



INDIAN SCHOOL AL WADI AL KABIR

Class: XII

DEPARTMENT: SCIENCE (2020-21)

SUBJECT: CHEMISTRY

HANDOUTS

TOPIC: CHEMICAL KINETICS

Note:

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NAME OF THE STUDENT

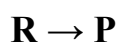
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CHAPTER 4 – CHEMICAL KINETICS

Rate of a chemical reaction

- The rate of a reaction is defined as the change in concentration of a reactant or product in unit time.
- **The rate can be expressed in terms of:**
 - (I) the rate of decrease in concentration of any one of the reactants.
 - (ii) the rate of increase in concentration of any one of the products.
- ❖ Consider a hypothetical reaction,



Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = - \frac{\Delta[R]}{\Delta t}$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta[P]}{\Delta t}$$

- These equations represent the average rate of a reaction, r_{av}
- Since, $\Delta[R]$ is a negative quantity, it is multiplied with -1 to make the rate of the reaction a positive quantity.

Instantaneous and average rate of a reaction

- Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.

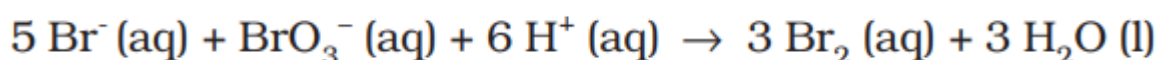
$$r_{\text{av}} = \frac{-\Delta[\text{R}]}{\Delta t} = \frac{\Delta[\text{P}]}{\Delta t}$$

- To express the rate at a particular moment of time, **instantaneous rate** is determined. It is obtained when the average rate at the smallest time interval, dt is considered. (i.e. when Δt approaches zero).
- Hence, for an infinitesimally small dt, instantaneous rate is given by:

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

EXAMPLE

- For the reaction,



$$\text{Rate} = -\frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = -\frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Factors influencing rate of a reaction

- Rate of reaction depends upon concentration of reactants (pressure in case of gases), temperature and catalyst.
- The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as **rate equation** or **rate expression**.
- Rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Rates generally increase when reactant concentrations increase.

Rate expression and Rate constant

- Consider a general reaction, $\mathbf{aA + bB \rightarrow cC + dD}$, where a, b, c and d are the stoichiometric coefficients of reactants and products.
- The rate expression for this reaction is

$$\text{Rate} \propto [\text{A}]^x [\text{B}]^y$$

where exponents x and y may or may not be equal to a and b.

- Above equation can also be written as

$$-\frac{d[\text{R}]}{dt} = k[\text{A}]^x [\text{B}]^y$$

This form of equation is known as **differential rate equation**.

RATE LAW

- Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

$$\text{Rate} = k [\text{A}]^x [\text{B}]^y$$

where **k** is a **proportionality constant called rate constant**.

- Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, *i.e.*, theoretically but must be determined experimentally.

Order of a reaction

- The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
- In the rate equation, $\text{Rate} = k [\text{A}]^x [\text{B}]^y$

Overall order of a reaction is $x + y$

- ❖ x and y represent the order with respect to the reactants A and B respectively.
- Order of a reaction can be 0, 1, 2, 3 and even a fraction.

Units of rate constant

- For a general reaction, $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

$\text{Rate} = k [\text{A}]^x [\text{B}]^y$, where $x + y = n = \text{order of the reaction}$.

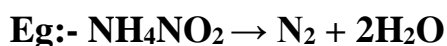
$$k = \frac{\text{Rate}}{[\text{A}]^x [\text{B}]^y}$$

$$= \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n}$$

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

Molecularity of a reaction

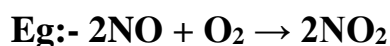
- The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.
- The reaction is said to be unimolecular when only one reacting species is involved.



- Bimolecular reactions involve simultaneous collision between two species.



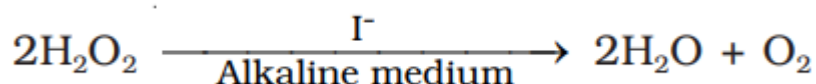
- Trimolecular or termolecular reactions involve simultaneous collision between three reacting species.



- The probability that more than three molecules can collide and react simultaneously is very small. Hence, **the molecularity greater than three is not observed.**

Rate determining step

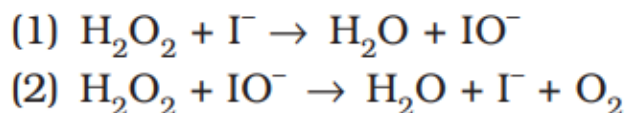
- The slowest step in a reaction called the rate determining step.
- Consider the decomposition of hydrogen peroxide



- The rate equation for this reaction is found to be

$$\text{Rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

- This reaction takes place in two steps:



The first step, being slow, is the *rate determining step*.

CONCLUSION

- (i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non-integer.
- (ii) The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions gives us the products, the reactions are called **complex reactions**.
- (iii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning.
- (iv) For complex reaction, order is given by the slowest step and generally, molecularity of the slowest step is same as the order of the overall reaction.

Zero Order Reactions

- Consider a reaction, $\text{R} \rightarrow \text{P}$

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^0$$

As any quantity raised to power zero is unity

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k \times 1$$

$$d[\text{R}] = -k dt$$

Integrating both sides

$$[\text{R}] = -k t + I$$

Integrating both sides,

$$[\text{R}] = -k t + I \quad \dots\dots\dots (1)$$

where, I is the constant of integration.

- At $t = 0$, the concentration of the reactant $\text{R} = [\text{R}]_0$, where $[\text{R}]_0$ is initial concentration of the reactant.
- Substituting in equation (1)

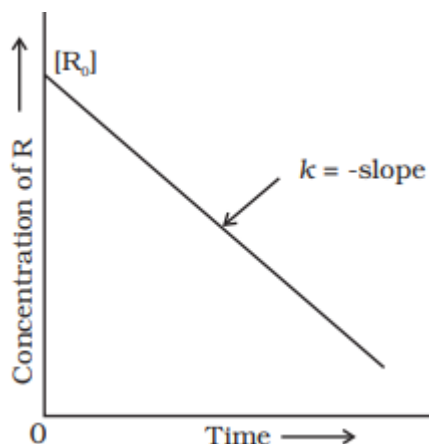
$$[R]_0 = -k \times 0 + I$$

$$[R]_0 = I$$

- Substituting the value of I in equation (1)

$$[R] = -kt + [R]_0 \dots\dots\dots (2)$$

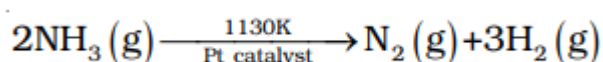
- Comparing equation (2) with equation of a straight line, $y = mx + c$, if a graph is drawn, $[R]$ against t , a straight line with slope = $-k$ and intercept equal to $[R]_0$ is obtained.



- Equation (2) on rearrangement

$$k = \frac{[R]_0 - [R]}{t}$$

- Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.
- The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure.



- At high pressure, the metal surface gets saturated with gas molecules. So, a further change in reaction conditions is unable to alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration.

First Order Reactions

- Consider a reaction, $R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R]$$

$$\frac{d[R]}{[R]} = -kdt$$

- Integrating the above equation,

$$\ln [R] = -kt + I \dots\dots\dots (1)$$

where I is the constant of integration.

- When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

- Therefore, equation (1) can be written as

$$\ln [R]_0 = -k \times 0 + I$$

$$\ln [R]_0 = I$$

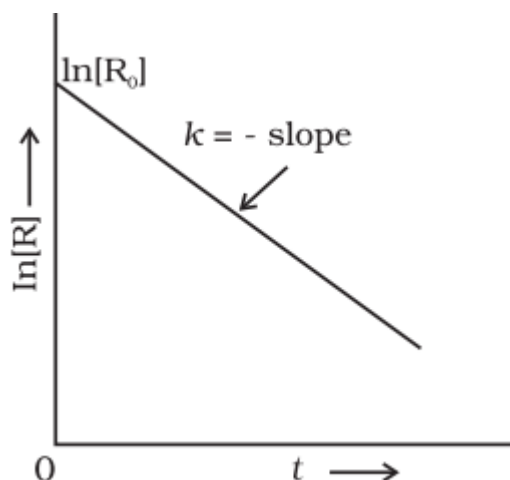
- Substituting the value of I in equation (1)

$$\ln[R] = -kt + \ln[R]_0 \dots\dots\dots (2)$$

Therefore,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \dots\dots\dots (3)$$

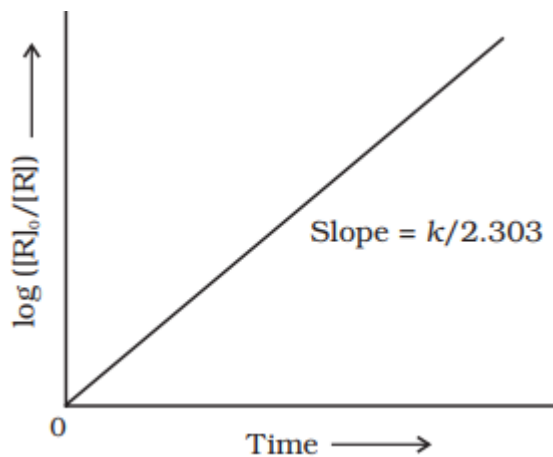
- Comparing equation (2) with equation of a straight line, $y = mx + c$, if a graph is drawn, $\ln [R]$ against t , a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$ is obtained.



- Equation (3) on rearranging

$$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303} \dots\dots\dots (4)$$

- Comparing equation (4) with equation of a straight line, $y = mx + c$, if a graph is drawn, $\log [R]_0/[R]$ against t , a straight line with slope = $k/2.303$ is obtained.



- At time t_1 from equation (2)

$$\ln[R]_1 = -kt_1 + \ln[R]_0 \quad \dots\dots\dots (5)$$

- At time t_2

$$\ln[R]_2 = -kt_2 + \ln[R]_0 \quad \dots\dots\dots (6)$$

- Subtracting equation (6) from (5) and rearranging,

$$k = \frac{1}{(t_2 - t_1)} \ln \frac{[R]_1}{[R]_2}$$

First order reactions in gas phase

- Consider a first order gas phase reaction, $A(g) \rightarrow B(g) + C(g)$
- Let p_i be the initial pressure of A and p_t the total pressure at time ‘t’. Integrated rate equation for such a reaction can be derived as
- Total pressure, $p_t = p_A + p_B + p_C$
- p_A , p_B and p_C are the partial pressures of A, B and C, respectively.

	$A(g)$	\rightarrow	$B(g)$	+	$C(g)$
At $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

where, p_i is the initial pressure at time $t = 0$.

$$p_t = (p_i - x) + x + x = p_i + x$$

$$x = (p_t - p_i)$$

$$\text{where, } p_A = p_i - x = p_i - (p_t - p_i)$$

$$= 2p_i - p_t$$

$$k = \left(\frac{2.303}{t} \right) \left(\log \frac{p_i}{p_A} \right)$$

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

HALF-LIFE OF A REACTION ($t_{1/2}$)

- The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

Half-Life of a zero order reaction

- For a zero order reaction, rate constant is given by equation

$$k = \frac{[R]_0 - [R]}{t}$$

$$\text{At } t = t_{1/2}, [R] = \frac{1}{2}[R]_0$$

The rate constant at $t_{1/2}$ becomes

$$k = \frac{[R]_0 - 1/2[R]_0}{t_{1/2}}$$

$$t_{1/2} = \frac{[R]_0}{2k}$$

- It is clear that $t_{1/2}$ for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

Half-Life of a first order reaction

- For the first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{at } t_{1/2} \quad [R] = \frac{[R]_0}{2}$$

So, the above equation becomes

$$k = \frac{2.303}{t_{1/2}} \log \frac{[R]_0}{[R]/2}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log 2$$

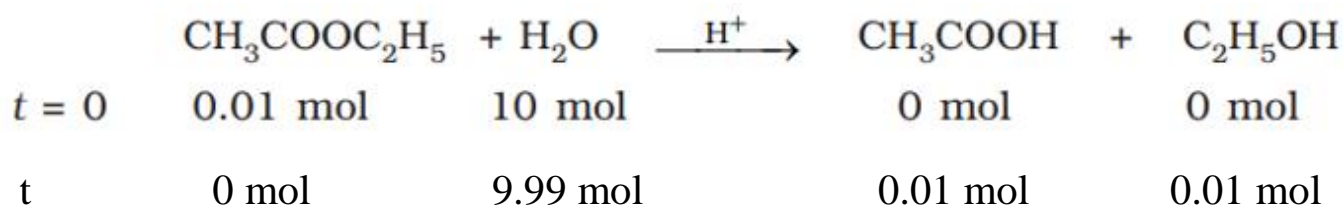
$$t_{1/2} = \frac{2.303}{k} \times 0.301$$

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

- It can be seen that for a first order reaction, half-life period is independent of initial concentration of the reacting species.

PSEUDO FIRST ORDER REACTION

- A Pseudo first order reaction can be defined as a reaction that is made to behave like a first order reaction. This occurs when one reacting material is present in great excess.
- During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are:



- The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

- The term $[\text{H}_2\text{O}]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

$$\text{where } k = k' [\text{H}_2\text{O}]$$

- The reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

Prepared by : Ms. Anoop Stephen	Checked by : HOD - SCIENCE
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