## Equilibrium

- The given equation is known as law of chemical equilibrium. Law of chemical equilibrium is for a reversible reaction at equilibrium, the ratio of the product of the concentrations of the products and the product of the concentrations of the reactants is constant at constant temperature when each concentration term is raised to the power equal to the corresponding stoichiometric coefficient in the balanced chemical equation. The ratio is known as equilibrium constant.


## Equilibrium Constant

- For a reaction,

$$
a A+b B \rightleftharpoons c C+d D
$$

Equilibrium constant, $K_{c}=\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$

- For a homogeneous gas phase reaction, the molar concentration of a substance is directly proportional to its partial pressure $p$ at constant temperature. Then equilibrium is denoted by $K_{p}$.

$$
K_{p}=\frac{\left(p_{C}\right)^{c} \times\left(p_{D}\right)^{d}}{\left(p_{A}\right)^{a} \times\left(p_{B}\right)^{b}}
$$

- Relation between $K_{p}$ and $\boldsymbol{K}_{c}$

$$
P=\frac{n}{V} R T=C R T
$$

- Characteristics of equilibrium constant

If for a reation, $A+B \rightleftharpoons C+D$, equilibrium constant, $K=\frac{[C][D]}{[A][B]}$

| Qhaweturducs | Reaction | Eequliorum constant |
| :---: | :---: | :---: |
| If reaction is reversed. | $A+B \rightleftharpoons C+D$ | $K^{\prime}=1 / K$ |
| If reaction is divided by factor $n$. | $\frac{1}{n} A+\frac{1}{n} B \rightleftharpoons \frac{1}{n} C+\frac{1}{n} D$ | $K^{\prime}=\sqrt[n]{K}$ |
| If reaction is multiplied by factor $n$. | $n A+n B \rightleftharpoons n C+n D$ | $K^{\prime}=K^{\prime \prime}$ |
| If reaction is written in $n$ number of steps. | $A+B \stackrel{K_{1}}{\rightleftharpoons} X+Y ; X+Y \xlongequal{\text { K2 }}$ ¢ $P+Q \ldots$. | $K^{\prime}=K_{1} \times K_{2} \times \ldots K_{n}$ |

## Tlustration ${ }^{2}$

A vessel at 1000 K contains carbon dioxide at a pressure of 0.5 atm . Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of $K$, if the total pressure at equilibrium is 0.8 atm .
Soln.: $\mathrm{CO}_{2}+\mathrm{C}_{\text {(graphite) }} \rightleftharpoons 2 \mathrm{CO}$
Let the decrease in pressure of $\mathrm{CO}_{2}$ after reaction $=$ $p \mathrm{~atm}$
Then, increase in pressure due to CO after reaction $=$
$2 p$ atm
Final total pressure $=(0.5-p)+2 p=0.8 \mathrm{~atm}$ $\Rightarrow \quad p=0.3 \mathrm{~atm}$
Thus after reaction, $p_{\mathrm{CO}_{2}}=0.5-0.3=0.2 \mathrm{~atm}$

$$
K_{p}=\frac{([C] R T)^{c}([D] R T)^{d}}{([A] R T)^{a}([B] R T)^{b}}=\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \cdot \times(R T)^{(c+d)-(a+b)}
$$

if $(c+d)-(a+b)=\Delta n$

$$
K_{p}=K_{c} R T^{\Delta n}
$$

$\Delta n=$ (number of moles of gaseous product) - (number of moles of gaseous reactants)

- Units of equilibrium constant $\left(K_{c}\right)=(\mathrm{mol} / \mathrm{L})^{\Delta n}$

$$
\left(K_{p}\right)=(\mathrm{atm})^{\Delta n}
$$

## Iliustration 1

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} ; K_{1}=1.8 \times 10^{-5}
$$

$$
2 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} ; K_{2}=1 \times 10^{14}
$$

Calculate equilibrium constant for

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{2} \mathrm{O}
$$

Soln.: It is given that

$$
\begin{gather*}
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}_{3} \mathrm{O}^{+} \\
K_{1}=1.8 \times 10^{-5}  \tag{i}\\
2 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}, K_{2}=1 \times 10^{-14} \tag{ii}
\end{gather*}
$$

$\therefore$ For reaction,

$$
\begin{equation*}
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{OH}^{-} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CeO}^{-}+\mathrm{H}_{2} \mathrm{O} \tag{iii}
\end{equation*}
$$

$$
K=\frac{K_{1}}{K_{2}}=\frac{1.8 \times 10^{-5}}{1 \times 10^{-14}}=1.8 \times 10^{9}
$$

$p_{\mathrm{CO}}=2 p=2 \times 0.3=0.6 \mathrm{~atm}$
$\Rightarrow K=\frac{p_{\mathrm{CO}}^{2}}{p_{\mathrm{CO}_{2}}}=\frac{(0.6)^{2}}{(0.2)}=1.8 \mathrm{~atm}$

- Factors affecting equilibrium constant : Equilibrium constant is only affected by temperature.
> In exothermic reversible reactions, as temperature increases, $K$ increases.
> In endothermic reversible reactions, as temperature increases, $K$ decreases.
- 

van't Hoff equation
$\log \frac{K_{2}}{K_{1}}=\frac{\Delta H^{\circ}}{2.303 R}\left[\frac{T_{2}-T_{1}}{T_{1} T_{2}}\right]$

