Class XII

Chemistry

Ch. 4: Chemical Kinetics

Chapter Notes

Key learnings:

1. Chemical kinetics: The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical kinetics.
2. Rate of reaction: It is defined as the change in concentration of reactant (or product) in unit time. Unit of rate of reaction is mol $L^{-1}s^{-1}$.
3. Average rate: The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$.
4. Instantaneous rate: It is the rate of reaction when the average rate is taken over a particular moment of time. It is equal to dx/dt.
5. Rate law or rate equation: It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
6. Rate constant: When the concentration of reactants is unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
7. Molecularity of a reaction: Total number of atoms, ions or molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number. It is never more than three. It cannot be zero.
8. Order of a reaction: The sum of the exponents (power) of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
9. Half- life of a reaction: The time taken for a reaction, when half of the starting material has reacted is called half- life of a reaction. For first order reaction $t_{\frac{1}{2}} = \frac{0.693}{k}$, where k is rate constant.

   It is independent of initial concentration for first order reaction.

10. Pseudo first order reaction: The reaction which is bimolecular but order is one is called pseudo first order reaction. This happens when one of the reactants is in large excess. E.g., acidic hydrolysis of ester (ethyl acetate).

    $$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

11. Activation energy (E_a): It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to the formation of product molecules.

12. Arrhenius equation of reaction rate: It gives the relation between rate of reaction and temperature.

    $k = Ae^{-E_a/RT}$

    where k = rate constant, A = frequency factor,

    E_a = energy of activation

    R = gas constant, T = temperature in Kelvin,

    $\ln k = \ln A - E_a/RT$

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

13. Mechanism of reaction: The sequence of elementary processes leading to the overall stoichiometry of a chemical reaction is known as mechanism of a reaction.

14. Activated complex: It is defined as unstable intermediate formed between reacting molecules. It is highly unstable and readily changes into product.

15. Rate determining step: The slowest step in the reaction mechanism is called rate determining step.

16. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Top Formulae:

1. Instantaneous rate = $\frac{dx}{dt}$, where dx is small change in conc. and dt is the smallest interval of time.

2. Average rate = $\frac{\Delta x}{\Delta t}$, where Δx is change in concentration and Δt is large interval of time.

3. $A + B \rightarrow C + D$

   Rate of disappearance of $A = \frac{-d[A]}{dt}$, where d[A] is small change in conc. of 'A' and dt is small interval of time

   Rate of disappearance of B $= \frac{-d[B]}{dt}$,

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

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

   $$\text{Rate} = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

   Unit of rate of reaction = mol $L^{-1}s\text{-}^{1}$

4. Order of reaction:

   If rate law expression for a reaction is

   Rate = $k\,[A]^x\,[B]^y$

   Order of reaction = x + y

   Remember: Order cannot be determined with a given balanced chemical equation. It can be experimentally determined.

5. Integrated rate law for zero order reaction:

   $R \rightarrow P$

   $$\frac{dx}{dt} = k[R]^0$$

   Unit of 'k' is mol $L^{-1}s^{-1}$

$$k = \frac{[R_o] - [R]}{t}$$

If we plot a graph between concentration of R vs time, the graph is a straight line with slope equal to -k and intercept is equal to $[R_o]$

6. Half- life reaction for a for zero order reaction:

$$t_{1/2} = \frac{[R_0]}{2k}$$

7. Rate law for Ist order reaction:

$$R \rightarrow P$$

$$k = \frac{2.303}{t} \log \frac{[R_o]}{[R]}$$

where 'k' is rate constant or specific reaction rate, $[R_o]$ is initial molar conc., [R] is final molar conc. after time't'

If we plot a graph between ln[R] with time, we get a straight line whose slope $= -k$ and intercept $\ln[R_o]$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

where 'a' is initial conc. in mol L^{-1}, x mol L^{-1} have reacted in time 't' final conc., after time 't' is (a – x)

8. Half- Life for a first order reaction is:

$$t_{1/2} = \frac{0.693}{k}$$

9. Formula to calculate rate constant for first order gas phase reaction of the type

$A(g) \rightarrow B(g) + C(g)$

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

Where:

p_i is initial pressure of A

p_t is total pressure of gaseous mixture containing A , B, C

Remember:

$p_t = p_A + p_B + p_C$

10. Arrhenius equation:

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

11. $$\log\frac{k_2}{k_1}=\frac{E_a}{2.303\ R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

12. $$\text{Rate}=P\,Z_{AB}.e^{\frac{-E_a}{RT}}$$

Where:

Z_{AB} represents the collision frequency of reactants, A and B

$e^{\frac{-E_a}{RT}}$ represents the fraction of molecules with energies equal to or greater than E_a

P is called the probability or steric factor