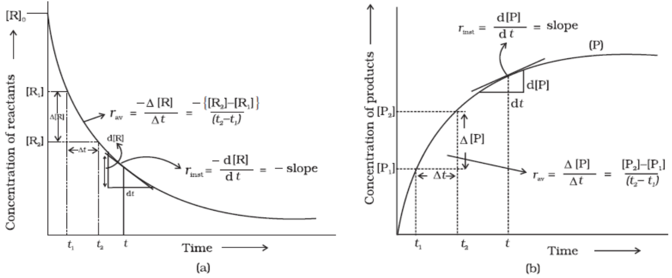
CHEMICAL KINETICS

Chemical Kinetics the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

Rate of a Chemical Reaction: the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It 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, R ---> P
One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then, $\Delta t = t_2 - t_1$, $\Delta[R] = [R]_2 - [R]_1$
$\Delta [P] = [P]_2 - [P]_1$
The square brackets in the above expressions are used to express molar concentration.
Rate of disappearance of R = Decrease in concentration of R / Time taken = - R/t (1)
Rate of appearance of P = Increase in concentration of P /Time taken = P/t (2)
Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity.
Equations (1) and (2) given above represent the average rate of a reaction, r_{av}.
Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. (Ref. ncert Fig. 4.1)



(a) (b)

Fig. 4.1: Instantaneous and average rate of a reaction

Units of rate of a reaction: The units will be **mol $L^{-1}s^{-1}$**.
In gaseous reactions, the units of the rate equation will be **atm s^{-1}**.

Factors affecting rate of reaction: The important factors are:

1. Concentration of the reacting species.
2. Temperature of the system.
3. Nature of reactant and products.
4. Presence of a catalyst.
5. Surface area.
6. Exposure to radiation.

Rate Law and Rate Constant:

Consider a general reaction: aA + bB ----> cC + dD
Where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is Rate $\propto [A]^x [B]^y$
Where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants. Above equation can also be written as
Rate = $k [A]^x [B]^y$
$-d[R]/dt = k[A]^x [B]^y$
This form of equation is known as differential rate equation, where k is a proportionality constant called **rate constant**.
The equation, Rate = $k [A]^x [B]^y$ which relates the rate of a reaction to concentration of reactants is called rate law or rate expression.
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.
For example:

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
Rate = $k [NO]^2 [O_2]$
$-d[R]/dt = k [NO]^2 [O_2]$

Order of reaction:

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

x and y indicate the rate is to the change in concentration of A and B.
Sum of these exponents, i.e., x + y in above equation gives the overall order of a reaction. whereas x and y represent the order with respect to the reactants A and B respectively.
Order of reaction is defined as the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.
Order of a reaction can be 0, 1, 2, 3 and even a fraction.
A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.
Units of rate constant:
Zero order rate of reaction: mol $L^{-1} s^{-1}$
First order rate of reaction: s^{-1}
Second order rate of reaction: L $mol^{-1} s^{-1}$

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.
For examples:

$NH_4NO_2 \longrightarrow N_2 + 2H_2O$	Unimolecular reaction
$2HI(g) \longrightarrow H_2(g) + I_2(g)$	Bimolecular reaction
$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$	Trimolecular reaction

Important points of distinction between order and molecularity

S.No.	**Order**	**Molecularity**
1	**Order** is the sum of powers of the concentration terms in the rate law	**Molecularity** is the number of reacting species undergoing simultaneous collision

	expression.	in the elementary or simple reaction.
2	Order of a reaction is determined experimentally.	Molecularity is a theoretical concept.
3	Order of a reaction can be zero.	Molecularity of a reaction cannot be zero.

Integrated rate equations:

Zero order reaction: Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

Consider the reaction,

R -----> P

Rate = $-d[R]/dt = k[R]^0$

Rate = $-d[R]/dt = k \times 1$

$d[R] = -k\,dt$

Integrating both sides

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

Where, I is the constant of integration

At t = 0 the concentration of reactant $[R] = [R]_0$

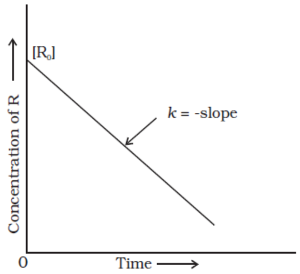
Where $[R]_0$ is the initial concentration of reactant.

$[R]_0 = -k \times 0 + I = I$, Substituting the value of I in the equation (1)

$[R] = -kt + [R]_0$

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

Variation in the concentration Vs time plot for a zero-order reaction



Example of Zero order reaction is the decomposition of gaseous ammonia.

$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

Rate = $k[NH_3]^0 = k$

the rate of the reaction is proportional to the

First Order Reactions: The rate of the reaction is proportional to the first power of the concentration of the reactant R.

For example:

R -----> P

Rate = $-d[R]/dt = k[R]$

$d[R]/[R] = -k\,dt$, Integrating this equation and we get

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

At t = 0, $\ln[R] = -k \times 0 + I$,

$I = \ln[R]_0$, Substituting the value of I in the equation (1)

$\ln[R] = -kt + \ln[R]_0$

$k = \{\ln[R]_0 - \ln[R]\}/t$ Remember that, ($\log a - \log b = \log(a/b)$

$k = (1/t)\ln\{[R]_0/[R]\}$

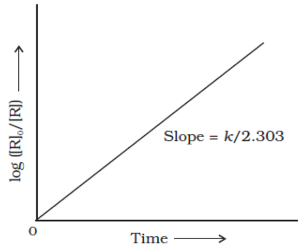
$\ln\{[R]/[R]_0\} = -kt$, taking antilog both sides

$[R] = [R]_0\, e^{-kt}$

We know that, ln a = 2.303 log a

$\boldsymbol{k = (2.303/t) \log\{[R]_0/[R]\}}$

If we plot a graph between log $[R]_0/[R]$ Vs t, the slope is k/2.303 for first order reaction



First order gas phase reaction: A(g) -----> B(g) + C(g)

Total pressure $p_t = p_A + p_B + p_C$

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

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

$x = (p_t - p_i)$

$p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

$k = (2.303/t) \log [p_i/ p_A]$

$k = (2.303/t) \log [p_i/(2p_i - p_t)]$

Half-life of a reaction: 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. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is

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

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

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

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

For a first order reaction, rate constant is

$k = (2.303/t) \log\{[R]_0/[R]\}$

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

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

$k = (2.303/t_{1/2}) \log 2$

$k = (2.303/t_{1/2})\ 0.3010$

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

For zero order reaction $t_{1/2} \propto [R]_0$.

For first order reaction $t_{1/2}$ is independent of $[R]_0$.

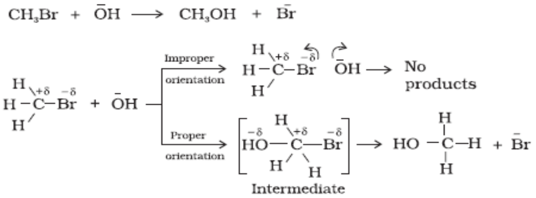
Collision Theory of Chemical Reactions:

Collision frequency: It is defined as the number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z).

Effective collision: The collisions in which molecules **collide with proper orientation**, breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions.**

Ineffective collision: The collisions in which molecules **collide with improper orientation** no products are formed are called as in**effective collisions.**

For example, formation of methanol from Bromoethane depends upon the orientation of reactant molecules. The proper orientation of reactant molecules lead to bond formation whereas improper orientation makes them simply bounce back and no products are formed. Diagram showing molecules having proper and improper orientation:-



Rate of reaction is proportional to

(i) the number of collisions per unit volume per second (collision frequency, Z) between the reacting species.

(ii) the fraction of effective collisions (properly oriented and possessing sufficient energy), f:
i.e., Rate = - dx/dt = f x Z

Temperature Dependence of the Rate of a Reaction: For the effect of temperature on reaction rates is that the rate of a reaction or rate constant becomes almost doubled for every 10° rise in temperature. Increase in the rate of reaction with the rise in temperature is mainly due to the increase in number of effective collisions.

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius equation.

Arrhenius equation and calculation of Activation energy:

$$k = A\ e^{-Ea\ /RT}$$

Where A is the Arrhenius factor or the frequency factor. It is also called pre-exponential factor. It is a constant specific to a particular reaction. R is gas constant and Ea is activation energy measured in joules/mole (J mol $^{-1}$).

Concept of Activation energy: The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy.

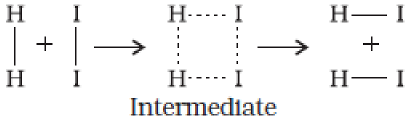
It is equal to the difference between the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules. That is,

Activation energy = Threshold energy - Average kinetic energy of the reacting molecules

Ea = Ea (threshold – Ea (reactants)
Low Activation energy: Fast reactions
High Activation energy: Slow reactions

It can be understood clearly using the following simple reaction:

$$H_2\ (g) + I_2\ (g) \longrightarrow 2HI\ (g)$$

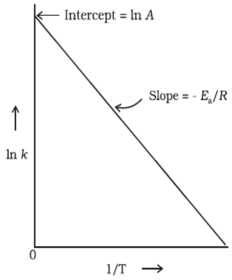


According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. The energy required to form this intermediate, called **activated complex**, is known as **activation energy (Ea)**.

$$k = A\ e^{-Ea/RT}$$

Taking logarithm both side

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



The plot of ln k Vs 1/T gives a straight line.
Slope = – Ea/R and intercept = ln A.
So we can calculate Ea and A using these values.

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

Converting to common logarithm lnX = 2.303 log X
2.303log k = 2.303log A – Ea/RT
log k = log A – Ea/2.303 RT
Let k1 and k2 are the rate constants for the reaction at two different temperatures T1 and T2 respectively.
log k_1 = log A – Ea/2.303 RT_1 …(i)
log k_2 = log A – Ea/2.303 RT_2 …(ii)
Subtracting eq. (i) from (ii)
log k_2 - log k_1 = Ea/2.303 R [$1/T_1 - 1/T_2$]

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Assignments:
Q1. Express the rate of the following reaction:
$5\ Br^-\ (aq) + BrO_3^-\ (aq) + 6\ H^+\ (aq) \longrightarrow 3\ Br_2\ (aq) + 3\ H_2O\ (l)$
Q2. For the reaction $R \longrightarrow P$, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
Ans. Average rate = 4×10^{-4} mol L^{-1} min^{-1}
Rate = 6.67×10^{-6} mol L^{-1} s^{-1}
Q3. Calculate the overall order of a reaction which has the rate expression:
(a) Rate = $k\ [A]^{1/2}\ [B]^{3/2}$
(b) Rate = $k\ [A]^{3/2}\ [B]^{-1}$

(a) Second order (b) half order.

Q4. Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1}

(ii) $k = 3 \times 10^{-4}$ s^{-1}

(i) Second order reaction (ii) first order reaction.

Q5. For a reaction, A + B $\longrightarrow$ Product; the rate law is given by, $r = k\,[A]^{1/2}\,[B]^2$.

What is the order of the reaction?

Ans. Order = 2.5

Q6. The initial concentration of N_2O_5 in the following first order reaction

N_2O_5 (g) $\longrightarrow$ 2 NO_2 (g) + 1/2O_2 (g) was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}.

Calculate the rate constant of the reaction at 318 K.

Answer: $k = 0.0304$ min^{-1}

Q7.Show that in a first order reaction, time required for completion of 99.9% is 10 times of half-life ($t_{1/2}$) of the reaction.

$t = 6.909/k$

For half-life of the reaction

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

$t/t_{1/2} = 10$

Q8. A first order reaction has a rate constant 1.15×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 3 g?

Ans. 444s

Q9. The rate constant for a first order reaction is 60 s^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

Ans. 4.6×10^{-2} seconds

Q10. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Ans. t(99%) = 2 x t (90%)

Q11. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Ans. 77.7 min.

Q12. What will be the effect of temperature on rate constant?

Q13. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate *E*a.

Ans. *E*a = 52.898 kJ

Q14. The rate constants of a reaction at 500K and 700K are 0.02s^{-1} and 0.07s^{-1} respectively. Calculate the values of *E*a and *A*.

Ans. *E*a = 18230.8 J

$k = A\,e\text{-}^{Ea/RT}$

0.02 = *A*e-18230.8/8.314 × 500

A = 0.02/0.012 = 1.61

Q15. The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of *A* is 4×10^{10}s^{-1}. Calculate *k* at 318K and *E*a.

Ans. *E*a = 76.623 Kj, k (318K) = 1.042×10^{-2} s^{-1}