

Chemical kinetics

OBJECTIVES

- Representation of rate of a reaction in terms concentration of reactants or products:
- Define the average and instantaneous rate of reaction:
- Distinguish between elementary and complex reaction:
- Differentiate between the elementary and order of a reaction:
- Define rate constant:
- Discuss the dependence of rate of reaction on concentration, temperature and catalyst:
- Derive integrated rate equations for the zero and first order reactions:
- Determine the rate constant for zero and first order reactions:
- Collision theory:

What do you mean by chemical

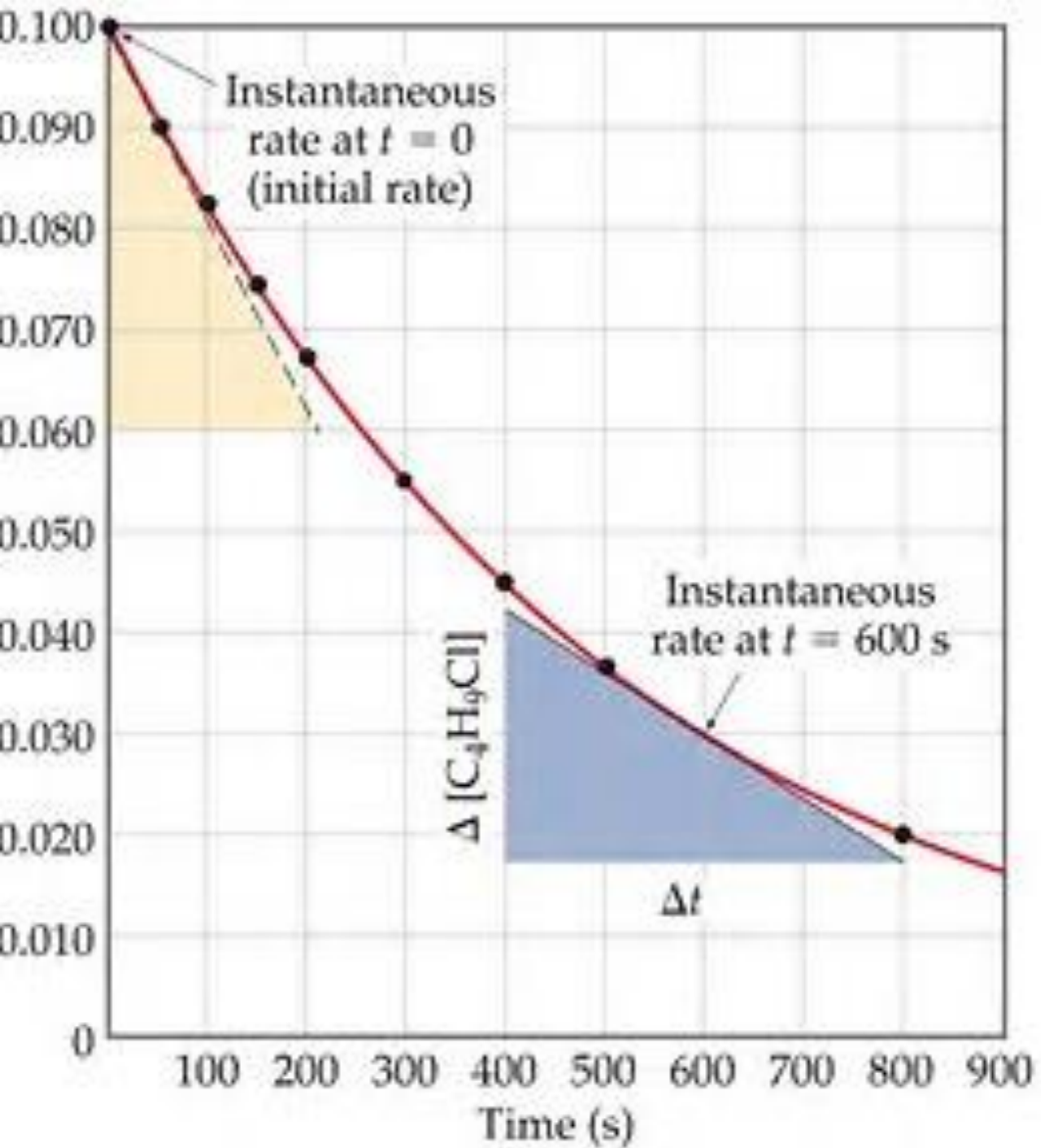
- The branch of chemistry, which deals with the rate of chemical reactions. the factors affecting the rate of reactions and the mechanism of the reaction. is called chemical kinetics.
- Chemical Reactions on the Basis of Rate of Reaction
- **1. Fast/instantaneous reactions:** Chemical reaction which completes in less than 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 complete 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.

Rate of Reaction

- Rate of a chemical reaction is the change in the concentration of any one of the reactants or products per unit time. It is expressed in $\text{mol L}^{-1} \text{s}^{-1}$ or Ms^{-1} or atm time^{-1} units.
- **Rate of reaction**
- = (decrease/increase in the concentration of reactant/product/time taken)
- This rate of reaction is known as average rate of reaction (r_{av}). (r_{av} can be calculated by dividing the concentration difference by the time interval).



Instantaneous
rate

- For a chemical reaction:
- $aA + bB \rightarrow cC + dD$
- Average rate of reaction, $r_{\text{ave}} = -1/a \Delta[A] / \Delta[t]$
- $= -1/b \Delta[B] / \Delta[t]$
- $= 1/c \Delta[C] / \Delta[t]$
- $= 1/d \Delta[D] / \Delta[t]$
- Rate of disappearance of A = $\Delta[A] / \Delta[t]$
- Rate of disappearance of B = $\Delta[B] / \Delta[t]$ and so on.

Instantaneous rate of a reaction

Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.

For a reaction



- Rate = $-\frac{[\Delta R]}{[\Delta t]}$ = $\frac{[\Delta P]}{\Delta t}$ As $\Delta t \rightarrow 0$
- Rate = $-\frac{d[R]}{dt}$ = $\frac{d[P]}{dt}$

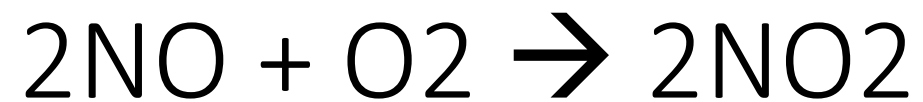
Units of rate of a reaction

- Rate = change in concentration of reactant or product/time
- = mol/Ls
- Rate of a reaction of the type
- $aA + bB \rightarrow cC + dD$ is
- Rate = $-1/a [\Delta A]/\Delta t = -1/b [\Delta B]/\Delta t = 1/c [\Delta C]/\Delta t = 1/d [\Delta D]/\Delta t$.
- The decomposition of N_2O_5 in CCl_4 has been studied. Initially the concentration of N_2O_5 is 2.33mol/L and after 184 minutes, it is reduced to 2.08mol/L . The reaction takes place according to the equation
- $2N_2O_5 \rightarrow 4NO_2 + O_2$. Calculate the average rate and rate of production of NO_2 .

Factors affecting rate of a reaction

- Methods for measuring reaction rate (i) pH measurement, (ii) change in optical activity, (iii) change in pressure, (iv) change in conductance.
- Slowest step of a reaction was called rate determining step by van't Hoff.
- Factors Affecting Rate of Reaction
 - 1. Nature and concentration of reactant. 2. Temperature
 - 3. Surface area of reactant 4. Radiations and catalyst
 - 5. Pressure of gas

Initial rate of formation of NO₂



Experiment	Initial [NO]	Initial[O ₂]	Initial rate of formation of NO ₂
1	0.30	0.30	0.096
2	0.60	0.30	0.384
3	0.30	0.60.	0.192
4	0.60	0.60	0.768

- From the above data it is clear that the rate of formation of NO_2 is proportional to square of the concentration of NO_2 and the concentration of O_2 or
- Rate = $k [\text{NO}_2]^2 [\text{O}_2]$ where 'k' is called rate constant.
- The sum of the powers, $2+1=3$ is called the order of the reaction.

Rate law or rate expression

- This indicates that rate of a reaction at a given temperature depends on the concentration of the reactant and it is not always proportional to the concentration to the power of one, it may be any whole number, or some fraction.
- Consider a reaction, $aA + bB \rightarrow Cc + dD$
- Rate $\propto [A]^x [B]^y$ or
- Rate = $k [A]^x [B]^y$
- **$-d[R]/dt = k [A]^x [B]^y$**
- where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactant.
- **$X+Y$ is the order of the reaction.**

- $-d[R]/dt = k [A]^x [B]^y$ is called **differential rate equation** and **k** is a proportionality constant called **rate constant**.
- Rate law expression 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.

Order and Molecularity of a reaction

Order : The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

- The **Molecularity** of a reaction is defined as the total number of reactant molecules or atoms taking part in the Chemical **Reaction**. The **reaction** are termed as unimolecular, bimolecular or termolecular etc. depending upon the number of reacting particles as 1,2,3 etc., in the rate determining step.
- If a reaction passes through different steps then the slowest step is the rate determining step.

Order	Molecularity
<p data-bbox="188 332 1243 546">It is sum of the concentration terms on which the rate of reaction actually depends or it is the sum of the exponents of the concentrations in the rate law equation.</p> <p data-bbox="188 561 1243 718">It need not be a whole number i.e. it can be fractional as well as zero. It can be determined experimentally only and cannot be calculated.</p> <p data-bbox="188 789 1230 889">It is for the overall reaction and no separate steps are written to obtain it.</p> <p data-bbox="188 903 1225 1061">Even the order of a simple reaction may not be equal to the number of molecules of the reactants as seen from the unbalance equation.</p>	<p data-bbox="1289 332 2356 489">It is the number of atoms, ions or molecules that must collide with one another simultaneously so as to result into a chemical reaction.</p> <p data-bbox="1289 561 2356 661">It is always a whole number. It can be determined experimentally only and cannot be calculated.</p> <p data-bbox="1289 675 2356 775">It can be calculated by simply adding the molecules of the slowest step</p> <p data-bbox="1289 789 2356 946">The overall molecularity of a complex reaction has no significance. It is only slowest step whose molecularity has significance for the overall reaction.</p> <p data-bbox="1289 1018 2356 1118">For simple reactions, the molecularity can usually be obtained from the Stoichiometry of the equation</p>

Instantaneous rate equation

- Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.
- For reaction,
-

Integrated rate equation for first order kinetics.



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

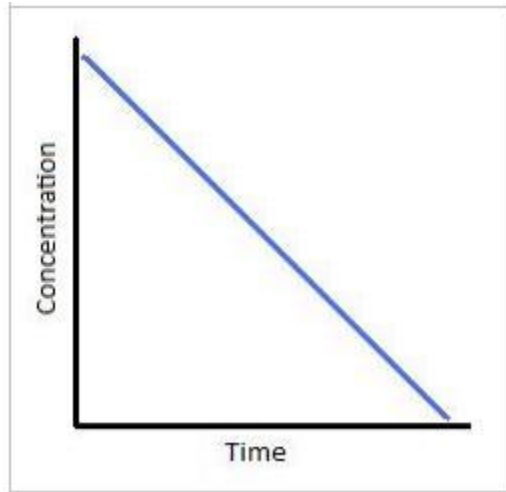
$$\text{Or } d[R]/[R] = -kdt.$$

Integrating this equation, we get

Integration

- $\ln[R] = -kt + I$ -----(1)
- Again , I is the constant of integration and its value can be determined easily.
- When $t=0, R=[R]_0$, where $[R]_0$ is the initial concentration of the reactant.
- Eq (1) became
- $\ln[R]_0 = k \times 0 + I$ or $\ln[R]_0 = I$

Variation in the concentration vs time plot for a zero order reaction. $k = [R]_0 - [R]/t$. The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction,



Unit of k for a zero order reaction

- $K = [R]_0 - [R]/t = \text{change in concentration of the reactant} / \text{time}$
- $= \text{mol/Ls}$
- Identify the reaction order from the following rate expression.
- $\text{Rate} = k[A]^{1/2}[B]^{3/2}$.
-
- 4.11 exercise and 4.2

Integrated rate equation for first order reaction

- Integrated rate equation for first order kinetics.
- $R \rightarrow P$
- Rate = $-d[R]/dt = k[R]$.
- Or $d[R]/[R] = -kdt$.
- Integrating this equation, we get
- $\ln[R] = -kt + I$ -----(1)

Again, I is the constant of integration and its value can be determined easily.

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

$$\ln[R]_0 = k \times 0 + I \text{ or } \ln[R]_0 = I$$

Substituting the value of I in eq (1)

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

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

Eq (1) became

- rearranging this
- $\ln[R]/[R]_0 = -kt$ or $k = 1/t \ln[R]/[R]_0$ or
- $k = 1/t \ln \frac{[R]_0}{[R]}$
- $\ln[R_1] - \ln[R_2] = \ln [R_1]/[R_2] = -kt_1 - (-kt_2)$
- $= kt_2 - kt_1 = k(t_2 - t_1)$ or
- $k = 1/t_2 - t_1 \times \ln [R_1]/[R_2] =$
- $2.303/t_2 - t_1 \times \log[R_1]/[R_2]$

- It can also be written as

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

Unit of k for a first order reaction is s^{-1} .

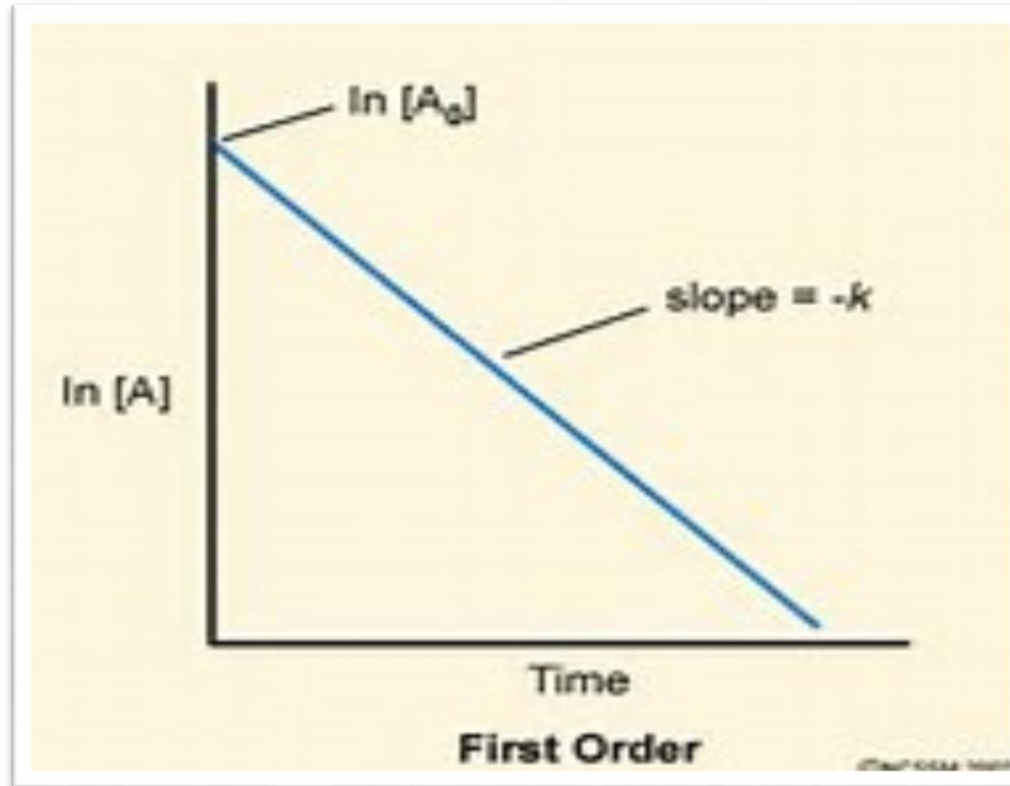
Identify the reaction order each of the following rate constants.

i) $k = 2.303 \times 10^{-5} \text{ Lmol}^{-1}\text{s}^{-1}$

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

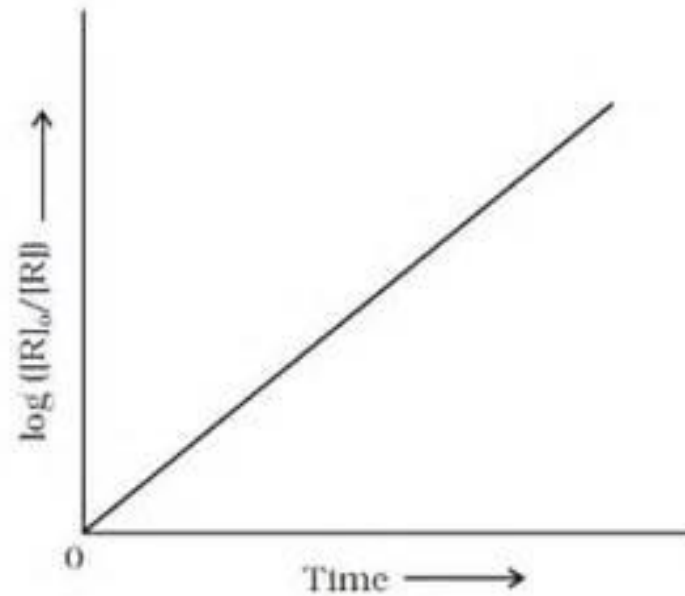
A plot of $\ln R$ and t for a first order reaction

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



A plot of $\log [R]_0 / [R]$ vs time for a first order reaction with respect to the equation, $\log \frac{[R]_0}{[R]}$

$= \frac{kt}{2.303}$ will give



Pseudo first order reaction

- Pseudo First Order Reaction
- Chemical reactions which appear to be of higher order but actually are of the lower order are called pseudo order reactions. In case of pseudo first order reaction, chemical reaction between two reactants takes place but the concentration of one of the reactant is present in excess. e.g., hydrolysis of ester. During the hydrolysis of 0.01 mol of ester with 10 mol of water 0.01 mol of water is only used up. The remaining 9.9 mol of water is left out. (10-0.01).
- $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$

- Thus the concentration does not alter much. 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
- $\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$ $\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$
- Where $k = k'[\text{H}_2\text{O}]$ and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions.

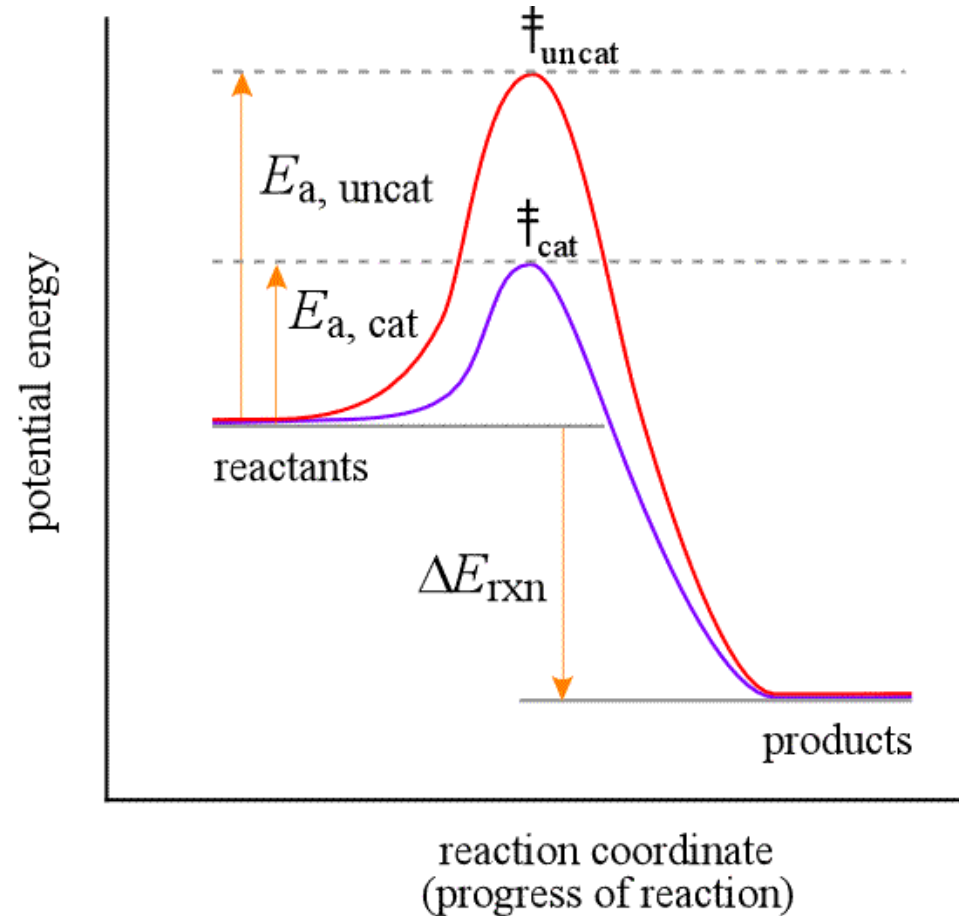
- Methods to Determine Order of Reaction
- (i) Graphical method : (refer the graph for zero order and first order)
-

- (ii) Initial rate method In this method, the order of a reaction is determined by varying the concentration of one of the reactants while others are kept constant.
- (iii) Integrated rate law method: In this method out different integrated rate equation which gives the most constant value for the rate constant corresponds to a specific order of reaction.
- (iv) Half-life period ($t_{1/2}$) method In general half-life period ($t_{1/2}$) of a reaction of n th order is related to initial concentration of the reactant as

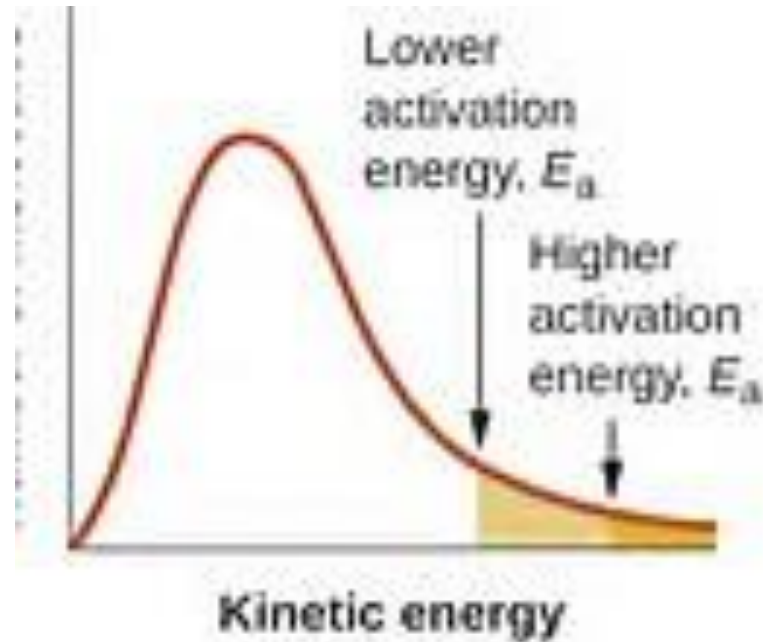
Temperature dependence of the rate of a reaction

- Temperature Dependence of Rate of a Reaction
- For every **10°C** rise in temperature, the **rate constant is doubled**. It can be explained by Arrhenius equation.
- Arrhenius equation is a mathematical expression to give a quantitative relationship between rate constant and temperature, and the expression is explained by Arrhenius equation.
- $k = Ae^{-E_a/RT}$ where, A = Arrhenius factor or frequency factor. It is called pre-exponential factor. It is a **constant specific** to a particular reaction. R is gas constant and E_a is activation energy measured in J/mol.

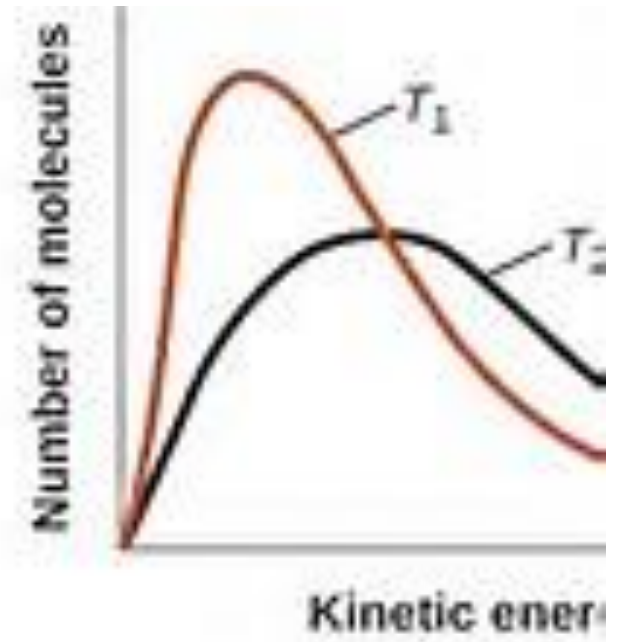
Diagram showing plot of potential energy vs reaction coordinate.



Distribution of curve showing energies among gaseous molecules. Threshold energy (E_a) The minimum amount of energy which the reactant must possess in order to convert into products is known as threshold energy

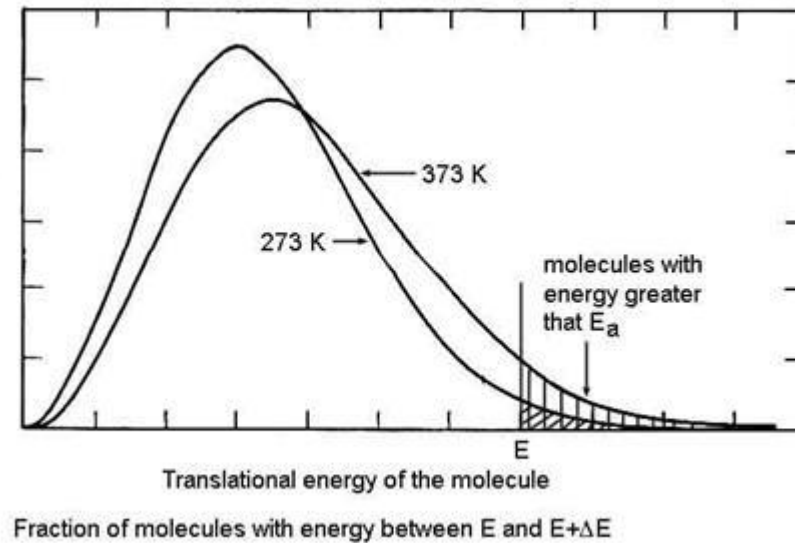


(a)



(b)

Distribution curve showing temperature dependence of rate of a reaction.



Taking logarithm on Arrhenius equation

- $\ln k = -\frac{E_a}{RT} + \ln A$ -----(1)

- Graph $\ln k$ vs $1/T$

- At two temperatures T_1 and T_2

- $\ln k_1 = -\frac{E_a}{RT_1} + \ln A$ and ----- (2)

- $\ln k_2 = -\frac{E_a}{RT_2} + \ln A$ and (since A is constant for a given reaction.-----)(3)

- Find(3) –(2)

Effect of catalyst

- A catalyst is a chemical substance which alters the rate of a reaction Without itself undergoing any permanent chemical change.
- In the chemical reactions, catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence. lowering the potential energy barrier. Graph.

COLLISION THEORY

- 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.

- $A + B \rightarrow \text{Products}$
- $\text{Rate} = Z_{AB} e^{-E_a/RT}$
- where, Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

- So, to account for effective collisions, another factor, **P called the probability or steric factor is introduced.**
- So, rate = $PZ_{AB} e^{-E_a/RT}$