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Deg-I (H) - Chemical-Kinetics

Topics — Kinetics of decomposition of H_2O_2 & inversion of Cane-Sugar.

Decomposion of H_2O_2:-

Decomposition of H_2O_2 in aquous solution takes place as

$$H_2O_2 \xrightarrow{Pt} H_2O + \frac{1}{2}O_2$$

The Kinetics of above reaction is studied by titrating against $KMnO_4$ solution. Equal amounts of H_2O_2 solution are titrated against the same $KMnO_4$ solution at regular interval of time

Experimental Observation

Volume of $KMnO_4$ solution used before the start of reaction (at zero time) is V_0. $V_0 \propto$ Initial concentration of H_2O_2 (a)

$$V_0 \propto a \quad \text{——— (1)}$$

again Volume of $KMnO_4$ solution used at any instant of time (t), $V_t \propto$ Amount of H_2O_2 present at that time is $(a-x)$

$$V_t \propto (a-x) \quad \text{——— (2)}$$

Putting the above value in first-order rate-Constant expression

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

$$\text{or} \quad K = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

By applying the above expression the value of K (rate-Constant) remain Constant which shows that it follows first order Kinetics.

Inversion of Cane-Sugar:-

The hydrolysis of Cane-Sugar (Sucrose) in presence of mineral acid take place is expressed by following reaction

$$\underset{\substack{\text{Sucrose} \\ \text{(dextro-Rotatory)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose} \\ \text{dextro-} \\ \text{Rotatory}}}{C_6H_{12}O_6} + \underset{\substack{\text{fructose} \\ \text{leavo} \\ \text{Rotatory}}}{C_6H_{12}O_6}$$

as a whole
leavo-Rotatory

laevo-Rotation of fructose (-92°) is more negative than the dextro-rotation of glucose ($+52.5^\circ$) thus the mixture as a whole is laevo-rotatory.
Thus upon hydrolysis the dextro-rotatory sucrose gradually changes into the laevo-rotatory mixture called Inversion of Sucrose.

Experimental - Observation

Kinetics measurement can be studied on the basis of observing the angle of rotation at different intervals of time with the help of Polarimeter.

Reading of Polarimeter

(I) At zero-time $= r_0$

(II) At any instant of time 't' $= r_t$

(III) At infinite time $= r_\infty$

It was observed that the reading at zero-time will be Positive & it regularly decreases with passage of time & finally it becomes negative.

Calculation

Angle of rotation at any instant of time $(r_0 - r_t)$ $\propto$ the amount of sucrose hydrolysed amount (x).

or, $(r_0 - r_t) \propto x$ — (I)

Angle of Rotation at infinite time $(r_0 - r_\alpha)$ $\propto$ the initial concentration of sucrose (a)

$(r_0 - r_\alpha) \propto a$ — (II)

From (I) & (II), we get

$$(a-x) \propto (r_0 - r_\alpha) - (r_0 - r_t)$$

$$\propto (r_t - r_\alpha)$$

Putting the value of a & $(a-x)$ in first order rate expression we get

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

$$= \frac{2.303}{t} \log \frac{(r_0 - r_\alpha)}{(r_t - r_\alpha)}$$

$$K = \frac{2.303}{t} \log \frac{r_0 - r_\alpha}{r_t - r_\alpha}$$