Le Chatelier's Principle

"If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed."

❖ Effect of change in concentration on equilibrium

As we add or remove reactant (or product) the ratio of new concentrations become 'Q' (reaction quotient)

$Q < K$: equilibrium will shift in forward direction.

$Q > K$: equilibrium will shift in backward direction.

❖ Effect of change in pressure

If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The equilibrium will shift in the direction in which there is decrease in number of moles *i.e.*, towards the direction in which there is decrease in volume.

❖ **Effect of change in pressure on melting point:** There are two types of solids:

(i) Solids whose volume decreases on melting, *e.g.*, ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

The process of melting is facilitated at high pressure, thus melting point is lowered.

(ii) Solid whose volume increase on melting, *e.g.*, Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

In this case the process of melting becomes difficult at high pressure, thus melting point becomes high.

❖ **Solubility of substances :** When solid substances are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

(i) For endothermic solubility process, solubility increase with increase in temperature.

(ii) For exothermic solubility process, decrease with increase in temperature.

❖ **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus increase of pressure will favour the dissolution of gas in liquid.

❖ **Effect of temperature:** For endothermic reaction as temperature increases reaction shift in forward direction. For exothermic reaction as temperature increases reaction shift in backward direction.

❖ **Addition of inert gas**

(i) For reactions in which $n_p = n_r$ there is no effect of adding an inert gas at constant volume or at constant pressure on the equilibrium.

(ii) For reactions in which $n_p \neq n_r$, there is no effect of adding inert gas on the equilibrium at constant volume but at constant pressure, equilibrium shifts towards larger mole side.

Applying Le Chatelier's principle, the favourable conditions for the formation of NH_3 by Haber's process

i.e., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -92.5$ kJ

are (i) High temperature (ii) Low pressure (iii) Removal of N_2 and H_2 (iv) Addition of inert gas at constant pressure.

❖ Physical Equilibrium

Only physical changes are involved.

Example : (i) Solid liquid equilibria

$$H_2O(s) \rightleftharpoons H_2O(l)$$

At equilibrium: Net rate of conversion of ice into water = Net rate of conversion of water into ice.

For $H_2O(l)$ normal freezing point is 273 K.

(ii) Liquid vapour equilibria :

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Equilibrium is characterized by constant value of vapour pressure of $H_2O(l)$ at certain temperature.

For $H_2O(l)$ normal boiling point is 373 K.