

Chemical Kinetics

Branch of physical Chemistry which deals with Rates of Chemical Reactions & various factors which affects the Rate of Reaction (ROR).

It also deals with mechanism of reaction

- Rate of Reaction (ROR)
- ⇒ Factors affecting ROR → Temp, Pressure
- Order of Reaction → Ist / IInd / IIIrd / nth / zero
- ⇒ Rate Law
- Molecularity of Reaction
- Methods to determine OOR (Order of Reaction)
- Mechanism of Reaction.

Rate of Reaction (ROR)

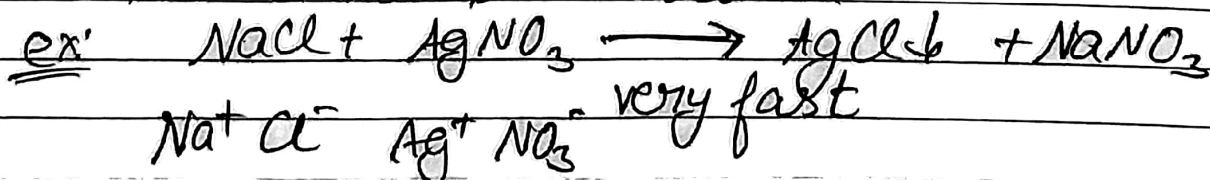
⇒ Speed of change in concentration of reactant / Product

⇒ Change in concentration of reactant / product per unit time

Very Fast Reactions :-

ionic reactions complete in microseconds

Rate cannot be measured



There is no dissociation or formation of bond

very slow reaction

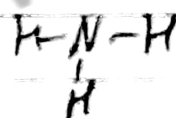
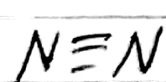
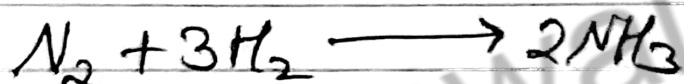
which requires years to complete

No practical use to determine Rate

Moderate Reactions \longrightarrow Rate is determined

\searrow Requires finite time for completion
which can be measured practically

example: Molecular Reaction



Bond Break \longrightarrow

takes
time

Bond formation

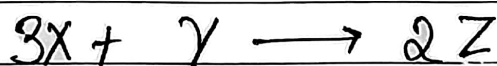
There are two types of rate:-

i) Average Rate of Reaction

ii) Instantaneous Rate of Reaction



$$\text{Average ROR} = -\frac{1}{2} \frac{[\Delta A]}{[\Delta t]} = -\frac{1}{3} \frac{[\Delta B]}{[\Delta t]} = +\frac{1}{4} \frac{[\Delta C]}{[\Delta t]}$$



$$\text{Average ROR} = -\frac{1}{3} \frac{[\Delta X]}{[\Delta t]} = -\frac{1}{1} \frac{[\Delta Y]}{[\Delta t]} = +\frac{1}{2} \frac{[\Delta Z]}{[\Delta t]}$$

$$\text{Rate of disappearance of X} = \left| \frac{[\Delta X]}{[\Delta t]} \right|$$

(R.O.D)

$$\text{Rate of disappearance of Y} = \left| \frac{[\Delta Y]}{[\Delta t]} \right|$$

(R.O.D)

$$\text{Rate of Appearance of Z} = \left| \frac{[\Delta Z]}{[\Delta t]} \right|$$

(R.O.A)

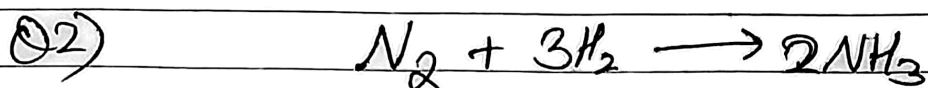
$$\text{Units of Rate of Reaction} = \frac{\text{Conc}}{\text{time}} \text{ mole l}^{-1} \text{ s}^{-1}$$

$$= \frac{\text{Pressure}}{\text{time}} \text{ atm s}^{-1}$$

Q1) Write the correct expression for Average Rate of Reaction :-



$$\text{Avg. ROR} = -\frac{1}{4} \frac{[\Delta\text{NH}_3]}{[\Delta t]} = -\frac{1}{5} \frac{[\Delta\text{O}_2]}{[\Delta t]} = +\frac{1}{4} \frac{[\Delta\text{NO}]}{[\Delta t]} = +\frac{1}{6} \frac{[\Delta\text{H}_2\text{O}]}{[\Delta t]}$$



During the formation of Ammonia, 2 moles of N_2 disappear in 60 s. If volume of vessel is 1 L. Find i) ROR ii) ROD of H_2 iii) ROA of NH_3

Solution

$$\text{i) ROR} = -\frac{1}{1} \frac{[\Delta\text{N}_2]}{[\Delta t]} = \frac{2 \text{ mole}}{\frac{1\text{L}}{60\text{s}}} = \frac{1}{30} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\text{ii) ROD of H}_2 = +\frac{[\Delta\text{H}_2]}{[\Delta t]}$$

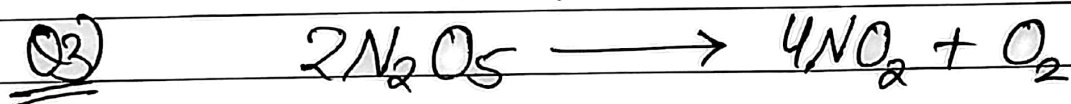
$$\text{ROR} = \frac{1}{3} \frac{[\Delta\text{H}_2]}{[\Delta t]}$$

$$\frac{[\Delta\text{H}_2]}{[\Delta t]} = 3\text{ROR} = 3 \times \frac{1}{30} = \frac{1}{10} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\text{iii) ROA of } \text{NH}_3 = \frac{[\Delta \text{NH}_3]}{[\Delta t]}$$

$$\text{ROR} = +\frac{1}{2} \frac{[\Delta \text{NH}_3]}{[\Delta t]}$$

$$\left| \frac{[\Delta \text{NH}_3]}{[\Delta t]} \right| = 2\text{ROR} = 2 \times \frac{1}{30} = \frac{1}{15} \text{ mol L}^{-1} \text{ s}^{-1}$$



If ROA of NO_2 is 2 mole/l sec . Find.

ROR & ROD of N_2O_5

Solution

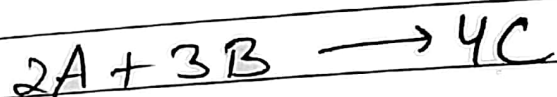
$$\text{ROR} = -\frac{1}{2} \frac{[\Delta \text{N}_2\text{O}_5]}{[\Delta t]} = +\frac{1}{4} \frac{[\Delta \text{NO}_2]}{[\Delta t]} = \frac{1}{1} \frac{[\Delta \text{O}_2]}{[\Delta t]}$$

$$\text{i) ROR} = +\frac{1}{4} \frac{[\Delta \text{NO}_2]}{[\Delta t]} = \frac{1}{4} \times 2 = \frac{1}{2} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{ii) ROR} = -\frac{1}{2} \frac{[\Delta \text{N}_2\text{O}_5]}{[\Delta t]}$$

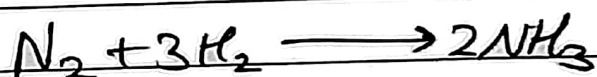
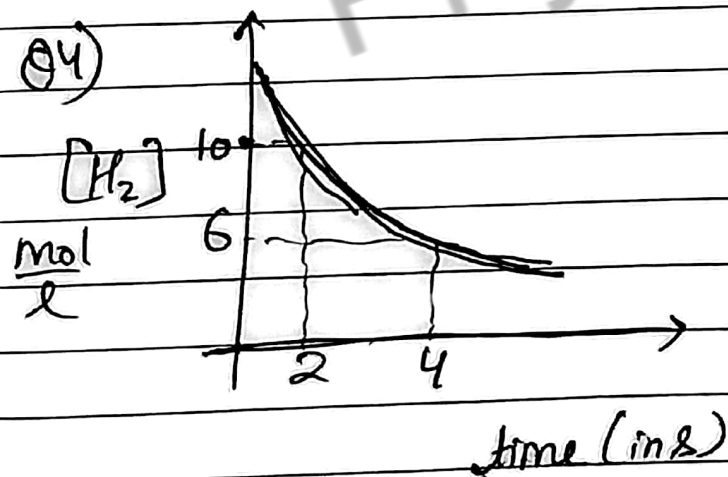
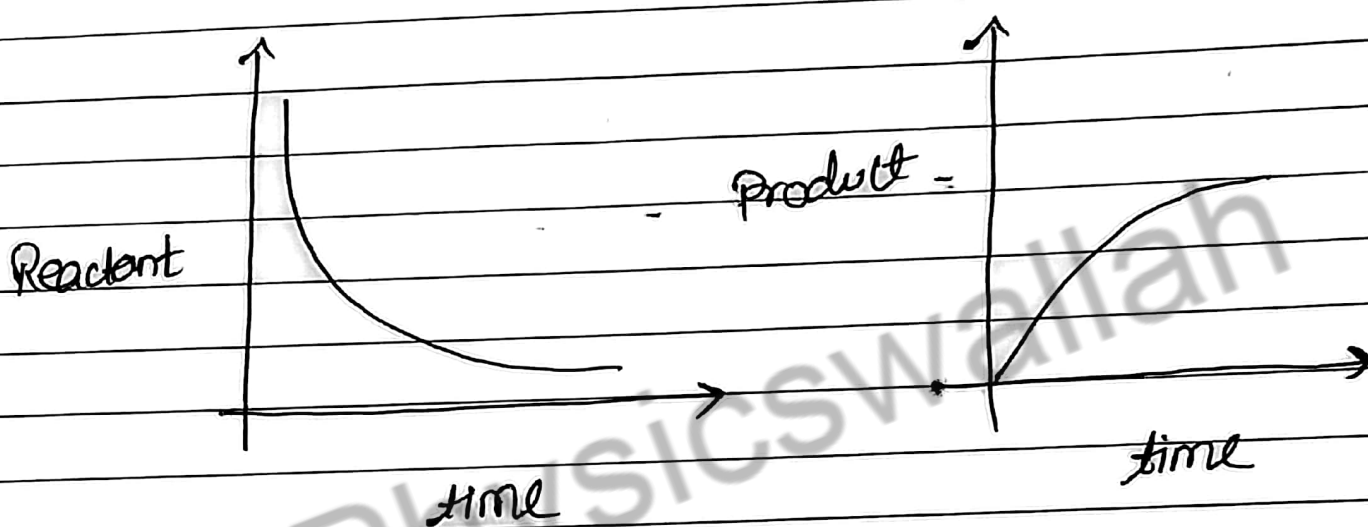
$$\left| \frac{[\Delta \text{N}_2\text{O}_5]}{[\Delta t]} \right| = 2\text{ROR} = 2 \times \frac{1}{2} = 1 \text{ mol L}^{-1} \text{ s}^{-1}$$

Instantaneous Rate of Reaction



$$\text{Inst. ROR} = -\frac{1}{2} \frac{dA}{dt} = -\frac{1}{3} \frac{dB}{dt} = +\frac{1}{4} \frac{dC}{dt}$$

Graphical Representation



Find i) ROR

ii) ROD of N_2

iii) ROA of NH_3

$$\frac{\Delta[H_2]}{\Delta t} = \frac{d[H_2]}{dt} = -\left(\frac{10-6}{4-2}\right) = -\frac{4}{2} = -2 \text{ mol l}^{-1} \text{ s}^{-1}$$

$$\text{ROR} = -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = -\frac{1}{3} \times -2 = \frac{2}{3} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$ROR = -\frac{1}{1} \frac{dN_2}{dt}$$

$$\Rightarrow \left| \frac{d[N_2]}{dt} \right| = ROR = \frac{2}{3} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$ROR = +\frac{1}{2} \frac{d[NH_3]}{dt}$$

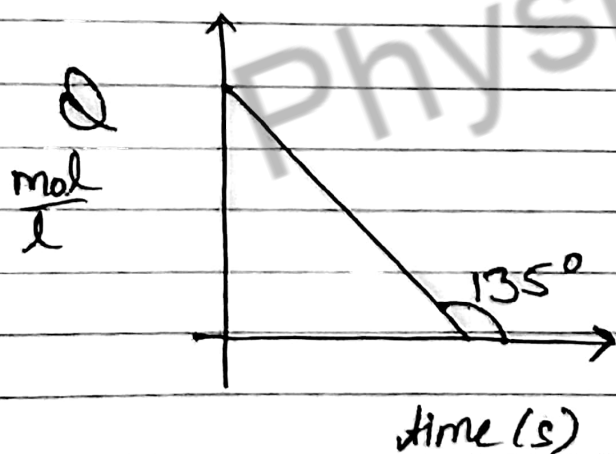
$$\left| \frac{d[NH_3]}{dt} \right| = 2ROR = \frac{4}{3} \text{ mol l}^{-1} \text{ s}^{-1}$$

Q5)



Find i) ROR

ii) ROA of R

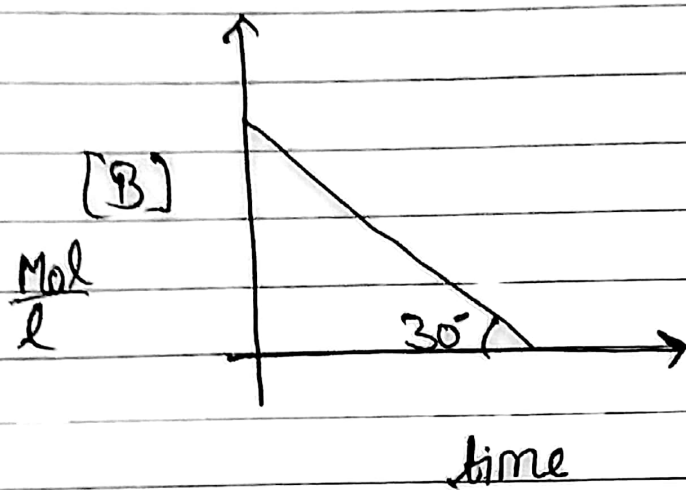
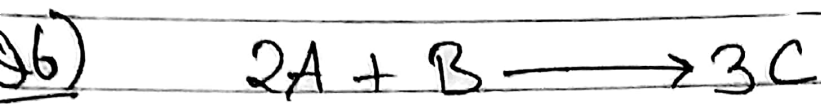


$$\frac{dQ}{dt} = \tan 135^\circ = -1$$

$$i) ROR = -\frac{1}{3} \frac{dQ}{dt} = -\frac{1}{3} \times -1 = \frac{1}{3} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$ROR = \frac{d[R]}{dt}$$

$$ii) \left| \frac{d[R]}{dt} \right| = ROR = \frac{1}{3} \text{ mol l}^{-1} \text{ s}^{-1}$$



Find i) RoR
ii) ROA of C

$$\frac{dB}{dt} = \tan 150^\circ = -\tan 30^\circ = -\frac{1}{\sqrt{3}}$$

i) $\text{RoR} = -\frac{1}{1} \frac{d[B]}{dt} = -1 \times -\frac{1}{\sqrt{3}} = \frac{1}{\sqrt{3}} \text{ mol l}^{-1} \text{ s}^{-1}$

ii) $\text{RoR} = \frac{1}{3} \frac{d[C]}{dt}$

$$\left| \frac{d[C]}{dt} \right| = 3 \text{RoR} = \sqrt{3} \text{ mol l}^{-1} \text{ s}^{-1}$$

In terms of Pressure

Q7)