B.Sc. III, Paper - V, Sub- chemistry
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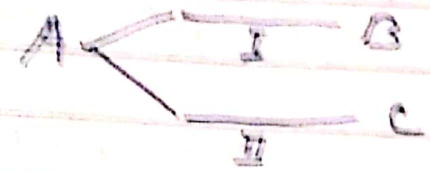
Kinetics of side reaction or parallel reaction

Let us consider a side reaction



Here A decomposes to form B and C simultaneously. If a is the initial concentration of A. After time t x mole of A decomposes to form B and C simultaneously.

therefore

Rate of disappearance of A $= -\frac{dx}{dt}$

Rate of formation of B and C $= \frac{dx}{dt}$ — (I)

Rate of formation of B $= \frac{dy}{dt}$ (II)

Rate of formation of C $= \frac{dz}{dt}$ (III)

As B and C is formed from A

$$\frac{dx}{dt} = \frac{dy}{dt} + \frac{dz}{dt} \quad \text{—— (IV)}$$

Now $\frac{dy}{dt} \propto a-x$ or, $\frac{dy}{dt} = k_1(a-x)$ — (V)

and similarly $\frac{dz}{dt} = k_2(a-x)$. — (VI)

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from equation (IV), (V) and (VI)

$$\frac{dx}{dt} = K_1(a-x) + K_2(a-x)$$

or $$\frac{dx}{dt} = (K_1+K_2)(a-x)$$

or $$\frac{dx}{a-x} = (K_1+K_2)\,dt = K\,dt \quad \text{— (VII)}$$

or Integrating we get

$$\int \frac{dx}{a-x} = \int K\,dt$$

or $$-\ln(a-x) = Kt + \text{Integration const} \quad \text{— (VIII)}$$

at $t=0$ $x=0$

$$-\ln a = 0 + \text{Integration Constant}$$

Hence eq (VIII) will be

$$-\ln(a-x) = Kt - \ln a$$

$$\therefore K = \frac{\ln a - \ln(a-x)}{t}$$

or $$\boxed{K = \frac{1}{t}\ln\frac{a}{a-x}}$$

From Wegscheider's test for side reaction amount of B and C formed depend upon rate of formation of B and C when order of both are same.

$$\frac{\text{amount of B formed}}{\text{amount of C formed}} = \frac{\text{Rate of formation of B}}{\text{Rate of formation}}$$

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or $\frac{\text{amount of B formed}}{\text{amount of C formed}} = \frac{K_1(a-x)}{K_2(a-x)} = \frac{K_1}{K_2} = K'$

or $\boxed{K' = \frac{K_1}{K_2}}$ ⟵ (IX)

from eqn (VII) and (IX)

$K = K_1 + K_2$ ⟵ (X)

and $K' = \frac{K_1}{K_2}$, $K_1 = K'K_2$

putting value of K_1 in eqn (X)

$K = K'K_2 + K_2$

or $K = K_2(K'+1)$.

or $\boxed{K_2 = \frac{K}{K'+1}}$ ⟶ (XI)

putting this value of K_2 in eqn (X)

$\boxed{K_1 = \frac{KK'}{1+K'}}$