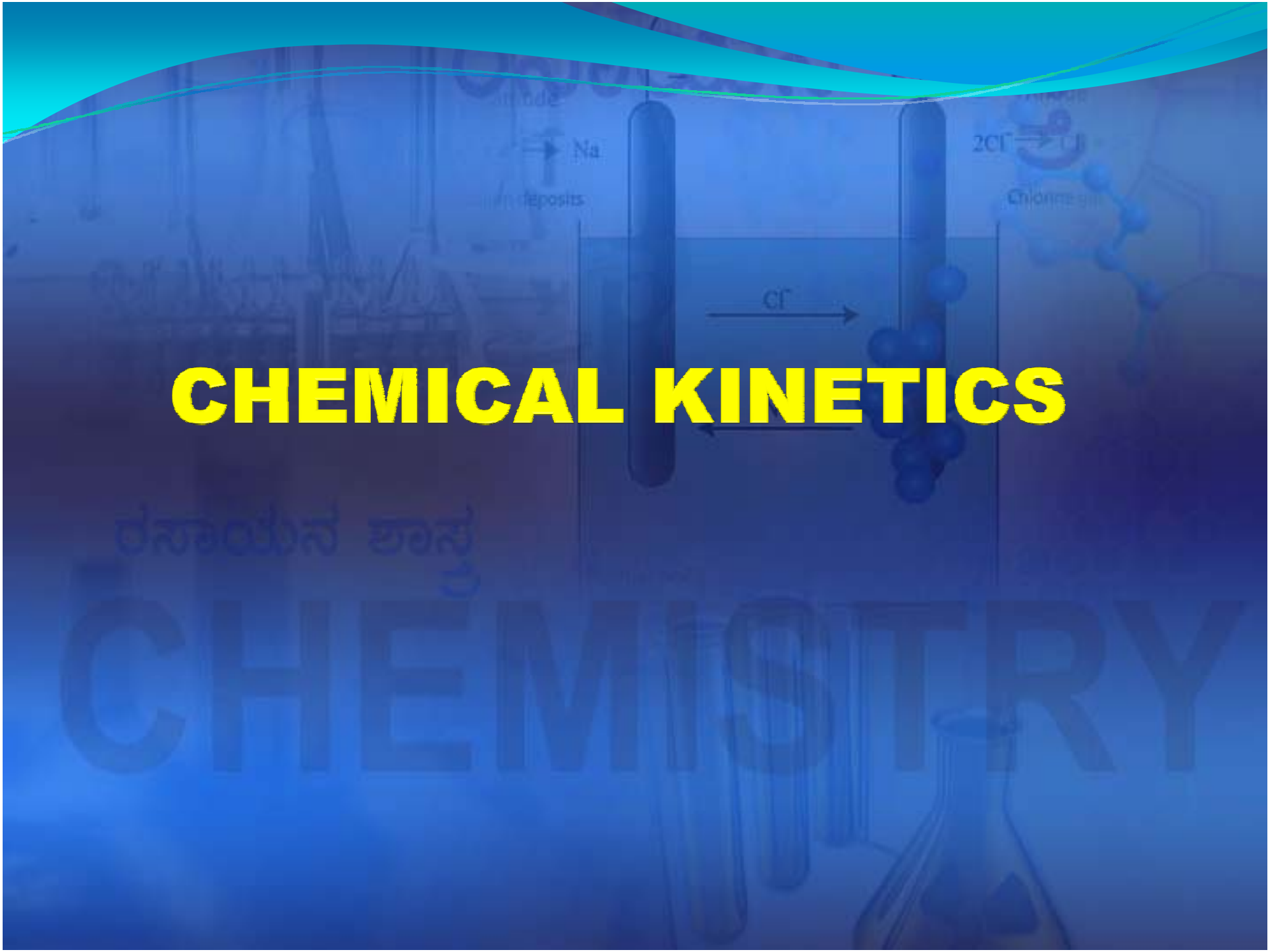



# CHEMICAL KINETICS

# CHEMICAL KINETICS AND THEORY OF DILUTE SOLUTIONS

# BLUE PRINT

| Name of the topic | No. of Teaching Hours | Marks Allotted | | | TOTAL |
|---|---|---|---|---|---|
| | | 1M | 2M | 3&4M | |
| 1) Chemical Kinetics | 5 | 1 | 2+2 | 3 | 8 |
| 2) Theory of dilute solutions | 3 | - | 2 | 3 | 5 |

# WHAT IS CHEMICAL Kinetics?

The branch of chemistry Which deals with the study of rate of a reaction is called chemical kinetics.

# What is rate of a reaction?

Change in concentration of reactants or products per unit time.

Rate is generally represented as

$$\pm \frac{dc}{dt}$$

Its unit is

$$mol\,dm^{-3}\,s^{-1}$$

## Explain the commercial importance of rate studies.

It helps to study the suitable conditions to get maximum yield of products.

It helps to understand the methods to control various steps in the formation of useful compounds.

# For a reaction

$$l\mathrm{A} + m\mathrm{B} \rightarrow x\mathrm{C} + y\mathrm{D}$$

$$-\frac{1}{l}\frac{d[A]}{dt} = -\frac{1}{m}\frac{d[B]}{dt} = +\frac{1}{x}\frac{d[C]}{dt} = +\frac{1}{m}\frac{d[D]}{dt}$$

# What is rate equation?

For a reaction

$$lA + mB \rightarrow xC + yD$$

Rate = $k [A]^l \times [B]^m$

# What is order of a reaction?

It is defined as the sum of the powers of the concentration terms in the experimentally determined rate equation

## What is zero order reaction? Give an example.

A zero order reaction is one

In which rate is independent

Of the concentration of reactants.

Eg;

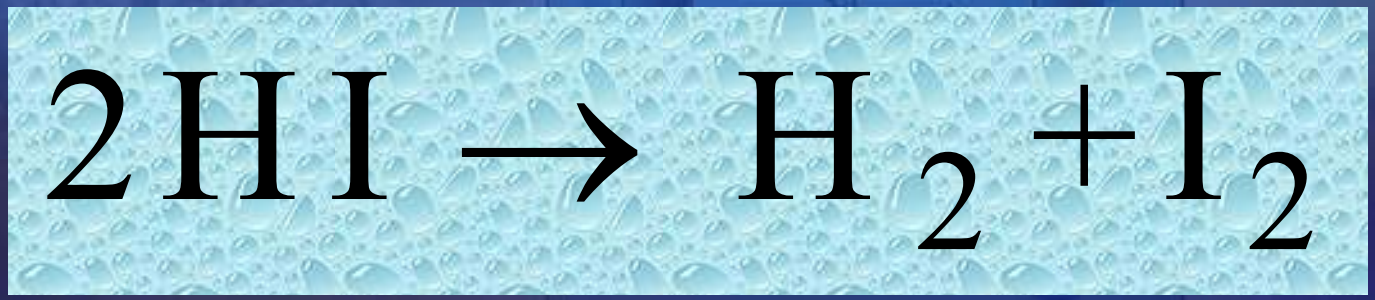
## What is first order reaction? Give an example.

A first order reaction is one

In which rate is directly proportional to the first power Of the concentration of reactants.

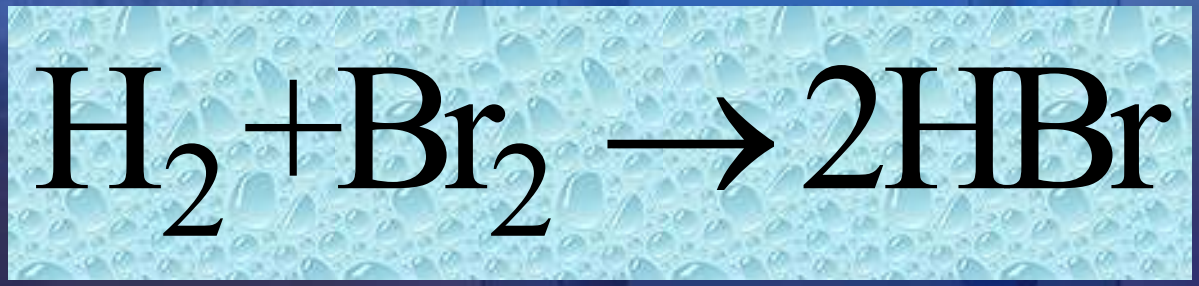
Eg; $2H_2O_2 \rightarrow 2H_2 + O_2$

## Give any two examples of second order reaction

1) 


2) Saponification or alkali hydrolysis of an ester

# Give an example of fractional order reaction

1) 


Rate = k $[H_2]^1$ x $[Br_2]^{1/2}$

order=1+1/2 =3/2

2) $CO + Cl_2 \rightarrow COCl_2$

order=5/2

## What is pseudo first order reaction? Give an example.

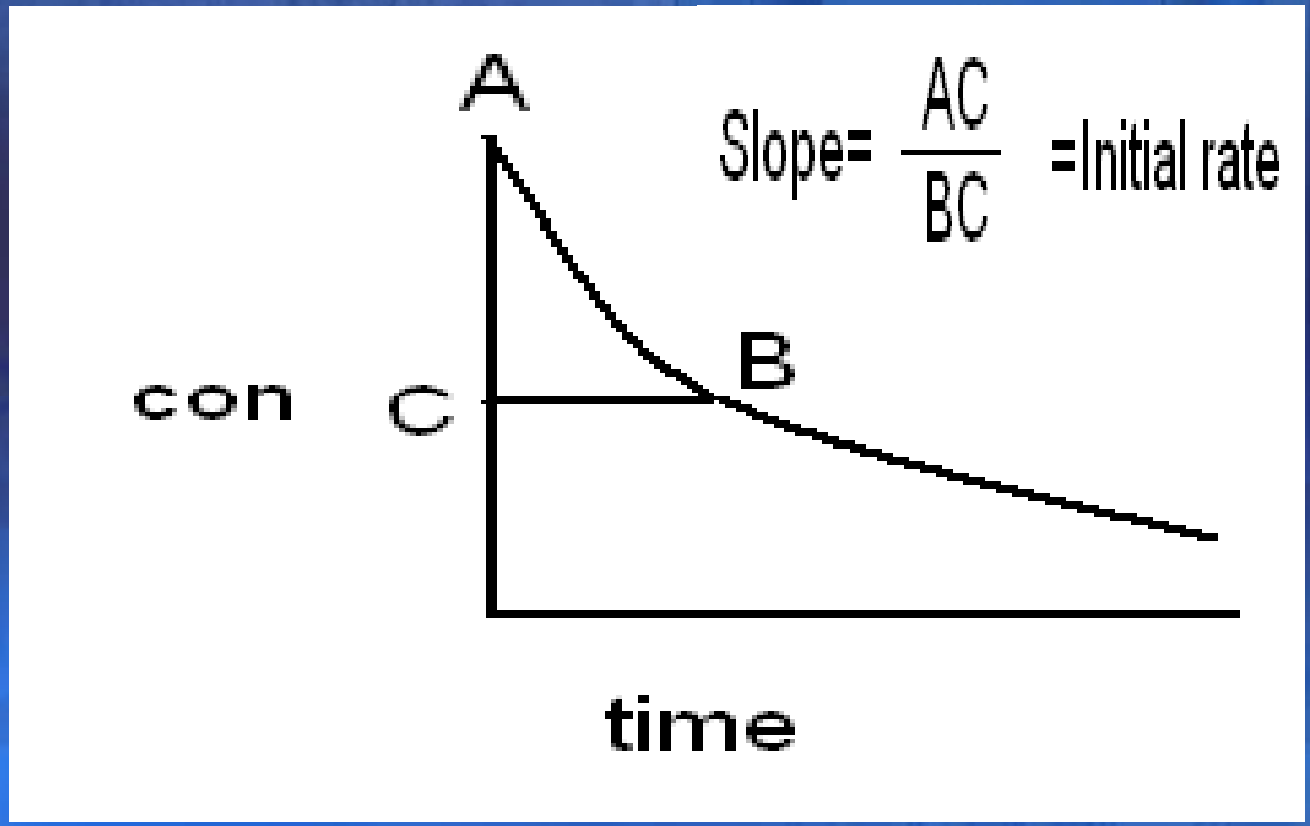
A reaction in which order is one but more than one reactants are participating in the reaction.

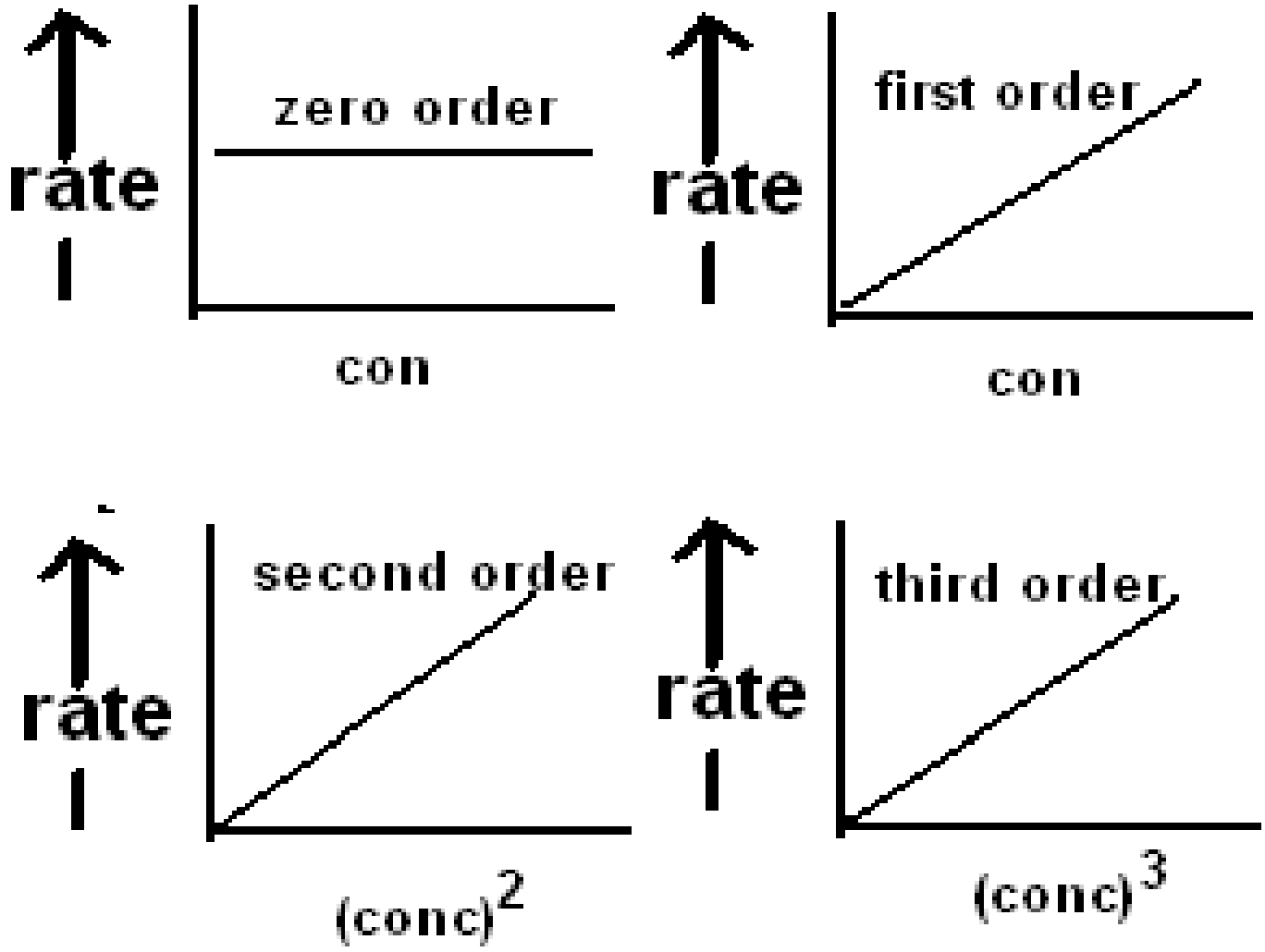
Eg: $CH_3COOCH_3 + H_2O \xrightarrow{HCl} CH_3COOH + CH_3OH$

## What are the factors affecting the order of a reaction? Explain.

1) Relative concentration of reactants:
2) Reaction mechanism:
   Rate depends on slowest step called rate determining step.

# Explain the graphical method of determining the order.




rate
zero order
con
rate
first order
con
rate
second order
(conc)2
rate
third order
(conc)3

# Explain Ostwald's isolation method of determining order.

For determining order of the Reaction A+B+C→ product , first A is taken in trace quantity others in excess then order wrt A is calculated ($n_1$ )

Next B in trace others in excess,let order wrt B is $n_2$ and so on then,

order= $n_1 + n_2 + n_3$

# Write the unit of rate constant of nth order reaction

- $(Moldm^{-3})^{1-n}s^{-1}$
- For 0 order $(Moldm^{-3})s^{-1}$
- For I order $s^{-1}$
- For II order $(Moldm^{-3})^{-1}s^{-1}$

  or $Mol^{-1}dm^3\ s^{-1}$

# Derive an expression for the rate constant period of a I order reaction

**For a I order reaction A→P**

**Rate =** $\frac{dx}{dt} = k\,[A]$ or $\frac{dx}{dt} = k\,[a-x]$

$$\frac{dx}{[a-x]} = k\,dt$$

**Integrating,**

$$\int \frac{dx}{[a-x]} = \int k\,dt$$

$$-\ln(a-x)=kt+C$$

**C is integration constant,**

**at t=0,x=0,a-x= a**

$$-\ln(a-0)=0+C \quad \text{or } C=-\ln a$$

**Substituting the value of C**

$$-\ln(a-x)=kt+-\ln a \text{ or } kt=\ln\left(\frac{a}{a-x}\right)$$

or $$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

- **What is half life period? Derive an expression for the half life period of a I order reaction.**

**“ Time required to reduce the concentration of reactants to half of its initial value”**

**At $t=t_{1/2}$ $x = a/2$ & $a-x = a-a/2 = a/2$**

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

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

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

**Write the relation between half life period & initial conc for $n^{th}$ order reaction.**

$$t_{1/2} \alpha \frac{1}{a^{n-1}}$$

- For 0 order : $t_{1/2} \alpha a$
- For I order: $t_{1/2}$ = constant
- For II order: $t_{1/2} \alpha 1/a$

## Define temperature coefficient.

The ratio of the rate constant of the reaction at (T+10)K to the rate constant at TK.

ie T.C= $\frac{k_{T+10}}{k_T}$ = 2 or 3

**The temperature coefficient of a reaction is 2. How many times the rate of the reaction increases by increasing the temperature from 300K to 330K?**

Rise in velocity = $(T.C)^n$

$= (2)^3 = 8$ times

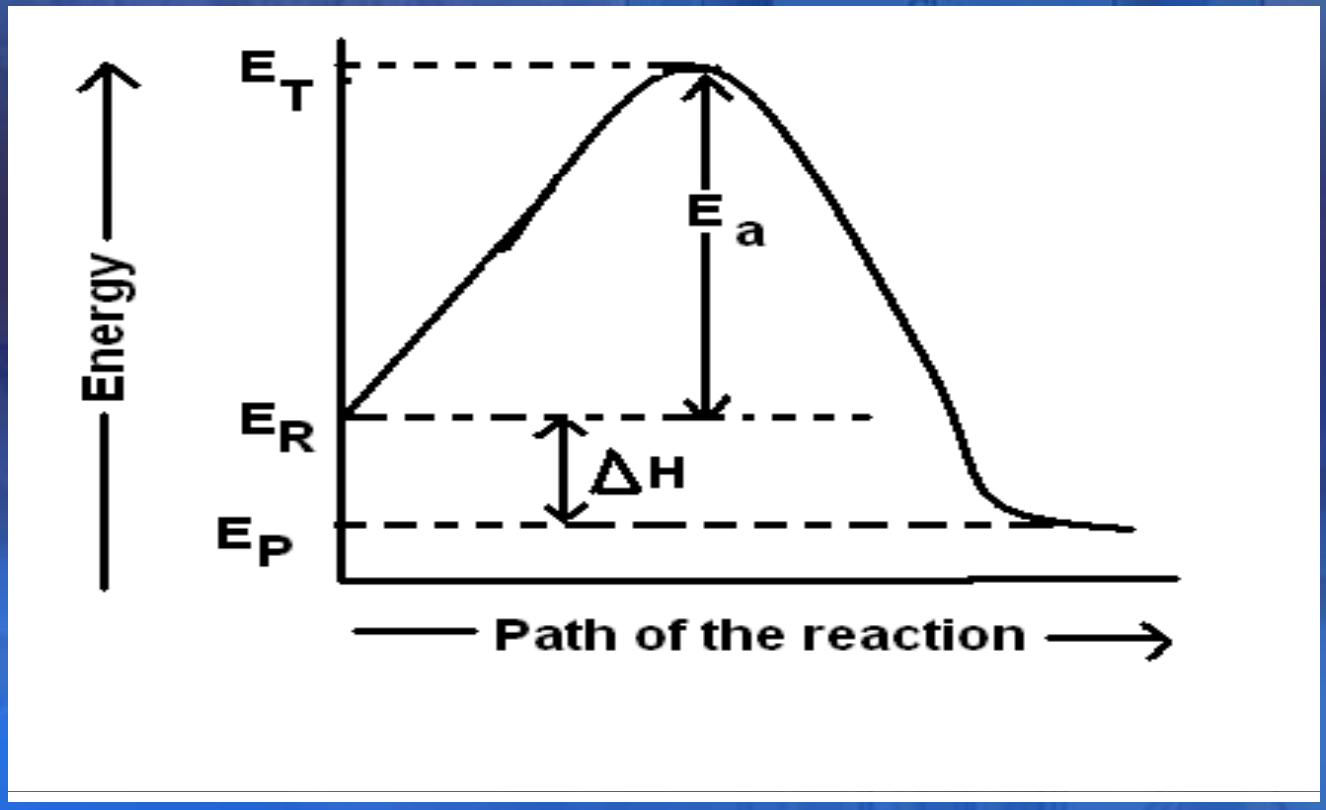
# Define threshold energy($E_T$).

The minimum amount of
Energy that the normal reactant
Molecules should possess
to form products upon collision.

# Define energy of activation($E_a$).

The minimum <u>extra</u> energy that the reactant molecules should possess to form products upon collision.

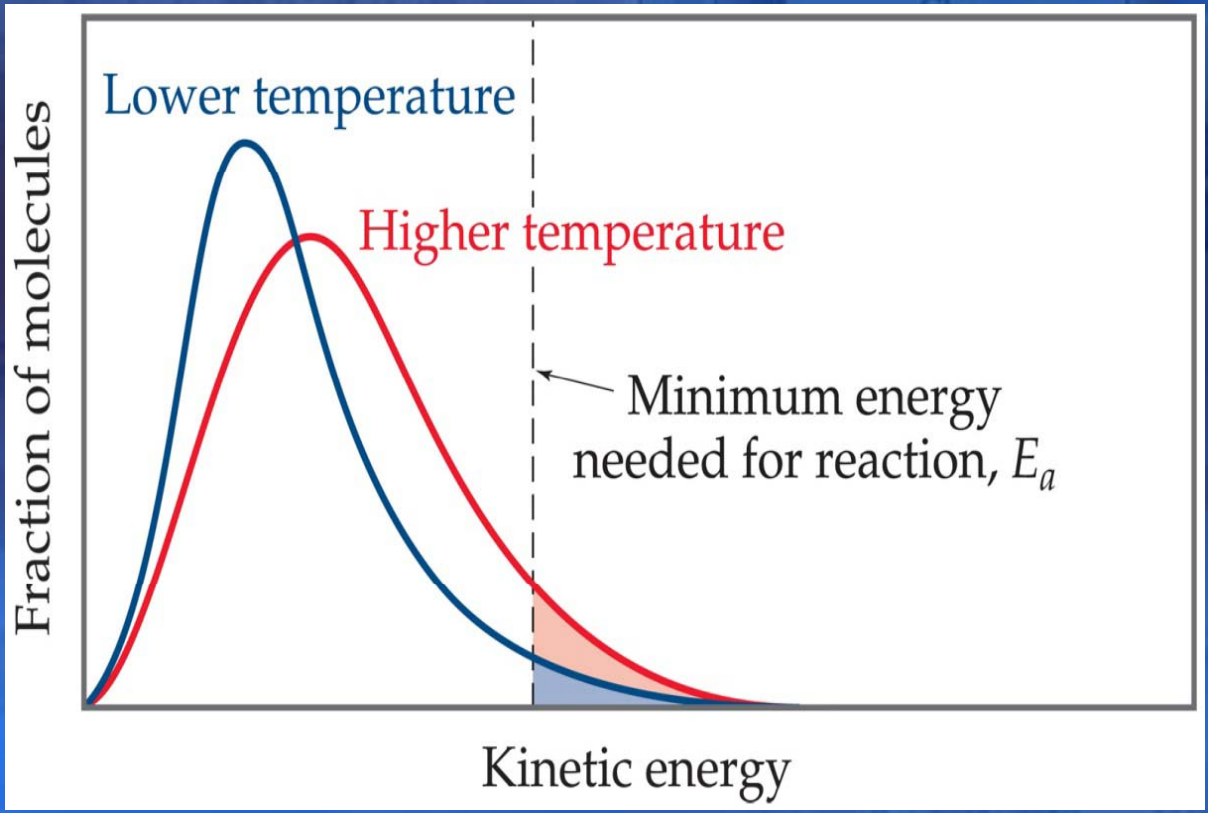
$$E_a = E_T - E_R$$



# Why rate of reaction doubles for every 10 degree rise in temp.

For every $10^0$c rise in temperature number of molecules having activation energy also doubles, which is evident from the graph.

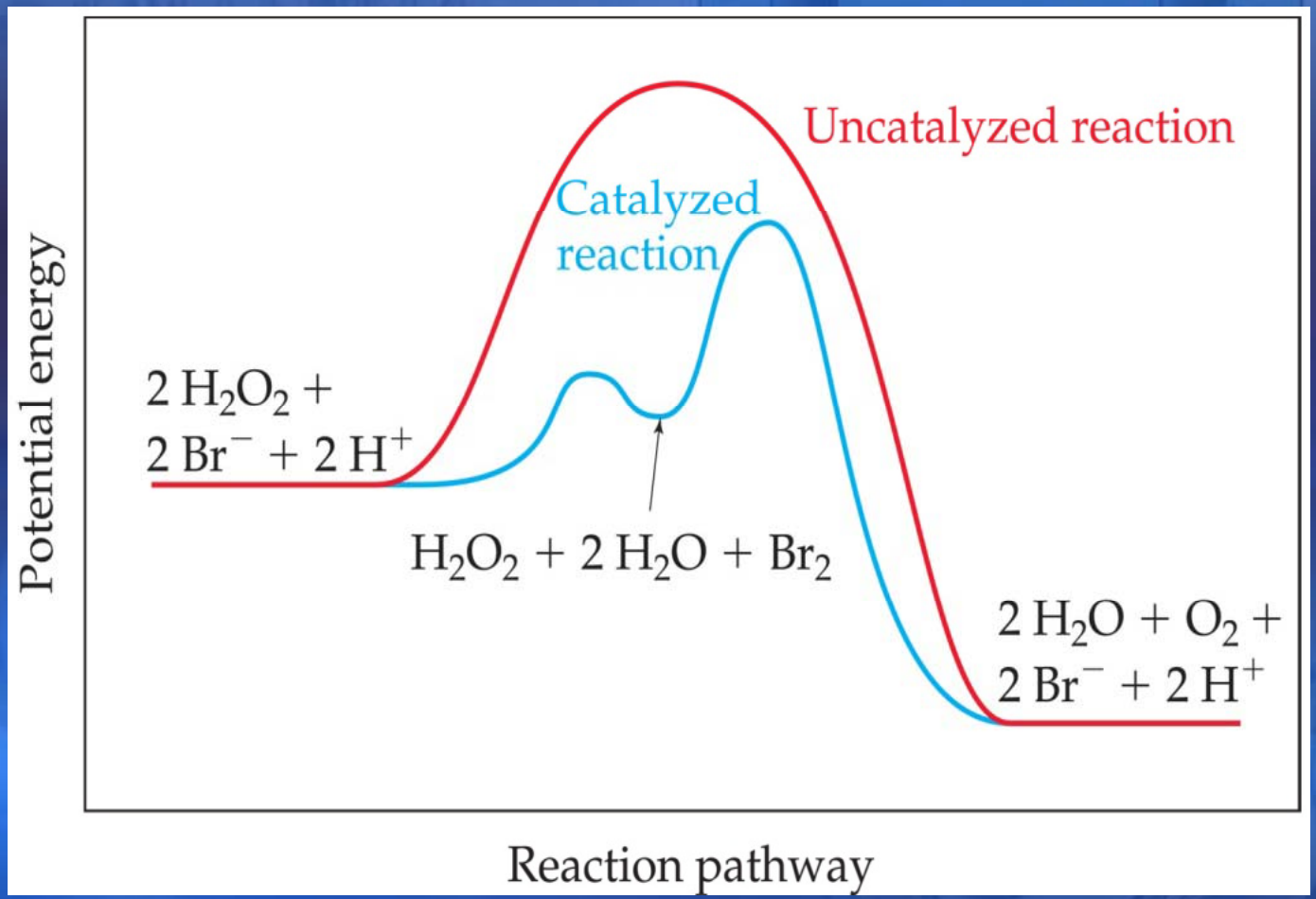
# Effect of temperature on the rate of a reaction.



# Explain the role of catalyst on the rate of a reaction.

Catalysts gives an alternative path in which energy of activation is less. It is evident from the energy profile diagram.

# Influence of catalyst on the rate of a reaction.



## Write Arrhenius equation & explain the terms.

$$k = A\, e^{\frac{-E_a}{RT}}$$

k is rate constant.

A is frequency factor.

$E_a$ is energy of activation.

$$\log k = \log A - \frac{E_a}{2.303RT}$$

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

**Problems:1) Half life period of I order reaction is 30 min.**

**Calculate its rate constant.**

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

**= 0.0231 $min^{-1}$**

**30% of a first order reaction is completed in 40 min. Calculate its velocity constant.**

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

**a =100,a-x = 70,t = 40.**

**k = 8.924 x$10^{-1}$$min^{-1}$**

**The rate constants of a reaction at $25^0$c & $35^0$c are 1.5 x$10^{-3}s^{-1}$ & 2.998 x$10^{-3}s^{-1}$ respectively. Calculate the energy of activation.**

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

$E_a$ =5284J.

$$\frac{P^0 - P}{P^0} = \frac{n_2}{n_1}$$

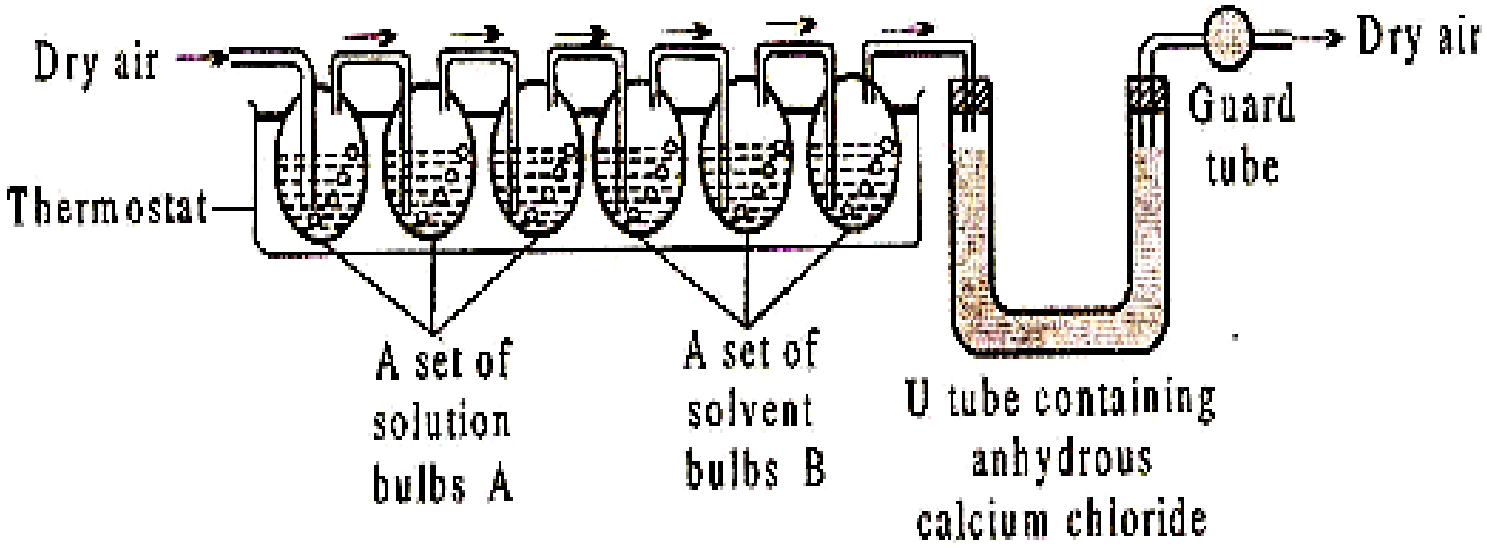
$$\frac{P^0 - P}{P^0} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{P^0 - P}{P^0} = \frac{W_2 M_1}{W_1 M_2}$$

$$M_2 = \frac{W_2 M_1 P^0}{W_1 (P^0 - P)}$$

$$M_2 = \frac{W_2 M_1}{W_1} \left[ \frac{1}{RLVP} \right]$$

# Explain Ostwald Walker method of determining molecular mass




Ostwald - Walker's apparatus

- Calculations:
  - Mass of the solute dissolved = $W_2$ g
  - Mass of the solvent taken = $W_1$ g
  - Loss in mass of solution bulbs = a $\alpha$ p
  - Loss in mass of solvent bulbs = b $\alpha$ ( $P^0$ – P)

Gain in mass of $Cl_2$ tube = c $\alpha$ $P^0$

Relative lowering of vapor pressure =

$$\frac{P^0 - P}{P^0} = \frac{b}{c}$$

$$M_2 = \frac{W_2}{W_1} \frac{M_1}{RLVP}$$

$$M_2 = \frac{W_2}{W_1} \frac{M_1}{b} \frac{c}{b}$$

# What are ideal/Non ideal solution.

1) **Ideal solution** **is a solution which obeys Raoult's law exactly at all concentrations and temperatures.**

- **i.e.** $P_A + P_B = P_{AB} = P_A^0 X_A + P_B^0 X_B$

Eg;Benzene+Tolune

2) **Non–Ideal solution** : It is a solution which do not obey Raoult's law

i.e. $P_A + P_B \neq P_A^0 X_A + P_B^0 X_B$

Eg; Ethanol + water

chloroform +acetone

# Differences between ideal and non-ideal solutions:-

| Ideal solution | Non Ideal solution |
| --- | --- |
| 1. It obeys Roult's law. | 1.It fails to obey Roult's law. |
| 2. $\Delta H_{mix} = 0$ | 2. $\Delta H_{mix} \neq 0$ |
| 3. $\Delta V_{mix} = 0$ | 3. $\Delta V_{mix} \neq 0$ |

4. The molecular interactions between solute and solvent molecules is equal solvent-solvent interactions

4. The molecular interactions between solute and solvent molecules is different from those of solute - solute interactions and solvent-solvent interactions.

**What are the two types of non ideal solutions? Give examples.**

**1) Non ideal solutions having positive deviation:**

**Here $\Delta H_{mix}$= +ve & $\Delta V_{mix}$= +ve .**

**Eg: Ethanol + water.**

**Ethanol + acetone.**

2) **Non ideal solutions having negative deviation from Raoult's law:**

Here $\Delta H_{mix}$= -ve &
$\Delta V_{mix}$= -ve .

**Eg:** HCl+ water.

Chloroform + acetone.

# Define elevation in boiling point ($\Delta T_b$)

"The difference between the boiling point of the solution and that of pure solvent "

$$\Delta T_b = \frac{1000 k_b W_2}{M_2 W_1} = k_b m$$

# Define depression in freezing point ($\Delta T_f$).

"The difference between the freezing point of the pure solvent and that of solution "

$$\Delta T_f = \frac{1000 k_f W_2}{M_2 W_1} = k_f m$$

**Problem:** A current of dry air was passed through a solution prepared by dissolving 3.75g of non volatile solute in 40.5 g of water & then distilled water. The loss in mass of solvent bulb was 0.055g.The gain in the mass of anhyd $CaCl_2$was2.9g.Calculate the molecular mass of the solute.

$$M_2 = \frac{W_2}{W_1} \frac{M_1}{b} \frac{c}{}$$

$$M_2 = \frac{3.75}{40.5} x \frac{18}{} x \frac{2.9}{0.055}$$

$$M_2 = 87.88$$