

Study material - I/A

Chemical Kinetics-, B.Sc-III, Paper-V.
By Dr. A.K.S. Bhosla, H.O.D. Chemistry,
Shershak college Sasaram.

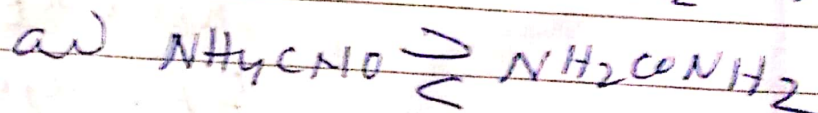
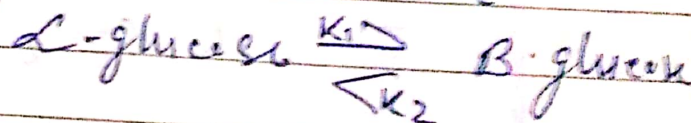
Kinetics of opposing reactions

When products formed in a chemical reaction reacts to form reactant or convert in reactant, the reaction is called reversible reaction or opposing reactions. 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



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



P.T.07

Let us consider the reversible reaction (i)



Here k_1 and k_2 represent the rate constants for forward and backward reactions. Let a be 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 reactions:
rate of forward reaction = $k_1(a-x)$
and rate of backward reaction = k_2x

Net rate of production of B

$$\frac{dx}{dt} = k_1(a-x) - k_2x \quad (ii)$$

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

$$\Rightarrow \frac{dx}{dt} = k_1(a-x_e) - k_2x_e = 0$$

$$\Rightarrow k_1(a-x_e) = k_2x_e$$

where x_e = concentration

of B at equilibrium.

$$\Rightarrow \text{K}_2 = \frac{\text{K}_1 (a - u_e)}{u_e} \quad \text{--- (iii)}$$

Put value of K_2 in equation (ii)

~~$$\frac{du}{dt} = \text{K}_1 (a - u) - \frac{\text{K}_1 (a - u_e)}{u_e} u$$~~

~~$$\frac{du}{dt} = \text{K}_1 (a - u) - \frac{\text{K}_1 (a - u_e)}{u_e} u$$~~

$$\frac{du}{dt} = \text{K}_1 (a - u) - \frac{\text{K}_1}{u_e} (a - u_e) u$$

~~$$= \text{K}_1 a - \text{K}_1 u - \frac{\text{K}_1}{u_e} a u + \frac{\text{K}_1}{u_e} u_e u$$~~

~~$$= \text{K}_1 a - \frac{\text{K}_1}{u_e} a u$$~~

~~$$= \text{K}_1 a \left[1 - \frac{u}{u_e} \right]$$~~

$$\text{or } \frac{du}{dt} \Rightarrow \frac{\text{K}_1 a}{u_e} \left[u_e - u \right] \quad \text{--- (iii)}$$

$$\Rightarrow \frac{du}{u_e - u} = \frac{\text{K}_1 a}{u_e} dt$$

Integrating both side

$$\int \frac{du}{u_e - u} = \frac{\text{K}_1 a}{u_e} \int dt$$

$$\Rightarrow -\ln(u_e - u) = \frac{\text{K}_1 a}{u_e} t + \text{Integration constant} \quad \text{--- (iv)}$$

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

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

Putting value of integration constant

in eqn (iv)

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

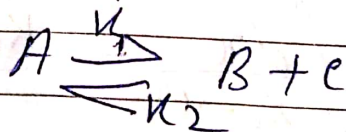
$$\text{or, } \ln x_e - \ln(x_e - x) = \frac{k_1 a t}{x_e}$$

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

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

This is kinetics of opposing reaction of type $A \rightleftharpoons B$.

Similarly kinetics of opposing reaction of type



will be calculated and it will be

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

example of this type of reaction is

(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 $A \rightarrow B \rightleftharpoons C + D$
 or $A \rightleftharpoons B + C$ etc.

Dr. A.K.S. Bhowla
 H.O.D. Chemistry,
 Shri Lal college
 Sasaram.