CHAPTER-6

CHEMICAL EQUILIBRIUM

6.1 EXTENT TO WHICH REACTIONS PROCEED·

All the chemical reactions do not proceed to the same extent, some proceed to completion and some never go to completion. The reactions which proceed to completion in a definite direction are called 'irreversible' or 'One way' reactions. For example,

$$\underset{\text{Reactants}}{NaCl + AgNO_3} \longrightarrow \underset{\text{Products}}{NaNO_3 + AgCl_{(S)}}$$

In these reactions, the reactants are completely converted into products.

There is vast number of reactions which never proceed to completion and are called 'reversible' or 'both way' reactions. For such reactions under the same conditions, both the forward and reverse reactions can occur at the same time if all the reactants and products are present in one container.

$$\text{Reactants} \rightleftharpoons \text{Products}$$

The double arrow ($\rightleftharpoons$) indicates that the reaction is reversible and that both the forward (left to right) and reverse (right to left) reactions can occur simultaneously. Some examples of reversible reactions are given below :

(i) Formation of Ethyl acetate (ester).

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(ii) Dissociation of Hydrogen iodide.

$$2HI \rightleftharpoons H_2 + I_2$$

(iii) Dissociation of Phosphorus pentachloride

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

(iv) Hydrolysis of Bismuth chloride

$$BiCl_3 + H.OH \rightleftharpoons BiOCl + 2HCl$$

(v) Synthesis of ammonia by Haber process

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

6.2 EQUILIBRIUM STATE

In a reversible reaction, both the changes, forward and the reverse occur simultaneously. Under these circumstances, a reaction might come to some kind of 'balance' in which the forward and reverse reactions occur at the same rate. Consider, for example, the following homogeneous reaction (i.e. entirely liquid or entirely gaseous).

$$A + B \rightleftharpoons C + D$$

In the beginning, forward reaction predominates, but as soon as C and D are formed, the reverse reaction 'builds up' until equilibrium position is reached where the forward as well as the reverse change proceeds with the same rate.

The equilibrium state of a chemical reaction, however, differs from these physical examples. The children on a see saw or a note book on a table are in a state of 'static' equilibrium, but the chemical equilibrium is 'dynamic', that is, it is an equilibrium involving the constant inter change of particles in motion (as it involves the balancing of two reactions occurring simultaneously). In static equilibrium, we can observe the fact that the children or the book are in equilibrium, but in dynamic equilibrium we can't observe the individual particles involved.

Although the idea of reactants and products is confusing in a reversible reaction, at equilibrium point, all the substances involved are present. That is to say that an equilibrium mixture is formed. The composition of this mixture remains constant due to same rate of forward and backward change. At this point, it apparently appears as if the reaction has stopped because we don't see an increase in the amount of products. But as mentioned earlier, a reversible reaction never stops – it is dynamic. The equilibrium state does not change with the lapse of time.

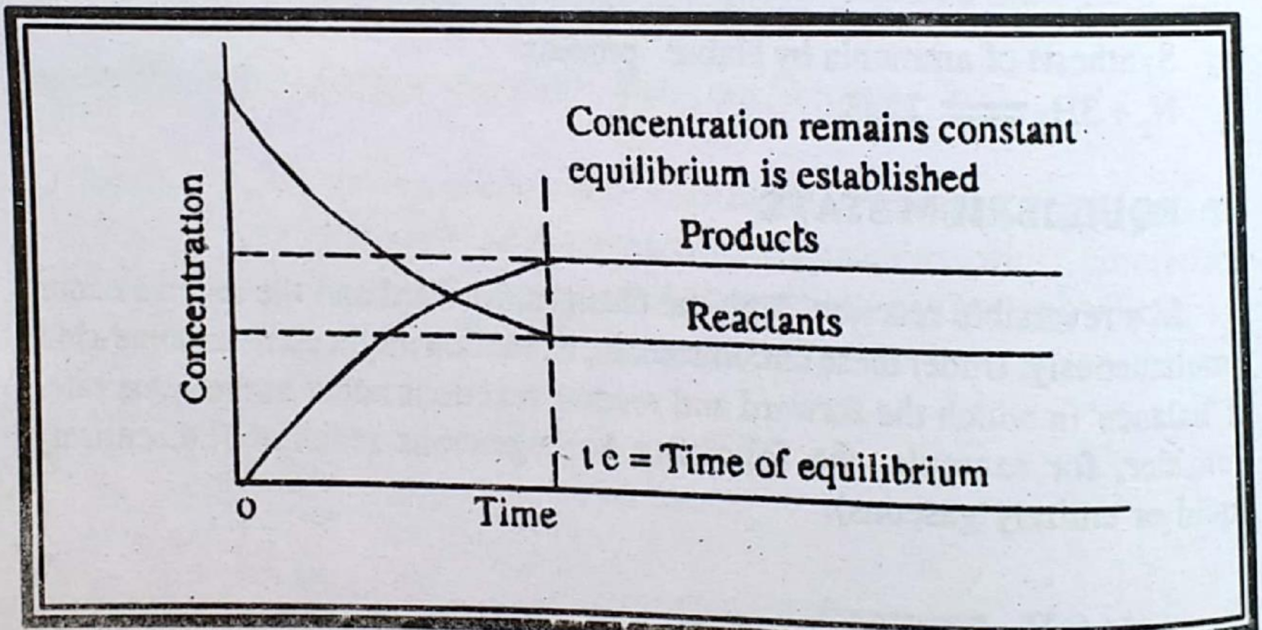

Fig.6.1

6.3 THE LAW OF MASS ACTION (EQUILIBRIUM LAW)

In 1864, the Scandinavian scientists, Guldberg and Waage formulated a generalization regarding the effect of concentration on reversible reactions in equilibrium. It is known as the law of mass action or law of equilibrium. It states that:

> "The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of reactants."

The term active mass' means the concentration in terms of moles/dm^3 (moles/litre). For example, the active mass of 4 gm H_2 is 2 moles/dm^3 and it is represented by means of square brackets such as $[H_2]$ = active mass of H_2

To derive the expressions of Equilibrium Constant, K_c. In order to find out the influence of concentration on chemical equilibrium, it is essential to derive the expression of its equilibrium constant which is denoted by K_c or K_p. Let us, for instance, apply the law of mass action to the following general reversible reaction in which 'm' moles of A and 'n' moles of B react to give 'x' moles of C and 'y' moles of D.

$$\boxed{mA + nB \rightleftharpoons xC + yD}$$

$$\begin{aligned}
\text{Rate of Forward reaction} &\propto [A]^m\ [B]^n \\
&= K_1\ [A]^m\ [B]^n \ \ldots\ (i) \\
\text{Rate of reverse reaction} &\propto [C]^x\ [D]^y \\
&= K_2\ [C]^x\ [D]^y \ldots\ldots (ii)
\end{aligned}$$

Since, at equilibrium state,

Rate of forward reaction = Rate of reverse reaction

$$\therefore \quad (i) = (ii)$$

$$K_1\ [A]^m\ [B]^n = K_2\ [C]^x\ [D]^y$$

$$\text{Or} \quad \frac{K_1}{K_2} = \frac{[C]^x\ [D]^y}{[A]^m\ [B]^n}$$

$$\text{Or} \quad K_c = \frac{[C]^x\ [D]^y}{[A]^m\ [B]^n}$$

This is the expression of K_c, in which active masses of products are placed in the mumerator while the active masses of reactants are placed in the denominator. In other words, equilibrium constant is the ratio of active masses of products and reactants at equilibrium. Thus, for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$K_c = \frac{[PCl_3]\ [PCl_2].}{[PCl_5]}$$

In case of gaseous equilibrium, a partial pressure is used instead of concentration because at a given temperature, partial pressure of a gas is proportional to its concentration. In this case, the equilibrium constant is expressed as K_p instead of K_c, for example, consider the following gaseous equilibrium.

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

$$K_p = \frac{[P_C][P_D]}{[P_A][P_B]},$$ where P_A, P_B, P_C, P_D are the partial pressures of gases A, B, C and D respectively.

Relation between K_C and K_p:

(i) $K_p = K_C$ in these cases where there is no change in volume such as

$$\underset{\text{1 Vol.}}{H_{2(g)}} + \underset{\text{1 Vol.}}{I_{2(g)}} \rightleftharpoons \underset{\text{2 Vol.}}{2HI_{(g)}}$$

(ii) $K_p > K_C$ when reactions occur with increase in volume such as

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

(iii) $K_p < K_C$ when there is decrease in volume on the product side such as

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

6.4 DETERMINATION OF EQUILIBRIUM CONSTANT

The value of equilibrium constant K_C does not depend upon the initial concentration of reactants. In order to find out the value of K_C, we have to find out the equilibrium concentration of reactants and products. Consider the following examples:

1. Ethyl Acetate Equilibrium :

Acetic acid (an organic acid) reacts with ethyl alcohol to form ethyl acetate (an ester) and water.

$$CH_3COOH + C_2H_5OH \underset{\text{Hydrolysis}}{\overset{\text{Esterification}}{\rightleftharpoons}} CH_3COO\,C_2H_5 + H_2O$$

Known masses of acetic acid and ethyl alcohol are taken in a stoppered sk. Let it be 'a' moles/dm³ acetic acid and 'b' moles/dm³ ethyl alcohol when uilibrium establishes after some time, the contents of the flask are cooled or enched' by adding crushed ice to 'fix' the equilibrium. Since equilibrium xture consists of unused reactants as well as the products, hence the amount of acid left at equilibrium is determined by titrating it against standard solution odium hydroxide. Suppose the amount of acetic acid consumed at equilibrium moles/dm³ which means the acid left at equilibrium is (a-x) mole/dm³. Note he above equation there is 1 molecule of acid, one molecule of alcohol which ct to form 1 molecule of ester and one molecule of water. In this case, therefore, amount of acid used up must be equal to the amount of alcohol used, which ans at equilibrium, the amount of acid left = $(a-x)$ moles/dm³, alcohol = x) moles/dm³, ester formed = x moles/dm³ and water produced = x moles/dm³.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

of moles at initial state =	a	b	Nil	Nil
of moles at equilibrium state =	$(a-x)$	$(b-x)$	x	x
centration at equilibrium state =	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

applying the law of mass action, we get:

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3\,COOH]\,[C_2H_5OH]}$$

$$K_c = \frac{\frac{(x)}{V} \times \frac{(x)}{V}}{\frac{(a-x)}{V}\frac{(b-x)}{V}} = \frac{x^2}{(a-x)\;(b-x)}$$

In separate experiments, different amounts of acetic acid and ethyl alcohol e made to react at constant temperature. Analysis of the equilibrium mixture e the following results:

Equilibrium Conc : (Moles/dm³)

Acetic Acid	Ethyl alcohol	Ethyl acetate	Water	$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$
18×10^{-3}	22×10^{-3}	40×10^{-3}	40×10^{-3}	4.04
63×10^{-3}	23×10^{-3}	75×10^{-3}	75×10^{-3}	3.88
75×10^{-3}	80×10^{-3}	160×10^{-3}	160×10^{-3}	4.26
28×10^{-3}	96×10^{-3}	105×10^{-3}	105×10^{-3}	4.10

For this system, the value of equilibrium constant, K_c is almost constant which averages to 4.

2. Hydrogen Iodide Equilibrium

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

To start with, suppose there are 'a' moles/dm³ of hydrogen and 'b' moles/dm³ of iodine which react in sealed bulbs at 444°C in the boiling sulphur for some length of time. In order to 'fix' the equilibrium, the equilibrium mixture is cooled. The bulbs are opened in the solution of sodium hydroxide which absorbs hydrogen iodide and iodine leaving behind hydrogen. Let the amount of hydrogen consumed at equilibrium be 'x' moles/dm³ which means the amount of hydrogen left at equilibrium is (a–x) moles/dm³. Since 1 mole of hydrogen reacts with 1 mole of iodine to form two moles of hydrogen iodide, hence the amount of iodine used is also 'x' moles/dm³. Thus 2x' moles/dm³ of hydrogen iodide are present at equilibrium. The equilibrium constant K_c is then calculated:

	$H_{2(g)}$ +	$I_{2(g)}$ $\rightleftharpoons$	$2HI_{(g)}$
No. of moles at initial state	a	b	Nil
No. of moles at equilibrium state	(a–x)	(b–x)	2x
Concentration at equilibrium state	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Applying the law of mass action

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

In separate experiments different amounts of hydrogen and iodine were made to react at constant temperature. Analysis of the equilibrium mixture gave the following results:

Equilibrium Amounts (Moles/dm³)

Hydrogen	Iodine	Hydrogen Iodide	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
0.00456	0.00074	0.01354	54.3
0.00356	0.00125	0.01559	54.6
0.00225	0.00234	0.01685	53.9
0.00048	0.00048	0.00353	54.1

For this system K_c averages to 54.

EXAMPLE 1. 4.6 gm of ethyl alcohol and 6.0 gm of acetic acid kept at constant temperature until equilibrium was established. 2.0 gm of unused acid were present. Calculate K_c.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

No. of moles at initial state	$\frac{6.0}{60} = 0.1$	$\frac{4.6}{46} = 0.1$	NIL	NIL
Suppose no. of moles at equilibrium	$(0.1-x)$	$(0.1-x)$	x	x

During the reaction 2 gms. of acetic acid were left which is $\frac{2}{60} = 0.033$ mole

or $0.1-x = 0.033$ mole

or $x = 0.1-0.033 = 0.067$ mole.

Therefore 0.067 mole of acetic acid and 0.067 mole of ethyl alcohol must have reacted. Hence 0.067 mole of each product (ethyl acetate and water) are formed.

∴ No. of moles at equilibrium state	0.033	0.033	0.067	0.067
Conc. at equilibrium state	$\frac{0.033}{V}$	$\frac{0.033}{V}$	$\frac{0.067}{V}$	$\frac{0.067}{V}$

$$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3COOH]\ [C_2H_6OH]} = \frac{\frac{0.067}{V} \times \frac{0.067}{V}}{\frac{0.033}{V} \times \frac{0.033}{V}} = \frac{0.067 \times 0.067}{0.033 \times 0.033} = 4.0$$

EXAMPLE 2. 9.2 gm of ethyl alcohol, 3.6 gm of acetic acid, 1.1 gm of ethyl acetate and 9.0 gm of water were mixed and allowed to attain equilibrium. If $K_c = 4$, what was the concentration of the resulting mixture?

$$CH_3\,COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

No. of moles at initial state $\frac{3.6}{60} = 0.06$, $\frac{9.2}{46} = 0.2$, $\frac{1.1}{88} = 0.0125$, $\frac{9.0}{18} = 0.5$

If *x* mole of acetic acid and *x* mole of ethyl alcohol react, then additional *x* mole of each product (ethylacetate and water) are formed.

No. of moles at initial state	−n	−n	+n	+n
No. of moles at equilibrium state	0.06−n	0.2−n	0.0125+n	0.5+n
Concentration at equilibrium state	$\frac{0.06-n}{V}$	$\frac{0.2-n}{V}$	$\frac{0.0125+n}{V}$	$\frac{0.5+n}{V}$

$$K_c = \frac{[CH_3COOC_2H_5]\ [H_2O]}{[CH_3\,COOH]\ [C_2H_5OH]}$$

$$K_c = \frac{\left(\frac{0.0125 + x}{V}\right) \left(\frac{0.5 + x}{V}\right)}{\left(\frac{0.06 - x}{V}\right) \quad \left(\frac{0.2 - x}{V}\right)}$$

$$3x^2 - 1.5525\,x + 0.04175 = 0$$

solving by the formula $ax^2 + bx + C = 0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = 0.49$ or $x = 0.029$ moles

Since the initial amounts of acetic acid and ethyl alcohol are less than 0.49 moles, hence $x = 0.49$ is ruled out. In other words $x = 0.029$ moles. Thus the equilibrium concentration of the mixture is given below:

Acetic acid = $0.06 - 0.029$ = 0.031 mole/dm^3
Ethyl alcohol = $0.2 - 0.029$ = 0.171 mole/dm^3
Ethyl acetate = $0.0125 + 0.029$ = 0.0415 mole/dm^3
Water = $0.5 + 0.029$ = 0.529 mole/dm^3

EXAMPLE 3. In a reaction $A + B \rightleftharpoons 2C$, when equilibrium was attained, the concentration was $[A] = [B] = 4$ moles/dm^3, $[C] = 6$ moles/dm^3. Calculate the equilibrium constant K_c and the initial concentrations of A and B.

Solution.

(a) The equilibrium constant of the above reaction is given by,

$$K_c = \frac{[C]^2}{[A]\,[B]}$$

$$K_c = \frac{(\frac{6}{V})^2}{(\frac{4}{V})\cdot(\frac{4}{V})} = \frac{36}{16} = 2.25$$

(b) Since one mole of A and one mole of B react to form two mole of C, hence 6 moles of C are produced from 3 moles of A and 3 moles of B. Thus the initial concentration of $A = B = 4 + 3 = 7$ moles/dm^3 each.

6.5 APPLICATIONS OF THE LAW OF EQUILIBRIUM

The law of equilibrium is used to calculate the equilibrium constant of a reversible reaction. The study of equilibrium expression and its constant K_c is very important to a chemist or to a manufacturer. Some valuable predictions can be made about a reaction. In fact, a chemist can control the direction and the extent of a chemical reaction by changing the conditions through the knowledge of K_c. Below are given the important applications of equilibrium constant:

(i) K_c is used to predict the direction of a reaction.
(ii) It is also used to predict the extent to which a reaction occurs.

(1) To predict the direction of a Reaction :

The value of equilibrium constant K_c is a valuable aid in predicting the direction in which a reaction will shift in order to achieve the equilibrium, provided the initial concentration of the reagents involved is known.

$$\text{Reactants} \rightleftharpoons \text{Products.}$$

As regards to the ratio of the initial concentration of the reagents $\dfrac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}}$, there are three possible cases.

(i) It is greater than K_c (ii) It is less than K_c (iii) It is equal to K_c.

(i) In the first case, when

$\dfrac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} > K_c$, the reaction will shift towards the reverse direction where less quantity of products is obtained and the ratio decreases to the value of K_c.

(ii) In the second case when

$$\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} < K_C,$$ the reaction will shift towards right where more quantity of products is formed and the ratio increases to the value of K_C.

(iii) In the Third case, when

$$\frac{[\text{Products}]_{\text{Initial}}}{[\text{Reactants}]_{\text{Initial}}} = K_C,$$ according to the law of mass action, equilibrium has been attained and there is no shifting of the reaction provided conditions are not changed.

EXAMPLE 4. The K_c for the dissociation of hydrogeniodide at 356°C is 1.3×10^{-2}. If there are 0.5 moles/dm³ Hydrogen, 1.5 moles/dm³ iodine and 5 moles/dm³ Hydrogeniodide, predict the direction in which the reaction moves so as to achieve the equilibrium.

The dissociation of Hydrogeniodide is represented by the equation,

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \quad K_C = 1.3 \times 10^{-2}$$

According to the law of mass action,

$$K_{\text{Initial}} = \frac{[H_2]_{\text{Initial}}\,[I_2]_{\text{Initial}}}{[HI]^2_{\text{Initial}}} = \frac{(0.5).(1.5)}{(5)^2} = \frac{0.75}{25} = 3 \times 10^{-2}$$

Since the calculated value of the ratio of the concentrations of the reagents is 3×10^{-2} which is greater than the actual value of K_C, hence the reaction will shift towards the reverse direction.

EXAMPLE 5. K_C for the reaction $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ at 448°C is 0.0194. If one litre vessel contains 0.2 moles. Hydrogen, 12 moles iodine and 15 moles Hydrogen iodide, predict the direction of reaction.

According to the law of mass action,

$$K_{Initial} = \frac{[H_2]_{Initial}\,[I_2]_{Initial}}{[HI]^2_{Initial}} = \frac{0.2 \times 12}{(15)^2} = \frac{2.4}{225} = 0.0106$$

Since the calculated ratio of the concentration of the products and reactants is less than the actual value, hence the reaction will move towards right i.e. towards the forward direction.

(2). To Predict the Extent of Reaction :

From the value of K_C, we can predict the extent to which a reaction will occur.

In the first case, when the value of K_C is very large, it is predicted that the forward reaction is almost complete. That is to say, the reactant is unstable. for example ozone, an allotropic form of oxygen, quickly decomposes to oxygen $2O_3 \rightleftharpoons 3O_2$. Its K_C is very large (10^{55}).

In the second case, when the value of K_C is very low, it is predicted that the forward reaction proceeds with negligible speed. That is to say, the reactant is fairly stable. For example, hydrogen fluoride unlike other hydrogen halides (HCl, HBr, HI) is very stable. Its dissociation in water is only 8%. That's why K_C for the reaction $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ is very low (10^{-13}).

In the third case, when the value of K_C is moderate – neither very high nor very low, the reaction occurs in both the directions and equilibrium will be attained after certain period of time. For example, K_C for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 10.

6.6 FACTORS AFFECTING BALANCE OF CHEMICAL EQUILIBRIUM (Le Chatelier's Principle).

The balance of a chemical equilibrium is disturbed by changing factors such as concentration, temperature and pressure. Le Chatelier's principle enables qualitative predictions to be made about the effects of the above mentioned factors on equilibrium position. This principle was enunciated in 1884 by Le-Chatelier.

"When a constraint or stress in a direction is applied to a system in equilibrium, the equilibrium position changes so as to undo the constraint"

By the term constraint we mean the changes concentration, pressure or temperature. According to this principle, if one of the factors involved in a chemical equilibrium is altered, the equilibrium shifts towards right or left in order to restore the balance of equilibrium.

1. **Effect of Concentration Change :**

By increasing the concentration of any substance present in the equilibrium mixture, the balance is disturbed, and the equilibrium moves away from that substance in order to decrease the concentration of the added substance. This is in accordance with the Le Chatelier's principle for the reaction $A + B \rightleftharpoons C + D$.

$$K_c = \frac{[C]\,[D]}{[A]\,[B]}$$

Without changing the other conditions, K_c is constant. If, for instance, the concentration of 'A' is increased, K_c decreases. To keep K_c constant, the concentration of 'C' and 'D' increases. Thus to get high yield of products, the concentration of cheaper reactant may be greatly increased.

Change in concentration	Effect on equilibrium position $A + B \rightleftharpoons C + D$
Increase in conc. of A or B	Equilibrium shifts to right and yield of products increases.
Increase in conc. of C or D	Equilibrium shifts to left i.e. more of A and B is formed.

2. Effect of Temperature Change :

For an exothermic reaction, K_c decreases with the rise of temperature. That is to say the concentration of products decreases. For an endothermic reaction, the rise of temperature favours the high yield of products. The effect of temperature on equilibrium can be explained in the light of Le Chatelier's principle.

In an exothermic reaction, heat is evolved in going from reactants to products. Increasing the temperature is a constraint to the equilibrium which is removed by absorbing heat in going from products to the reactants. In an endothermic reaction, heat is absorbed in going from reactants to the products. Increasing the temperature is the stress to the equilibrium which is nullified by absorbing heat in going from left towards right, i.e., from reactants to the products.

Nature of Reaction $A + B \rightleftharpoons C + D$	Change in Temperature	Effect on Equilibrium
Exothermic, eg. $2NO_{(g)} + O_{2(g)} = 2NO_{2(g)}$	Increase	Equilibrium shifts to left i.e. more NO and O_2 are formed.
	Decrease	Equilibrium shifts towards right and more products are formed (yield of NO_2 increases).
Endothermic, e.g. $N_{2(g)}+O_{2(g)} \rightleftharpoons 2NO$	Increase	Equilibrium moves towards right to give high yield of products (NO)
	Decrease	Equilibrium is driven towards left and more N_2 and O_2 are present in equilibrium mixture.

3. Effect of Pressure Change :

Change of pressure is related to the change of volume. Since solids and liquids are almost incompressible, hence their volumes are very little affected by the changes in pressure. In other words, pressure will only affect gaseous equilibria in which there is a volume change. If volume is same on both sides, pressure will have no effect on equilibrium.

If a reaction proceeds with increase in volume,($2NH_3 \rightleftharpoons N_2 + 3H_2$) the increase of pressure (constraint) shifts the equilibrium towards reactant side to remove the constraint of increased pressure. This is in accordance with the Le Chatelier's principle.

If a reaction proceeds with decreasing volume (e.g. $PCl_3 + Cl_2 \rightleftharpoons PCl_5$), the increase of pressure forces the equilibrium to be driven to right hand side.

Volume involved $mA + nB \rightleftharpoons xC + yD$	Change in pressure	Effect on equilibrium position
(i) If $x + y > m + n$ volume of products is greater than reactants e.g. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$	Increase	Equilibrium moves towards left i.e., more O_3 is present in equilibrium mixture.
	Decrease	Equilibrium position moves towrds right, i.e. more O_2 is present in the equilibrium mixture.
(ii) If $x + y < m + n$ volume of products is less than the reactants. e.g. $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$	Increase	Equilibrium position is driven towards right, i.e. yield of N_2O_4 increases.
	Decrease	Equilibrium shifts towards left, i.e. N_2O_4 dissociates more and more NO_2 is present in the equilibrium mixture.
(iii) If $x + y = m + n$	No effect	

4. Effect of Catalyst on Equilibrium :

A catalyst has no effect on the equilibrium position, but it enables equilibirum to be reached more quickly by decreasing the 'energy of activation'. In fact a catalyst affects forward and reverse rates equally.

6.7 IMPORTANT INDUSTRIAL APPLICATIONS OF LE CHATELIER'S PRINCIPLE

A Chemist or a manufacturer is always ambitious in getting maximum yield of his products in the shortest possible time. For this purpose he uses the knowledge of equilibrium constant and Le Chatelier's principle to sort out the most suitable and favourable conditions under which the reaction is to be carried.

How far this knowledge is useful in various industries, is described with special reference to the synthesis of Ammonia by Haber's process and the manufacture of sulphuric acid by contact process.

EXAMPLES :

1. The Haber's Process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad (\Delta H = -46.2 \text{ KJ/mole})$$

1 Vol   3 Vol   2 Vol.

The reaction between nitrogen and hydrogen to produce ammonia is accompanied by decrease in volume and it is exothermic.

(i). Effect of concentration. If more nitrogen is added at equilibrium, according to Le-Chatelier's principle, the equilibrium is forced towards right in order to reduce the concentration of nitrogen. This increases the yield of NH_3. In actual practice, however, there is no practical advantage in using excess nitrogen or hydrogen. The two gases are mixed in the theoretical ratio of 1:3 by volume.

(ii). Effect of Temperature. Synthesis of ammonia is exothermic, that is, heat is liberated in the forward reaction. If, at equilibrium, temperature is kept low, according to Le-Chatelier's principle, the equilibrium shifts to right where heat is liberated; in this way balance of equilibrium position is maintained. In other words, the low temperature favours the formation of ammonia. The high temperature, at equilibrium, would obviously favour the reverse reaction, In actual practice, the reaction is carried out at high temperature of 450°C – 500°C which produces reduced yield at much higher rate. A catalyst of finely divided iron is used.

(iii). Effect of Pressure : The formation of ammonia proceeds with the reduction in volume (4 volumes on the reactant side and 2 volumes on the product side). The reaction, is therefore, carried out under high pressure, the equilibrium is forced to right as the formation of ammonia lowers the volume and by Le-Chatelier's principle, relieves the pressure. The pressures vary from 400 to 1000 atmospheres.

2. **Contact Process :** In Pakistan, sulphuric acid is manufactured largely by the Contact process in which the most important step is the oxidation of sulphur dioxide to sulphur trioxide in presence of catalyst vanadium pentoxide.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad (\Delta H = -395 \text{ KJ/mole})$$

2 Vol 1 Vol 2 Vol

This oxidation process is exothermic and occurs with the reduction of volume. In order to sort out suitable conditions under which high yield of SO_3 is produced, Le-Chatelier's principle is applied.

(i). Effect of Concentration: If at equilibrium position, the concentration of oxygen is increased, the Le-Chatelier's principle requires the system to react to oppose this change, that is, to reduce the concentration of oxygen. This is done with the conversion of more SO_2 to SO_3.

(ii). Effect of Temperature : If, at equilibrium, the temperature is decreased, according to Le-Chatelier's principle, the system tends to react so as to oppose the change, that is, to raise the temperature. This is achieved when more of SO_3 is produced. In actual practice, the reaction is carried out at 450°C (since a fast rate is more important than a high yield). A catalyst such as V_2O_5 is also added to speed up the reaction.

(iii). Effect of Pressure: Increasing yield of SO_3 is favoured by increased pressure (since the volume of products is less than the reactants). In practice, the reaction is carried out at one atmospheric pressure (since the volume is not large enough to justify the expense of high pressure vessel).

6.8 SOLUBILITY PRODUCT

When a saturated solution of sparingly or slightly soluble salt is in contact with undissolved salt, an equilibrium is established between the dissolved ions and the ions in the solid phase of the undisssolved salt. For example, AgCl is only very slightly soluble in water and the following equilibrium exists.

$$\underset{\text{Undissolved}}{AgCl_{(s)}} \rightleftharpoons \underbrace{Ag^{+}_{(aq)} + Cl^{-}_{(aq)}}_{\text{Dissolved}}$$

According to the equilibrium law (law of mass action),

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl_{(s)}]}$$

But at saturation, the concentration of the solid AgCl is constant

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

$$K_c \times K' = [Ag^+]\,[Cl^-]$$

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

K_{sp} is termed as the solubility product. It is the product of ionic concentration of the dissolved ions and it varies with the temperature. Similarly. For CaF_2:

$$K_{SP} = [Ca^{2+}]\,[F^-]^2$$

The solubility product is expressed in the chemical units of concentration i.e. molar concentration.

Calculation of solubility product from the solubility.

Solubilities are normally given in grams per cubic decimetre (g/dm^3) which are the physical units of concentration. The solubility of AgCl is 1.4×10^{-3} g/dm^3 at 25°C. Since the molecular mass of AgCl is 143.5, hence its solubility in terms of molarity is calculated:

$$\text{Molarity} = \frac{1.4 \times 10^{-3}}{143.5} = 0.98 \times 10^{-5} \quad \text{mole dm}^{-3}$$

Hence the concentration of Ag^+ is 0.98×10^{-5} moles dm^{-3}, the concentration of the Cl^- is also 0.98×10^{-5} mole dm^{-3} because there is one Cl^- ion for each Ag^+ ion. Now,

$$K_{SP}\ AgCl = [Ag^+]\,[Cl^-] = 0.98 \times 10^{-5} \text{ mole dm}^{-3} \times 0.98 \times 10^{-5} \text{ mol dm}^{-3}$$
$$K_{SP}\ AgCl = 0.96 \times 10^{-10} = 9.6 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

Solubility products of some salts are given in the following table:

Table 6.1 Solubility products of salts at 18° – 25°C.

Compound	Formula	Solubility product
Lead chloride	$PbCl_2$	1×10^{-4} mole^3 dm^{-9}
Lead sulphide	PbS	8.4×10^{-28} mole^2 dm^{-6}
Nickel sulphide	NiS	1.8×10^{-21} mole^2 dm^{-6}
Mercuric sulphide	HgS	3.5×10^{-52} mole^2 dm^{-6}
Copper sulphide	CuS	8.7×10^{-36} mole^2 dm^{-6}
Cobalt sulphide	CoS	3.0×10^{-26} mole^2 dm^{-6}
Calcium carbonate	$CaCO_3$	1.0×10^{-8} mole^2 dm^{-6}
Barium sulphate	$BaSO_4$	1.0×10^{-10} mole^2 dm^{-6}

Calculation of Solubility from Solubility product :

If we know the value of solubility product, we can calculate the solubility of salt. For example, the solubility product of lead iodide (PbI_2) at 25°C is 1.00×10^{-9} mol³ dm⁻⁹

$$\underset{\text{undissolved}}{PbI_{2(S)}} \rightleftharpoons \underbrace{Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}}_{\text{Dissolved}}$$

$$K_{SP} = [Pb^{2+}]\,[I^{-}]^2 = 1.00 \times 10^{-9}\ mol^3\ dm^{-9}$$

If x moles per dm³ of PbI_2 dissolve (i.e ionize),

$[Pb^{2+}] = x$ and $[I^-] = 2x$

$$K_{SP} = [Pb^{2+}]\,[I^-]^2 = 1.00 \times 10^{-9}\ mol^3\ dm^{-9}$$

or
$$(x)\,(2x)^2 = 1.00 \times 10^{-9}\ mol^3\ dm^{-9}$$
$$4x^3 = 1.00 \times 10^{-9}\ mol^3\ dm^{-9}$$
$$x = 0.63 \times 10^{-3}\ mol\ dm^{-3}\ PbI_2 \text{ dissolved.}$$

Molecular mass of PbI_2 = 461 moles per dm³ is converted into g/dm³ (Chemical units into physical unit of concentration) as follows:

$$\text{Moles.} = \frac{\text{Mass in g}}{\text{molecular mass}}$$

$$\therefore \text{ Mass in g} = \text{moles} \times \text{molecular mass}$$
$$= 0.63 \times 10^{-3} \times 461$$
$$= 0.00063 \times 461$$
$$= 0.29\ g$$

Solubility of PbI_2 at 25°C = 0.29 g/dm³.

Application of Solubility Product :

The solubility product (K_{sp}) is used to determine whether a precipitate should form from a solution of known ionic concentrations. The value of solubility product represents the equilibrium condition between the dissolved ions and undissolved solid phase of solute i.e. when a solution is saturated.

When the product of the ionic concentrations is equal to the solubility product, a saturated solution is said to exist. If the ionic product is less than the solubility product, the solution is not saturated i. e. more amount of the solute can go in to the solution. If the ionic product is larger than the solubility product, the solution is said to be super saturated and the excess of solute should precipitate so as to restore the equilibrium conditions. For example, the solubility product of calcium sulphate solution is 2.4 x 10^{-5} mole/dm^3.

$$CaSO_{4(S)} \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4\ (aq)}$$

$$K_{SP} = [Ca^{2+}]\,[SO_4^{2-}] = 2.4 \times 10^{-5}$$

If,

$$[Ca^{2+}]\,[SO_4^{2-}] > 2.4 \text{ X } 10^{-5}$$

$CaSO_4$ would form precipitates so as to reach the value of 2.4 x 10^{-5}. If, on the other hand,

$[Ca^{2+}]\,[SO_4^{2-}] < 2.4 \times 10^{-5}$ it means the solution is not saturated and more solute could go into the solution till the product becomes equal to 2.4 x 10^{-5}.

Problem :

Should $PbCrO_4$ precipitate from a solution prepared by mixing 100 cm^3 of 2.5 x 10^{-4} M Pb (NO_3) and 300 cm^3 of 1.5 x 10^{-8} M K_2CrO_4? (K_{SP} of $PbCrO_4$ = 1.8 x 10^{-14}).

Solution:

The equation for the equilibrium is:

$$\underset{\text{Undissolved}}{PbCrO_{4(S)}} \rightleftharpoons Pb^{2+}_{(aq)} + \underset{\text{Dissolved}}{CrO_4{}^{2-}{}_{(aq)}}$$

$$K_{SP} = [Pb^{2+}]\,[CrO_4^{2-}] = 1.8 \times 10^{-14}$$

Total volume of the solution = 100 cm³ + 300 cm³ = 400 cm³. This volume contains the equivalent of 100 cm³ $Pb(NO_3)_2$ and 300 cm³ of K_2CrO_4. The concentration of each ion is calculated:

$$[Pb^{2+}] = \left(\frac{100cm^3\ Pb(NO_3)_2}{400\ cm^3\ \text{Total solution}}\right) \times 2.5 \times 10^{-4} M = 6.25 \times 10^{-5} M$$

$$[CrO_4^{2-}] = \left(\frac{300Cm^3\ K_2CrO_4}{400\ cm^{-3}\ \text{Total solution}}\right) \times 1.5 \times 10^{-8} M = 1.125 \times 10^{-8} M$$

The ionic product of $PbCrO_4$ is:

$[Pb^{2+}]\ [CrO_4^{2-}] = (6.25 \times 10^{-5})\ (1.125 \times 10^{-8}) = 7.03 \times 10^{-13}$

Since the ionic product (7.03×10^{-13}) is larger than the solubility product (1.8×10^{-14}), hence $PbCrO_4$ should precipitate out from the solution.

6.9 COMMON ION EFFECT

The equilibrium law can be applied to sparingly soluble salts such as AgCl. It is very slightly soluble in water and the following equilibrium exists between the solid ionic salt and its ions in the aqueous phase.

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

The decrease in the solubility of the salt in a solution that already contains an ion common to that salt, is called common ion effect.

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

Since the concentration of solid AgCl is constant in its saturated solution, hence

$$K_c[AgCl] = K_{sp} = [Ag^+][Cl^-]$$

K_{sp} is known as the solubility product which is equal to the product of the ionic concentration. Similarly, for magnesium chloride ($MgCl_2$).

$$K_{sp} = [Mg^{2+}][Cl^{1-}]^2$$

Precipitation of an electrolyte is caused when the concentration of its ions exceeds the solubility product. It is achieved by increasing the concentration of any one of the ions. That is to say, by adding common ion, solubility product can be exceeded. For example, precipitation of AgCl is caused by adding Cl^- as common ion in the shape of NaCl. With the addition of common ion, either Cl^- or Ag^+, the ionization of AgCl is suppressed and it forms precipitate. This is known as common ion effect.

$$\left.\begin{array}{l} AgCl_{(S)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)} \\ KCl_{(S)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)} \end{array}\right\} \text{ Common ion } (Cl^-)$$

Common ion effect finds useful application in qualitative salt analysis.

EXAMPLE : Cations of II and IV groups are precipitated as sulphides but under different conditions due to their different solubility products. In fact the solubility product of IV group sulphides is higher than that of II group sulphides.

TABLE – SOLUBILITY PRODUCTS AT 18°C

SULPHIDES OF II GROUP	SULPHIDES OF IV GROUP
PbS 3.4×10^{-28}	MnS 1.4×10^{-16}
CdS 3.6×10^{-29}	ZnS 1.2×10^{-23}
CuS 8.5×10^{-45}	NiS 1.4×10^{-24}
HgS 4.1×10^{-54}	CoS 3×10^{-26}

In order to precipitate the sulphides of II group, H_2S is passed through the original solution (O.S.) in presence of HCl.

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

HCl furnishes H^+ as common ions which shift the above equilibrium to left according to Le-Chatelier's principle. In other words, addition of HCl suppresses the ionization of H_2S there by lowering the concentration of sulphide ion (S^{2-}) which is however just enough to exceed the solubility product of II group sulphides. In this way group II cations are precipitated such as CuS, PbS, CdS etc.

IV group sulphides having higher solubility product are precipitated by H_2S in presence of NH_4OH. The OH^- of NH_4OH combines with H^+ of H_2S to form H_2O ($H^+ + OH^- \rightarrow H_2O$). The removal of H^+ from the product side shifts the equilibrium to right ($H_2S \rightleftharpoons 2H^+ + S^{2-}$). In this way, the concentration of sulphide ion (S^{2-}) increases which is enough to exceed the solubility product for the precipitation of sulphides, e.g. CoS, NiS, ZnS.

Group III cations are precipitated as hydroxides by NH_4OH in presence of NH_4Cl. The common ion in this case is NH_4^+ which suppresses the ionization of NH_4OH

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Thus with the addition of common ion (NH_4^+) the equilibrium is shifted towards left and the concentration of OH^- decreases. Under these conditions, the solubility product of the hydroxides of Al, Fe and Cr is only exceeded due to which they are precipitated. The hydroxides of other cations such as Zn, Ni, Co etc. are not precipitated due to their higher solubility product.

In addition to salt analysis, common ion effect is very useful in industries also. Chemical yields in manufacturing processes can be controlled and greatly increased by making use of common ion effect.

The common ion effect changes the equilibrium point of a reaction from a less to a more favourable position.

PROGRESS TEST 6

1. What are reversible and irreversible changes? Describe an experiment to demonstrate a reversible change.

2. (a) State and explain the law of equilibrium. Describe its applications.
   (b) What do you understand by K_c and K_p? Describe their relationship.

3. What is meant by solubility product and the common ion effect. Discuss the application of common ion effect in the qualitative salt analysis.

4. How is the balance of chemical equilibrium influenced? Explain giving examples.

5. For the gaseous equilibrium $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}; \Delta H = 87.9$ KJ/mole, explain the effect upon the material distribution of (a) increased temperature (b) increased pressure (c) higher concentration of Cl_2 (d) higher concentration of PCl_5 (e) presence of a catalyst.

6. A quantity of PCl_5 was heated in a 12 dm³ vessel at 250°C.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

At equilibrium, the vessel contains 0.21 mole PCl_5, 0.32 mole PCl_3 and 0.32 mole Cl_2. Compute the equilibrium constant K_c. ($K_c = 0.040$) Ans.

7. Consider the following equilibria:

(i) $3O_{2(g)} \rightleftharpoons 2\,O_{3(g)}$ ΔH = positive
(ii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ ΔH = positive
(iii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ ΔH= negative

(a) Write the equilibrium constant expressions.
(b) In which direction will each equilibrium change as the temperature is raised?
(c) Which of the equilibria will not be affected by change in total pressure?

8. One mole of HI is introduced into a vessel held at constant temperature. When equilibrium is reached, it is found that 0.1 mole of I_2 have been formed. Calculate the equilibrium constant K_c. ($K_c = 0.0125$) Ans.

9. What effect on the position of equilibrium $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ for which $\Delta H = +176 KJ/mole$, does each of the following changes have: (a), adding $CaCO_3$ (b), adding CaO (c), decreasing the volume of the container (d), raising the temperature (e) removing CO_2.

10. State Le-Chatelier's principle. What are its industrial applications?

11. Write note on : (i) Reversibility of a chemical change (ii) dynamic equilibrium (iii), K_c and K_p.

12. When 1 mole of pure ethyl alcohol (C_2H_5OH) is mixed with 1 mole of acetic acid (CH_3COOH) at room temperature, the equilibrium mixture contains $^2/_3$ mole each of ester ($CH_3COOC_2H_5$) and water. (a), What is the equilibrium constant K_c, (b) how many moles of ester are formed at equilibrium when 3 moles of alcohol are mixed with 1 mole of acid? All substances are liquids at room temperature. (a) Kc = 4; (b) ester = 0.9 moles Ans.

solution for (b) Let x = no. of moles of alcohol reacting.

	Alcohol +	Acid $\rightleftharpoons$	Ester +	water
No. of moles at initial state	3	1	NIL	NIL
Change by reaction	$-x$	$-x$	$+x$	$+x$
No. of moles at equilibrium state	$(3-x)$	$(1-x)$	x	x
Concentration at equilibrium state	$\frac{(3-x)}{V}$	$\frac{(1-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = 4 = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{3-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{3-4x+x^2}$$

$x^2 = 4(3-4x+x^2)$ or $3x^2 - 16x + 12 = 0$. Solving by quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a} = \frac{+16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2\,(3)} = \frac{16 \pm 10.6}{6}$$

$x = 4.433$ or $x = 0.9$

In the problem we started with 3 moles alcohol and one mole acid, hence we cannot form more than one mole ester even if all the acid is used up. Therefore correct root of quadratic is 0.9, that is, 0.9 mole ester is produced.

13. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Calculate the number of moles of Cl_2 produced at equilibrium when one mole of PCl_5 is heated at 250°C in a vessel having a capacity of 10 dm³. At 250°C, $K_C = 0.041$ for the dissociation.
(0.465 moles) Ans.

14. (a) What is meant by the equilibrium constant and how it is determined experimentally?

(b) To determine the value of K_C for the reaction $CH_3COOH_{(l)} + C_2H_5\,OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$ 1 mole of $CH_3\,COOH$ and 1 mole of $C_2H_5\,OH$ in 1 dm³ of solution in an inert solvent containing a small amount of acid catalyst were warmed until no further change occurred. At equilibrium, 0.667 mole of water was present. Calculate the value of K_C.
($K_C = 4$) Ans.

15. "At equilibrium all processes come to a halt." What is wrong with this statement when applied to chemical systems?

16. (a) What is meant by the solubility product? Give its uses.

(b) What is the solubility of lead chromate in moles per dm³ at 25°C. K_{SP} for $PbCrO_4 = 2.8 \times 10^{-13}$ mole/dm³

17. (a) Will Cadmium hydroxide precipitate from 0.01M solution of $CdCl_2$ at pH 9. K_{SP} of $Cd(OH)_2 = 2.5 \times 10^{-14}$ mole³/dm⁶. (Since ionic product of $Cd(OH)_2$ is greater than K_{SP} so it will precipitate).

(b) The solubility of $Mg(OH)_2$ at 25°C is 0.00764 g/dm³. What is the solubility product of $Mg(OH)_2$? ($K_{SP} = 9.0 \times 10^{-12}$ mole³/dm⁹) Ans.

Should AgCl precipitate from a solution prepared by mixing 400 ml of 0.1M NaCl and 600 ml of 0.03 M $AgNO_3$?
K_{SP} of $AgCl = 1.6 \times 10^{-10}$ moles/dm³. (Ionic product is larger than K_{SP} AgCl will precipitate). Ans.