

# KINETICS AND THERMODYNAMICS OF REACTIONS

**Key words:** Enthalpy, entropy, Gibbs free energy, heat of reaction, energy of activation, rate of reaction, rate law, energy profiles, order and molecularity, catalysts

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# INTRODUCTION

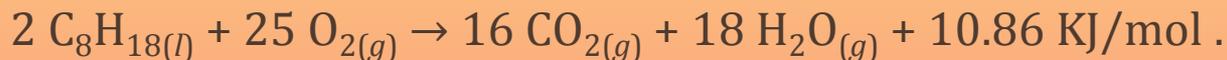
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- ✘ This module offers a very preliminary detail of basic thermodynamics. Emphasis is given on the commonly used terms such as free energy of a reaction, rate of a reaction, multi-step reactions, intermediates, transition states etc.,

# FIRST LAW OF THERMODYNAMICS.

- Law of conservation of energy. States that,
- Energy can be neither created nor destroyed.
- Total energy of the universe remains constant.
- Energy can be converted from one form to another form.

eg. Combustion of octane (petrol).



Conversion of potential energy into thermal energy.

# ESSENTIAL FACTORS FOR REACTION.

- ❖ For a reaction to progress.
- The equilibrium must favor the products-
- Thermodynamics(energy difference between reactant and product) should be favorable
- Reaction rate must be fast enough to notice product formation in a reasonable period.
  - Kinetics( rate of reaction)

# ESSENTIAL TERMS OF THERMODYNAMICS.

## ❖ Thermodynamics.

- ❖ Predicts whether the reaction is thermally favorable.
- ❖ The energy difference between the final products and reactants are taken as the guiding principle.
- ❖ The equilibrium will be in favor of products when the product energy is lower.
- ❖ Molecule with lowered energy possesses enhanced stability.

## ✕ Essential terms

- Free energy change ( $\Delta G$ ) –  
Overall free energy difference between the reactant and the product
- Enthalpy ( $\Delta H$ ) –  
Heat *content* of a system *under a given pressure*.
- Entropy ( $\Delta S$ ) –  
The energy of disorderness, not available for work  
in a thermodynamic process of a system.

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❖ The Gibbs free energy is the *maximum* amount of non-expansion work that can be extracted from a closed system which can be attained only in a completely reversible process.

❖ The Gibbs free energy change at temperature T is expressed as,

$$\Delta G = \Delta H - T \Delta S$$

○ In terms of standard states, when reactants and products at 1 M concentrations (or 1 atmosphere pressure), the free energy change is expressed as,

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$

# FREE ENERGY ( $\Delta G$ )

- ❖ For a reaction to be spontaneous
- The overall free energy at any concentrations of reactant and product is:

$$\Delta G = \Delta G^\circ + RT \ln[\text{product}]/[\text{reactant}]$$

Where R(gas constant) =  $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$  and

T(temperature) = in  $^\circ\text{K}$

At equilibrium,

$$\Delta G^\circ + RT \ln[\text{product}]/[\text{reactant}] = 0$$

$$\Delta G^\circ = -RT \ln K_{\text{eq}}$$

$$= -2.303 RT \log K_{\text{eq}}$$

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For a reaction, equilibrium shifts in the direction of lower species. Hence ,

$G^0_{\text{(reactant)}} > G^0_{\text{(product)}}$  then,

- reaction is spontaneous since  $\Delta G^0 < 0$ .  
i.e. negative and  $K_{\text{eq}} > 1$

$G^0_{\text{(reactant)}} < G^0_{\text{(product)}}$  then,

- reaction is nonspontaneous since  $\Delta G^0 > 0$   
i.e. positive and  $K_{\text{eq}} < 1$

- 
- ❖ Calculation of equilibrium constant with respect to  $\Delta G$  at 298 °K for a reaction.

$\Delta G^\circ$ in kcal mol <sup>-1</sup>	Calculated values of $K_{eq}$	Amount at equilibrium
-4.2	$10^3$	Products (99.99%)
-1.4	$10^1$	Product=(10 times of reactant)
0	1	Equal (product=reactant)
+1.4	$10^{-1}$	Reactant =(10 times of reactant).
+4.2	$10^{-3}$	Reactant (99.99%).

- It can be noted from the above calculation that a small change in  $\Delta G$  can produce considerable change to the value of  $K_{eq}$ .
- The values for product concentration decreases as  $\Delta G^\circ$  becomes progressively more +ve.

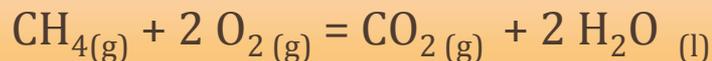
# ENTHALPY ( $\Delta H$ )

- Enthalpy can be regarded as thermodynamic potential.
- It is a *state function* and an *extensive quantity*.
- It also refers to the difference in bond energies between the reactant and product.
- In short enthalpy is 'the heat absorbed (or released) by a chemical reaction'.

# CALCULATION OF ENTHALPY

- ✘ Enthalpy is a measure of difference in bond energy between reactants and products.

E.g. Combustion of methane.



$$\Delta H_{\text{reaction}} = \sum n_p H(\text{reactants}) - \sum n_r H(\text{products})$$

$$\begin{aligned} \Delta H^{\circ}_{\text{comb}} &= \Delta H^{\circ}_{\text{f, methane}} + 2 \Delta H^{\circ}_{\text{f, oxygen}} - 2 \Delta H^{\circ}_{\text{f, water}} - \Delta H^{\circ}_{\text{f, carbon dioxide}} \\ &= 75 + 0 - (2 \times 286 + 394) \quad (\Delta H^{\circ}_{\text{f, oxygen}} = 0 \text{ as oxygen is a pure element.}) \\ &= -891 \text{ KJ mol}^{-1} . \end{aligned}$$

$\Delta H^{\circ}$  is +ve when reaction is endothermic (endergonic).

$\Delta H^{\circ}$  is -ve when reaction is exothermic (exergonic).

# SOME FACTS ABOUT ENTROPY ( $\Delta S$ )

- ✘ The second law of thermodynamics states that the entropy of any closed system, not in thermal equilibrium, will almost always increase.
- ✘ Entropy is a thermodynamic property, it is the measure of energy not used to perform work but is dependent on temperature as well as volume.
- ✘ Entropy is directly proportional to **Spontaneity**.
- ✘ Comparison of entropies: Gases > liquids > solids (bromine gas has greater entropy than when in liquid state)
- ✘ Entropy is greater for larger atoms (as we move down in groups in periodic table) and molecules with larger number of atoms.
- ✘ Entropy is a measure of the number of ways particles as well as energy can be arranged.
- ✘ More configurations (different geometries), more will be the entropy.
- ✘ Entropy of an irreversible system always increases.

# CALCULATION OF ENTROPY.

- ✗ The **standard entropy** ( $\Delta S^\circ$ ) of a substance is the value of entropy of the substance at 298 K and 1 atm.
- ✗  $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
- ✗ From the Table of Thermodynamic Data, the Standard entropies of the substances involved in the above reaction are:

✗ <b>Substances</b>	<b><math>\Delta S</math> (J/K.mol)</b>
$\text{CH}_4(\text{g})$	186
$\text{O}_2(\text{g})$	205
$\text{CO}_2(\text{g})$	214
$\text{H}_2\text{O}(\text{l})$	70

The entropy change of the reaction can be calculated as:

$$\Delta S^\circ_{\text{reaction}} = \sum n_p S(\text{products}) - \sum n_r S(\text{reactants})$$

$$\Delta S^\circ = [214 + 70 * 2] - [186 + 205 * 2] = -242 \text{ J/K.}$$

- ✗  $\Delta S^\circ = +\text{ve}$  when there is **decrease** in order.
- ✗  $\Delta S^\circ = -\text{ve}$  when there is **increase** in order.

# THERMODYNAMICS

## VARIATION OF $\Delta G$ IN RELATION WITH $\Delta H$ & $\Delta S$

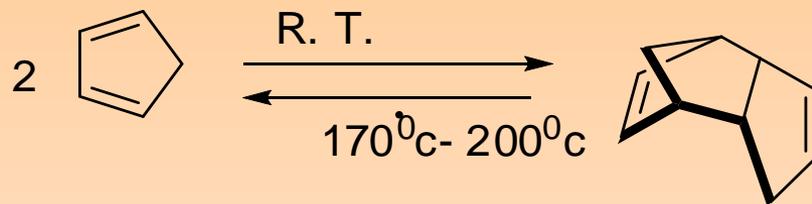
Enthalpy Change	Entropy Change	Spontaneous Reaction?
Exothermic ( $\Delta H < 0$ )	Increase ( $\Delta S > 0$ )	Yes, $\Delta G < 0$
Exothermic ( $\Delta H < 0$ )	Decrease ( $\Delta S < 0$ )	Only at low temps, if $ T \Delta S  <  \Delta H $
Endothermic ( $\Delta H > 0$ )	Increase ( $\Delta S > 0$ )	Only at high temps, if $ T \Delta S  >  \Delta H $
Endothermic ( $\Delta H > 0$ )	Decrease ( $\Delta S < 0$ )	No, $\Delta G > 0$

# ILLUSTRATIVE EXAMPLES ON THERMODYNAMICS

## PERICYCLIC REACTIONS

### DIELS ALDER REACTION

- × **Diels Alder reaction** (4+2 cycloaddition , converting two weaker  $\pi$ -bonds into two stronger  $\sigma$ -bonds)
- × **Dimerization of Cyclopentadiene :-**

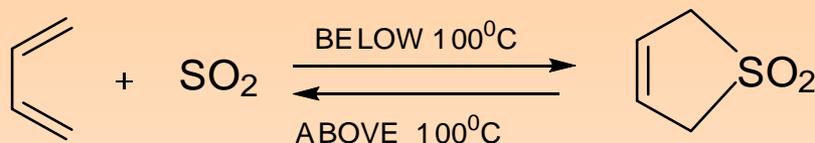


- × Cyclopentadiene at normal temperatures exists as a dimer with selective endo product and exists as a monomer at  $200^{\circ}\text{C}$
- × At normal temperature, the dimerization is favored due to  $-ve \Delta G$  ( $-9.61 \text{ Kcal mol}^{-1}$ ) which is  $+ve$  at  $200^{\circ}\text{C}$  ( $0.05 \text{ Kcal mol}^{-1}$ ) hence increasing spontaneity.

# CHELETROPIC ADDITION OF SO<sub>2</sub>

## × Cheletropic Addition of SO<sub>2</sub>

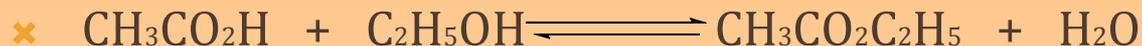
- × Reaction involving two sigma bonds directed to a single atom of a ring are made or broken concertedly resulting in decrease or increase of one pi bond. An example is the reversible addition of sulfur dioxide to 1,3-butadiene shown here.



- ×  $\Delta H^\circ = -16.5 \text{ kcal/mole}$
- × Below 100° C the equilibrium favors the addition product with  $\Delta H^\circ = -16.5 \text{ kcal/mole}$ . Above 100° C the cyclic sulfone decomposes to 1,3-butadiene. The equilibrium constant is close to unity at 100°C. The entropy change calculated is as follows:-

# INFLUENCE OF $\Delta G^\circ$ IN LACTONE FORMATION REACTION (MUKIYAMA ESTERIFICATION)

✘ Consider the reaction,



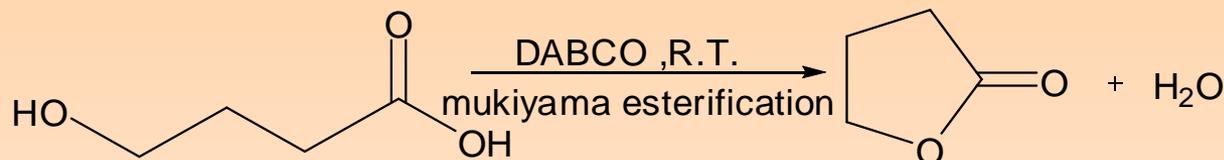
$$\Delta H^\circ = -0.80 \text{ kcal/mol}$$

$$\Delta S^\circ = +1.6 \text{ cal/ } ^\circ\text{K mol}$$

$$\Delta G^\circ = -1.28 \text{ kcal/mol}$$

✘ This reaction is considerably slow, requires a good amount of catalyst, and continuous removal of water to favor yield more than 90%.

✘ Exactly reverse is the condition with lactone formation



4-hydroxybutanoic acid

cyclic 5 membered lactone.

$$\Delta H^\circ = +1.10 \text{ kcal/mol}$$

$$\Delta S^\circ = +13.9 \text{ cal/ } ^\circ\text{K mol}$$

$$\Delta G^\circ = -3.1 \text{ kcal/mol}$$

There is 1.90 kcal/mol increase in  $\Delta H^\circ$  is due to combination of angle, eclipsing and other conformational strains contributing to overall ring strain, hence we can expect  $\Delta G^\circ$  to be less negative.

✘ This lactonization is known to occur in  $(\text{CH}_2)_n$  when  $n=2,3$

Below this ( $n=1$ ) lactonization is unfavored as it may result in highly strained ring increasing  $\Delta H^\ominus$  so much that  $\Delta S^\ominus$  cannot counterbalance it, thus leading to a +ve  $\Delta G^\ominus$  value and decrease in spontaneity.

Above this ( $n>3$ ) particularly in 7 or 8 membered rings, the probability of  $-\text{OH}$  and  $-\text{COOH}$  group coming closer is low. Hence dimerization or polymerization can be preferred over intramolecular lactonization reaction.

# MOLECULARITY AND IT'S DETERMINATION

- ✘ It is the total count of number of atoms, molecules or ions colliding together in the slow rate-determining step of a reaction.
- ✘ **Classification of molecularity**
- ✘ Molecularity is classified on basis of number of molecules taking part in reaction, illustrated as follows
  - Unimolecular :-when one reactant disintegrate to form products.
  - e.g.,  $\text{N}_2\text{O}_5 \longrightarrow \text{N}_2\text{O}_4 + 1/2\text{O}_2$
  - Bimolecular :-when two molecules collide to form products.
  - ✘ e.g.,  $\text{C}_{12}\text{H}_{22}\text{O}_{12}(\text{sucrose}) + \text{H}_2\text{O}_{(\text{excess})} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{Glucose}) + \text{C}_6\text{H}_{12}\text{O}_6(\text{fructose})$
  - ✘ Termolecular :- when three molecules collide to form products.
  - ✘ e.g.,  $2\text{Cl}\cdot + \text{Cl}_2 \longrightarrow 2\text{Cl}_2$
  - $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$

# KINETICS OF REACTION

- ✘ Kinetics is the study of

  - How fast the reactant is converted to product.

  - Relates to reaction rates.

  - Pathway for the reaction.

- ✘ Kinetics depend on following factors,

  - Activation energy to cross the barrier.

  - Concentration

  - Temperature of the reaction

  - Catalyst and co-catalyst (lowers the activation energy for the reaction without affecting reactant or products).

## RELATION OF KINETICS WITH REACTION RATES.

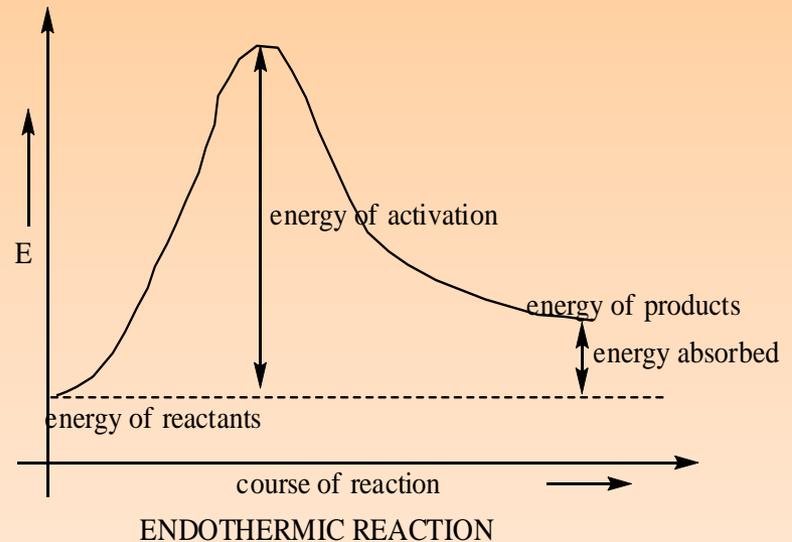
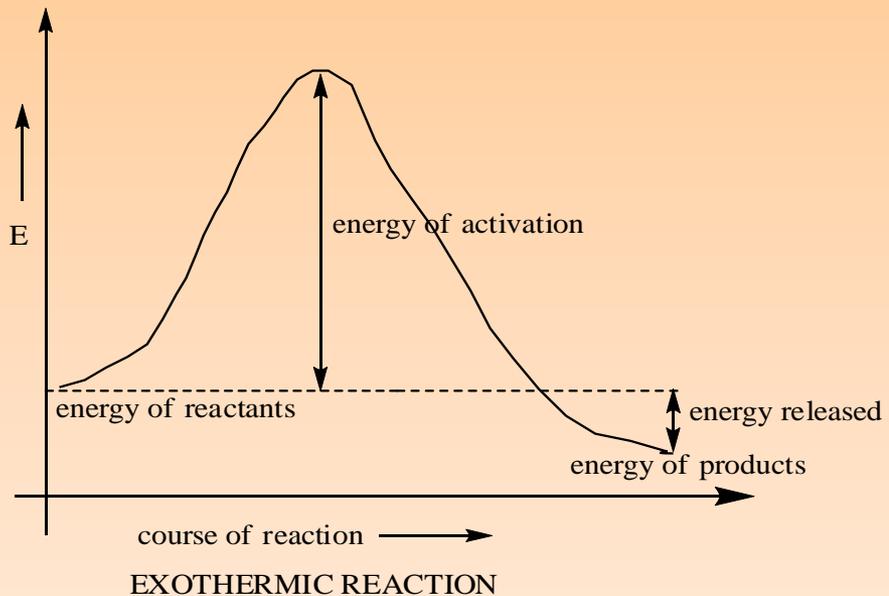
- As per the Arrhenius equation the **rate constant (small k)** is inversely proportional to the **energy of activation ( $E_a$ )**.
- Faster the reaction is larger will be the rate constant
- Catalyst increases the rate of reaction by forming a different pathway which decreases the  $E_a$  and hence increasing the rate constant k.
- The rate law and rate equation are experimentally determined quantities (not involving theoretical calculations). They show the relations between the **concentration of reactant** with the **reaction rate**.

# ENERGY PLOTS.

- ✘ It is a schematic plot representing the the changes in  $\Delta H^\circ$  or  $\Delta G^\circ$  of system with respect to the reaction progresses (from reactant to product).
- ✘  $\Delta H^\circ$  or  $\Delta G^\circ$  are -ve when the reaction is exothermic or exergonic respectively i.e., the products having lower energy than the reactants.
- ✘  $\Delta H^\circ$  or  $\Delta G^\circ$  are +ve when the reaction is endothermic or endorgenic respectively i.e. the product having higher energy than the reactant .
- ✘ They are plotted with energy on the Y-axis and the reaction coordinate (on simpler terms, progress of reaction) on the X-axis.
- ❖ The maxima on the energy profile is typically transition states, the energy required to attain that level is the energy of activation represented by  $E_a$ .

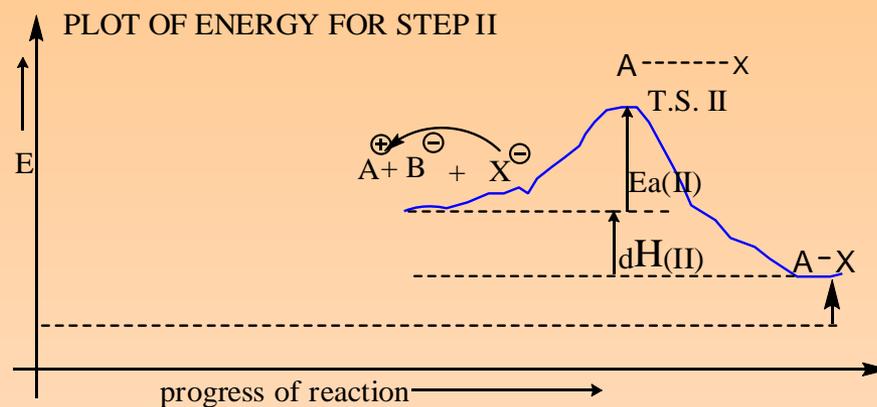
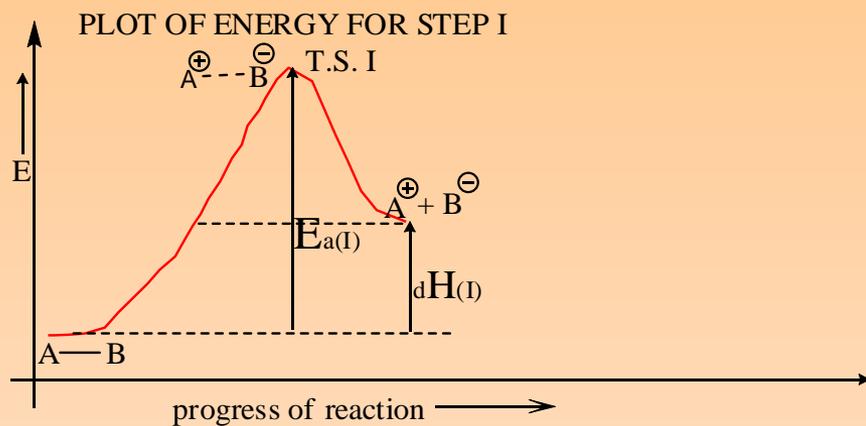
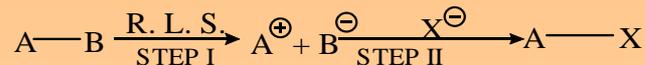
# EXOTHERMIC AND ENDOTHERMIC REACTIONS

## ✘ Exothermic and endothermic reactions

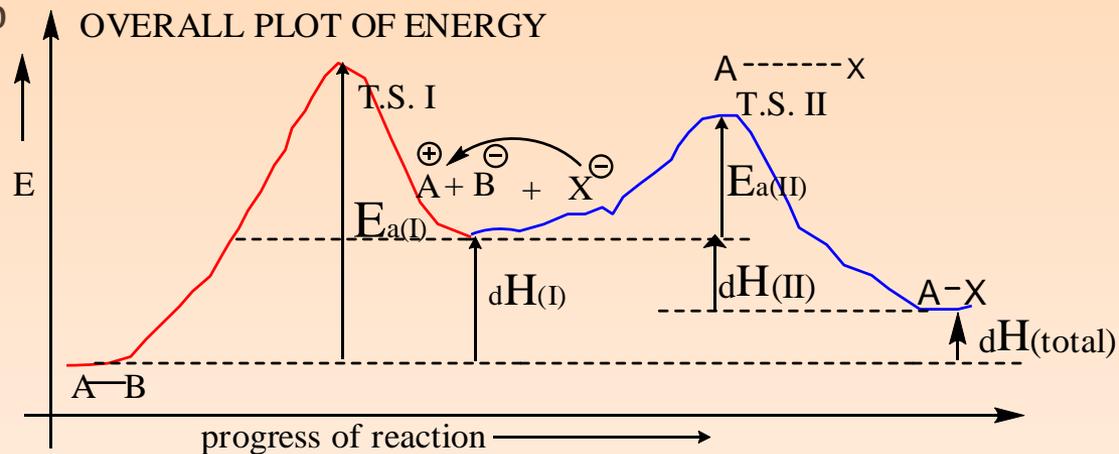


# ENERGY DIAGRAM FOR A TWO STEP PROCESS

- Consider a two step process in which a nucleophile  $X^-$  attack the AB molecule giving AX as products.



- The highest transition state is for step I (higher  $E_a$ ). This will be the slowest step and hence is the Rate Determining step.
- The overall reaction is endothermic ( $\Delta H$  is +ve).
- Each step is characterized by its own  $\Delta H$  &  $E_a$  values.
- Step II is faster step having lower activation energy.



# RATE OF REACTION (MEASURE OF HOW FAST A REACTION PROCEED)

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- ✗ It is a measure of the rate with which reactant are consumed to form products (which may vary from a few seconds to years).
- ✗ It can be expressed as decrease of concentration as a function of time.  
Rate = -  $\frac{\Delta[A]}{\Delta t}$
- ✗  $\Delta[A]$  = concentration of reactant A in **mol dm<sup>-3</sup>**.
- ✗  $\Delta t$  = time expressed in **seconds**.
- ✗ The rate of reaction is by two theories
- ✗ The rate of reaction depends on **Activation energy, Frequency of collisions, and a Probability factor** (factor specifying that molecule have proper orientation).

# FACTOR AFFECTING RATE OF REACTION

- × **TEMPERATURE**:- increase in temperature result in higher speed of molecules effecting successful collision.
- × **PRESSURE**:- increase in pressure, lesser the volume, particles are more closer (mostly in case of gaseous reactant).
- × **CONCENTRATION**:-rate of reaction is directly related to increase in concentration as more number of molecule result in more collisions.
- × **SURFACE AREA**:- more surface area results in greater space, increasing probability of collisions (mostly in solid reactant).
- × **CATALYST**:- catalyst speed up the reaction by providing alternative path which decreases the activation energy hence reactant don't have to overcome the much higher activation barrier as in an uncatalysed reaction.
- × **INHIBITORS**:- they act as obstacles in the rate of reaction which may decrease the rate to considerable extent or completely.

# RATE LAWS AND RATE CONSTANT

- ✗ Rate law is a mathematical expression, which relates the decreases in **concentration** of a reactant with **time** and it is determined experimentally.
- ✗ **Order of reaction** :-the power to which the concentration term of reactant is raised in the rate equation determine the order of reaction. ~~Order of reaction has no relation with stoichiometry of reactant.~~
- ✗  $aA_{(l)} \rightarrow pA_{(l)}$  products
- ✗  $\text{Rate} = k[A]^m$  here m represents order of the reaction with respect to reactant (A in the present case).
- ✗ Larger the value of k is the faster will be the reaction.
- ✗ k is independent of concentration.

# UNITS FOR RATE CONSTANT OF A REACTION

- ✗ The equation of rate is given as,  $\text{RATE} = \text{--- mol L}^{-1}\text{s}^{-1}$
- ✗ Concentration of A is given as  $[\text{A}] = \text{--- mol L}^{-1}$
- ✗ Hence, we get  $k = \text{---} [\text{mol L}^{-1}]^{(1-n)}\text{s}^{-1}$
- ✗  $k(\text{for a gaseous reactant}) = \text{--- atm}^{(1-n)}\text{s}^{-1}$
- ✗ For of reaction of various order the unit of k can be written as

ORDER OF REACTION	UNITS	Units for gaseous reactant.
I <sup>st</sup>	$\text{s}^{-1}$	$\text{s}^{-1}$
II <sup>nd</sup>	$\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$ or $\text{mol}^{-1}\text{L s}^{-1}$	$\text{Atm}^{-1}\text{s}^{-1}$
III <sup>rd</sup>	$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$ or $\text{mol}^{-2}\text{L}^2\text{s}^{-1}$	$\text{Atm}^{-2}\text{s}^{-1}$

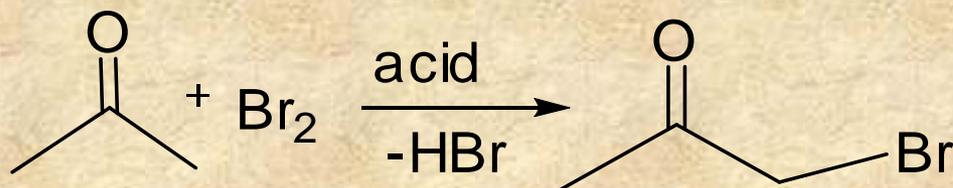
- ✘ The overall order is the sum of the exponents of all the reactants in a rate equation. Reaction rates are classified as zero order, first order, second order or mixed order.
- ✘ The order of a reaction is determined experimentally by following methods.
- ✘ Half rate method, initial rates methods, graphical method, etc.,
- ✘ **Half rate method**
- ✘ Half time ( $t_{1/2}$ ) is the time taken for one half part of reactant to react.
- ✘ Faster reaction have larger rate constant and shorter half life.
- ✘ The ( $t_{1/2}$ ) for various order is deduced from following equations

Order of reactant	Half time ( $t_{1/2}$ )
0	$[A]_0/2k$
1	$\ln 2/k$ or $0.693/k$
2	$1/\{k[A]_0\}$

## ✘ Initial rates methods:-

✘ In this method, the concentration of reactants is kept constant, except that of one reactant, in each experiment for which the rate is determined.

✘ Example: Bromination of acetone



$$\text{Rate of reaction} = k[\text{acetone}]^a [\text{Br}_2]^b$$

✘ The data obtained is as follows,

Experiment	[acetone] $\text{mol}^{-1}\text{dm}^3$	[Br <sub>2</sub> ] $\text{mol}^{-1}\text{dm}^3$	Rate in $\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$
1	0.1	0.1	$1.64 \times 10^{-5}$
2	0.2	0.1	$3.29 \times 10^{-5}$
3	0.1	0.2	$1.645 \times 10^{-5}$

✘ Hence, Rate =  $k[\text{acetone}]^1 [\text{Br}_2]^0$

✘ The rate is first order in the case of acetone and zero order in the case of bromine, hence the overall order is  $a+b=0+1=1$  (first order reaction).

## ✘ Graphical method (Valid for one reactant)

✘ Also called pseudo rate law method

✘ Consider a reaction  $A + B \longrightarrow$  Products

✘ Initially the concentration of A is kept 100 times greater and the rate equation is deduced for a constant concentration of B

$$\text{Rate} = k[B]^n$$

✘ The same procedure is followed by keeping reactant A constant & concentration of reactant B 100 times greater than A

$$\text{Rate} = k[A]^m$$

✘ The rate of reaction can be determined graphically by plotting the co-ordinate as follows, the graph which give a straight line plot correspond to the order of reaction.

X-axis	Y-axis	Integrated Rate law	Rate law	Order
[A]	t	$[A] = [A]_0 - kt$	Rate = k	0
ln [A]	t	$[A] = \ln[A]_0 - kt$	Rate = k[A]	1
1/[A]	t	$[A] = [A]_0 / \{1 + k t [A]_0\}$	Rate = k [A] <sup>2</sup>	2