# Chapter-7

CHEMICAL EQUILIBRIUM

Reversible Chemical Reactions:

"The reactions which occur both in forward as well as in reverse or backward direction under given conditions" are called reversible reactions.

- Actually almost all reactions occur in both directions, however some reactions occur up to negligibly small extent in one direction and in other direction to a very high extent almost to completion, such reactions are called irreversible reactions. e.g

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$
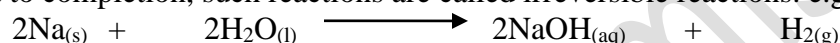
While the reactions which occur to reasonable extents in both directions under same conditions are called reversible reactions e.g.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
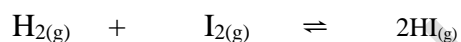
- A reversible reaction never goes to completion.
- A reversible reaction ultimately achieves equilibrium between forward and backward reaction.

Chemical equilibrium:

"A stage during a reversible reaction at which rate of forward reaction becomes equal to rate of reverse reaction" is called chemical equilibrium.

e.g. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ is a reversible reaction

At beginning only forward reaction occurs and no reverse reaction as no products are there. But then backward reaction also starts. With the passage of time rate of forward reaction becomes slow and slow as concentrations of reactants drop first rapidly and then slowly, while rate of reverse reaction becomes fast and fast as concentration of products increases first rapidly and then slowly, and ultimately two rates become equal. This stage of the reaction is called equilibrium.

In above mentioned case, reaction started with formation of Hydrogen Iodide but with passage of time rate of formation of Hydrogen Iodide becomes slow and slow while rate of its dissociation becomes fast and fast and ultimately the two rates becomes equal and equilibrium establishes.
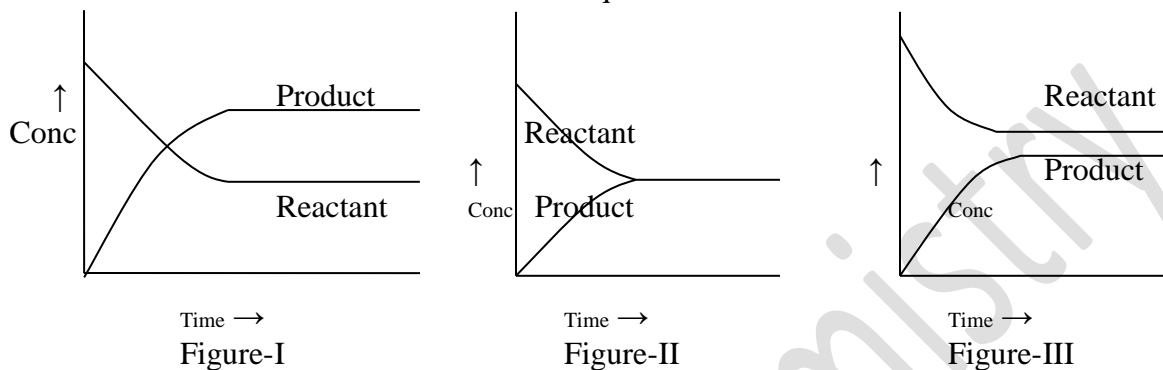
At equilibrium:

(i)   Rate of forward and reverse reaction becomes equal.

(ii)   Concentrations of reactants and products become constant i.e. no further change in concentration of reactants or products occurs. Figure-I, II & III representing three different reversible reactions and their equilibriums.

Figure-I   Figure-II   Figure-III

(iii)   For equilibrium to exist, a close system is usually necessary so that neither reactants nor products escape.

- Equilibriums are of two types (i) Static equilibrium and (ii) Dynamic equilibrium.
- Static equilibrium is the one in which system is stationary e.g. a book lying on table is in static equilibrium.
- Dynamic equilibrium is the one in which system is moving with constant speed e.g. Earth is moving around Sun with constant speed so its equilibrium is dynamic equilibrium, similarly chemical equilibrium is also dynamic equilibrium.

Law of Mass Action:

In 1864 the Norwegian chemists Cato Guldberg and Peter Waage put forward this law. The law states that
"The rate at which a substance reacts is directly proportional to its active mass raised to the power of its stoichiometric coefficient (i.e. its number of moles in balanced equation) and the rate at which a chemical reaction proceeds is proportional to the product of the active masses of the reactants raised to the power of their number of moles in the balanced chemical equation."

Consider a general reaction $aA + bB \rightleftharpoons cC + dD$
Rate of forward reaction can be given as   Rate $= K_f [A]^a[B]^b$
and rate of reverse reaction can be given as   Rate $= K_r [C]^c[D]^d$
But at equilibrium   Rate of forward reaction = rate of reverse reaction

So $\qquad K_f [A]^a[B]^b \ldots\ldots = K_r [C]^c[D]^d$

On rearranging we can write

$$K_c = \frac{K_f}{K_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \ldots\ldots \text{ (1)}$$

Above mentioned expression is called equilibrium expression in terms of molar concentration. K_c is equilibrium constant in terms of molar concentrations.

Now consider an actual case $\qquad N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
Its equilibrium expression can be written as

$$K_c = \frac{[NH_3]^2}{[N_2] [H_2]^3}$$

If reactants and products are gases, their concentration can also be expressed in terms of their partial pressures so equilibrium expression can also be written in terms of partial pressures e.g. for above case we can write

$$K_p = \frac{(P_{NH3})^2}{(P_{N2}) (P_{H2})^3}$$

Kp is equilibrium constant in terms of partial pressure.

And for general reaction $\qquad aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$
Equilibrium expression in terms of partial pressure is written as

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a (P_B)^b} \qquad \ldots\ldots \text{ (2)}$$

Equilibrium expression in terms of mole fraction is written as

$$K_x = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b} \qquad \ldots\ldots \text{ (3)}$$

Equilibrium expression in terms of mole is written as

$$K_n = \frac{(n_C)^c (n_D)^d}{(n_A)^a (n_B)^b} \qquad \ldots\ldots \text{ (4)}$$

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Relationship between K_p and K_c:

According to ideal gas equation $PV = nRT$

Or $P = \dfrac{n}{V} RT$

Or $P = C_i RT = [i]RT$ as $^n/V = C_i = [i]$

Thus for a particular gas 'i', we can write $P_i = C_i RT$ or $P_i = [i] RT$

Therefore $P_A = [A] RT$, $P_B = [B] RT$, $P_C = [C] RT$ and $P_D = [D] RT$

So eq-2 can be written as

$$K_p = \frac{([P]RT)^p ([Q]RT)^q}{([A]RT)^a ([B]RT)^b .}$$

$$K_p = \frac{[P]^p [Q]^q}{[A]^a [B]^b} \quad x \quad \frac{(RT)^p (RT)^q}{(RT)^a (RT)^b}$$

Comparing with equation-1 we can write

$$K_p = K_c \frac{(RT)^{(p+q.....)}}{(RT)^{(a+b.....)}}$$

$$K_p = K_c (RT)^{(p+q.....) - (a+b.....)}$$

$$\boxed{K_p = K_c (RT)^{\Delta n}} \qquad \ldots\ldots\ldots(5)$$

Where $\Delta n = \Sigma n_{(products)} - \Sigma n_{(reactants)}$

Comparison of K_c and K_p of a reaction:

      (i) When $\Delta n = 0$, then $K_p = K_c$
      (ii) When $\Delta n = +ve$, then $K_p > K_c$
      (iii) When $\Delta n = -ve$, then $K_p < K_c$

Relationship between K_p and K_x:

According to Dalton law of partial pressure for a particular gas "i" we can write

$$P_i = X_i P$$

Therefore $\quad P_A = X_A P, \quad\quad P_B = X_B P, \quad\quad P_C = X_C P \quad\quad$ and $\quad P_D = X_D P$

So eq-2 can be written as

$$K_p = \frac{(X_P P)^p (X_Q P)^q}{(X_A P)^a (X_B P)^b}$$

$$K_p = \frac{(X_P)^p (X_Q)^q \quad x \quad (P)^p (P)^q}{(X_A)^a (X_B)^b \quad x \quad (P)^a (P)^b}$$

Comparing with equation-3 we can write

$$K_p = K_x \frac{(P)^{(p+q.....)}}{(P)^{(a+b.....)}}$$

$$K_p = K_x (P)^{(p+q.....) - (a+b.....)} = K_x (P)^{\Delta n}$$

Also ideal gas equation for one mole is $PV = RT \quad$ or $\quad P = RT/V$

SO $\quad K_p = K_x (P)^{\Delta n} = K_x (RT/V)^{\Delta n}$

$$\boxed{K_p = K_x (P)^{\Delta n} = K_x (RT/V)^{\Delta n}} \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

Relationship between Kp and Kn:

According to Dalton law of partial pressure for a particular gas "i" we can write

$$P_i = X_i P$$

Or $\quad\quad P_i = \dfrac{n_i}{N} P \quad\quad\quad\quad$ as $X_i = n_i/N$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ N = Avogadro's number

Therefore $\quad P_A = \dfrac{n_A}{N} P, \quad\quad P_A = \dfrac{n_B}{N} P, \quad\quad P_C = \dfrac{n_C}{N} P$ and $\quad P_C = \dfrac{n_D}{N} P$

So eq-2 can be written as

$$K_p = \frac{\left(\dfrac{n_P P}{N}\right)^p \left(\dfrac{n_Q P}{N}\right)^q}{\left(\dfrac{n_A P}{N}\right)^a \left(\dfrac{n_B P}{N}\right)^b}$$

$$K_p = \frac{(n_{P_-})^p (n_Q)^q}{(n_A)^a (n_B)^b} \times \frac{\left(\frac{P}{N}\right)^p \left(\frac{P}{N}\right)^q}{\left(\frac{P}{N}\right)^a \left(\frac{P}{N}\right)^b}$$

Comparing with equation-4 we can write

$$K_p = K_n \times \frac{\left(\frac{P}{N}\right)^{(p+q)}}{\left(\frac{P}{N}\right)^{(a+b)}}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{(p+q.....) - (a+b.....)}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{(\Delta n)}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{(\Delta n)}$$

$$\boxed{K_p = K_n (P/N)^{\Delta n}}$$ ………………………(7)

Equilibrium constants Kp, Kx, Kn and Kc in terms of partial pressure, mole fraction, number of moles and molar concentration respectively are related to one another. The relationship is given as

$$\boxed{K_p = K_c (RT)^{\Delta n} = K_x (RT/V)^{\Delta n} = K_n (P/N)^{\Delta n}}$$ ……….. (6)

Where
P = total pressure
    of gaseous Mix
N = total moles

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Factors affecting Value of Kc:

- Value of K_c is independent of initial concentrations.
- Value of K_c dependents upon temperature, for endothermic reactions higher is the temperature high will be K_c and vice versa while reverse is true for exothermic reactions.
- Value of K_c dependents upon pressure. When sum of stoichiometric coefficients of reactants is more than that of products then increase in pressure will increase Kc and vice versa. On other hand when sum of stoichiometric coefficients of reactants is less than that of products then increase in pressure will decrease Kc and vice versa. If sum of stoichiometric coefficients of reactants is equal to that of products then pressure does not change Kc.

Types of Chemical Equilibrium:

On the basis of states or phases of reactants and products, we can divide chemical equilibrium into two types.
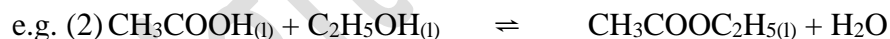
(i) Homogeneous equilibrium:

When all reactants and products are in same phase or state, the equilibrium is called homogeneous equilibrium e.g.
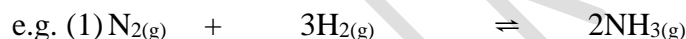
e.g. (1) $N_{2(g)}$ + $3H_{2(g)}$ ⇌ $2NH_{3(g)}$

Its equilibrium expression can be written as

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

e.g. (2) $CH_3COOH_{(l)} + C_2H_5OH_{(l)}$ ⇌ $CH_3COOC_2H_{5(l)} + H_2O$

Its equilibrium expression can be written as

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

(ii) Heterogeneous equilibrium:

When all reactants and products are not in same phase or state, the equilibrium is called heterogeneous equilibrium. While writing equilibrium expression of heterogeneous equilibrium, concentrations of pure solid and liquids are taken as constant (unity).

e.g.(i) $3Fe_{(s)}$ + $4H_2O_{(g)}$ ⇌ $Fe_3O_{4(s)}$ + $4H_{2(g)}$
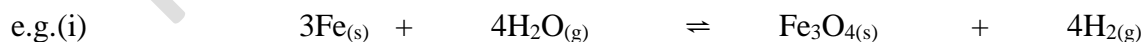
Its equilibrium expression can be written as

$$K_c = \frac{[H_2]^4}{[H_2O]^4} \quad \text{and} \quad K_p = \frac{(P_{H2})^4}{(P_{H2O})^4}$$

e.g.(ii) $CaCO_{3(s)}$ ⇌ $CaO_{(s)}$ + $CO_{2(g)}$

Its equilibrium expression can be written as $K_c = [CO_2]$ and $K_p = (P_{CO2})$

e.g.(iii) $\quad\quad\quad\quad\quad$ $Zn_{(s)}$ + $\quad$ $CuSO_{4(aq)}$ $\quad$ ⇌ $\quad$ $Cu_{(s)}$ + $\quad$ $ZnSO_{4(aq)}$

Its equilibrium expression can be written as

$$K_c = \frac{[ZnSO_4]}{[CuSO_4]}$$

Significance (Importance)   or   Applications of Equilibrium Constant:

(I)   Prediction of the Direction of Reaction:

We can predict the direction of reaction by comparing reaction quotient (Q_c) with K_c of reaction. Q_c has same algebraic form of concentration terms as does K_c. Q_c is ratio of initial concentrations of reactants and products while K_c is is ratio of equilibrium concentrations of reactants and products.

For a general reaction $\quad\quad\quad$ $aA + bB + ………$ ⇌ $\quad\quad$ $pP + qQ + ………$

$$Q_c = \frac{[\text{Initial conc of P}]^p\ [\text{Initial conc of Q}]^q}{[\text{Initial conc of A}]^a\ [\text{Initial conc of B}]^b}$$

While predicting about direction of a reaction we come across three cases

(i)   When $Q_c = K_c$ the reaction is already in equilibrium.

(ii)   When $Q_c > K_c$ the reaction is not in equilibrium and net reaction will occur in reverse direction to attain equilibrium.

(iii)   When $Q_c < K_c$ the reaction is not in equilibrium and net reaction will occur in forward direction to attain equilibrium.

(II)   Prediction of the Extent of Reaction:

The magnitude of K_c shows the extent to which a reaction occurs. In this regard we come across three cases.

(i)   When K_c is very small: Then reaction will occur to negligibly small extent in forward direction and vice versa. e.g.

$$N_2 + O_2 ⇌ 2NO$$
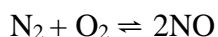
$$K_c = \frac{[NO]^2}{[N_2][O_2]} = 1 \times 10^{-30} \text{ at } 25^oC$$
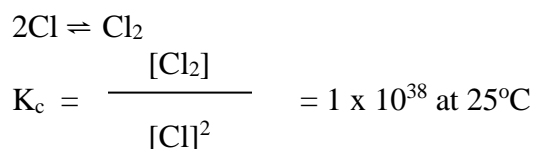
As K_c of above mentioned reaction is very very small which means that nitrogen and oxygen almost do not react to produce nitric oxide at room temperature.

(ii)   When K_c is very large: Then reaction will occur to very large extent in forward direction and vice versa. In other words forward reaction almost goes to completion. e.g.

$$2Cl \rightleftharpoons Cl_2$$

$$K_c = \frac{[Cl_2]}{[Cl]^2} = 1 \times 10^{38} \text{ at } 25^oC$$

As K_c of above mentioned reaction is very large which means that almost all atomic chlorine changes to molecular chlorine at room temperature.

(iii)   When K_c is neither very large nor very small: Then reaction will occur to reasonable extent both in forward as well as in reverse direction. e.g.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 64 \text{ at } 400^oC$$
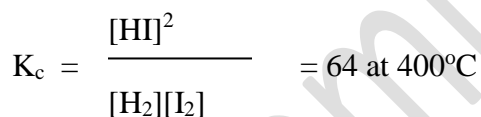
As K_c of above mentioned reaction is neither very large nor very small so this reaction occurs to reasonable extent in both directions.

(III)   Prediction of the Effect of Change in Conditions on the Equilibrium of the Reaction:
     The effect of change in conditions on the equilibrium of a reaction can be explained by Le Chatelier's Principle. This principle was put forward by a French chemist Le

Chatelier in 1888. It states:
"*If a system in equilibrium is disturbed by change in conc or pressure or temp the system will readjust itself to counteract the effect of applied change.*"
It means that the system tries to minimize the effect of applied change and attains a new equilibrium.
(A)*Effect of Change in Concentration*:
An increase in conc of any one of the reactants will shift the equilibrium to the right while increase in conc of any one of the products will shift the equilibrium to the left.

e.g.(i) consider the reaction $N_2O_4 \rightleftharpoons 2NO_2$
                                          Colourless   Brown
There are four ways to disturb the equilibrium of above mentioned reaction.
     (a)   By adding N_2O_4:   Reaction will occur in forward direction to decrease N_2O_4
     (b)   By removing N_2O_4:   Reaction will occur in reverse direction to make N_2O_4
     (c)   By adding NO_2:   Reaction will occur in reverse direction to decrease NO_2
     (d)   By removing NO_2:   Reaction will occur in forward direction to make NO_2

e.g. (ii)   Consider reaction $FeCl_3 + 3NH_4CNS \rightleftharpoons Fe(CNS)_3 + 3NH_4Cl$
                                     Yellow   Colourless   Blood red   Colourless

Addition of FeCl$_3$ will shift equilibrium to the right and blood red colour becomes dark. On other hand addition of NH$_4$Cl will shift the equilibrium to the left and blood red colour will fade.

Some Industrial Processes:
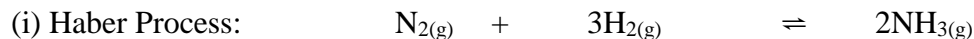
(i) Haber Process: $\qquad$ N$_{2(g)}$ + 3H$_{2(g)}$ ⇌ 2NH$_{3(g)}$
Formation of ammonia can be increased either by adding nitrogen or hydrogen or by removing ammonia. But economical way to obtain more ammonia is addition of nitrogen of air.
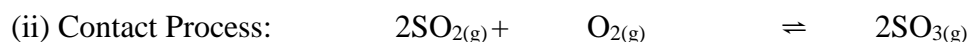
(ii) Contact Process: $\qquad$ 2SO$_{2(g)}$+ O$_{2(g)}$ ⇌ 2SO$_{3(g)}$
Formation of Sulphur trioxide can be increased either by adding Sulphur dioxide or Oxygen or by removing Sulphur trioxide. But economical way to obtain more Sulphur trioxide is addition of Oxygen of air.

(iii) Birkland Eyed Process: $\qquad$ N$_{2(g)}$ + O$_{2(g)}$ ⇌ 2NO$_{(g)}$
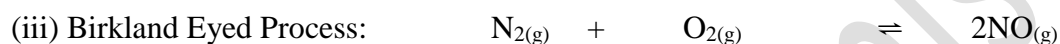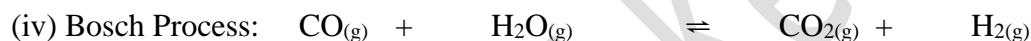Formation of Nitric oxide can be increased either by adding Nitrogen or Oxygen or by removing Nitric oxide. But economical way to obtain more Nitric oxide is addition of air which will increase nitrogen as well as oxygen and equilibrium will shift to the right and more Nitric oxide will be obtained.

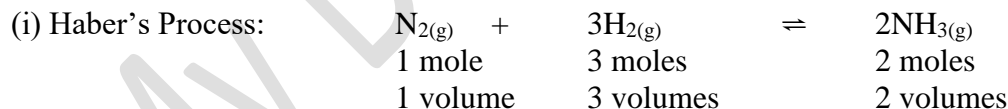(iv) Bosch Process: $\quad$ CO$_{(g)}$ + H$_2$O$_{(g)}$ ⇌ CO$_{2(g)}$ + H$_{2(g)}$
Equilibrium could be shifted to the right either by adding carbon monoxide or steam or by removing carbon dioxide or hydrogen. But economical way to oxidize carbon monoxide is addition of steam.
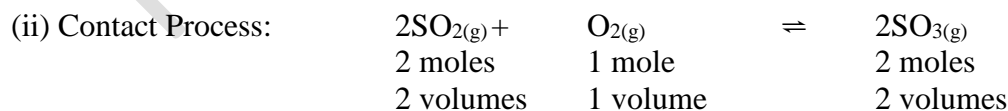
(B)*Effect of Change in Pressure*:
$\qquad$ Change in pressure affects the position of equilibrium of reactions in which total number of moles or volume is not equal on reactant and product side. An increase in pressure will shift equilibrium to the side where number of moles or volume will decrease and a decrease in pressure will shift equilibrium to the side where number of moles or volume will increase.

Some Industrial Processes:

(i) Haber's Process: $\qquad$ N$_{2(g)}$ + 3H$_{2(g)}$ ⇌ 2NH$_{3(g)}$
$\qquad\qquad\qquad\qquad\qquad$ 1 mole $\quad$ 3 moles $\qquad\quad$ 2 moles
$\qquad\qquad\qquad\qquad\qquad$ 1 volume $\quad$ 3 volumes $\qquad$ 2 volumes
High pressure will shift equilibrium to the right as numbers of moles or volumes in this direction are less and thus high pressure will favour formation of ammonia. Thus in Haber's process high pressure i.e. 200-300 atm pressure is applied.

(ii) Contact Process: $\qquad$ 2SO$_{2(g)}$+ O$_{2(g)}$ ⇌ 2SO$_{3(g)}$
$\qquad\qquad\qquad\qquad\qquad$ 2 moles $\quad$ 1 mole $\qquad\quad$ 2 moles
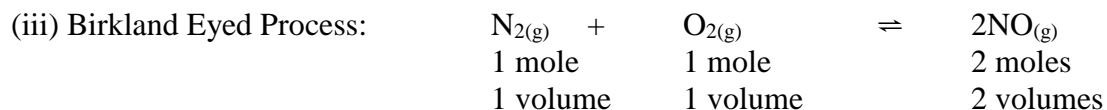$\qquad\qquad\qquad\qquad\qquad$ 2 volumes $\quad$ 1 volume $\qquad$ 2 volumes
High pressure will shift equilibrium to the right as numbers of moles or volumes in this direction are less and thus high pressure will favour formation of sulphur trioxide. Thus in Contact process high pressure is applied.
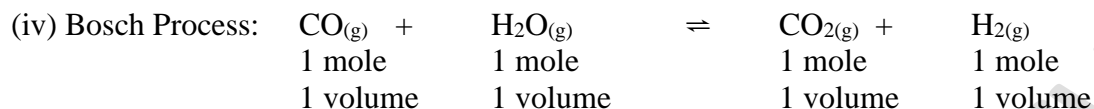
(iii) Birkland Eyed Process:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

1 mole	1 mole	2 moles
1 volume	1 volume	2 volumes

As there is no change in number of moles or volumes so change in pressure will not affect the position of equilibrium. Thus we cannot increase the formation of Nitric oxide by changing pressure.

(iv) Bosch Process:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

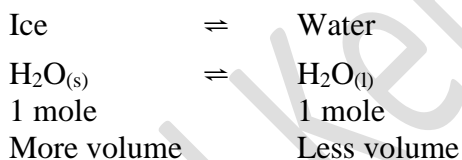|			
1 mole	1 mole	1 mole	1 mole
1 volume	1 volume	1 volume	1 volume

As there is no change in numbers of moles or volumes so change in pressure will not affect the position of equilibrium. Thus we cannot increase the oxidation of carbon monoxide by changing pressure.

Melting of ice by applying pressure:

Ice can be melted at $0^{o}C$ without heating and by just applying pressure.

$$\text{Ice} \rightleftharpoons \text{Water}$$

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$

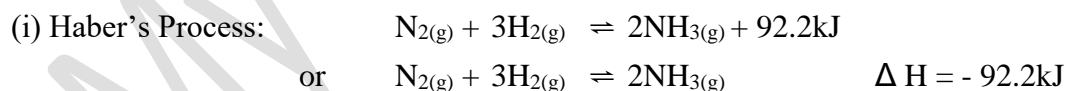|	
1 mole	1 mole
More volume	Less volume

Ice has less density and more volume than water at same temperature. As here, volume in forward direction decreases so high pressure will shift equilibrium to the right and, therefore, ice can be melted by applying pressure and without heating at $0^{o}C$.
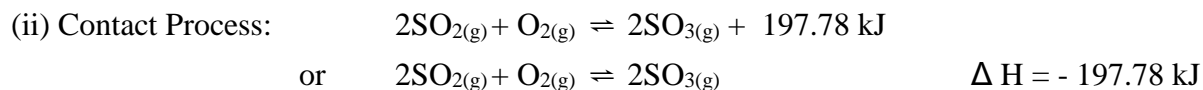
(C)*Effect of Change in Temperature*:

Change in temperature affects the equilibrium of both exothermic and endothermic reactions. If a reversible reaction is exothermic in one direction then it will be endothermic in the opposite direction. An increase in temperature favours endothermic reaction while decrease in temperature favours exothermic reaction.

Some Industrial Processes:

(i) Haber's Process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92.2kJ$$

or

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.2kJ$$

As this reaction is exothermic in forward direction, so low temperature will favour the formation of ammonia. Best temperature for this process is $450\text{-}500^{o}C$. At temperature lower than this, energy of molecules will be less than activation energy and no reaction will occur.

(ii) Contact Process:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + 197.78 \text{ kJ}$$

or

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -197.78 \text{ kJ}$$
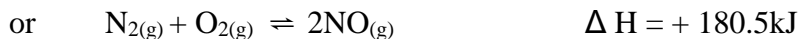
As this reaction is exothermic in forward direction, so low temperature will favour the formation of sulphur trioxide. Best temperature for this process is $400^{o}C$. At temperature lower than this, energy of molecules will be less than activation energy and no reaction will occur.

(iii) Birkland Eyed Process:

$$N_{2(g)} + O_{2(g)} + 180.5kJ \rightleftharpoons 2NO_{(g)}$$

$$\text{or} \qquad N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \qquad \Delta H = + 180.5kJ$$

As this reaction is endothermic in forward direction, so high temperature will favour the formation of nitric oxide. Best temperature for this process is 2000-3000°C.

(iv) Bosch Process: $\quad CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} + 41.84kJ$

$$\text{or} \qquad CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad \Delta H = - 41.84kJ$$

As this reaction is exothermic in forward direction, so low temperature will favour the oxidation of carbon monoxide.. Best temperature for this process is 500°C. At temperature lower than this, energy of molecules will be less than activation energy and no reaction will occur.

(D)*Effect of Catalyst*:

Catalyst does not alter the position of equilibrium of a reversible reaction. It only changes the time to achieve equilibrium. By using catalyst equilibrium will be achieved in a shorter time.

Calculations of Equilibrium Concentrations:

(i) Equilibrium concentrations of reactants and products can be calculated if initial concentrations and Kc of the reaction is known e.g. 'a' moles of CH_3COOH and and 'b' moles of C_2H_5OH are made to react to get equilibrium mixture, then

	Acetic acid	Ethyl alcohol	Ethyl acetate	Water
	CH_3COOH +	C_2H_5OH $\rightleftharpoons$	$CH_3COOC_2H_5$ +	H_2O
Initial concentration	a	b	0	0

Let x moles of CH_3COOH are consumed, then x moles of C_2H_5OH will also be consumed, while x moles of $CH_3COOC_2H_5$ and x moles of H_2O will be produced.

| Equilibrium concentration | a – x | b – x | x | x |

Now write equilibrium expression and put values

$$Kc = \frac{[CH_3COOC_2H_5] \, [H_2O]}{[CH_3COOH] \, [C_2H_5OH]}$$

$$Kc = \frac{[x] \, [x]}{[a – x] \, [b – x]}$$

Now solve above equation for x and then calculate equilibrium concentrations.

(ii) Equilibrium concentrations of reactants and products can also be calculated if initial concentrations of all species and equilibrium concentration of one of the species is known. By using stoichiometric calculations, equilibrium concentrations cab be worked out.
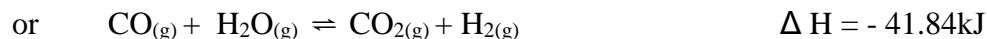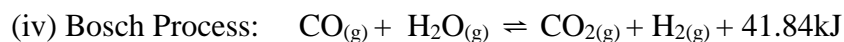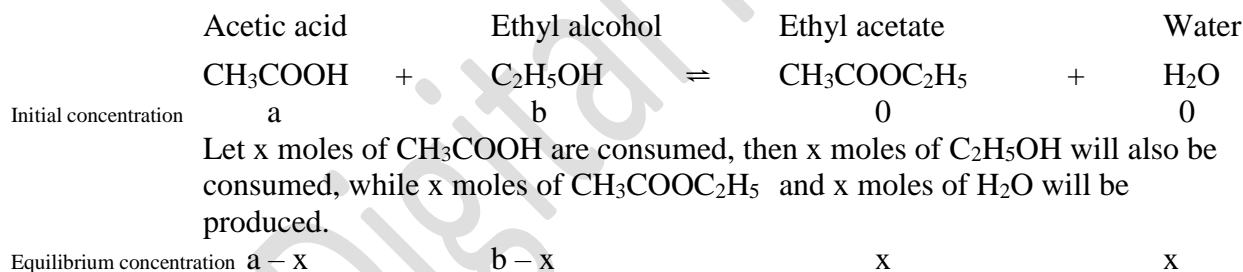
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Solubility Product:

When a soluble ionic solute is dissolved in water it dissociates completely into ions. But on other hand sparingly soluble solutes e.g. AgCl, $PbCl_2$, $PbSO_4$ etc dissociate very little. So in case of sparingly soluble solutes, in the solution solid solute and ions both are present.

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The solution contains silver ions, chloride ions and undissociated silver chloride. Its equilibrium expression will be written as

$$K_c = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

Being sparingly soluble salt concentration of AgCl almost remains constant, so

$$K_c\,[AgCl] = [Ag^+]\,[Cl^-]$$

Product of two constant will be another constant i.e. $K_c[AgCl] = K_{sp}$, therefore

$$K_{sp} = [Ag^+]\,[Cl^-]$$

This new constant 'K_{sp}' is called solubility product constant. K_{sp} for AgCl is 1.8×10^{-10}.

- *K_{sp} of substance is temperature dependant.*

For a general sparingly soluble substance, A_mB_n

$$A_mB_n \rightleftharpoons mA^{+n} + nB^{-m}$$

$$K_{sp} = [A^{+n}]^m\,[B^{-m}]^n.$$

"*The solubility product is the product of equilibrium concentrations of ions of the electrolyte raised to the power of their stoichiometric coefficients in the chemical equation.*"

e.g.   Consider $PbCl_2 \rightleftharpoons Pb^{+2} + 2Cl^-$
Its K_{sp} expression is written as $K_{sp} = [Pb^{+2}]\,[Cl^-]^2$
K_{sp} for $PbCl_2$ is 1.6×10^{-5}

Applications of K_{sp}:

(i) It determines the solubility of a solute. Higher is the K_{sp} of a solute more will be its solubility and vice versa e.g. K_{sp} for $PbCl_2$ is 1.6×10^{-5} and that of AgCl is 1.8×10^{-10}, so $PbCl_2$ is more soluble than AgCl.

(ii) It can be used to check whether a solution is unsaturated, saturated or supersaturated. This can be done by comparing the ionic product of the solution of a solute with K_{sp} of the solute.

      If $[A^{+n}]^m [B^{-m}]^n < K_{sp}$ then solution is unsaturated
      and if $[A^{+n}]^m [B^{-m}]^n = K_{sp}$ then solution is saturated
      and if $[A^{+n}]^m [B^{-m}]^n > K_{sp}$ then solution is supersaturated

(iii) It can be used to predict whether precipitation will occur or not.

      If $[A^{+n}]^m [B^{-m}]^n > K_{sp}$ then solution is supersaturated and precipitation will occur.

(iv) It can be used to predict which solute will suppress the solubility of other solute. The solute having higher K_{sp} suppresses the ionization or solubility of solute having lower K_{sp} e.g. $PbCl_2$ ($K_{sp} = 1.6 \times 10^{-5}$) suppresses the ionization or solubility of AgCl ($K_{sp} = 1.8 \times 10^{-10}$).

(v) It can be used to predict whether a solute can be replaced by other solute in a solution or not. A solute having higher Ksp can remove other having low Ksp and certain ion common between them. For AgCl ($K_{sp} = 1.8 \times 10^{-10}$) can be replaced by $PbCl_2$ ($K_{sp} = 1.6 \times 10^{-5}$)

Common Ion Effect:

"The phenomenon of suppression of ionization or solubility of a less ionizable solute (having low Ksp) in presence of a more ionizable solute (having higher Ksp) having certain ion common between them is called common ion effect."

e.g. (i) When calcium oxalate is dissolved in water, it get ionized and establishes following
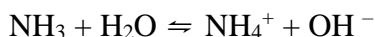
equilibrium. $CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$

If now $CaCl_2$ is added to this solution it being more ionizable so it ionizes to greater extent and concentration of common Ca^{+2} ion increases considerably.

$$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl^-$$

According to Le-Chatelier's principle equilibrium of the 1st reaction shifts to the left and thus ionization or solubility of CaC_2O_4 suppresses.

e.g. (ii) When ammonia is dissolved in water, it establishes following equilibrium.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

If NH_4Cl is added to this solution it being more ionizable so it ionizes to greater extent and concentration of common NH_4^+ ion increases considerably.

$$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$$

According to Le-Chatelier's principle equilibrium of the 1st shifts to the left and thus ionization of NH_3 suppresses and it become more weak base.

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e.g. (iii)   Purification of NaCl: We can use common ion effect method for purification of NaCl. For this pupose hot saturated solution of NaCl will be prepared, which establishes following equilibrium.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Now HCl gas which is more ionizible, will be passed through this solution. It gives following

equilibrium. $$HCl \rightleftharpoons H^+ + Cl^-$$

The concentration of common Cl^- ion will be considerably increased so first equilibrium will shift to the left. Solid NaCl will settle down where as impurities will be left with in solution. Crystals of pure NaCl will then be separated by filtration.

Common ion effect method can be used to extract a less ionizable solute from a solution by adding a more ionizable solute having certain common ion.

Applications:
- Due to common ion effect we can remove a substance from solution. For this purpose we add a solute to the solution which has higher Ksp than this solute and has certain ion common to it.
- Common ion effect can be applied to remove soluble impurities e.g. purification of NaCl by passing HCl gas through brine.

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