Crash Course for NEET 2020

KEY NOTES ON Chemical kinetics

Biomentors Classes Online, Mumbai

NCERT Based - Very Important Points

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Rate of a reaction : The rate of a reaction can be defined as the change in concentration of a reactant or a product in unit time. For the reaction,

$R \longrightarrow P$, Rate $= -\frac{\Delta[R]}{\Delta t}$ or $+\frac{\Delta[P]}{\Delta t}$

Rate law and rate constant : The equation that correlates the rate of reaction with concentration of reactants is known as rate law. For a simple reaction, $A + B \rightarrow C + D, so\ Rate = k[A][B]$ where k is a rate constant which is equal to the rate of the reaction when the concentration of each of the reactant is unity.

Types of chemical reactions

(1) **Very fast or instantaneous reactions :** These reactions occur at a very fast rate It is almost impossible to determine the rates of these reactions.

Examples

(i) $AgNO_3 + NaCl \rightarrow \underset{(PPt.)}{AgCl} + NaNO_3$ (*Precipitation reaction*)

(ii) $\underset{(acid)}{HCl} + \underset{(base)}{NaOH} \rightarrow \underset{(Salt)}{NaCl} + H_2O$ (*Neutralization reaction*)

(2) **Moderate reaction :** These reactions proceed with a measurable rates at normal temperature and it is *these reactions are studied in chemical kinetics*. Mostly these reactions are molecular in nature.

Examples

Decomposition of H_2O_2 : $2H_2O_2 \rightarrow 2H_2O + O_2$

(3) **Very slow reactions :** These reactions are extremely slow and take months together to show any measurable change.

Examples

(i) *Rusting of iron* : $Fe_2O_3 + xH_2O \rightarrow \underset{\text{Hydrated ferric oxide (Rust)}}{Fe_2O_3.xH_2O}$

Factors affecting rate of a reaction

rate of a chemical reaction depends on the following things

1. **Nature of reactants**
   a. Physical state of reactants : This has considerable effect over rate of reaction.

$$\xrightarrow[\text{Decreasing rate of reaction}]{\text{Gaseous satae} > \text{Liquid state} > \text{Solid state}}$$

   b. Physical size of the reactants : Among the solids, rate increases with decrease in particle size of the solid.

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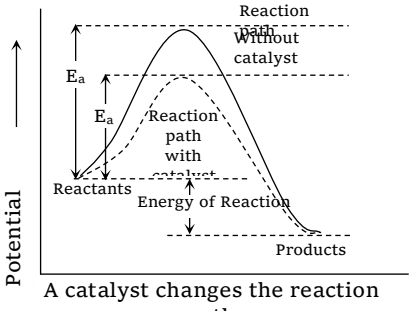
2. Effect of temperature : The rate of chemical reaction generally increases on increasing the temperature.

3. Concentration of reactants : The rate of a chemical reaction is directly proportional to the concentration of the reactants means rate of reaction decreases with decrease in concentration.

4. Presence of catalyst : The function of a catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate.



5. Effect of sunlight : There are many chemical reactions whose rate are influenced by radiations particularly by ultraviolet and visible light. Such reactions are called photochemical reactions. For example, Photosynthesis, Photography, Blue printing, Photochemical synthesis of compounds etc.

Law of mass action

The rate at which a substance reacts is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances.

- For a reaction, $aA + bB \rightarrow$ product

Rate $= \left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$; $\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$

Where *k* is called **rate constant** or **velocity constant**.

When $[A] = [B] = 1\ mol/litre$, then $\frac{dx}{dt} = k$

Thus, rate constant *k* is also called **specific reaction rate**.

- The value of rate constant depends on, nature of reactant, temperature and catalyst. It is independent of concentration of the reactants.

- Unit of rate constant $= \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1} = \left[\frac{\text{mol}}{\text{litre}}\right]^{1-n} \times \text{sec}^{-1}$

Where $n =$ order of reaction.

Order of the reaction: It is experimentally determined and indicates the dependence of observed reaction rate on the concentration of reactant

For the reaction $xA + yB \rightarrow$ Products

The rate law is $\text{Rate} = [A]^x[B]^y$

Then the overall order of reaction. $n = x + y$

where *x* and *y* are the orders with respect to individual reactants

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Order and molecularity of some reaction

S. No.	Chemical equation	Molecularity	Rate law	Order w.r.t.		
				First reactant	Second reactant	Overall
1.	$aA + bB \rightarrow$ product	*a* + *b*	$\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$	*a*	b	*a* + *b*
2.	$aA + bB \rightarrow$ product	*a* + *b*	$\left(\frac{dx}{dt}\right) = k[A]^2[B]^0$	2	zero, if *B* is in excess	2
3.	$2H_2O_2 \xrightarrow{Pt,\Delta} 2H_2O + O_2$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[H_2O_2]$	1*	-----	1
4.	$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[CH_3COOC_2H_5]$	1*	Zero, if H_2O is in excess	1
5.	$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[C_{12}H_{22}O_{11}]$	1*	Zero, if H_2O is in excess	1
6.	$(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[(CH_3)_3CCl]$	1*	Zero, if OH^- does not take part in slow step	1
7.	$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[CH_3Cl][OH^-]$	1	1	2
8.	$C_6H_5N_2Cl \xrightarrow{\Delta} C_6H_5Cl + N_2$	1 Unimolecular	$\left(\frac{dx}{dt}\right) = k[C_6H_5N_2Cl]$	1	----	1
9.	$CH_3CHO \xrightarrow{\Delta} CH_4 + CO$	1 Unimolecular	$\left(\frac{dx}{dt}\right) = k[CH_3CHO]^{3/2}$	1.5	----	1.5
10.	$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$	5	$\left(\frac{dx}{dt}\right) = k[H_2O_2][I^-]$	1	1 ($H^+$is medium)	2
11.	$2O_3 \rightarrow 3O_2$	2 Bimolecular	$\left(\frac{dx}{dt}\right) = k[O_3]^2[O_2]$	1	-1 with respect to O_2	1

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Rate law, integrated rate law, half-life, units of rate constant and graph for the reactions of different orders

Order	Rate law	Integrated rate law	Half-life	Units of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	mol L^{-1} s^{-1}	$[A]$ *vs* t; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln [A]_0$	$t_{1/2} = 0.693/k$	s^{-1}	$\ln[A]$ *vs* t; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k\,[A]_0$	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
2	Rate = $k[A]\,[B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	–	L mol^{-1} s^{-1}	$1/[A]$ *vs* t; slope = k
n	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}$	$t_{1/2} = \frac{2^{n-1}-1}{k(n-1)\,[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n}$ s^{-1}	$\frac{1}{[A]^{n-1}}$ *vs* t; slope = k

Methods for determination of order of a reaction

1. **Integration method** (Hit and Trial method)

   (i) The method can be used with various sets of a, x and t with integrated rate equations.

   (ii) The value of k is determined and checked for all sets of a, x and t.

   (iii) If the value of k is constant, the used equation gives the order of reaction.

   (iv) If all the reactants are at the same molar concentration, the kinetic equations are :

   $k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ (*For first order reactions*)

   $k = \frac{1}{t}\left[\frac{1}{a} - \frac{1}{a-x}\right]$ (*For second order reactions*)

   $k = \frac{1}{2t}\left[\frac{1}{(a-x)^2} - \frac{1}{a^2}\right]$ (*For third order reactions*)

2. **Half-life method :** This method is employed only when the rate law involved only one concentration term.

   $t_{1/2} \propto a^{1-n}$; $t_{1/2} = ka^{1-n}$; $\log t_{1/2} = \log k + (1-n)\log a$

   A plotted graph of $\log t_{1/2}$ *vs log a* gives a straight line with slope $(1-n)$, determining the slope we can find the order *n*. If half-life at different concentration is given then,

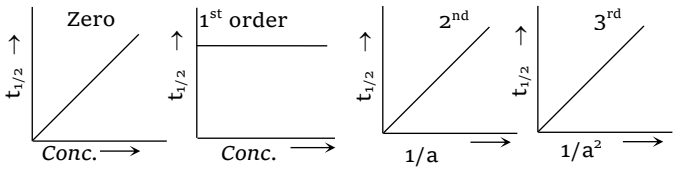
   $(t_{1/2})_1 \propto \frac{1}{a_1^{n-1}}$; $(t_{1/2})_2 \propto \frac{1}{a_2^{n-1}}$; $\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$

   $\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2 = (n-1)[\log_{10} a_2 - \log_{10} a_1]$

   $n = 1 + \frac{\log_{10}(t_{1/2})_1 - \log_{10}(t_{1/2})_2}{(\log_{10} a_2 - \log_{10} a_1)}$

   This relation can be used to determine order of reaction '*n*'

   Plots of half-lives Vs concentrations ($t_{1/2} \propto a^{1-n}$)



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3. **Graphical method :** A graphical method based on the respective rate laws, can also be used.

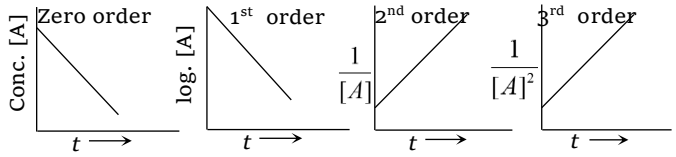
(i) If the plot of $\log(a-x)$ Vs t is a straight line, the reaction follows first order.

(ii) If the plot of $\frac{1}{(a-x)}$ Vs t is a straight line, the reaction follows second order.

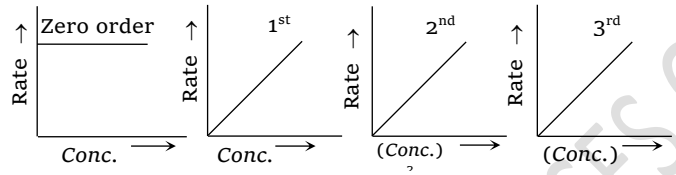
(iii) If the plot of $\frac{1}{(a-x)^2}$ Vs t is a straight line, the reaction follows third order.

(iv) In general, for a reaction of nth order, a graph of $\frac{1}{(a-x)^{n-1}}$ Vs t must be a straight line.

Plots from integrated rate equations



Plots of rate Vs concentrations [Rate = k(conc.)^n]



4. **Van't Haff differential method :** The rate of reaction varies as the n^{th} power of the concentration Where $'n'$ is the order of the reaction. Thus for two different initial concentrations C_1 and C_2 equation, can be written in the form,

$\frac{-dC_1}{dt} = kC_1^n$ and $\frac{-dC_2}{dt} = kC_2^n$

Taking logarithms,

$$\log_{10}\left(\frac{-dC_1}{dt}\right) = \log_{10} k + n\log_{10} C_1 \qquad \text{.....(i)}$$

and $$\log_{10}\left(\frac{-dC_2}{dt}\right) = \log_{10} k + n\log_{10} C_2 \qquad \text{.....(ii)}$$

Subtracting equation (ii) from (i),

$$n = \frac{\log_{10}\left(\frac{-dC_1}{dt}\right) - \log_{10}\left(\frac{-dC_2}{dt}\right)}{\log_{10} C_1 - \log_{10} C_2} \qquad \text{.....(iii)}$$

$\frac{-dC_1}{dt}$ and $\frac{-dC_2}{dt}$ are determined from concentration Vs time graphs and the value of $'n'$ can be determined.

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(5) **Ostwald's isolation method** (Initial rate method)

This method can be used irrespective of the number of reactants involved *e.g.,* consider the reaction, $n_1A + n_2B + n_3C \rightarrow \text{Products}$.

This method consists in finding the initial rate of the reaction taking known concentrations of the different reactants (*A*, *B*, *C*).

Suppose it is observed as follows,

(i) Keeping the concentrations of *B* and *C* constant, if concentration of *A* is doubled, the rate of reaction becomes four times. This means that, Rate $\propto [A]^2$ *i.e.,* order with respect to *A* is 2

(ii) Keeping the concentrations of *A* and *C* constant, if concentration of B is doubled, the rate of reaction is also doubled. This means that, Rate $\propto$ [*B*] *i.e.,* order with respect to *B* is 1

(iii) Keeping the concentrations of *A* and *B* constant, if concentration of *C* is doubled, the rate of reaction remains unaffected. This means that rate is independent of the concentration of *C i.e.,* order with respect to *C* is zero. Hence the overall rate law expression will be, Rate = $k[A]^2\,[B]\,[C]^0$

$\therefore$ Overall order of reaction = 2 + 1 + 0 = 3.

Collision theory of reaction rate

The main points of ***collision theory*** are as follows,

(a) For a reaction to occur, there must be collisions between the reacting species.

(b) Only a certain fraction of the total number of collisions is effective in forming the products.

(c) For effective collisions, the molecules should possess sufficient energy as well as orientation.

Arrhenius equation

Arrhenius proposed a quantitative relationship between rate constant and temperature as,

$$k = A\,e^{-E_a/RT} \qquad \text{.....(i)}$$

The equation is called ***Arrhenius equation***.

In which constant *A* is known as ***frequency factor***. This factor is related to number of binary molecular collision per second per litre.

E_a is the activation energy.

T is the absolute temperature and

R is the gas constant

Both A and E_a are collectively known as ***Arrhenius parameters***.

Taking logarithm equation (i) may be written as,

$$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad \text{.....(ii)}$$

The value of activation energy (E_a) increases, the value of *k* decreases and therefore, the reaction rate decreases.

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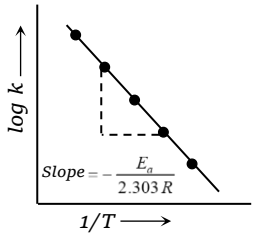
When log *k* plotted against $1/T$, we get a straight line. The intercept of this line is equal to log *A* and slope equal to $\frac{-E_a}{2.303\ R}$.

Therefore $E_a = -2.303\ R \times \text{slope}$.



Rate constants for the reaction at two different temperatures T_1 and T_2,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \text{.....(iii)}$$

where k_1 and k_2 are rate constant at temperatures T_1 and T_2 respectively $(T_2 > T_1)$.

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