

D. B. College (Jaynagar)

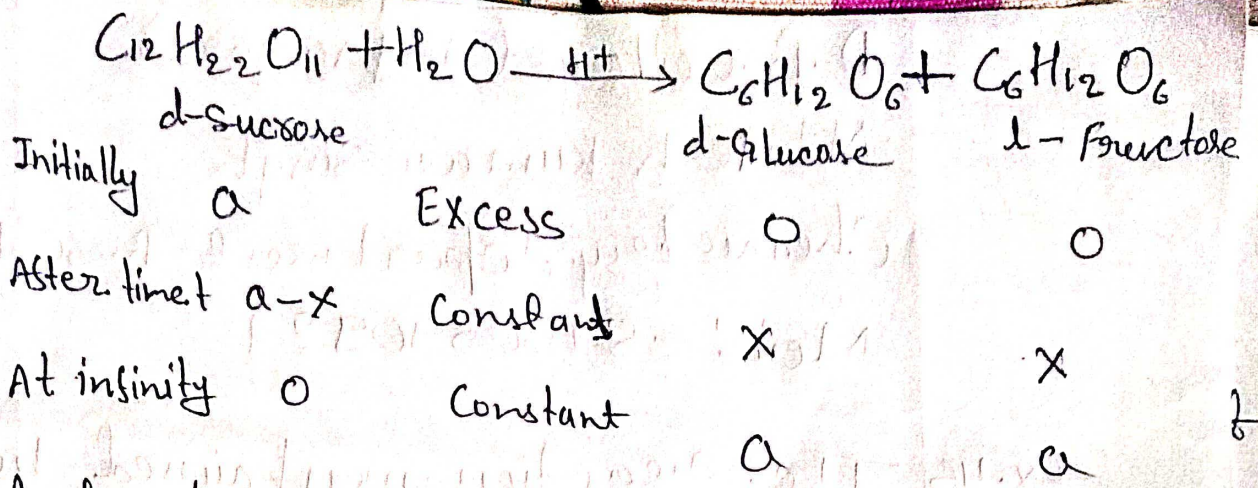
Lect:- 1

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Ex. 45 The reaction mentioned below is first order w.r.t sucrose and zero order w.r.t water, since water is in large excess as compared to sucrose. That is, it is an example of pseudo unimolecular reaction. Sucrose glucose and fructose all are optically active substances. Therefore, the progress of the reaction can be followed by measuring angle of rotations of the reaction mixture at various time intervals. During the reaction, angle of rotation goes on decreasing and after sometime there is reversal of the direction of rotation, i.e. from dextro to laevo and hence, the reaction is called "inversion of Cane Sugar" or inversion of sucrose.



Angle of optical rotation is measured by means of an instrument called polarimeter. Optical rotation is mathematically expressed as,

$$R_{obs} = l \cdot C \cdot [\alpha]_D^t$$

l = length of the polarimeter tube

C = concentration of test solution

$[\alpha]_D^t$ = Specific rotation

For a given sample and polarimeter, l and $[\alpha]_D^t$ are constant.

$$R_{obs} \propto l, \text{ or } R_{obs} = Kc,$$

If α_0 , α_t and α_∞ be the observed angle of rotations of the sample at zero time, time t and infinity respectively, and k_1 , k_2 and k_3 be proportionate in terms of ~~source~~ sucrose, glucose and fructose, respectively.

Then,

$$r_0 = k_1 a$$

$$r_1 = k_1(a-x) - k_2 x + k_3 x$$

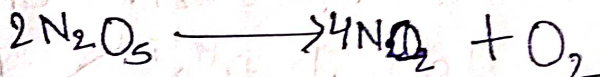
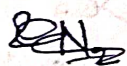
$$r_{\infty} = k_2 a + k_3 a$$

From these equations it can be shown that

$$\frac{a}{a-x} = \frac{r_0 - r_{\infty}}{r_1 - r_{\infty}}$$

So, the expression for the rate constant of this reaction in terms of the optical rotational data may be put as $k = \frac{2.303}{t} \log \frac{r_0 - r_{\infty}}{r_1 - r_{\infty}}$

Ex 46



At $t=0$

P_0

0

0

At $t=t$

$P_0 - 2x$

$4x$

x

At $t=\infty$

0

$2P_0$

$\frac{1}{2}P_0$

The progress of the reaction can be followed by measuring the pressure of the gaseous mixture in a closed vessel, i.e. at constant volume. The expression for the rate constant in terms of pressure data will be as given below.

$$k = \frac{2.303}{t} \log \frac{P_0}{P_t}, \text{ where } P = P_0 - 2x$$

If total pressure after any time t and at ∞ is given, then it is possible to find P_0 and x and hence k may be calculated.