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Class  $\Rightarrow$  B.Sc.(Hons.) Part-I

Subject  $\Rightarrow$  Chemistry

Chapter  $\Rightarrow$  Chemical Kinetics

Topic  $\Rightarrow$  Examples of Second order reaction, Half-life period, unit of rate constants

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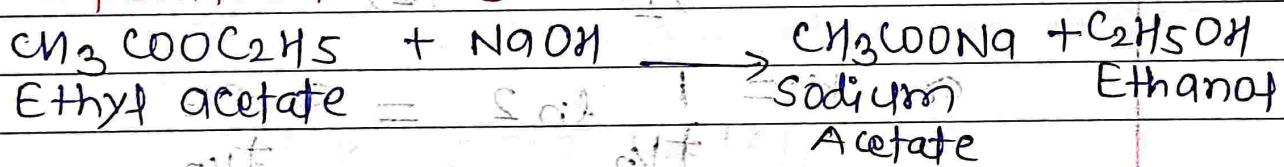
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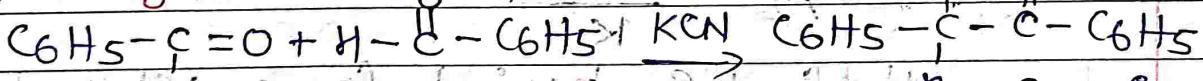
### Examples of Second order Reaction

(1) Hydrolysis of an Ester by NaOH

Saponification of esters  $\Rightarrow$



(2) Benzoin Condensation  $\Rightarrow$

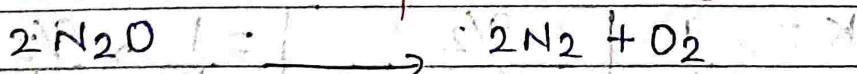


(3) Conversion of ammonium cyanate to form urea  $\Rightarrow$

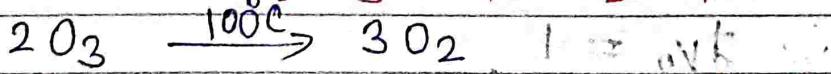


Ammonium cyanate  $\xrightarrow{\text{heat}}$  Urea

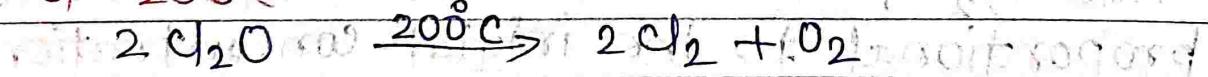
(4) Thermal decomposition of  $\text{N}_2\text{O}$



(5) Conversion of  $\text{O}_3$  into  $\text{O}_2$  at  $100^\circ\text{C}$



(6) Thermal decomposition of  $\text{Cl}_2\text{O}$  to  $\text{Cl}_2$  and  $\text{O}_2$  at  $200^\circ\text{C}$



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## Half-life period

The time required for the reaction to be half completed is called Half-life period.

OR

The time required for the concentration of a reactant to decrease to half its initial value is called Half-life period of a reaction.

Half life period is denoted by  $t_{1/2}$ .

$t_{1/2}$  for a first order Reaction.

$$\alpha = \frac{1}{2} \quad \text{and} \quad t = t_{1/2}$$

from first order rate equation

$$K = \frac{1}{t_{1/2}} \ln \frac{9}{9 - (9/2)}$$

$$\therefore K = \frac{1}{t_{1/2}} \ln 2 = \frac{0.693}{t_{1/2}}$$

$$\therefore t_{1/2} = 0.693$$

i.e. Half-life period for a 1st order reaction is independent of the initial concentration.

$t_{1/2}$  for a Second order Reaction

for 2nd order reaction  $\alpha = \frac{1}{2}$ ,  $t = t_{1/2}$

Putting this value in 2nd order Reckn.

$$K = \frac{1}{t_{1/2}} \left[ \frac{\frac{1}{2}}{9(9 - \frac{1}{2})} \right] = \frac{1}{t_{1/2}} \times \frac{\frac{1}{2}}{9(\frac{17}{2})} = \frac{1}{9t_{1/2}}$$

$$\therefore t_{1/2} = \frac{1}{K_9}$$

Thus  $t_{1/2}$  of a second order reaction is inversely proportional to the initial concentration of

(1)

the reactant and thus, it does not remain constant as the reaction proceeds.

### Units of Rate Constant

The units of rate constant for different orders are different.

#### Unit of zero order Rate Constant

for zero order reaction, the rate constant

$$k = \frac{d[A]}{dt} = \frac{\text{mol}}{\text{litre time}}$$

$$\therefore \text{unit of } k = \text{mol l}^{-1} \text{time}^{-1}$$

$\Rightarrow$  Time may be given in seconds, minutes, days or years

#### Unit of first order Rate Constant

The rate constant of a first order reaction is given by

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

thus the rate constant for the 1st order reac. is independent of the concentration. It has the unit

time<sup>-1</sup>

#### Unit of 2nd order Rate Constant

The rate constant for a second order reaction is expressed as

$$k = \frac{1}{t} \times \frac{x}{[A]_0([A]_0 - x)}$$

$$\text{or } k = \frac{\text{Concentration}}{\text{Concentration} \times \text{Concentration} \times \text{time}} \times 1$$

$$\text{or } k = \frac{1}{\text{Concentration} \times \text{time}} \times 1$$

$$\text{or } k = \frac{1}{\text{mol/litre} \times \text{time}} \times 1$$

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$k = \text{mold time}$  (in paper cut)

Thus, the unit of  $k$  for a second order reaction,  
 $\text{mold time}$