CHEMICAL KINETICS

Concepts of chemical kinetics, rate of reaction and factors affecting the rate of reaction

VERY SHORT ANSWER QUESTIONS

1. What is rate of reaction?

Ans: Rate is usually expresses as the ratio of the amount of change in some quantity to the time required to produce that change.

Rate = (Change in some quantity)/(Time taken for the change) = $\Delta X/\Delta t$

The term ΔX means $X_{final} - X_{initial}$ and Δt is the amount of time elapsed

2. What is order of reaction?

Ans: Let us consider a good reaction:

$m_1A + m_2B + m_3C \rightarrow$ product

Let active moles of 'A', 'B' and 'C' be 'α', 'β' and 'γ' respectively. Then, rate of reaction may be given as:

Rate = $k[A]^{\alpha}[B]^{\beta}[C]^{\gamma}$

Sum of powers of concentration terms involved in rate law expression is called order of reaction.

$\alpha + \beta + \gamma$ order

3. What are the factors that affect rate of reaction?

Ans: i) Nature of the reactants:

(ii) Concentration of reactants

(iii) Effect of temperature

(iv) Presence of a positive catalyst

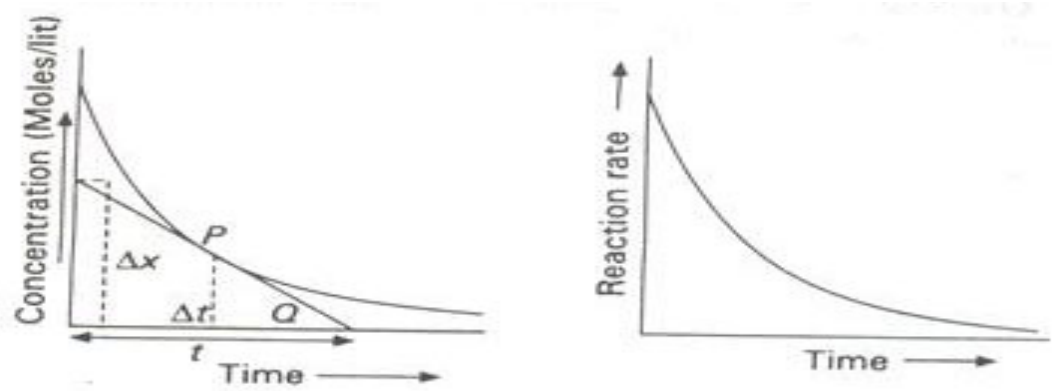
(v) Presence of negative catalyst

SHORT ANSWER QUESTIONS

1. How does rate of reaction change with time?

Ans: **Expression of Rate**

Since the concentrations of the reactants keep on decreasing with time, the rate of reaction correspondingly decreases with time. Thus, the rate of reaction will depend on the stage considered during progress of the reaction. The rate of reaction is maximum at the initial stage and decreases with time. Theoretically, infinite time would be required for a reaction to complete. But the reaction rate becomes so slow after a certain time that for all practical purposes, the reaction can be considered to be completed. It is evident from fig 8.2 (b) that the rate of reaction is varying from moment to moment.

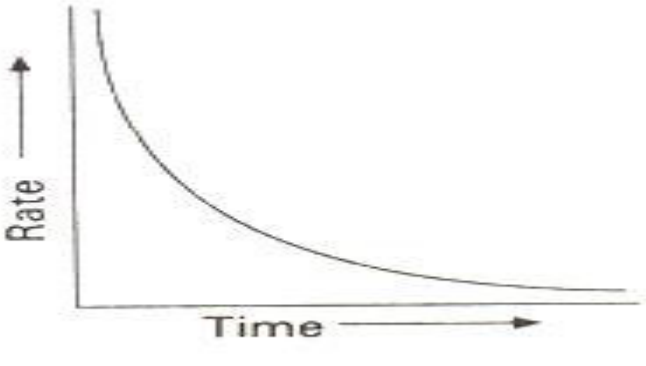


3. How is rate of reaction effected by change of concentration of reactants?

Ans: Concentration of reactants affects the rate of reaction.

Let us consider the reaction:

$A + B \rightarrow C + D$; Rate = k[A][B]



Rate of the above reaction decreases with the passage of time because the concentration of reactants A and B will decrease as time pass on.

4. Explain the effect of temperature on rate of reaction.?

Ans: Effect of temperature

The rate of reaction increases considerably with an increase in temperature. The rates of many reactions are approximately doubled or tripled for every 10^oC rise in temperature. The temperature coefficient of a chemical reaction is defined as the ratio of the specific reaction rates of a reaction at two temperature differing by 10^oC.

μ = Temperature coefficient= $k_{(r+10)}/k_t$

Let temperature coefficient of a reaction be ' μ ' when temperature is raised from T_1 to T_2; then the ratio of rate constants or rate may be calculated as

$$\mathbf{k_{T2}/k_{T1} = (\mu)^{(T_2 - T_1)/10} = \mu^{\Delta T/10}}$$

$$\mathbf{\log_{10}(k_{T2}/k_{T1}) = \Delta T/10 \log_{10}\mu}$$

$$\mathbf{k_{T2}/k_{T1} = \text{antilog}\,[\Delta T/10 \log_{10}\mu]}$$

Its value lies generally between 2 and 3.

LONG ANSWER QUESTIONS

Ans: Factors influencing rate of reaction:

1) Nature of the reactants:

- The rate of reaction depends on the nature of reactants.
- Reactants which require less activation energy react faster than the reactants which require higher activation energy.
- Ionic reactions and neutralisation reactions are very fast in solution as they involve simple exchange of ions.
- Reactions between covalent molecules are generally slow as they involve shuffling of bonds.
  The reactions which involve greater bond rearrangements are slow and the reactions involving lesser bond rearrangements are fast.

Fast reactions	**Slow reactions**
i) $H^+ + OH^- \rightarrow H_2O$	$2H_2O + O_2 \rightarrow 2H_2O$
ii) $2NO + O_2 \rightarrow 2NO_2$	$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

2) Effect of concentration of reactants:

- According to law of mass action, the rate of a chemical reaction is directly proportional to the product of concentration of reactants.
- In case of gaseous reactions, rate is directly proportional to the product of partial pressures of reactants.
- If concentration is higher, the number of molecules per unit volume is, more and the number of active collisions increases. According to collision theory, rate of reaction increases with increase in the number of collisions.
- The dependence of rate of reaction on the concentration of reactants can be mathematically expressed as $-\frac{dc}{dt} = k.C^n$ (n can take any simple value including zero)

3) Effect of temperature:

- With increase in temperature rate of reaction increases because the number of active collisions or activated molecules increases.

- According to Arrhenius for most of the reactions rate of reaction doubles or triples for every 10° rise in temperature.

  Temperature coefficient ( ) = $\frac{K_{T+10}}{K_T} = 2$ (or) 3

- Arhenious suggested a simple empirical relation between specific rate and temperature.

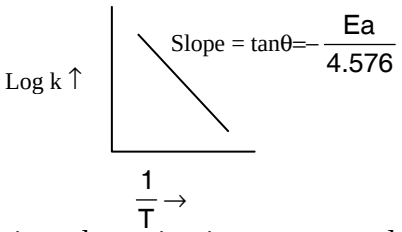
  $K = A.e^{-Ea/RT}$

  $\ell n\, K = \ell n\, A - Ea/RT$

  $2.303\ \ell og\, K = 2.303\ \ell og\, A - Ea/RT$

  $\ell og\, K = \ell og\, A - \frac{Ea}{2.303R} \times \frac{1}{T}$

  Plot of log k Vs $\frac{1}{T}$ gives a linear graph with –ve slope.



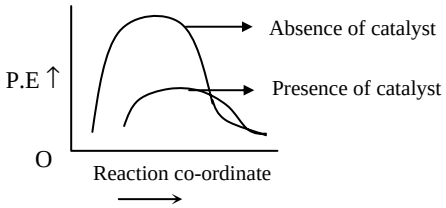
- Slope gives the activation energy and intercept gives frequency factor.

4) Effect of catalyst:

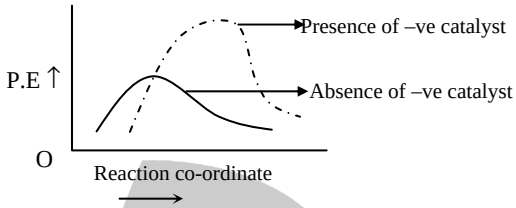
- Catalyst alters the speed of reaction by changing the activation energy.
- Catalyst alters the activation energy by changing the path of the reaction or

mechanism of reaction.

- A positive catalyst increases the rate of reaction by decreasing the activating energy. In case of some reactions, rate is proportional to the concentration of catalyst.
  Ex : Acid catalysed hydrolysis of ester.



- A negative catalyst decreases the rate of reaction by increasing the activation energy.



- Enzymes are biocatalysts for biochemical reactions.

5) Effect of radiation:

- Some chemical reactions take place very fast by absorbing sunlight. Such chemical reactions are called photocatalysed or photo accelerated or photosensitized reactions.

6) Physical state of reactants:

- In heterogeneous system, collisions are not much effective as that of in homogeneous system. There fore reactions are much faster in gaseous and liquid states.
  Rate of reaction:
  Gaseous state > Liquid state >Solid state

7) Physical size of reactants:

- In case of solids, rate increases with decrease in the size of particle. Rate is faster in powdered state than that of undivided state because surface area increases and the possibility of contact between reactant molecules increases.