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Chemical Equilibrium

(2) Le-Chatelier's Principle -

This principle gives the qualitative effect of the change of temperature, pressure and concentration on the equilibrium of a reversible reactions. According to this principle,

"If a system in equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium automatically shifts in the direction, where the effect of change is minimized or cancelled."

This principle can be explained under following heads-

(1)Effect of change of Concentration

According to Le - Chatelier's principle, if concentration of any species is increased at equilibrium, then the equilibrium (reaction) shifts in the direction where the increased conc. of respective species decreases and vice versa.

Let us consider following reversible reaction-

$$A + B \leftrightharpoons C + D$$

Here, if conc. of reactant A or B or both is increased at equilibrium, then the reaction shifts in forward direction, where the increased conc. of the reactants decreases. Similarly, if conc. of products C or D or both is decreased at equilibrium then also, the reaction shifts in forward direction, where the decreased conc. of the products increases. Thus, in both of these two cases more products are formed at equilibrium.

On the other hand, if conc. of reactant A or B or both is decreased or that of products C or D or both is increased at equilibrium, then following Le- Chatelier's principle, the equilibrium shifts in backward direction. Thus,

(1) Increase of the conc. of any or all the reactants
Or
(2) Decrease of the conc. of any or all the products
→ **Shifts the reaction** → **in forward direction**

(3) Increase of the conc. of any or all the products
Or
(4) Decrease of the conc. of any or all the reactants
→ **Shifts the reaction** → **in backward direction**

For example, for following reaction-

$$N_2\,(g) + 3H_2\,(g) \leftrightharpoons 2NH_3\,(g)$$

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Here, if conc. of reactant $N_2(g)$ or $H_2(g)$ or both is increased or conc. of product $NH_3(g)$ is decreased at equilibrium, then following Le- Chatelier's principle, the reaction will shifts in forward direction and more ammonia will formed. Thus, in order to get more ammonia, the conc. of the reactants $N_2(g)$ and H_2 (g) should be high, while that of product $NH_3(g)$ should be low in reaction mixture. Thus, reactants $N_2(g)$ and $H_2(g)$ should be constantly added to the reaction mixture, while product $NH_3(g)$ should be constantly drawn off from the reaction mixture, so that the reaction will continuously shift in forward direction and more ammonia will formed.

On the other hand, if conc. of reactant $N_2(g)$ or $H_2(g)$ or both is decreased at equilibrium or the conc. of products $NH_3(g)$ is increased at equilibrium, then the reaction will shift in backward direction i.e. the ammonia formed will start dissociating.

Similarly, for following reaction-

$$PCl_5\,(g) \;\leftrightharpoons\; PCl_3\,(g) + Cl_2(g)$$

In order to get more products, the conc. of the reactant $PCl_5(g)$ should be high, while that of products $PCl_3(g)$ and $Cl_2(g)$ should be low in reaction mixture. Thus, reactant $PCl_5(g)$ should be constantly added to the reaction mixture, while the products $PCl_3(g)$ and $Cl_2(g)$ should be constantly drawn off from the reaction mixture, so that the reaction will continuously shift in forward direction and more products will formed.

On the other hand, if conc. of reactant $PCl_5(g)$ is decreased at equilibrium or the conc. of products $PCl_3(g)$ and $Cl_2(g)$ is increased at equilibrium, then the reaction will shift in backward direction i.e. $PCl_3(g)$ and $Cl_2(g)$ will recombine together to form un-dissociated $PCl_5(g)$.

(2)Effect of change of Temperature

In reversible reactions, both exothermic and endothermic reactions occur simultaneously. If forward reaction is exothermic then backward is endothermic and vice versa. For example,

$$N_2\,(g) + 3H_2\,(g) \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\leftrightharpoons}} 2NH_3\,(g) + \text{Heat}$$

(Haber's process)

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$$PCl_5\,(g) \underset{\text{Exothermic}}{\overset{\text{Endothermic}}{\rightleftharpoons}} PCl_3\,(g) + Cl_2(g) - \text{Heat}$$

Here, if temperature is increased at equilibrium (by heating the system), then following Le- Chatelier's principle, the reaction shifts in the direction where the increased temperature decreases i.e. in endothermic direction, where heat provided is absorbed. On the other hand, if temperature is decreased at equilibrium then the reaction shifts in the direction, where the decreased temperature increases i.e. in exothermic direction. Thus,

(1) Increase of the temperature Or High temperature } $\xrightarrow{\text{Shifts the reaction}}$ in endothermic direction

(2) Decrease of the temperature Or Low temperature } $\xrightarrow{\text{Shifts the reaction}}$ in exothermic direction

For example, for following reaction-

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + \text{Heat}$$

Here, if temperature is increased at equilibrium (by heating the system), then following Le- Chatelier's principle, the reaction will shift in backward direction which is endothermic. Hence, ammonia formed will start dissociating. Thus, increase of temperature i.e. high temperature will not be favourable for preparing more ammonia in Haber's process.

On the other, if temperature is decreased at equilibrium, then the reaction will shift in the forward direction, which is exothermic. Hence, more ammonia will formed. Thus, decrease of temperature i.e. low temperature will be favourable for preparing more ammonia in Haber's process.

Similarly, for following reaction-

$$PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - \text{Heat}$$

Here, if temperature is increased at equilibrium (by heating the system), then following Le- Chatelier's principle, the reaction will shift in the forward direction which is endothermic. Hence, more $PCl_5(g)$ will dissociate to give more $PCl_3(g)$ and

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Cl_2(g). Thus, increase of temperature i.e. high temperature will be favourable for more dissociation of PCl_5 (g).

On the other, if temperature is decreased at equilibrium, then the reaction will shift in the backward direction, which is exodothermic. Hence, PCl_3 (g) and Cl_2(g) will combine together to form undissociated PCl_5(g). Thus, low temperature will not be favourable for dissociation of PCl_5(g).

(3)Effect of change of Pressure

Pressure change affects only gaseous equilibria and especially those gaseous equilibrium in which number of gaseous moles changes. If the number of gaseous moles does not change, the pressure change has no effect on the equilibrium. For example, pressure change has no effect on following equilibrium-

$$N_2\,(g) + O_2\,(g) \leftrightharpoons 2NO\,(g)$$
$$H_2\,(g) + I_2\,(g) \leftrightharpoons 2HI\,(g)$$

If pressure is increased at equilibrium, then the volume gets decreased, and therefore, the number of gaseous moles per unit volume gets increased. To overcome this effect, following Le- Chatelier's principle, the equilibrium shifts in the direction in which lesser number of gaseous moles are formed.

On the other hand, if pressure is decreased at equilibrium, then the volume gets increased, and therefore, the number of gaseous moles per unit volume gets decreased. To overcome this effect, following Le - Chatelier's principle, the equilibrium shifts in the direction in which more number of gaseous moles are formed.

Thus,

(1) Increase of pressure Or High pressure $\xrightarrow[\text{In the direction}]{\text{shifts the reaction}}$ where lesser number of gaseous moles are formed

(2) Decrease of pressure Or Low pressure $\xrightarrow[\text{In the direction}]{\text{shifts the reaction}}$ where more number of gaseous moles are formed

For example, for following reaction-

$$N_2\,(g) + 3H_2\,(g) \leftrightharpoons 2NH_3\,(g)$$ (Haber's process)

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Here, if pressure is increased at equilibrium, then the equilibrium will shift in forward direction, where lesser number of gaseous moles are formed. Hence, more ammonia will formed. Thus, increase of pressure or high pressure is favourable for preparing more ammonia in Haber's process. On the other hand, if pressure is decreased at equilibrium, then the equilibrium will shift in backward direction, where more number of gaseous moles are formed. Hence, ammonia formed will start dissociating. Thus, decrease of pressure or low pressure is not favourable for preparing more ammonia in Haber's process.

Similarly, for following reaction-

$$PCl_5\,(g) \quad \leftrightharpoons \quad PCl_3\,(g) + Cl_2(g) - \text{Heat}$$

Here, if pressure is increased at equilibrium, then the equilibrium will shift in backward direction, where lesser number of gaseous moles are formed. Hence, PCl_3 and Cl_2 will combine together to form undissociated PCl_5. Thus, increase of pressure or high pressure is not favourable for dissociation of PCl_5. On the other hand, if pressure is decreased at equilibrium, then the equilibrium will shift in forward direction, where more number of gaseous moles are formed. Hence, more PCl_5 will dissociate to give more PCl_3 and Cl_2. Thus, decrease of pressure or low pressure is favourable for more dissociation of PCl_5.

(4) Effect of adding inert gas

If an inert gas (He, Ne, Ar etc.) is added in reaction mixture at constant pressure, then the volume gets increased, and therefore, the number of gaseous moles per unit volume gets decreased. To overcome this effect following Le - Chatelier's principle, the equilibrium shifts in the direction where more number of gaseous moles are formed.

Thus,

Addition of an inert gas at constant pressure $\xrightarrow[\text{in the direction}]{\text{shift the reaction}}$ where more number of gaseous moles are formed

For example, for following reaction

$$PCl_5\,(g) \quad \leftrightharpoons \quad PCl_3\,(g) + Cl_2(g) - \text{Heat}$$

Here, if an inert gas is added at constant pressure, then the equilibrium will shift in forward direction, where more number of gaseous moles are formed. Hence, more PCl_5 will dissociate to give more PCl_3 and Cl_2. Thus, addition of an inert gas

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at constant pressure is favourable for more dissociation of PCl_5.

On the other hand, For following reaction-

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g) \quad \text{(Haber's process)}$$

Here, if an inert gas is added at constant pressure, then the equilibrium will shift in backward direction, where more number of gaseous moles are formed. Hence, NH_3 formed will dissociate to give back $N_2(g)$ and $H_2(g)$. Thus, addition of an inert gas at constant pressure is not favourable for preparing more ammonia in Haber's process.

If an inert gas (He, Ne, Ar etc.) is added at constant volume, then the internal pressure of gaseous mixture gets increased, but the number of reacting gaseous moles per unit volume remains unchanged and therefore, the equilibrium remains unaffected. Thus, the addition of inert gas at constant volume does not affect the equilibrium.

Application of Le-Chateliers principle on Physical Equilibria-

(1) Fusion of Ice- Fusion of ice is an endothermic process and involves a decrease in volume.

$$\text{Ice (s)} + \text{Heat} \leftrightharpoons \text{Water (l)}$$

Hence, following Le-Chateliers principle, high temperature and high pressure will shift this equilibrium in forward direction and therefore, will be favourable in fusion of ice. On the other hand, if temperature or pressure or both are decreased, the equilibrium will shift in backward direction and therefore, more water will convert into ice.

(2) Vaporisation of Water- Vaporisation of Water is an endothermic process and involves the increase in volume.

$$\text{Water (l)} + \text{Heat} \leftrightharpoons \text{Water vapour (g)}$$

Hence, following Le-Chateliers principle, high temperature and low pressure will shift this equilibrium in forward direction and therefore, will be favourable in vaporisation of water. On the other hand, if temperature is decreased or pressure is increased, the equilibrium will shift in backward direction and therefore, more water vapours will condensed to liquid water.

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(3) Solubility of Substances in water- The dissolution of certain substances like NaCl, KCl, NH_4Cl, $CuSO_4$, $FeCl_3$ etc. in Water is endothermic and involves the absorption of heat. For example,

$$NH_4Cl\ (s) + Heat \leftrightharpoons NH_4^+\ (aq) + Cl^-\ (aq)$$

Following Le-Chateliers principle, high temperature will shift this equilibrium in forward direction and will be favourable in dissolution of NH_4Cl (s) in water . Thus, high temperature is favourable in dissolution of such substances in water. If temperature is decreased, the equilibrium will shift in backward direction and therefore, solubility of these substances in water will get decreased.

On the other hand, the dissolution of substances like NaOH, KOH, CaO, $Ca(OH)_2$, etc. in Water is exothermic and involves the release of heat. For example,

$$Ca(OH)_2\ (s) \overset{Water}{\leftrightharpoons} Ca^{2+}\ (aq) + 2OH^-\ (aq) + Heat$$

Following Le-Chateliers principle, low temperature will shift this equilibrium in forward direction and will be favourable in dissolution of $Ca(OH)_2$ in water. Thus, low temperature is favourable in dissolution of such substances in water. If temperature is increased, the equilibrium will shift in backward direction and therefore, solubility of these substances in water will get decreased.

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