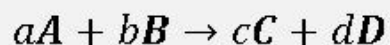


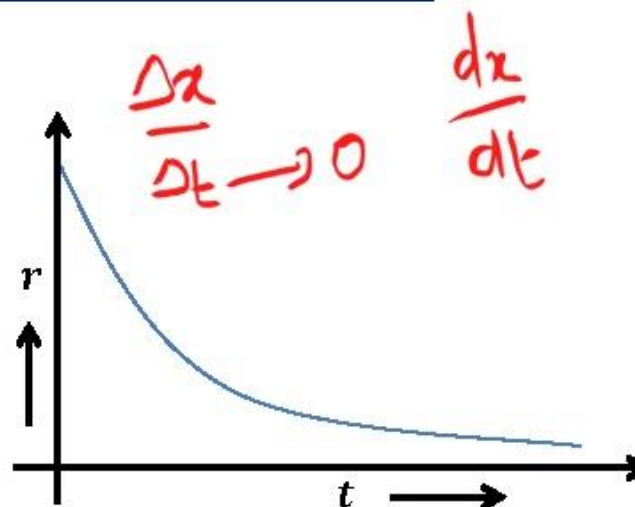
## Instantaneous Rate And Average Rate Of A Reaction

For a general reaction



Note that rate of reaction decreases gradually with the progress of reaction

Average  $\rightarrow$  Instantaneous rate



$$\therefore \text{instantaneous reaction rate} = \frac{-1}{a} \frac{d[A]}{dt}, \text{ at any time } t$$

Over a finite time interval  $\Delta t$  concentration change is given by average reaction rate

$$\frac{-1}{a} \frac{\Delta[A]}{\Delta t}$$

## Simple And Complex Reaction

Simple reactions:

Reaction which occur in a single step

elementary  
↓  
mechanism ✗

Example :  $H_2 + I_2 \rightarrow 2HI$

$$r = k_1[H_2][I_2]$$

Order → Experimental  
(  
0, +ve, -ve, fractional

Complex reactions:

Reaction which take place in two or more steps

↓  
mechanism ✓

Example :  $H_2 + Br_2 \rightarrow 2HBr$

$$r = k_2[H_2][Br_2]^{\frac{1}{2}}$$

Note that for determination of rate of complex reactions mechanism should be known and then the rate of slowest step is the rate of overall reaction

## Rate Constant (k) Of A Reaction

For a general reaction  $aA + bB \rightarrow cC + dD$

$$r = k[A]^m[B]^n$$

$k$  is defined as rate of reaction when concentration of each reactant is unity

Note that value of  $k$  is for a specific reaction represented by a balanced equation

Value of  $k$

✓ Does not depend on [reactants] or [products]

✓ Does not depend on time

✓ Depend on temperature of reaction

✓ Depends on catalyst used

## Differential Rate Law

For a general reaction  $aA + bB \rightarrow cC + dD$

$$r \propto [A]^a [B]^b \quad \text{ToR} = a+b$$

$$r \propto [A]^m [B]^n$$

Since reaction rate is proportional to concentration of reactant

OR  $\text{ToR} = m+n$

Complex reaction  $\rightarrow$  Series of elementary reaction

Elementary reaction

$k$  is known as rate constant

$$r = k[A]^m [B]^n$$

The exponents  $m$  and  $n$  are known as order of reaction with respect to  $A$  and  $B$  respectively

AND

$(m + n)$  gives overall order of reaction

Note that  $m$  or  $n$  may and may not be equal to stoichiometric coefficients

$a$  and  $b$

## Concept Of Molecularity

✓ It has the minimum number of reacting particles that come together or collide in a rate determining step to form products

Unimolecular ✓

Bimolecular ✓

Termolecular ✓

It has meaning only for simple reactions



### Note that

- it is a theoretical concept ✓
- it can not be zero , negative , fractional , infinite or imaginary ✓
- it can not be greater than 3 since it is difficult for more than 3 molecules to collide ✓
- it is invariant (i.e. independent of pressure , temperature etc.) for a chemical equation ✓

## Concept Of Order Of A Reaction

Mathematically : order = sum of powers to which concentration terms are raised to determine rate of a reaction

$$k = \text{lit mol}^{-1} \text{sec}^{-1}$$



Example for reaction  $aA + bB \rightarrow cC + dD$

$$r = k[A]^m[B]^n$$

$$\text{Order} = m + n$$



Note that order is an experimentally determined quantity . ✓

It can be zero , negative , fractional or greater than 3 (but not infinite)

Note that for simple reaction, order = molecularity ✓

$$r = k[\text{HBr}]^1(\text{HOB})^1$$

## Concept Of Order Of A Reaction

Mathematically : order = sum of powers to which concentration terms are raised to determine rate of a reaction

$$\text{Units of } k = \frac{(\text{moles})^{1-n} (\text{Lit}^n)^{n-1} \text{ time}^{-1}}{}$$

Example for reaction  $aA + bB \rightarrow cC + dD$

$$r = k[A]^m[B]^n \longrightarrow \text{Order} = m + n$$

Zero { mole Lit<sup>n</sup> sec<sup>-1</sup>  
 1st { sec<sup>-1</sup> ✓  
 2nd { Lit mol<sup>-1</sup> sec<sup>-1</sup>  
 3rd { Lit<sup>2</sup> mol<sup>-2</sup> sec<sup>-1</sup>

Note that order is an experimentally determined quantity .

It can be zero , negative , fractional or greater than 3 (but not infinite)

Note that for simple reaction, order = molecularity

## Law Of Mass Action

This law relates rate of reaction with active mass

$$pH = -\log H^+$$

$$\text{active mass} = \frac{\text{number of moles of the substance}}{\text{volume in litres}}$$

dilute solution = 1 (active mass = Molarity)

At a given temperature:

rate of reaction ( $r$ ) is proportional to the product of active masses of the reactant at that instant and raised to their stoichiometric equation

[activity = molarity  $\times$  activity coefficient] for concentrated solution  $< 1$

pH of  $10^{-13} M H^+$   
 $pH = -\log(H^+)$   
 13✓

$10^2 M HCl$  pH?  $pH = -2 \times$

$$pH = -\log a_{H^+}$$

## Law Of Mass Action

This law relates rate of reaction with active mass

$$\text{active mass} = \frac{\text{number of moles of the substance}}{\text{volume in litres}}$$

Units of  $k = \frac{(\text{moles})^{1-n} (\text{Litre})^{n-1}}{\text{time}}$

At a given temperature:

rate of reaction ( $r$ ) is proportional to the product of active masses of the reactant at that instant and raised to their stoichiometric equation

Zero / mole Litre<sup>-1</sup> sec<sup>-1</sup>  
 1st / sec<sup>-1</sup> ✓  
 2nd / Lit<sup>2</sup> mol<sup>-2</sup> sec<sup>-1</sup>  
 3rd / Lit<sup>3</sup> mol<sup>-3</sup> sec<sup>-1</sup>

## Law Of Mass Action

This law relates rate of reaction with active mass

*Molarity (moles Litre<sup>-1</sup>)*

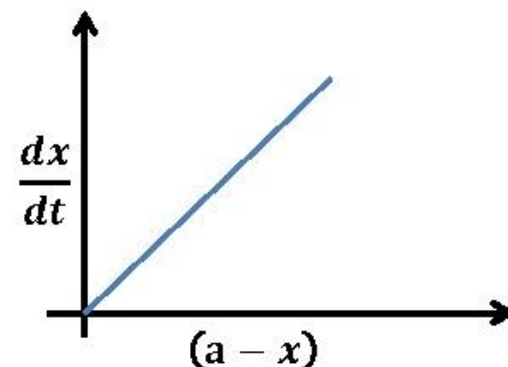
$$\text{active mass} = \frac{\text{number of moles of the substance}}{\text{volume in litres}}$$

At a given temperature:

rate of reaction ( $r$ ) is proportional to the product of active masses of the reactant at that instant and raised to their stoichiometric equation

## First Order Reaction

	$A \longrightarrow$	Product
Initial concentration	$a$	$0$
Concentration at time $t$	$(a - x)$	$x$



$$k = \frac{1}{t} \ln \frac{C_0}{C_t}$$

$$\ln \frac{C_0}{C_t} = kt$$

$$\frac{C_0}{C_t} = e^{kt}$$

OR

$$\frac{-d[a-x]}{dt} = k_1[a-x]$$

$$k_1 = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right)$$

$$k_1 = \frac{2.303}{t} \log \left( \frac{[A]_0}{[A]_t} \right)$$

$$\frac{C_0}{C_t}$$

Note that unit of  $k_1$  is per time

Note that for 1<sup>st</sup> order reaction time required to complete any definite fraction (say  $\frac{1}{n}$ ) of the reaction is independent of a initial concentration

$$\frac{C_t}{C_0} = e^{-kt}$$

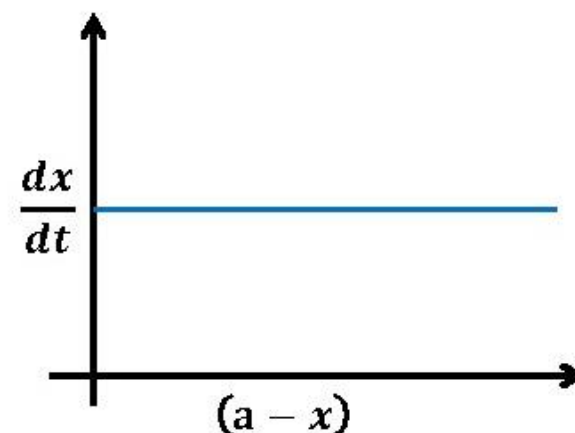
$$t_{\frac{1}{n}} = \frac{2.303}{k_1} \log \left( \frac{1}{1 - \frac{1}{n}} \right)$$

$$1 - \frac{C_t}{C_0} = 1 - e^{-kt}$$

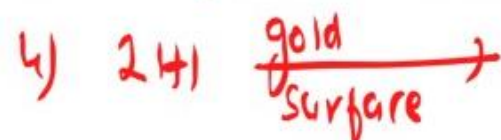
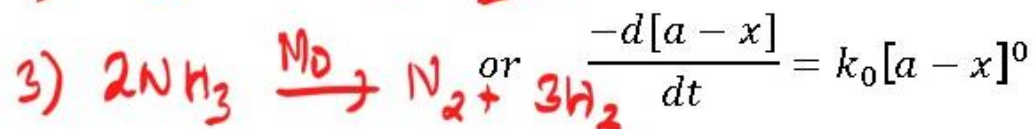
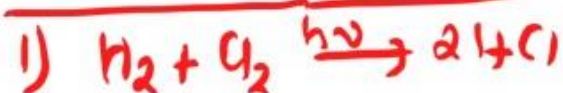
$$\alpha = 1 - e^{-kt}$$

## Zero Order Reaction

	$A$	$\longrightarrow$	Product
Initial concentration	$a$		$0$
Concentration at time $t$	$(a - x)$		$x$



Photochemical reactions



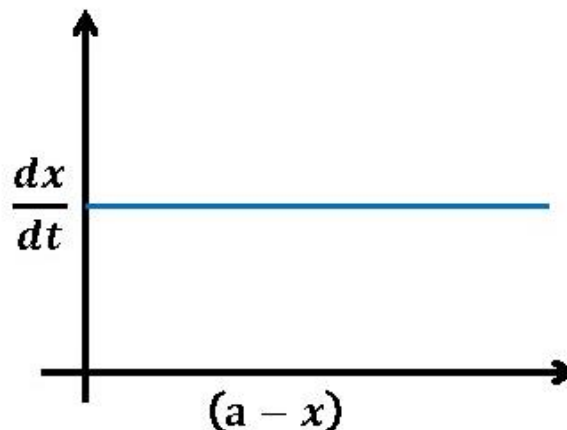
$$\Rightarrow \frac{dx}{dt} = k_0 \Rightarrow x = k_0 t$$

i.e.  $k_0 t = a - (a - x) = [A]_0 - [A]_t$

Note that rate constant is equal to the rate of reaction at all concentration

## Zero Order Reaction

	$A$	$\longrightarrow$	Product
Initial concentration	$a$		$0$
Concentration at time $t$	$(a - x)$		$x$



$$k = \frac{x}{t} = \frac{a - (a-x)}{t}$$

$\downarrow$   $\downarrow$   
 $C_0$   $C_t$

$$K = \frac{C_0 - C_t}{t}$$

$$\frac{-d[A]}{dt} = k_0 [A]^0$$

or  $\frac{-d[a-x]}{dt} = k_0 [a-x]^0$

$$\Rightarrow \frac{dx}{dt} = k_0 \Rightarrow x = k_0 t$$

i.e.  $k_0 t = a - (a - x) = [A]_0 - [A]_t$

Note that rate constant is equal to the rate of reaction at all concentration

## Half Life Period: $t_{\frac{1}{2}}$

It is the time required for half the reaction to change

Order of reaction	Expression for rate constant	$t_{\frac{1}{2}}$
Zero	$k_0 = \frac{x}{t}$	$\frac{a}{2k_0}$
One	$k_1 = \frac{2.303}{t} \log \left( \frac{a}{a-x} \right)$	$\frac{0.693}{k_1}$
Two	$k_2 = \frac{1}{t} \frac{x}{a(a-x)}$	$\frac{1}{ak_2}$
$n$ (for $n \geq 2$ )	—	$\frac{2^{n-1} - 1}{k_2(n-1)a^{n-1}}$

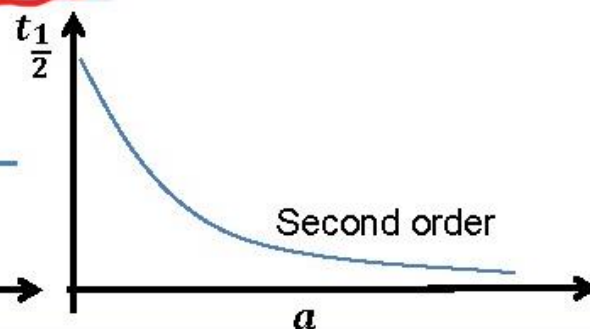
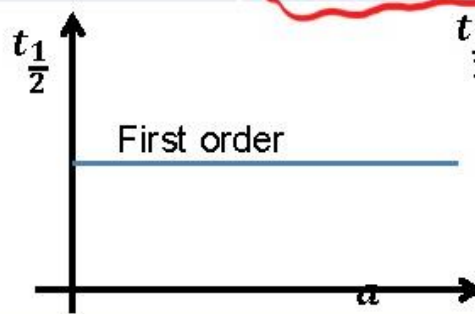
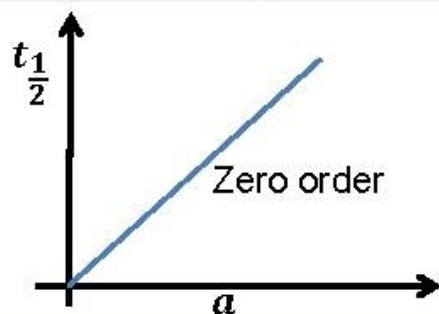
$$k = \frac{C_0 - C_t}{t - t_{\frac{1}{2}}} = \frac{C_0}{2t_{\frac{1}{2}}}$$

→ directly proportional to 'a'

→ independent of 'a'

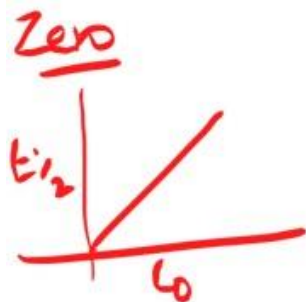
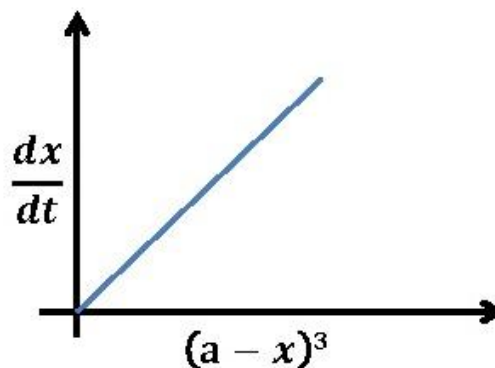
→ inversely related to 'a'

→ inversely related to 'a<sup>n-1</sup>'



## Third Order Reaction Of Simplest Type

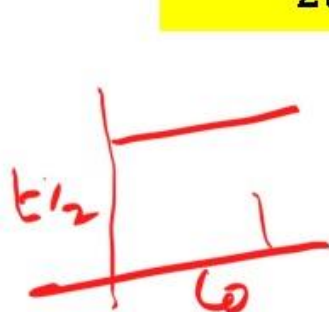
	$A \longrightarrow$	Product
Initial concentration	$a$	$0$
Concentration at time $t$	$(a - x)$	$x$



$$\frac{-d[a-x]}{dt} = k_3[a-x]^3$$

$$k_3 = \frac{1}{2t} \left\{ \frac{x(2a-x)}{a^2(a-x)^2} \right\}$$

Unit of  $k_3$  is concentration<sup>-2</sup>time<sup>-1</sup>



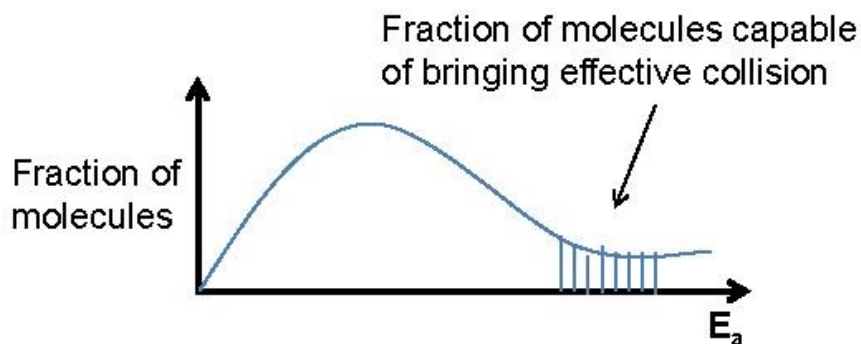
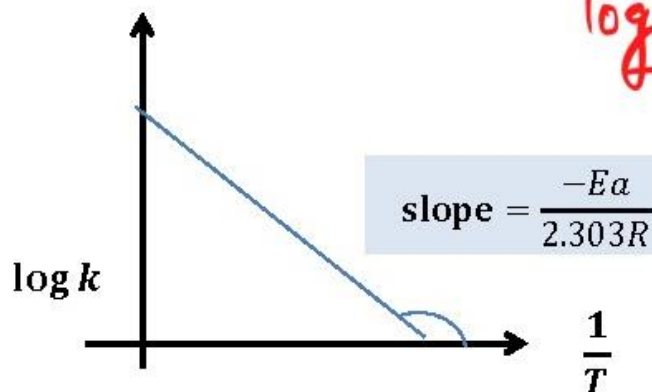
$$t_{1/2} \propto \left( \frac{1}{C_0} \right)^{n-1}$$

$$\frac{(t_{1/2})_I}{(t_{1/2})_{II}} = \left( \frac{C_{0II}}{C_{0I}} \right)^{n-1}$$

## Arrhenius Equation

$$k = Ae^{\frac{-E_a}{RT}}$$

Where  $A$  = Frequency factor  
 $E_a$  = activation energy



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

$E_a \downarrow \quad \frac{E_a}{RT} \downarrow \quad -\frac{E_a}{RT} \uparrow$   
 $e^{-E_a/RT} \uparrow \quad k \uparrow$   
Reaction speed up