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## CLASS 11th

## Chemical and Ionic Equilibrium



## 01. Irreversible and Reversible Reactions

Chemical reactions can be classified as irreversible and reversible reactions. The reactions which move in one direction only are called irreversible reactions.

$$
2 \mathrm{HClO}_{3} \xrightarrow[\text { Heat }]{\mathrm{MnO}_{2}} 2 \mathrm{HCl}+3 \mathrm{O}_{2}
$$

In these reactions products do not react to produce original reactants. In such reactions an arrow $(\rightarrow)$ is placed between reactants and products. $2 \mathrm{HI} \rightleftharpoons \mathrm{H}_{2}+\mathrm{I}_{2}$ The chemical reactions which take place in both directions under similar conditions are called reversible reactions. In such reactions products also react with each other to produce reactants again. The sign $(\rightleftharpoons)$ is placed between reactants and products.

## 02. Chemical Equilibrium

Chemical equilibrium is the most important characteristic property of reversible reactions. It is the state at which both forward and backward reactions occur at the same speed.
At equilibrium state,
Rate of forward = Rate of backward reaction


At equilibrium state, the concentrations of the reactants and products do not change with time. The following are the characteristics of the equilibrium state.


## Chemical and Ionic Equilibrium

(i) It can be achieved only if the reversible reaction is carried out in a closed space.
(ii) It is characterised by constancy of certain properties such as concentration, pressure, density, colour, etc.
(iii) It can be attained from either side of the reaction.
(iv) It can be attained in lesser time by use of a catalyst.
(v) It is dynamic in nature, i.e. reaction does not stop, but both the forward and backward reactions move with the same speed.
(vi) Change of pressure, concentration or temperature favours one of the reaction and thus shifts the equilibrium point in one direction.

## Reversible chemical reactions are classified into two types :

(i) Heterogeneous reactions : The reversible reaction in which more than one-phase is present.
(ii) Homogeneous reactions : The reversible reactions in which only one-phase is present. These are further classified into three types :
(a) When there is no change in the number of molecules, i.e., $\Delta n=0$.
(b) When there is an increase in the number of molecules, i.e., $\Delta n=+\mathrm{ve}$.
(c) When there is a decrease in the number of molecules, i.e., $\Delta n=-\mathrm{ve}$.

## 03. Law of Chemical Equilibrium (Application of Law of Mass Action)

Consider the general homogeneous reversible reaction in which equilibrium has been attained at a certain temperature.

$$
m_{1} A_{1}+m_{2} A_{2}+m_{3} A_{3}+\ldots \rightleftharpoons n_{1} B_{1}+n_{2} B_{2}+n_{3} B_{3}+\ldots
$$

Rate of forward reaction $=$ Rate of backward reaction

$$
k_{f}\left[A_{1}\right]^{m_{1}}\left[A_{2}\right]^{m_{1}}\left[A_{3}\right]^{m_{3}} \ldots=k_{b}\left[B_{1}\right]^{n_{1}}\left[B_{2}\right]^{n_{1}}\left[B_{3}\right]^{n_{3}} \ldots
$$

or $\quad \frac{\left\{\left[B_{1}\right]^{n_{1}}\left[B_{2}\right]^{n_{2}}\left[B_{3}\right]^{n_{3}} \ldots\right\}}{\left\{\left[A_{1}\right]^{m_{1}}\left[A_{2}\right]^{m_{2}}\left[A_{3}\right]^{m_{3}} \ldots\right\}}=\frac{k_{f}}{k_{b}}=K_{c}$
The equilibrium constant, $\mathrm{K}_{\mathrm{c}}$, at a given temperature, is the ratio of rate constants of forward and backward reactions. It is also defined as the ratio between the molar concentrations of the products to the molar concentrations of the reactants with each concentration term raised to the power equal to stoichiometric coefficient in the balanced chemical equation.
The value of equilibrium constant is independent of the following factors :
(i) Initial concentration of reactants.
(ii) The direction from which equilibrium has been attained.
(iii) The presence of a catalyst.
(iv) The presence of inert materials.

The value of equilibrium constant depends upon the following factors :
(i) The mode of representation of the reaction : Consider the reversible reaction.

$$
\begin{aligned}
& \mathrm{A}+\mathrm{B} \rightleftharpoons \mathrm{C}+\mathrm{D} \\
& K_{c}=\frac{[C][D]}{[A][B]}
\end{aligned}
$$

The products are made the reactants, i.e., the reaction is reversed.

$$
\mathrm{C}+\mathrm{D} \rightleftharpoons \mathrm{~A}+\mathrm{B}
$$

$$
K_{c}^{\prime}=\frac{[A][B]}{[C][D]}
$$

So, $\quad K_{c}^{+}=\frac{1}{K_{c}}$
(ii) Stoichiometric representation of chemical equation : The value of equilibrium constant will be numerically different if the reaction can be written with the help of two or more stoichiometric equations.
i.e., $2 \mathrm{NO}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) ; \quad K_{c}=\frac{\left[N_{2}\right]\left[O_{2}\right]^{2}}{\left[\mathrm{NO}_{2}\right]^{2}}$
or $\mathrm{NO}_{2}(\mathrm{~g}) \rightleftharpoons(1 / 2) \mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) ; \quad K_{c}^{\prime}=\frac{\left[N_{2}\right]^{1 / 2}\left[O_{2}\right]}{\left[N O_{2}\right]}$
Thus, $\quad K_{c}^{\prime}=\sqrt{K_{c}}$
(iii) Use of partial pressures : When the reactants and products are in gaseous state, the partial pressures can be used instead of concentrations at a definite temperature.
$m_{1} A_{1}+m_{2} A_{2}+m_{3} A_{3}+\ldots \rightleftharpoons n_{1} B_{1}+n_{2} B_{2}+n_{3} B_{3}+\ldots$

$$
\begin{aligned}
K_{p} & =\frac{\left(P_{B_{1}}\right)^{n_{1}}\left(P_{B_{2}}\right)^{n_{2}}\left(P_{B_{3}}\right)^{n_{3}} \cdots}{\left(P_{A_{1}}\right)^{m_{1}}\left(P_{A_{2}}\right)^{m_{2}}\left(P_{A_{3}}\right)^{m_{3}} \cdots} \\
K_{p} & =K_{c}(R T)^{\Delta n}
\end{aligned}
$$

where, $\Delta \mathrm{n}=$ total number of molecules of products - total number of molecules or reactants.
When
and

$$
\begin{array}{ll}
\Delta \mathrm{n}=0, & \mathrm{~K}_{\mathrm{p}}=\mathrm{K}_{\mathrm{c}} ; \\
\Delta \mathrm{n}=+\mathrm{ve}, & \mathrm{~K}_{\mathrm{p}}>\mathrm{K}_{\mathrm{c}} ; \\
\Delta \mathrm{n}=-\mathrm{ve}, & \mathrm{~K}_{\mathrm{p}}>\mathrm{K}_{\mathrm{c}} ;
\end{array}
$$

(iv) Temperature : The value of equilibrium constant changes with temperature. The values of equilibrium constants at two different temperatures are related by the following equation:

$$
\log K_{2}-\log K_{1}=-\frac{\Delta H}{2.303 R}\left[\frac{1}{T_{2}}-\frac{1}{T_{1}}\right] \quad T_{2}>T_{1}
$$


(a) Endothermic reaction (Plots or $\log \mathrm{K}$ versus T )

(b) Endothermic reaction

