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CHEMICAL KINETICS

- **Chemical Kinetics:** The branch of physical chemistry which deals with the study of rate of reaction and factors affecting rate.

RATE OF A CHEMICAL REACTION

- Rate of chemical reaction: The change in concentration of any reactant or product per unit time is called rate of reaction.

AVERAGE RATE AND INSTANTANEOUS RATE

- **Average rate of reaction:** The rate of reaction measured over the long time interval is called average rate of reaction.

$$\text{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta\,[p]/\Delta t$$

- **Instantaneous rate of reaction:** The rate of reaction measured at a particular time is called instantaneous rate of reaction.

$$\text{Avg rate } \Delta x/\Delta t = -\Delta[R]/\Delta t = +\Delta\,[p]/\Delta t$$

FACTORS AFFECTING RATE OF A REACTION

1. The concentration of reactants: Generally the rate of a reaction increases as the concentration of the reactants is increased.

2. Temperature: A reaction is faster when the reaction temperature is increased.

3. Presence of a catalyst: A catalyst alters the reaction rate without being consumed by the reaction.

DEPENDENCE OF REACTION RATE UPON CONCENTRATION

- **Rate law:** The rate of reaction is directly proportional to the product of concentration of reactant and each concentration is raised to some power which may or may not be equal to stereochemistry experimentally. For a reaction, aA + bB $\rightarrow$ cC + dD

$$\text{Rate law} = k[A]^p[B]^q$$

Where, powers p and q are determined experimentally.

ORDER AND MOLECULARITY OF A REACTION

- **Molecularity:** The total number of reactants taking part in elementary chemical reaction is called molecularity.
- **Order of reaction:** The sum of powers to which the concentration terms are raised in a rate law expression is called order of reaction.

For above case, **Order = P + Q**

Orders of reaction are determined experimentally.

UNITS OF RATE CONSTANT

- The units of the rate constant, k, depend on the overall reaction order. The units of k for a zero-order reaction are M/s, the units of k for a first-order reaction are 1/s, and the units of k for a second-order reaction are 1/(M·s).
- In general for any order n the unit for rate constant k is given as $\mathbf{k = (mol\ L^{-1})^{1-n}\ s^{-1}}$

Zero Order Reactions

- Zero order reactions are those whose rate is proportional to zeroth power of concentration, that is, the rate is independent of concentration of the reactant.
- Integrated rate law equation for zero order reaction is given as below :

(a) $k = \dfrac{[R]_0 - [R]_t}{t}$

Where k is rate constant and $[R]_0$ is initial molar concentration.

(b) $t_{1/2} = \dfrac{[R]_0}{2k}$ $\quad t_{1/2}$ is half-life period of zero order reaction.

First Order Reaction

- **A first-order reaction** is a chemical reaction in which the rate varies based on the changes in the concentration of only one of the reactants.
- **Integrated rate law equation for first order reaction :**

$$\text{(a)} \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

Where, k is rate constant, $[R]_0$ is initial molar concentration and [R] is final concentration at time 't'.

(b) Half-life period ($t_{1/2}$) for first order reaction:

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

- **Pseudo chemical reaction:** The chemical reaction which looks like higher order reaction but in real it follows lower order reaction.

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k[CH_3COOC_2H_5]^1$$

Order = 1

COLLISION THEORY OF REACTION RATES

- According to this theory, the reactant molecules are assumed to be hard spheres and the reaction is postulated to occur, when molecules collide with each other.
- The number of collisions between the reacting molecules taking place per second per unit volume is known as collision frequency (Z_{AB}).
- But only those collisions in which the colliding species are associated with certain minimum amount of energy and collide in proper orientation result in the product formation, such collisions are called fruitful collisions or effective collision.
- Here, rate = – (dv/dt) = collision frequency x fraction of effective collision = Z_{AB} x f = Z_{AB} x $e^{-E_a/RT}$

DEPENDENCE OF REACTION RATE ON TEMPERATURE

- **Arrhenius Equation:** Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is:

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

or $$\ln k = \ln A - \frac{E_a}{RT}$$

or $$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

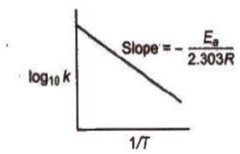


Fig. 14.3 Graphical determination of Ea.

Where, A = frequency or Arrhenius factor. It is also called pre-exponential factor, R = gas constant and Ea = activation energy

- **Half-life period:** The time during which the concentration of the reactant is reduced to half of its initial concentration is called half-life period.
- **Activated complex (or transition state):** Activated complex is the highest energy unstable intermediate between the reactants and products and gets decomposed immediately (having very short life), to give the products. In this state, bonds of reactant are not completely broken while the bonds of products are not completely formed.

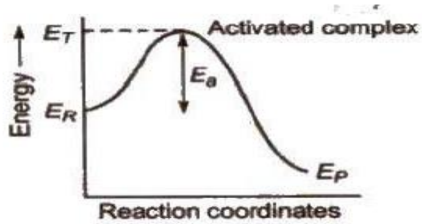


Fig. 14.2 Energy diagram for a reaction

- **Threshold energy (E_T)**: The minimum amount of energy which the reactant must possess in order to convert into products is known as ***threshold energy***.
- **Activation energy (E_a):** The additional amount of energy, required by the reactant so that their energy becomes equal to the threshold value is known as ***activation energy***.
- **Activation energy = Threshold energy ñ Kinetic energy**

$$\Rightarrow E_a = E_T - E_R$$

- Energy of activation can be evaluated as:

$$\text{Log}[K2/K1] = \text{Ea}\ (1/T1-1/T2)/2.303RT$$

$$\text{Log}[K2/K1] = \text{Ea}(1/T1-1/T2)\ /\ 19.15$$

- **Temperature coefficient:** The ratio of rate constant at two temperatures having difference of 10ºC is called temperature coefficient. **Temperature coefficient = Rate constant at T + 10ºC/Rate constant at TºC**
- **Photochemical Reactions:** Chemical reactions that occur on exposure to visible radiation are called photochemical reactions. φ = (number of reactant molecules reacting in a given time / number of photons (quanta) of light absorbed ill the same time).
- **Chemical Reactions on the Basis of Rate of Reaction**:

  1. Fast/instantaneous reactions: Chemical reaction which completes in less than Ips (10^{-12} s) time IS known as fast reaction. It IS practically impossible to measure the speed of such reactions, e.g., ionic reactions. Organic substitution reactions.

  2. Slow reactions: Chemical reactions which completes in a long time from some minutes to some years are called slow reactions. e.g., rusting of iron, transformation of diamond etc.

  3. Moderately slow reactions: Chemical reactions which are intermediate between slow and fast reactions are called moderately slow reactions.

Factors affecting Rate of Reaction:

1. Concentration of reactant
2. Surface area
3. Temperature
4. Nature of reactant
5. Presence of catalyst
6. Radiation in photochemical reaction

- **Examples of Zero Order Reactions:** Some reactions show zero order under certain conditions.

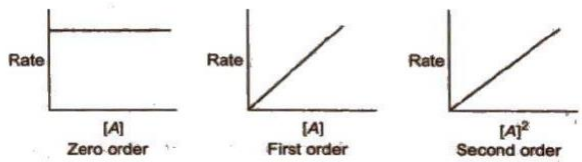
(1) Decomposition of HI on the surface of gold catalyst when the pressure of HI is high.

(2) Photochemical combination of H_2 and Cl_2 to form HCl when carried out over water.

(3) Enzyme reactions when the substrate concentration is high in comparison to the enzyme concentration.

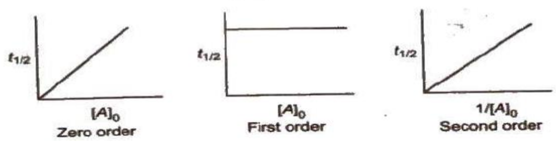
Methods to Determine Order of Reaction

(i) Graphical method:



Half-life period ($t_{1/2}$) method

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$



Check Yourself

1. What will be the fraction of molecules having energy equal to or greater than activation energy, E_a?

(A) K (B) A

(C) $Ae^{-Ea/Rt}$ (D) $e^{-Ea/Rt}$

2. For a chemical reaction A→B, it is found that the rate of reaction doubles when the concentration of A is increased four times. The order of reaction is

(A) Two (B) One

(C) Half (D) Zero

3. The half life of the first order reaction having rate constant K = 1.7 x $10^{-5}s^{-1}$ is

(A) 12.1 h (B) 9.7 h

(C) 11.3 h (D) 1.8 h

4. The rate of a chemical reaction tells us about

(A) The reactants taking part in the reaction

(B) the products formed in the reaction

(C) How slow or fast the reaction is taking place

(D) None of the above

5. The average rate and instantaneous rate of a reaction are equal

(A) At the start (B) At the end

(C) In the middle

(D) When two rates have a time interval equal to zero

Stretch Yourself

1. If the rate constant of a reaction is k = 3 × 10^{-4} s^{-1}, then identify the order of the reaction.

2. For a reaction R → P, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?

3. A reaction is of second order with respect to a reactant. How will the rate of reaction be affected if the concentration of this reactant is

(i) Doubled, (ii) Reduced to half?

4. The rate constant for a reaction of zero order in A is 0.0030 mol L^{-1} s^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M?

5. Distinguish between 'rate expression' and 'rate constant' of a reaction.

Test Yourself

Question: What do you understand by the rate law and rate constant of a reaction? Identify the order of a reaction if the units of its rate constant are: (i) L^{-1} mol s^{-1} (ii) L mol^{-1} s^{-1}

Answer: Rate=k $[A]^x$ $[B]^y$

⇒ Order=x+y

The reaction order from each of the following units of reaction rate constant:

(i)$L^{-1}mols^{-1}$: Zero order

(ii)$Lmol^{-1}s^{-1}$: Second order

Answers

Check Yourself

Answer: 1(D); 2(C); 3(C); 4(C); 5(B)

Stretch Yourself

1. On the basis of unit of rate constant (s^{-1}), the order of the reaction is first order.

2. Second Order

3. 1. A reaction is second order with respect to a reactant.

Rate =k[A]2

(i) If the concentration of the reactant is doubled, the rate of reaction becomes 4 times.

(ii) If the concentration of the reactant is reduced to half, the rate of reaction becomes one fourth.

4. For a zero order reaction

$$K = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$[A]_0 = 0.10M \qquad [A] = 0.075M$$

$$K = \frac{[A]_0 - [A]}{t}$$

$$t = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s}$$

5. Do it by yourself.