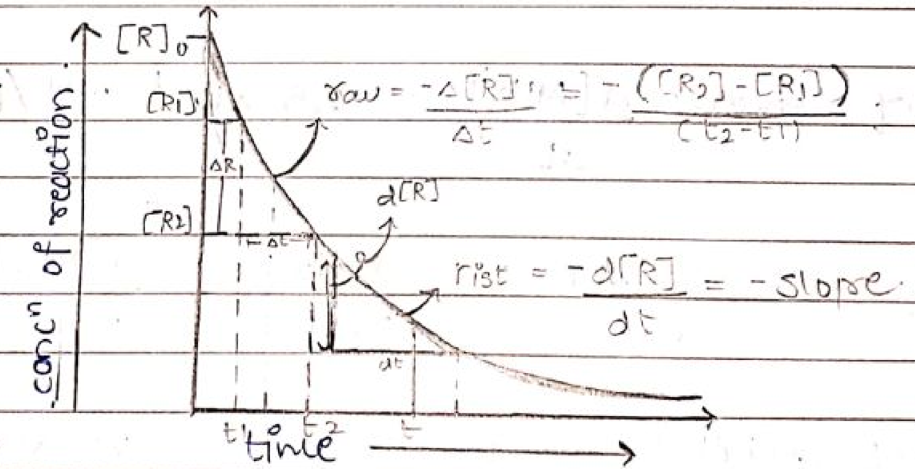
- rate of reaction when average rate is taken over a particular moment of time.
- for general reaction $R \longrightarrow P$

$$\text{Instantaneous rate} = (\text{Average rate})_{\lim\ \Delta t \to 0}.$$

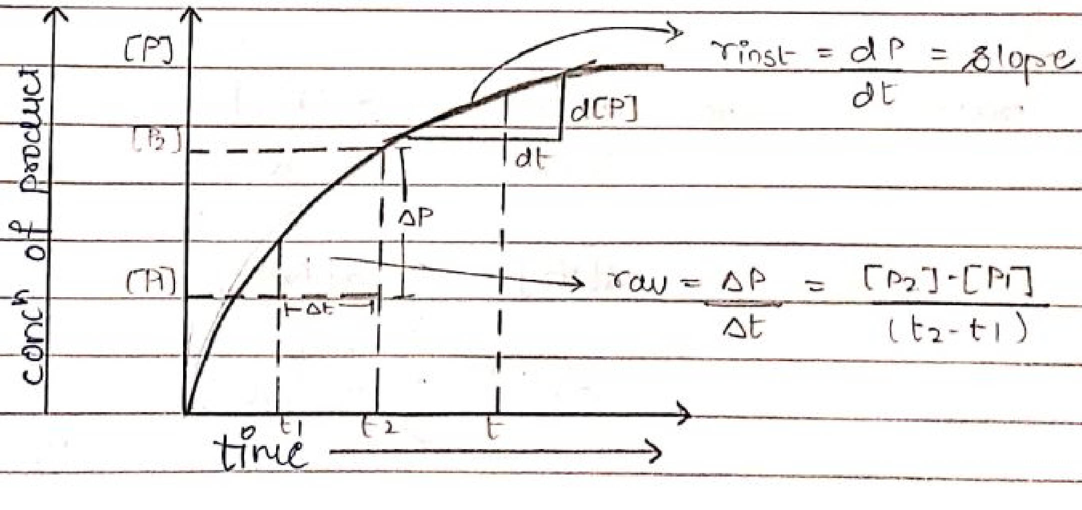
$$r_{inst} = -\left[\frac{\Delta[R]}{\Delta t}\right]_{\lim\ \Delta t \to 0} = \left[\frac{\Delta[P]}{\Delta t}\right]_{\lim\ \Delta t \to 0}.$$

$$r_{inst} = \frac{-d[R]}{dt} = \frac{d[p]}{dt}.$$

(A)



(B)



* General Expression for ROR:

NEET

- rate of disappearance of reactant and rate of appearance of product are equalised by dividing them with coefficient in the balanced chemical reaction.

- for a general reaction;

Q:2 →

$$aA + bB \longrightarrow cC + dD.$$

$$\boxed{r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{-1}{c}\frac{d[C]}{dt} = \frac{-1}{d}\frac{d[D]}{dt}}$$

Q:1 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ rate of appearance of NH_3 is 2.5×10^{-4} mol/L·sec. ROR & ROD of H_2 will be Q:3

→ $$N_2 + 3H_2 \longrightarrow 2NH_3$$ →

rate of appear.: $\frac{d[NH_3]}{dt} = 2.5 \times 10^{-4}$ mol/ltr·sec

625
32
50

rate of rxn: $\frac{-d[N_2]}{dt} = -\frac{d[H_2]}{3 \cdot dt} = \frac{d[NH_3]}{2 \cdot dt}$

rate: $\frac{d[NH_3]}{2 \cdot dt} \Rightarrow \frac{2.5 \times 10^{-4}}{2} \Rightarrow 1.25 \times 10^{-4}$ mol/ltr·sec

∴ $\underline{ROR = 1.25 \times 10^{-4} \text{ mol/ltrs}}$

rate of disapp: $\frac{d[H_2]}{3 \cdot \cancel{dt}} = \frac{d[NH_3]}{2 \cdot \cancel{dt}}$ Q:4.

$$d[H_2] = \frac{3}{2}\, d[NH_3]$$

$$d[H_2] = \frac{3}{\cancel{2}} \cdot \overset{1.25}{\cancel{2.5}} \times 10^{-4}$$

∴ $\underline{ROD = 3.75 \times 10^{-4}}$

Or

NEET

$$\frac{\text{mole of } H_2}{3} = \frac{\text{mole of } NH_3}{2}$$

$$\text{mole of } H_2 = \frac{3}{2} \text{ mole of } NH_3 .$$

Q:2 in above que; find ROD of N_2 gas.

→ ROD: $\frac{d[N_2]}{dt} = \frac{d[NH_3]}{2 \cdot dt}$

$$d[N_2] = \frac{2.5 \times 10^{-4}}{2} \longrightarrow 1.75 \times 10^{-4} \text{ mol/ltr·sec}$$

Q:3 Rate of formation of SO_3 in $2SO_2 + O_2 \longrightarrow 2SO_3$ is 100 g/min. ROD of O_2 is:

→ $\text{mole} = \frac{100}{80} \longrightarrow 1.25 \text{ moles}$

625
32

$$\frac{\text{moles of } O_2}{1} = \frac{\text{moles of } SO_3}{2}$$

$$\text{mole } O_2 = \frac{1.25}{2} \longrightarrow 0.625 \text{ moles}$$

∴, wt = mole × mol. wt

$= 0.625 \times 32 \longrightarrow 20 \text{ g/min}$

Q:4. for given rxn: $2A \longrightarrow 3B$. initially 10 moles of A taken in vessel after 10 secs we found that moles of A in container is 4 moles. find:

⟶ (A) ROD of A (B) ROF of B.

ans. (A) ROD of A = $\frac{4-10}{10}$ = $\frac{-6}{10}$ ⟶ −0.6 mol/ltr.sec.

(B) ROF of B ⇒ $\frac{\text{moles of B}}{3}$ = $\frac{\text{moles of A}}{2}$

moles of B = $\frac{3}{2}$ × 0.6 ⟹ $\underline{0.9 \text{ mole}}$

ROF of B = 0.9 mol/ltr.sec.

Q:5 Rxn: $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

ROD of N_2O_5 = 6.25 ×10^{-3} mole/ltr.sec

find ROF of NO_2 and O_2.

→ $\frac{\text{mole of } NO_2}{2}$ = mole N_2O_5

∴ mole of NO_2 = 2 · 6.25 ×10^{-3}

= $\underline{12.5 \times 10^{-3}}$

$\frac{\text{mole of } O_2}{1/2}$ = $\frac{\text{mole } N_2O_5}{1}$

∴ mole of O_2 = 6.25 ×10^{-3}/2

= $\underline{\underline{3.125 \times 10^{-3}}}$

* Factors affecting Rate of chemical reaction:

a) Nature of reactant: ionic substances more rapidly than substance with covalent bond

b) concentration of reactant: rate of reactions increases with increase in concentration of reactants

c) Temperature: rate of reaction increase with temp↑.
(for endothermic) temp↑ | for exothermic temp↓ |

d) Presence of catalyst: In presence of catalysts, rate of reaction generally increases and equilibrium state is attained quickly in reversible rxn.

e) Surface area reactants: smaller particle size, greater surface area and faster is reaction.

f) Radiations: some reactions are of considerable speed when exposed to sunlight or UV radiations, i.e. photochemical reactions.
eg: photosynthesis of carbohydrates ; photography etc

elementary = 1 step rxn.
complex = >1 steps

* **Rate law [rate eq^n] and Rate constant:**

- rate law or rate equation for chemical reaction is an equation that links reaction rate with conc^n or pressure of reactants and constant parameter (like rate coefficient and partial rxn orders).

$$aA + bB \longrightarrow cC + dD$$

→ a, b, c and d are stoichiometric coefficients of reactants and products.

→ rate expression

$\text{Rate} \propto [A]^x [B]^y$ rate $= K[A]^x [B]^y$

- this eq^n relates ROR to concentration of reactants called rate law or rate expression, where exponents x and y may or may not equal to stoichiometric coeff. (a & b) of reactants and K is prop. constant

K = rate constant

if [A] = [B] = 1 mole/ltr then,

$$Rate = K$$

- thus ROR at unit concentration of reactants is called rate constant or specific reaction rate.
- value of 'K' does not depend on concentration of reactant but it may depend on conditions such as temperature, catalyst, etc.

$$\frac{-d[R]}{dt} = K[A]^x[B]^y$$

- this form of eqn is called Differential rate equation

* Types of chemical reaction:

- On the basis of number of steps:

(1.) Elementary rxn:

- reaction that takes place in one step.
- they've exponential form in rate law, which equals to stoichiometric coefficients of reactant

- if $A + B \longrightarrow$ product ; (elementary rxn).
  $ROR = K[A][B]$.

* zero order reaction can never be elementary reaction.

* for elementary rxn, fractional order is not possible

(2.) Complex rxn:

- multistep reactions.
- for complex reactions, overall ROR is controlled by slowest step which is known as rate determining steps.
- for those reactions, rate law expression depends on concentration of reactants of slowest step which must be free from intermediate.

eg: $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$.

- reaction is complex reaction because it is carried out in following 2 steps:

$NO_2Cl \longrightarrow NO_2 + Cl$ (slow step)

$2NO_2Cl + Cl \longrightarrow 2NO_2 + Cl_2$ (fast step).

- for that rxn, rate law is determined by slowest step.

$ROR = K[NO_2Cl]$.

eg: $R-X + KCN \longrightarrow R-CN$

Step-1: $R-X \longrightarrow R^+$

(it is slow step and is rate determining step)

Step-2: $R^+ + CN^- \longrightarrow R-CN$

(fast step).

$ROR = K[R-X]$

* **Molecularity:**

- total numbers of molecules, atoms or ions (reacting step) participating in an elementary reaction is called Molecularity of reaction.
- it is always in whole number and it can never be zero or negative or fractional
- reactions can be unimolecular, bimolecular & trimolecular for molecularity 1, 2, 3 respect.

(imp) - molecularity or order is never more than three because probabilities of more 3 molecules colliding simultaneously is rare so it does not extend beyond.

- molecularity can be defined only for elementary reactions and has no meaning for complex rxn
- in elementary reaction, molecularity is equal to its order.

- in complex reaction, generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction.
[except, when slowest step contain intermediate]

* **Order of reaction:**

- sum of powers of concentration of reactant in rate law expression.
- order of rxn can be zero, positive, negative and even fraction.
- order cannot be determined with given balanced chemical eq^n which can be derived experimentally

- for reactions;

$$aA + bB \longrightarrow cC + dD.$$

$\text{rate} = K[A]^x [B]^y$ here; x = Order of Rxn wrt A

y = Order of Rxn wrt B

[$x + y = n$ (overall order of rxn)]

* unit of K:

- for n^{th} order reaction,

$$a \longrightarrow \text{product}$$

$$\text{rate} = K[A]^n$$

$$K = \frac{\text{rate}}{[A]^n}$$

$$K = \frac{\text{concentration}}{\text{time}} \times \frac{1}{\text{conc}^n \text{ of } n}$$

$$K = (\text{concentration})^{1-n} \cdot \text{time}^{-1}$$

- SI unit: mol/ltr time: secs

* unit of K for different reaction order are:

(a.) zero order reaction:

→ $n = 0$ unit of K = mol/ltr.sec

b.) First order reaction:

→ $n = 1$ unit of K = sec^{-1}

c.) Second order reaction:

→ $n = 2$ unit of K = $\text{mole}^{-1}\ \text{ltr} \cdot \text{sec}^{-1}$

*** NOTE:**

- for gaseous reaction unit of K maybe $(atm)^{1-n}$ $time^{-1}$

Q:6 → write diff. b/w molecularity and order of rxn

* Zero order reaction: Important (board)

- those chemical reaction whose rate does not depend upon the concentration of reactant.
- for a general chemical reaction,

$$R \longrightarrow P$$

$$-\frac{d[R]}{dt} = K[R]^n$$

(∵ Order of rxn (n) = 0)

then,

$$\boxed{-\frac{d[R]}{dt} = K}$$

(differentiated form of zero order rxn)