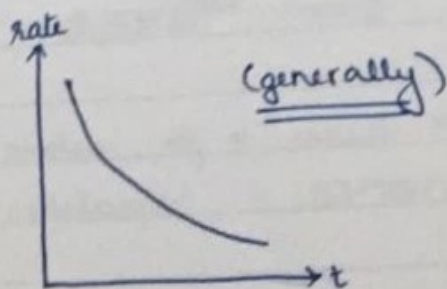
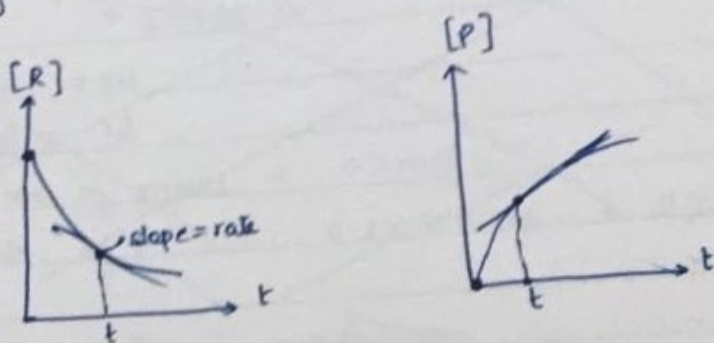


CHEMICAL KINETICS

- Rate of rxn: $R \rightarrow P$
- avg. rate w.r.t reactants = $-\frac{\Delta[R]}{\Delta t} = -\frac{(C_2 - C_1)}{t_2 - t_1}$

[(-) indicates a decrease.]

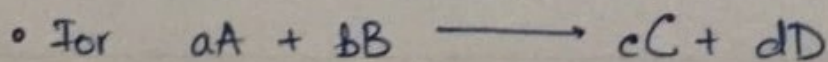
- avg. rate w.r.t products = $\frac{\Delta[P]}{\Delta t} = \frac{C_2 - C_1}{t_2 - t_1}$



- Generally rate of a rxn decreases with time and hence we use instantaneous rate i.e. rate at a given time. i.e.

$$\text{rate} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Units: $\frac{\text{mol/l}}{\text{time}} = \boxed{\text{mol l}^{-1} (\text{time})^{-1}}$



$$\frac{1}{a} \left(-\frac{d[A]}{dt} \right) = \frac{1}{b} \left(-\frac{d[B]}{dt} \right) = \frac{1}{c} \left(\frac{d[C]}{dt} \right) = \frac{1}{d} \left(\frac{d[D]}{dt} \right)$$

rate of decomposition of A rate of formation of C



If rate of decomposition of N_2 is $4 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$ then what is the rate of formation of NH_3 and rate of rxn?

A. Rate of formation of $NH_3 = x$.

$$\frac{1}{2} \times x = 1 \times 4 \times 10^{-2}$$
$$x = 8 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$$

Rate of rxn = $4 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$

→ Factors:

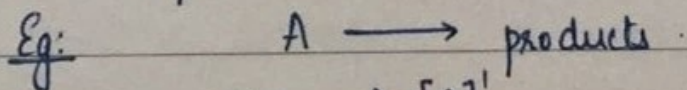
1. Nature of reactants:

- Ionic reactions faster than covalent rxn as covalent rxns involve bond breakage and formation.
- Greater the no. of bonds to be broken, slower the rate of rxn.

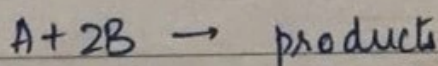
2. Conc. of reactants:

- Rate $\propto [R]^n$
 $\text{rate} = k [R]^n$ [where $n = \text{order of the rxn.}$]
rate law / rate eqn. of the rxn.

- For simple rxns [single step rxns], we can write the rate eqn by seeing the balanced chemical eqn.



$$\text{rate} = k [A]^1$$

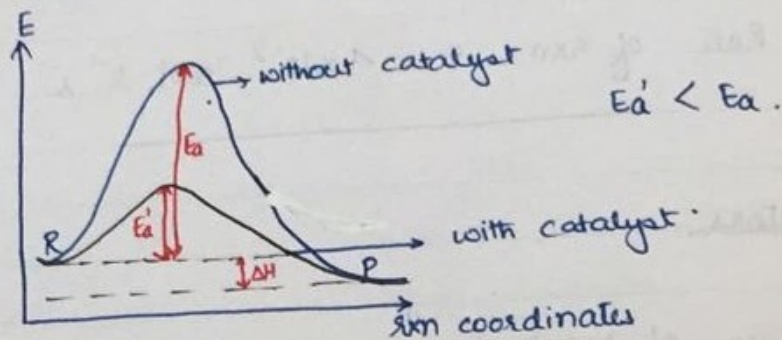


$$\text{rate} = k [A][B]^2$$

→ For complex rxns, rate eqn. is to be written by experiment.

3. Catalyst :

On using catalyst (+ve catalyst) the rate of rxn increases: "as the rxn. path changes in a way in which the activation energy is decreased."



4. Temperature :

With increase in temp., KE & collision freq. of reactants increases to increase the rate of rxn.

[Here, we have considered E_a to remain constant within certain range of temperature].

Generally, for every 10°C rise in temp, rate of rxn doubles.

i.e. eg: $\frac{k_{35^\circ\text{C}}}{k_{25^\circ\text{C}}} \approx 2$

$$\frac{k_{(t+10)^\circ\text{C}}}{k_{t^\circ\text{C}}} = 2$$

ratio called - temperature co-efficient.

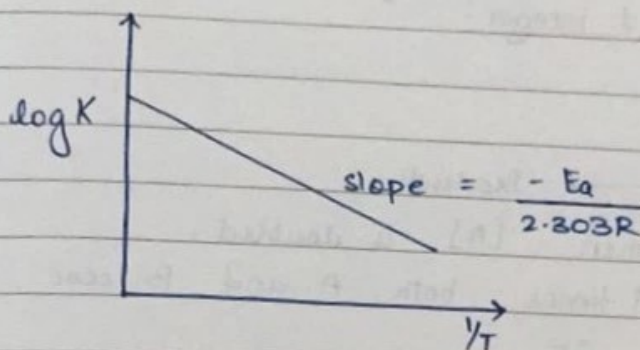
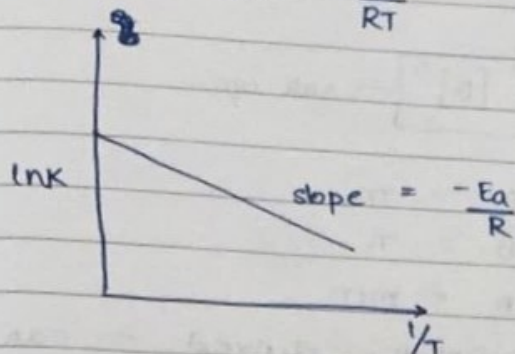
Arrhenius eqn:

$$k = A e^{-E_a/RT}$$

↓
Arrhenius const.

• A → constant within temperature range.

$$\ln K = \ln A - \frac{E_a}{RT}$$



$$* \log K = \log A - \frac{E_a}{2.303RT}$$

$$\log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

E_a is +ve.

$$\text{If } \underline{\underline{T_2 > T_1}} \Rightarrow \underline{\underline{k_2 > k_1}}$$

* Rate constant K increases with temperature for all reactions whether exothermic / endothermic.

[But equi. constant increases with temp. for endothermic
decreases " " " " exothermic.]

* For some particular rxns, rate depends upon the pH, intensity of light ($\propto I$) and dielectric constant ($\propto \epsilon$) and strength of electrical E , magnetic fields, particle size of the reactants ($\propto \frac{1}{r}$) and physical state of rxns.