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Study material - IA

Chemical Kinetics -, B.Sc - III, Paper - V.
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Kinetics of opposing reaction

When products formed in a chemical reaction reacts to form reactant or convert in reactant, the reaction is called reversible reaction or opposing reaction. In this type of reaction an equilibrium state comes after some time at which forward reaction rate and backward reaction rates become equal.

Let us consider a simple opposing reaction of type

$$A \rightleftharpoons B \quad \text{--- (1)}$$

Practical example is inversion or mutarotion of α-D-glucose to β-D-glucose or conversion of ammonium cyanate into urea.

$$\alpha\text{-glucose} \underset{K_2}{\overset{K_1}{\rightleftharpoons}} \beta\text{-glucose}$$

and $NH_4CNO \rightleftharpoons NH_2CONH_2$

P.T.O.

Let us consider the above equation (i)

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

Here K_1 and represent the rate constant for forward and backward reaction. Let a is the initial concentration of A and after time t concentration of A is $a-x$ and concentration of B will be x.

From Rate law of chemical reaction,
rate of forward reaction $= K_1(a-x)$
and rate of backward reaction $= K_2 x$.

Net rate of production of B

$$\frac{dx}{dt} = K_1(a-x) - K_2 x \quad \text{(ii)}$$

At equilibrium $\frac{dx}{dt} = 0$

$$\Rightarrow \frac{dx}{dt} = K_1(a-x_e) - K_2 x_e = 0$$

$$\Rightarrow K_1(a-x_e) = K_2 x_e$$

where x_e = concentration of B at equilibrium.

$\Rightarrow$ $k_2 = k_1 \dfrac{(a - x_e)}{x_e}$ —— (iii)

put value of k_2 in equation (ii)

~~[illegible]~~

~~[illegible]~~

$$\frac{dx}{dt} = k_1(a-x) - \frac{k_1}{x_e}(a-x_e)x$$

$$= k_1 a - k_1 x - \frac{k_1}{x_e} a x + \frac{k_1}{x_e} x_e x$$

$$= k_1 a - \frac{k_1}{x_e} a x$$

$$= k_1 a \left[1 - \frac{x}{x_e}\right]$$

or $\dfrac{dx}{dt} = \dfrac{k_1 a}{x_e}\left[x_e - x\right]$ —— (iii)

$\Rightarrow$ $\dfrac{dx}{x_e - x} = \dfrac{k_1 a}{x_e}\, dt$

Integrating both side

$$\int \frac{dx}{x_e - x} = \frac{k_1 a}{x_e}\int dt$$

$\Rightarrow$ $-\ln(x_e - x) = \dfrac{k_1 a}{x_e} t + I$ Integration constant —— (iv)

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When $t=0$, $x=0$ and eqn (iv) will be.

$$-\ln x_e = 0 + \text{Integration constant}$$

Putting value of integration constant in eq^n (iv)

$$-\ln(x_e - x) = \frac{k_1 a}{x_e} t - \ln x_e.$$

or, $$\ln x_e - \ln(x_e - x) = \frac{k_1 a}{x_e} \cdot t$$

or, $$\ln \frac{x_e}{(x_e - x)} = \frac{k_1 a}{x_e} \cdot t.$$

or, $$\boxed{k_1 = \frac{1}{t} \cdot \frac{x_e}{a} \cdot \ln \frac{x_e}{x - x_e}}$$

this is kinetics of oppossing reaction of type $A \rightleftharpoons B$.

Similarly kinetics of ~~of~~ oppossing reaction of type

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C$$

will be calculated and it will be

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$$K_1 = \frac{x_e}{t(2a - x_e)} \ln \frac{a x_e + x(a - x_e)}{a(x_e + x)}.$$

example of this type of reaction are
(i) Hydrolysis of Ester ethyl acetate.

Note – student are advice to write down the kinetics of opposing reaction of type $A \rightleftharpoons B$. It is not essential to write all opposing types of reaction kinetics as $A + B \rightleftharpoons C + D$ or $A \rightleftharpoons B + C$ etc.

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