

Chemical kinetics involves in the study of ^{the} rate of chemical reaction.

→ Rate = velocity or speed of the reaction which can be denoted by $\pm \frac{dc}{dt}$.

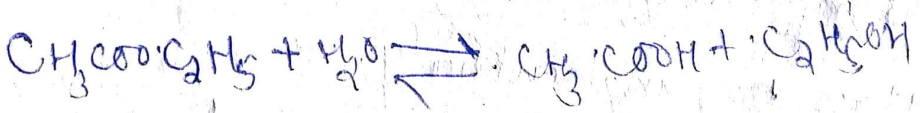
Application of chemical kinetics in pharmacy

- The stability of the drug can be ~~assess~~ ^{assess} by chemical kinetics.
- The dissolved & drug release can be calculated by chemical kinetics.
- The pharmacokinetic like AOMF follows the chemical kinetic process.
- By interaction of membrane or any receptors can be interpreted by chemical kinetics.

~~also~~

Rate process / law of mass action

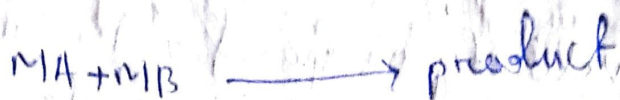
The hydrolysis of ethyl acetate can be considered for this process



$$\begin{aligned} \text{Rate} &= -\frac{dc}{dt} = \frac{-d[CH_3COOC_2H_5]}{dt} \\ &= \frac{-d[H_2O]}{dt} \end{aligned}$$

According to law of mass action, the rate of chemical reaction is proportional to the

product of molar concentration of the reactants ^{each} raised to the power equal to the no. of molecules ^{undergo} undergoing reaction



$$\text{Rate} = -\frac{1}{m} \frac{d[A]}{dt} = -\frac{1}{n} \frac{d[B]}{dt}$$

$$= k_{m+n} [A]^m [B]^n$$

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

$$r = k_{m+n} [A]^m [B]^n$$

k_{m+n} = specific rate constant

or
equilibrium rate constant

$[A]^m [B]^n$ = molar concentration of reactant

A B B

Df = 26/02/20

Molecularity of the reaction :-

molecularity is defined as the no. of molecules or atoms that react to form a product.

unimolecular reaction :-

Here the molecularity is one.

ex - isomerization trans-stilbene to cis-stilbene



Here the molar ratio is 2:2

ex - oxidation of hydrogen peroxide



Termolecular reaction:

The reaction ~~is~~ terminated by ~~the~~ ~~and~~ ~~of~~ molecularities are seldom observed.

Order of the reaction:

The order of the reaction is defined as the concentration term on which the rate of reaction depends when determined experimentally.

Zero order reaction

Zero order reaction is defined as the reaction in which the rate does not depend upon the concentration term of the reactant. This is mathematically expressed as

$$- \frac{dc}{dt} = k_0$$

$k_0 =$ zero order rate constant

$$\frac{dc}{dt} = R \cdot t \cdot c$$

ex - oxidation of B. Vitamine + A. in oily solution.

→ Photochemical degradation of chloroform in aqueous solution.

Derivation:

$$- \frac{dc}{dt} = k_0 \quad (1)$$

then by cross multiplication $\int dC = -k_0 \int dt$
 \rightarrow integrating the equation number (2) we

get

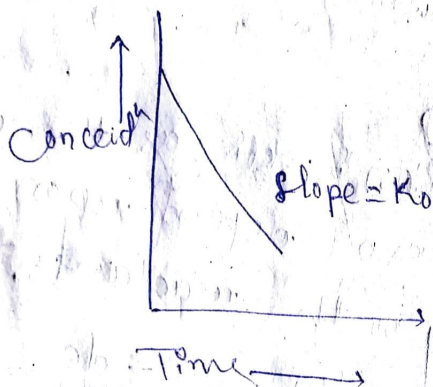
$$\int_{C_0}^C dC = -k_0 \int_0^t dt$$

$$\Rightarrow C - C_0 = -k_0 t$$

$$\Rightarrow k_0 = -\left(\frac{C - C_0}{t}\right)$$

$$= \frac{C_0 - C}{t} \quad \text{--- (3)}$$

\Rightarrow if we plot a graph concentration ^C in y-axis and time t in x-axis it will give a straight line graph where the slope is equal to k_0 .



\rightarrow $\frac{1}{2}$ life

It is the time required for the concentration of the reactant to become half of its initial concentration.

\rightarrow As per the definition $C = \frac{C_0}{2}$ when $t = t_{1/2}$

so from the eqn (3) we get

$$t_{1/2} = \frac{C_0 - \frac{C_0}{2}}{k_0}$$

Then by cross multiplication

Half life:-

It is defined as the time required for the concentration of the reactant to become 90% of its initial concentration.

As per the definition $C = 0.9C_0$ when $t = t_{90}$ it can be calculated by eq-(3)

$$t_{90} = \frac{C_0 - 0.9C_0}{k_0}$$

$$= \frac{0.1C_0}{k_0}$$

$$t_{90} = \frac{C_0}{10k_0}$$

1st order reaction:-

→ 1st order reaction is defined as the reaction in which the rate of reaction depends on concentration of one reactant.

ex- Acid hydrolysis of ethyl acetate & methyl acetate ~~esters~~

- Inversion of sugar i.e sucrose.
- Disintegration of radioactive element.
- The rate expression for 1st order reaction

$$-\frac{dC}{dt} = k_1 C \quad \text{--- (1)}$$

→ By cross multiplication or rearrangement the equation

$$-\frac{dc}{c} = k_1 dt$$

$$\text{or } \frac{dc}{c} = -k_1 dt$$

By integrating the above equation

$$\int_{c_0}^{c_t} \frac{d.c}{c} = -k_1 \int_0^t dt$$

$$\left[\ln c \right]_{c_0}^{c_t} = -k_1 [t]_0^t$$

$$\ln c_t - \ln c_0 = -k_1 t$$

$$\boxed{\ln c_t = \ln c_0 - k_1 t} \quad \text{--- (3)}$$

Converting equation (3) into logarithm base 10

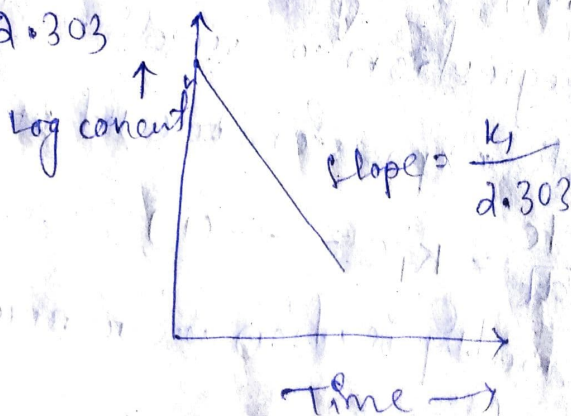
$$\boxed{\log c_t = \log c_0 - \frac{k_1 t}{2.303}} \quad \text{--- (4)}$$

By rearrangement, we'll get

$$\boxed{k_1 = \frac{2.303}{t} \cdot \log \frac{c_0}{c_t}} \quad \text{--- (5)}$$

if we plot a graph by taking logarithm in y-axis and time = t in x-axis then we will get a straight line graph having

$$\text{slope} = \frac{k_1}{2.303}$$



$$k_1 = \frac{2.303}{t_{1/2}} \log \frac{C_0}{C_{0/2}}$$

$$t_{1/2} = \frac{2.303}{k_1} \log \frac{C_0}{C_{0/2}}$$

$$\boxed{t_{1/2} = \frac{0.693}{k_1}}$$

Shelf Life: -

→ As per the definition $C_t = 0.9C_0$ where $t = t_{90}$

→ Substituting this equation we will get

$$t_{90} = \frac{2.303}{k} \log \frac{C_0}{0.9C_0}$$

$$t_{90} = \frac{2.303}{k} \log \frac{10}{9}$$

$$\boxed{t_{90} = \frac{0.105}{k_1}}$$

Dt: 27/02/20

Pseudo 1st order reaction: -

A pseudo 1st order reaction is defined as the reaction which is originally 2nd order but make to behave like a 1st order reaction.

→ Pure 2nd order reaction the rate expression will be $-\frac{dc}{dt} = k_2 [A][B]$

where, A & B = reactant

k_2 = 2nd order rate constant

\Rightarrow If the concentrⁿ of one reactant is very large
~~excess~~ ^{excess} then compare to the other concentrⁿ
 other, here the concentrⁿ of one reactant
 doesn't change in compare to other
 so this expression can be changed into

$$-\frac{dc}{dt} = k_2 [A] [B]$$

$$-\frac{dc}{dt} = k_2 [A] [\text{Excess}]$$

[B] concentrⁿ is very large in compare
 to A

$$\text{So } \frac{dc}{dt} = k_1 [A]$$

example

Hydrolysis of ester in presence of H^+ ion
 \rightarrow Base catalysed oxidation, degradation
 or prednisolone, in aqueous solution etc.

2nd order reaction:

\Rightarrow Second order reaction is defined as the
 reaction in which the rate depends on
 concentrⁿ terms of 2 reactants each raise
 to ^{the} power one.

consider the following equation



Rate equation can be written as,

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2 [A]^1 [B]^1 \quad \text{--- (1)}$$

or rate = $k_2 [A]^1 [B]^1$

- Alkaline hydrolysis of ester.
- Hydrolysis of chlorobutanol in presence of sodium hydroxide.

Derivation:

Let a & b be the initial concentration of A & B respectively, and x be the concentration of each species and reacting in time t .

Then eqn (1) can be written as

$$\frac{dx}{dt} = k_2 (a-x)(b-x) \quad \text{--- (2)}$$

If $a = b$ then the eqn (2) can be written as

$$\frac{dx}{dt} = k_2 (a-x)^2 \quad \text{or } k_2 (b-x)^2 \quad \text{--- (3)}$$

Integrating the eqn (3) we'll get

$$\int_0^x \frac{dx}{(a-x)^2} = k_2 \int_0^t dt$$

$$\left[\frac{1}{-1(a-x)} \right]_0^x = k_2 [t]_0^t$$

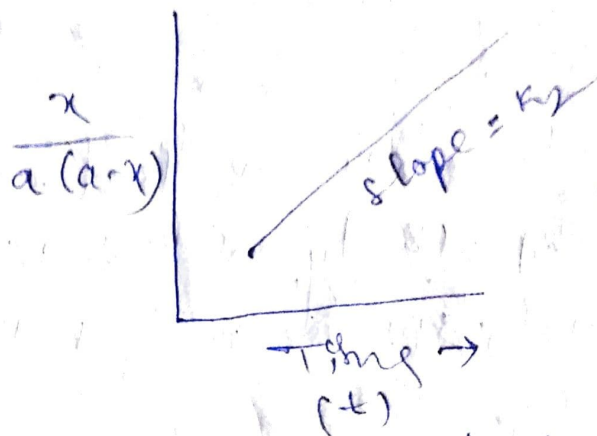
$$\frac{1}{a-x} - \frac{1}{a-0} = k_2 (t-0)$$

$$\frac{a-a+x}{a(a-x)} = k_2 t$$

$$\text{or } \frac{x}{a(a-x)} = k_2 t \quad \text{--- (4)}$$

$$\text{or } k_2 = \frac{1}{at} \cdot \frac{x}{(a-x)} \quad \text{--- (5)}$$

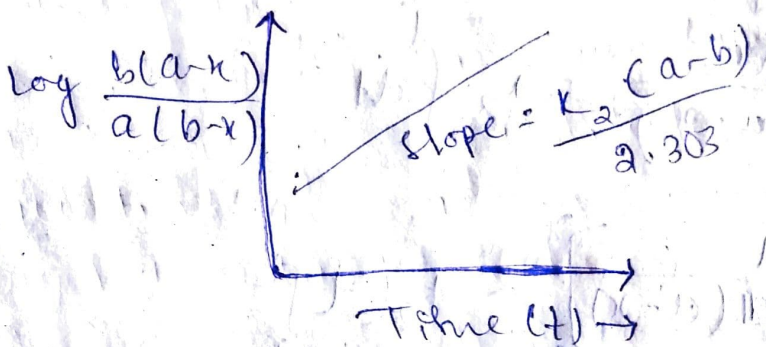
If we plot a graph of $\frac{x}{a-x}$ vs time on y-axis we will get a straight line graph of slope $= k_2$



If $0 \neq b$ then k_2 will be

$$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

If we draw a graph by taking $\log \frac{b(a-x)}{a(b-x)}$ vs time, then a straight line will be obtained having slope $= \frac{k_2(a-b)}{2.303}$



$t_{1/2}$ life:

As per the definition $a-x$ will be $\frac{a}{2}$ when $t = t_{1/2}$ putting this value in equation we get

$$k_2 = \frac{1}{t} \cdot \frac{x}{a-x}$$

$$= \frac{1}{at_{1/2}} \cdot \frac{a/2}{a/2}$$

$$k_2 = \frac{1}{at_2}$$

$$\boxed{t_{1/2} = \frac{1}{at_2}} \quad \text{--- (6)}$$

shelf life: ---

when $a-x = 0.9a$ when $t =$

putting the value in eq (5)

$$k_2 = \frac{1}{at} \cdot \frac{x}{a-x}$$

$$= \frac{1}{at_{90}} \cdot \frac{0.1a}{0.9a}$$

$$\boxed{t_{90} = \frac{0.11}{at_2}} \quad \text{---}$$

shelf life ---