## 2 Kinetics of opposing or Reversible Reactions

In opposing reactions the products formed also react to give back the reactants.

Initially, the rate of forward reaction is very large which decreases with passage of time and the rate of backward or reverse reaction is zero which increases with passage of item.

A stage is reached when two rates become equal. This ~~equation~~ situation is called the chemical equilibrium.

⟹ Consider the simplest case of an opposing reaction in which the forward as well as the backward reactions are both first-order.

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

| | | |
|---|---|---|
| Initial Conc$^n$. | $[A]_0$ | 0 |
| Conc$^n$ after time $t$ | $[A]$ | $[B]$ |

Where $K_f$ and $K_b$ are the rate constants of the forward and backward reactions.

The overall rate of reaction is given by

Rate of Reaction = Rate of forward reaction − Rate of backward reaction

i.e. $$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = K_f[A] - K_b[B] \quad \text{——— (1)}$$

If $[A]_0$ is the initial concentration of A and $x$ moles of it have reacted in time $t$. Then

$$[A]_t = [A]_0 - x \quad \text{and}$$
$$[B] = x$$

Putting these values in eqn. ① we get

$$\frac{dx}{dt} = K_f([A]_0 - x) - K_b \cdot x \quad \text{——— ②}$$

At equilibrium

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

Hence,

$$K_f([A]_0 - x_{eq.}) = K_b \cdot x_{eq.} \quad \text{——— ③}$$

Where $x_{eq.}$ is the conc$^n$. of A that has reacted into B at equilibrium.

from eqn ③ we have

$$K_b = K_f\left(\frac{[A]_0 - x_{eq.}}{x_{eq.}}\right)$$

Substituting the value of $K_b$ in eqn. ②, we get

$$\frac{dx}{dt} = K_f([A]_0 - x) - K_f\left(\frac{[A]_0 - x_{eq.}}{x_{eq.}}\right)x$$

Integrating this equation between the limits $t=0$, $x=0$ and $t=t$, $x = x_{eq.}$ we have

$$\int_0^x \frac{dx}{x_{eq.} - x} = K_f \frac{[A]_0}{x_{eq.}} \int_0^t dt$$

$$= -\ln(x_{eq.} - x) + \ln x_{eq.} = K_f \frac{[A]_0 t}{x_{eq.}}$$

or, $$\ln \frac{x_{eq.}}{x_{eq.} - x} = K_f \frac{[A]_0}{x_{eq.}} t$$

from this eqn. we calculate the value of $K_f$ from the quantities $[A]_0$, $x_{eq.}$ and $x$ at time $t$.

from the value of $K_f$, the value of $K_b$

can be calculated by using the relation

$$K_b = K_f \left( \frac{[A]_0 - x_{eq.}}{x_{eq.}} \right)$$

Examples of opposing Reactions

(i) Dissociation of Hydrogen Iodide

$$2HI \underset{K_b}{\overset{K_f}{\rightleftharpoons}} H_2 + I_2$$

(ii) Isomerisation of cyclopropane into Propene.

Cyclopropane $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ $CH_3 - CH = CH_2$ Propene

(iii) Isomerisation of ammonium cyanate into urea in aqueous solution.

$NH_4CNO$ Ammonium cyanate $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ $NH_2 - \overset{O}{\overset{\|}{C}} - NH_2$ Urea

(iv) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution.

$R^+NH_3CNO^-$ Alkyl ammonium cyanate $\underset{K_b}{\overset{K_f}{\rightleftharpoons}}$ $NH_2 - \overset{O}{\overset{\|}{C}} - NHR$ Alkyl urea.

(V) Reaction between gaseous CO and $NO_2$

$$CO + NO_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} CO_2 + NO$$

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