Chapter 6 Chemical Equilibrium

Multiple Choice Questions (M.C.Qs)

Choose the correct answer for each the given option:

01 **When the product of ionic concentration of sparingly soluble salt is equal to its solubility product (K_{sp}) the solution is said to be a:**

(a) dilute (b) saturated (c) supersaturated (d) very dilute

02 **For the reaction $2NH_3 \longrightarrow N_2 + 3H_2$, choose the correct K_c expression:**

(a) $K_C = \frac{[2NH_3]}{[N_2][3H_2]}$ (b) $K_C = \frac{[N_2][H_2]^3}{[NH_3]^2}$ (c) $K_C = \frac{[N_2][3H_2]}{[2NH_3]}$ (d) $K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

03 **Precipitation occurs if the ionic concentration is:**

(a) less than K_{sp} (b) more then K_{sp} (c) equal to K_{sp} (d) none of these

04 **For the reaction $2NH_3 \longrightarrow N_2 + 3H_2$, the relationship between K_c and K_p is:**

(a) $K_p = K_c$ (b) $K_p > K_c$ (c) $K_p < K_c$ (d) $K_p \leq K_c$

05 **If K_c is very small:**

(a) reverse reaction will occur (b) forward reaction will take place
(c) more products will be formed (d) equilibrium has been attained

06 **Which of the reaction has the same value of K_C and K_p ?**

(a) $N_2 + 3H_2 \longrightarrow 2NH_3$ (b) $H_2 + I_2 \longrightarrow 2HI$
(c) $PCl_5 \longrightarrow PCl_3 + Cl_2$ (d) $2SO_2 + O_2 \longrightarrow 2SO_3$

07 **The solubility product (K_{sp}) of AgCl is 1×10^{-10} mole^2 dm^{-6}. Its precipitation occurs if the product of ionic concentration is:**

(a) less then K_{sp} (b) greater then K_{sp} (c) equal to K_{sp} (d) twice of K_{sp}

08 **For the reaction: $2SO_{2\,(g)} + O_{2(g)} \longrightarrow 2SO_3$:**

(a) $K_p = K_c$ (b) $K_p < K_c$ (c) $K_p > K_c$ (d) None of them

09 **Chemical reaction which proceed in both forward and backward directions under the given conditions are called:**

(a) reversible reaction (b) irreversible reaction
(c) substitution reaction (d) decomposition reaction

10 **For the reaction: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the unit for K_c is:**

(a) dm^5 mol^{-2} (b) mol^2 dm^{-6} (c) mol dm^{-3} (d) No unit

11 ***Increase of temperature increases the rate of reaction due to:***
(a) shortening of mean free path *(b) lowering of activation energy.*
(c) increase in number of collision of the molecule
(d) decrease in number of activated molecule

12 ***The concentration is an expression of the equilibrium constants are given in units of :***
(a) mol / ml *(b) g / l* *(c) gram equivalent/l* *(d) moles / l*

13 ***Precipitation and neutralization reactions are:***
(a) reversible *(b) irreversible* *(c) homogeneous* *(d) heterogeneous*

14 ***Active mass of a substance is equal to:***
(a) molar concentration *(b) molal concentration*
(c) normal concentration *(d) None of the above*

15 ***K_c is symbol for:***
(a) rate constant *(b) equilibrium constant*
(c) gas constant *(d) Planck's constant*

16 ***When a rate for forward reaction is equal to the rate of backward reaction then the chemical equilibrium established which is a:***
(a) neutral equilibrium *(b) static equilibrium*
(c) dynamic equilibrium *(d) none of these*

17 ***Alcohols and acids react to from water and:***
(a) halides *(b) esters* *(c) amines* *(d) ketones*

18 ***Very small value of K_c indicates:***
(a) high yield *(b) low yield* *(c) moderate yield* *(d) no yield*

19 ***Very large value of K_c indicates that the reaction is:***
(a) partially completed *(b) incomplete*
(c) almost completed *(d) tends to complete*

20 ***Le Chatelier's principle is connected with:***
(a) catalysis *(b) photolysis* *(c) photosynthesis* *(d) chemical equilibrium*

21 ***Considering the following reaction*** $2SO_2 + O_2 \longrightarrow 2SO_3$ ΔH = - ve ***the yield of SO_3, will be maximum if :***
(a) temperature is increased pressure kept constant
(b) temperature is reduced, pressure increased
(c) temperature and pressure are both increased
(d) temperature and pressure are both decreased

22 ***The ionization of NH_4OH is suppressed by adding:***
(a) NaCl *(b) HCl* *(c) NH_4OH* *(d) NH_4Cl*

23 ***Le Chatlier's principle applied to a:***
(a) reversible reaction *(b) irreversible reaction*
(c) none of these *(d) both A & B*

24 ***At the equilibrium:*** $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ ΔH = + ve
The concentration of $Cl_{2(g)}$ at equilibrium will be increased by:
(a) lowering of temperature *(b) adding PCl_3 to the mixture*
(c) adding PCl_5 to the mixture *(d) increasing the pressure*

Chemical Equilibrium

25 ***The process in which ionization of an electrolyte is suppressed by the addition of another strong electrolyte containing one same ion is termed as:***
(a) electrolysis (b) hydrolysis (c) hydration (d) common ion effect

26 ***If the volume of reactants and product are same the equilibrium is not affected by:***
(a) temperature (b) pressure (c) concentration (d) None

27 ***When*** $\frac{[Product]}{[Reactant]} < K_c$ ***then reaction will proceed in:***
(a) reverse direction (b) forward direction (c) equilibrium (d) none

28 ***The law of mass action was given by:***
(a) Arrhenius (b) Vant Hoff (c) Berthelot (d) Guldberg & Waage

29 ***For the reaction*** $A + B \rightleftharpoons C + D$, ***the increase in concentration of "A" will shift the reaction in:***
(a) forward direction (b) backward direction (c) equilibrium state (d) none

30 ***For the reaction:*** $N_2 + O_2 \rightleftharpoons 2NO \quad \Delta H = +ve$ ***to get maximum yield of product the temperature should be:***
(a) increased (b) decreased (c) remain the same (d) none of them

31 ***For the reaction,*** $H_2 + I_2 \rightleftharpoons 2HI$, ***if volume is reduced to half, the value of*** K_c ***will be:***
(a) become half (b) become double (c) increase 4 times (d) not changed

32 ***For a reversible reaction if the concentration of the reactants are doubled, the equilibrium constant is:***
(a) halved (b) also doubled
(c) ¼ of the original volumes (d) not changed

33 ***Solubility of*** $KClO_3$ ***can be decreased in*** H_2O ***by:***
(a) adding KCl from outside (b) adding $NaNO_3$ *from outside*
(c) by removing K^+ *ions from solution (d) by removing* ClO_3 *ion from solution*

34 ***Precipitate will form when the product of ionic concentration:***
(a) exceed their solubility product (b) is less than solubility product
(c) is equal to solubility product (d) none of the above

35 $3O_2 \rightleftharpoons 2O_3, \quad \Delta H = +ve$
In which direction will reaction proceed when temperature is raised?
(a) forward (b) backward (c) remain the same (d) none of the above

36 ***In the equilibrium reaction:*** $AgCl \rightleftharpoons Ag^+ + Cl^-$, ***if AgCl is added to the solution of AgCl, then equilibrium will:***
(a) shift towards left (b) shift towards right (c) not disturbed (d) slightly disturbed

37 ***Which of the following reaction is reversible endothermic?***
(a) $2SO_2 + O_2 \rightleftharpoons 2SO_3 + heat$ *(b)* $N_2 + O_2 + heat \rightleftharpoons 2NO$
(c) $CuSO_4 + Fe \rightleftharpoons FeSO_4 + Cu$ *(d) None of above*

38 ***In which of the following case does the reaction go fastest to completion?***
(a) $K_c = 10^5$ *(b)* $K_c = 10^{-2}$ *(c)* $K_c = 10$ *(d)* $K_c = 1$

39 ***Synthesis of ammonia gas requires :***
(a) removal of hydrogen (b) low temperatures
(c) low pressure (d) addition of catalyst

40 ***In which of the following reaction increase in pressure favours the products?***

(a) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ (b) $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$

(c) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ (d) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_3$

41 ***An electrolyte is precipitated from its solution when the concentration of its ions exceeds the:***

(a) pressure (b) volume (c) density (d) solubility product

42 ***The value of K_c is independent of :***

(a) initial concentration of reactants (b) volume

(c) catalyst (d) pressure

43 ***At equilibrium, the concentration of reactants and product becomes:***

(a) equal (b) different (c) constant (d) same

44 ***Equilibrium constant of a reaction is equal to:***

(a) $K_c = \frac{[Reactant]}{[Product]}$ (b) $K_c = \frac{[Product]}{[Reactant]}$

(c) $K_c = \frac{[Mass]}{[Volume]}$ (d) $K_c = \frac{[Density]}{[Volume]}$

45 ***When the ionic product is less than the K_{sp}, the solution will be:***

(a) unsaturated (b) saturated (c) ionic (d) super saturated

Answer Key

1. (b)	8. (b)	15. (b)	22. (d)	29. (a)	36. (a)	43. (c)
2. (b)	9. (a)	16. (c)	23. (a)	30. (a)	37. (b)	44. (b)
3. (b)	10. (d)	17. (b)	24. (c)	31. (d)	38. (a)	45. (a)
4. (b)	11. (c)	18. (b)	25. (d)	32. (d)	39. (b)	
5. (a)	12. (d)	19. (c)	26. (b)	33. (a)	40. (d)	
6. (b)	13. (b)	20. (d)	27. (b)	34. (a)	41. (d)	
7. (b)	14. (a)	21. (b)	28. (d)	35. (a)	42. (a)	

Short / Detailed Answer Questions

Q.01 ***Describe irreversible reaction.*** ***Karachi Board: 2005***

Ans. The reaction which proceed to completion when stoichiometric amounts of reactants are taken are called irreversible reaction. These reaction take place in one direction only.

$$A + B \longrightarrow C + D$$

For example:

$$2H_{2(g)} + O_{2(g)} \xrightarrow[\text{spark}]{\text{Electric}} 2H_2O_{(l)}$$

Q.02 ***Describe reversible reactions.*** ***Karachi Board: 2008***

Ans. The reactions which do not proceed to completion are called reversible reactions. These reaction take place both in the forward and backward directions.

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

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

Q.03 ***What is chemical equilibrium? Illustrate it with the help of graph.***

Ans. The state of a reversible reaction at which composition of the reaction mixture does not change is called state of chemical equilibrium.

Consider the following general reversible reaction to illustrate the state of chemical equilibrium.

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

Let the initial concentration of A & B are equal. A reacts with B to produce C and D. As the reaction proceeds concentration of both A and B first rapidly, then slowly and finally their concentration stop to decrease. Similarly concentrations of both C and D increase first rapidly, then slowly and finally their concentration stop to increase. As the composition of the reaction mixture does not change at this state, so it is the state of equilibrium.

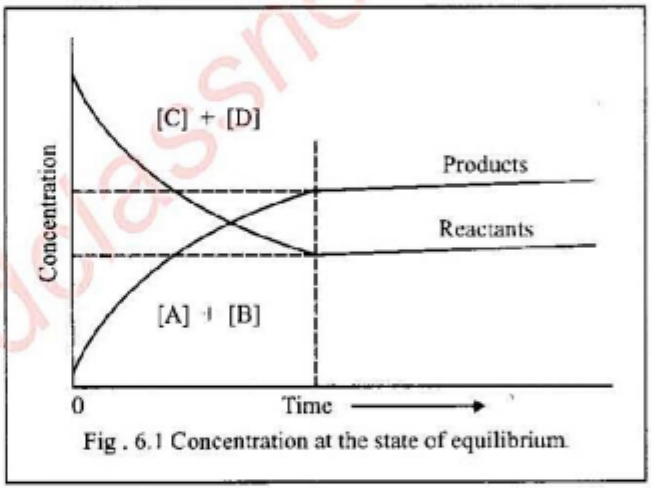

Fig . 6.1 Concentration at the state of equilibrium

Q.04 ***State law of mass action. What is its significance?*** ***Karachi Board: 2008, 2014, 2018***

Ans. ***This law was derived by Gulbberg and Waage in 1864.***

Statement of the Law: This law is stated as "the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants".

Significance: This law helps to determine the concentration of the reactants and products at the equilibrium state.

Q.05 ***What is active mass?***

Ans. The term active mass represents the concentration in mole dm^{-3} of the reactants and the products for a dilute solution.

Q.06 ***State the law of mass action & derive the equilibrium constant for the following reaction:*** $mA + nB \rightleftharpoons xC + yD$ ***Karachi Board: 2007, 2008, 2014, 2018***

Ans. The rate at which a substance reacts is directly proportional to the multiplication of active masses of the reacting substance at constant temperature.

Chemical Equilibrium

The rate at which a substance reacts is directly proportional to the multiplication of active masses of the reacting substance at constant temperature.

Explanation: Law of mass action can be explained on the basis of collision theory which tells that the chemical change occurs due to the effective collision of reacting molecules.

The rate of a forward reaction is directly proportional to the concentration of reactants and the rate of backward reaction is directly proportional to the concentration of product.

Derivation of Equilibrium Constant:

Consider the following general reversible reaction

$$mA + nB \longrightarrow xC + yD$$

Rate of forward reaction $\propto [A]^m [B]^n = K_f [A]^m [B]^n$ ..... (i)

Rate of forward reaction $\propto [C]^x [D]^y = K_r [C]^x [D]^y$ ..... (ii)

Since at equilibrium state:

Rate of forward reaction = Rate of backward reaction

$$K_f [A]^m [B]^n = K_r [C]^x [D]^y$$

On re-arranging:

$$\frac{K_f}{K_r} = \frac{[C]^x [D]^y}{[A]^m [B]^n} \quad \left[\frac{K_f}{K_r} = K_c\right]$$

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

The above equation is known as equilibrium constant expression and K_c is known as equilibrium constant in which active masses of products are placed in the numerator while those of the reactants would be written as denominator.

Q.07 ***Write K_c expression for the following reaction:***

(i) $CaCO_3 \rightleftharpoons CaO + CO_2$ ***(ii)*** $N_2 + 3H_2 \rightleftharpoons 2NH_{3(g)}$

(iii) $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$ ***(iv)*** $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Karachi Board: 2004, 2005, 2006

Ans.

(i) $CaCO_3 \rightleftharpoons CaO + CO_2$

$$K_c = \frac{[CaO]\ [CO_2]}{[CaCO_3]}$$

(ii) $N_2 + 3H_2 \rightleftharpoons 2NH_{3(g)}$

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

(iii) $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$

$$K_c = \frac{[BiOCl]\ [HCl]^2}{[BiCl_3]\ [H_2O]}$$

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\ [O_2]}$$

Q.08 ***Explain relation between K_c and K_p.*** ***Karachi Board: 2013***

Ans. ***Relationship between K_c & K_p:***

(i) ***$K_p = K_c$:*** If there is no change in the volume of reactant and product, then the value of $K_p = K_c$.

e.g. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$
1 vol 1 vol 2 vol

(ii) $K_p > K_c$: If the reaction occurs with increase in volume of product, then the value of K_p is greater than K_c.

e.g. $2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$
2 vol 1 vol 3 vol

(iii) $K_p < K_c$: If the reaction occurs with decrease in volume of product, then the value of K_p is smaller then K_c.

e.g. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
2 vol 1 vol 2 vol

Q.09 ***Apply the equilibrium constant expression for the formation of ester from an organic acid and alcohol.***

Ans. ***Formation of ester from an organic acid and alcohol:*** Acetic acid reacts with ethyl alcohol to form ethyl acetate (an ester) and water.

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_{5(aq)} + H_2O_{(l)}$$

Let 'a' moles of CH_3COOH and 'b' moles of C_2H_5OH are allowed to react in the presence of a mineral acid used as a catalyst. To determine the equilibrium concentrations of the reactants and products, a small portion of the reaction mixture is withdrawn and titrated against standard solution of NaOH to determine the moles of un-reacted CH_3COOH. After regular interval small portion of the reaction mixtures are withdrawn and titrated till constant moles of un-reacted CH_3COOH is obtained which is represented by (a-x) moles i.e., the moles of un-reacted CH_3COOH at equilibrium state. From this moles of C_2H_5OH, $CH_3COOC_2H_5$ and H_2O at equilibrium state an calculated which are (b-x), x and x moles respectively. Moles of the reactants and products at equilibrium state are divided by the volume "V" of the reaction mixture to get their equilibrium concentration, which are substituted in equilibrium constant expression to calculate the value of K_c.

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftharpoons CH_3COOC_2H_5 + H_2$$
'a' mol 'b' mol 0 mol 0 mol

No. of moles at equilibrium state = a - x mol, b - x mol, x mol, x mol

Concentration at equilibrium state = $\frac{a-x}{v}$, $\frac{b-x}{v}$, $\frac{x}{v}$, $\frac{x}{v}$

On applying the law of mass action, we get:

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

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{a-x}{v}\right)\left(\frac{b-x}{v}\right)} = \frac{\left(\frac{x^2}{v^2}\right)}{\frac{(a-x)(b-x)}{v}}$$

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

It is clear from the above expression that volume "V" of the reaction has no effect on the equilibrium position.

Q.10 ***Determine the equilibrium constant in hydrogen iodide.***

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

Ans. Consider the reaction:

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

Suppose there are (a) moles/dm³ of hydrogen and (b) moles/dm³ of iodine kept in a closed vessel (volume 'v') at 445°C. In order to fix he equilibrium established, the equilibrium is cooled. Suppose the amount of hydrogen consumed in at equilibrium is (x) moles / dm³ and the amount of un-reacted hydrogen at equilibrium is (a-x) moles / dm³.

When the 2x moles / dm³ of HI are obtained, the equilibrium constant K_c is calculated as follows:

	$H_{2(g)}$ +	$I_{2(g)}$ ⇌	$2HI_{(g)}$
No. of moles at initial state:	a	a	nil
No. of moles at equilibrium state:	(a - x)	(b - x)	(2x)
Concentration at equilibrium state:	$\frac{(a-x)}{v}$	$\frac{(b-x)}{v}$	$\frac{(2x)}{v}$

By the law of mass action:

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

$$K_c = \frac{4x^2}{(a-x)(b-x)}$$

Q.11 ***What are the applications of law of equilibrium? Explain with examples.***

Ans. ***Karachi Board: 2010***

Law of equilibrium predicts the following:

(i) Direction of the reaction.
(ii) Extent of the reaction.
(iii) Effect of change in concentration, pressure and temperature on the equilibrium position.

(i) K_c predicts the direction of the reaction:

Consider the following reversible reaction

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

Calculate the following ratio and then compare it with the value of K_c of the reaction.

$$\text{Ratio} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- If ratio < K_c then reaction will proceed towards the forward direction till the establishment of equilibrium state.
- If rate > K_c then reaction will proceed towards the backward direction till the establishment of equilibrium state.
- If ratio = K_c then reaction is at equilibrium state, and will proceed in both direction with equal rates.

(ii) ***K_c predicts the extent of the reaction:***

Larger the value of K_c, larger would be extent of the reaction.

(a) The large value of K_c of the following reaction indicates that O_3 decomposes to very large extant to O_2. It means that at equilibrium state, concentration of O_2 would be very large as compared to that of O_3.

e.g. $2O_3 \rightleftharpoons 3O_{2(g)}$ $K_c = 10^{55}$ at 25°C

such reactions proceed near to completion.

(b) The small value of K_c of the following reaction indicates that HF decomposes to very small extent to H_2 and F_2. It means that at equilibrium state concentration of H_2 and F_2 would be very small as compared to that of HF.

e.g., $2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ $K_c = 10^{-13}$ at 2000°C

such reactions do not proceed appreciably in the forward direction.

(c) The value of K_c is neither very large nor very small. This indicates that the reaction occurs in both directions and the equilibrium will be attained after certain period of time.

e.g., $N_{2(g)} + 3H_2 \rightleftharpoons 2NH_{3(g)}$ $K_c = 10$ at 300°C

Q.12 ***State Le-Chatelier's principle and give its significance.***

Karachi Board: 2007-2008-2009-2013-2015-2017-2019

Ans.

This principle was stated by Le-Chatelier's in 1884, It is a general principle with the help of which we can predict the influence of change in temperature, pressure or concentration on a system in equilibrium.

Statement: If a systems in equilibrium is subjected to stress the equilibrium position changes so as to minimize the effect of stress.

Significance: Le-Chatelier's principle predicts the effect of changes on equilibrium systems. It predicts:

(i) the effect of change in concentrations.
(ii) the effect of change in pressure
(iii) the effect of change in temperature.

Q.13 ***Describe the effect of change in concentration in different manners by applying Le-Chatelier's principle.***

Ans. ***Effect of change in concentration by applying Le-Chatelier's principle:***

Consider the following reaction:

$$N_2O_4 \rightleftharpoons 2NO_{2(g)}$$

Four possibilities are there to explain the effect when the reaction is at equilibrium.

(i) ***Addition of the reactant i.e., N_2O_4:***

This will cause to increase the concentration of N_2O_4 which will disturb the equilibrium. According to Le-Chatelier's principle, effect of increase in concentration of N_2O_4 will be nullified by the decrease in the concentration of N_2O_4. To do so position of equilibrium will shift to the right to re establish equilibrium.

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

(ii) ***Removal of the reactant i.e., N_2O_4:***

This will cause to decrease the concentration of N_2O_4 which will disturb the equilibrium. This effect of decrease in concentration of N_2O_4 will be adjusted by the increase in concentration of N_2O_4. To do so the position of equilibrium will shift to the left direction to re-establish equilibrium.

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$$

(iii) ***Addition of the product i.e., NO_2:***

This will cause to increase the concentration of NO_2 which will disturb the equilibrium. According to Le-Chatelier's principle, effect of increase in concentration of NO_2 can be adjusted by the decrease in the concentration of NO_2. To do so, the equilibrium will shift to the left and the reaction will more in the backward direction to re-establish equilibrium.

$$N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$$

(iv) ***Removal of the product i.e., NO_2:***

This will cause to decrease the concentration of NO_2 which will disturb the equilibrium. According to Le-Chatelier's principle, effect of decrease in concentration of NO_2 will be removed by the increase in the concentration of NO_2. To do so the position of equilibrium will shift to the right i.e. the reaction will move in the forward direction to re-establish equilibrium.

Q.14 ***Discuss the effect of increase in temperature and pressure on the following systems at equilibrium:***

(a) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3 + heat$

(b) $N_{2(g)} + O_2 + heat \rightleftharpoons 2NO_{(g)}$ ***Karachi Board: 2012***

Ans. *(a)* $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3 + heat.$

Solution: It in an exothermic reaction. On increase in temperature reaction will shift in backward direction. Volume of product are less than the reactants, so if we increase the pressure, reaction will shift in forward direction and if we decrease the pressure reaction will shift in backward direction.

(b) $N_{2(g)} + O_2 + heat \rightleftharpoons 2NO_{(g)}$

Solution: It is an endothermic reaction. On increase in temperature, reaction will shift in forward direction and on decrease the temperature the reaction will shift in backward direction. As the volume of reactant and product are same so there is no effect of pressure.

Q.15 ***Describe the effect of change in pressure or volume by applying Le-Chateliers principle.***

Ans. ***Effect of change in pressure be applying Le-Chatelier's principle:***

A change of pressure in gaseous systems at equilibrium affects the yield of product. In such reaction when pressure is increased, their position of equilibrium shift in the direction having less number of moles.

Note: A change of pressure on the system, containing only liquids and solids, has virtually no effect on the position of equilibrium.

There are three types of reactions, which show the effect of pressure change:

(i) ***When the number of moles of reactants are greater:***

In these reactions with the increase of pressure more products are formed. Consider the following reaction:

$$\underbrace{N_{2(g)} + 3H_{2(g)}}_{\text{4 moles}} \rightleftharpoons 2NH_{3(g)}$$

According to this reaction the increase will shift the equilibrium towards right and hence more ammonia will form.

(ii) ***When the number of moles of reactants are lesser:***

In these reactions, the increase of pressure will result in the backward reaction. Consider the following reaction:

$$\underset{\text{1 mole}}{N_2O_{4(g)}} \rightleftharpoons \underset{\text{2 moles}}{2NO_{2(g)}}$$

In such reaction the increase in pressure does not favour the formation of product.

(iii) ***When the number of moles of reactants and the products are same:***

In these reactions the change in pressure does not change the state of equilibrium. Consider the following reaction:

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

Thus in the above equation it in clear that increase of pressure does not affect the yield of product HI, and hence no change in equilibrium is taken place.

Q.16 ***Describe the effect of change in temperature by applying Le-Chatelier's principle.***

Ans. Changes in the concentration of reactants and products affect only the position of equilibrium whereas change in temperature not only affect the position of equilibrium but also the equilibrium constant.

(a) Endothermic reactions are favoured by the increase in temperature. In such reactions the value of K_c increases with the increase in temperature.

(b) Exothermic reaction are favoured by the decrease in temperature. In such reactions the value of K_c increase with the decrease in temperature.

(i) ***Effect of temperature on the formation of NO_2:***

$$N_2O_{4(g)} + \text{heat} \rightleftharpoons 2NO_{2(g)}$$

It is an endothermic reaction, heat is consumed as the N_2O_4 is consumed. When heat is added by increasing temperature, it disturbs equilibrium. According to Le-Chatelier's principle, the effect of increase in temperature will be set by consumption of heat. To do so the reaction will move in the forward direction to re-establish the equilibrium.

(ii) ***Effect of temperature on the formation of N_2O_4:***

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)} + \text{heat}$$

It is an exothermic reaction. Heat is produced as one of the product. When heat is removed by decreasing temperature, it disturb equilibrium. According to Le-Chatelier's principle, the effect of decrease in temperature will be adjusted by evolution of heat. To do so the reaction will move in the forward direction to re-establish the equilibrium. In other words decrease in temperature favoured the formation of N_2O_4. However, at low temperature much time is required to establish equilibrium.

Q.17 ***Briefly describe the effect of catalyst on equilibrium constant by applying Le-Chatelier's principle.***

Ans. ***Effect of catalyst on equilibrium constant by applying Le-Chatelier's principle:***

In most of the reversible reactions, the equilibrium is not always reached within a suitable short time, so an appropriate catalyst is added. A catalyst does not effect the equilibrium position of the reaction. It increases the rates of both forward and backward reactions and this reduces the time to attain the state of equilibrium.

Q.18 ***Write down the application of chemical equilibrium in the synthesis of ammonia industry.*** ***Karachi Board: 2007, 2009, 2015***

Ans. The principle of chemical equilibrium can predict the effect of charge in concentration, temperature and pressure. It is applied to select the favourable conditions necessary to get maximum amount of NH_3 during its industrial production by Haber's process.

- ***Effect of change in concentration on the production of NH_3.***

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

Addition of any one of the reactant at equilibrium state will cause to increase the concentration of that reactant which will disturb equilibrium. According to Le-Chatelier's principle, the effect of increase in the concentration of added reactant will be nullified by the decrease in the concentration of the added reactant. To do so position of equilibrium will shift to the right i.e., the reaction moves in the forward direction to re-establish equilibrium.

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

- ***Effect of pressure on the production of ammonia.***

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

This reaction proceeds with decrease in number of moles i.e., 4 moles of the reactant converts into 2 moles of the product). When pressure is increased on this reaction in equilibrium position, this disturbs the equilibrium and shift the equilibrium towards the direction having less number of moles. Hence more ammonia is formed. The reaction is carried at 200-600 atm pressure.

- ***Effect of temperature on the production of ammonia:***

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

It is an exothermic reaction. When heat is removed by decreasing temperature, it disturbs equilibrium. According to Le-Chatelier's principle, the effect of decease in temperature will be nullified by evolution of heat. To do so the position of equilibrium will move to the right i.e., the reaction will move in the forward direction to re-establish the equilibrium. To get maximum amount of NH_3 in less time the reaction is carried out at 400°C - 500°C.

Q.19 ***Describe the application of Le-Chatelier's principle in manufacturing of SO_3 by contact process.*** ***Karachi Board: 2017-2019***

Ans. - ***Effect of charge in concentration on the production of SO_3:***

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

Addition of any reactant at equilibrium state will cause to increase the concentration of that reactant which will disturb equilibrium. According to Le-Chatelier's principle, the effect of increase in the concentration of added reactant will be nullified by the decrease in the concentration of the added reactant. To do so the position of equilibrium will shift to the right i.e., the reaction will move in forward direction to re-establish equilibrium.

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

In this way maximum amount of SO_3 is obtained by increasing the concentration of any one of the reactants.

- ***Effect of pressure on the production of SO_3:***

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

This reaction proceeds with decrease in number of moles i.e., 3 moles of the reactant converts into 2 moles of the product. When pressure is increased on this reaction this disturbs the equilibrium. According to Le-Chatelier's principle, the effect of increased pressure is nullified by the decrease in pressure. Since the pressure is directly proportional to the number of moles, therefore to increase the pressure, position of equilibrium shift towards the direction having less number of moles. Hence more SO_3 is formed. The reaction is carried at 1.5 - 1.7 atm pressure.

- ***Effect of temperature on the production of SO_3:***

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

It is an exothermic reaction. Heat is produced in the above reaction when heat is removed by decreasing temperature, it disturbs equilibrium. According to Le-Chatelier's principle, the effect of decrease in temperature will be nullified by evolution of heat. To do so the position of equilibrium will move to the right i.e., the reaction will move in the forward direction to re-establish equilibrium. The reaction is carried out at 450°C. A catalyst V_2O_5 is also added to speed up the reaction.

Q.20 ***Define solubility and solubility product.*** ***Karachi Board: 2008, 2010, 2016***

Ans. ***Solubility:*** The solubility of a substance is the amount of substance that dissolves in a given quantity of a solvent at a given temperature to produce a saturated solution. Solubility is usually expressed in grams of solute per 100g of solvent.

Solubility Product: The product of molar concentration of dissolved ions of a sparingly soluble salt at specific temperature is known as solubility product. Solubility product is expressed in molar concentration.

Q.21 ***Derive the solubility product expression of sparingly soluble compound AgCl.***

Ans. When AgCl (slightly soluble salt) is dissolved in water to from saturated solution. An equilibrium exists between solid and its ions in aqueous phase.

$$\underset{\text{un-dissolved}}{AgCl} \rightleftharpoons \underset{\text{Dissolved ions}}{Ag^+_{(aq)} + Cl^-_{(aq)}}$$

According to law of mass action.

$$[AgCl] \rightleftharpoons [Ag^+]\ [Cl^-]$$

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

Concentration of solid $AgCl$ is constant in solution which is expressed by K'.

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

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

$$K_c \times K' = K_{sp}$$

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

where K_{sp} is called the solubility product. It is the ionic product of dissolved ions.

Q.22 ***State relationship between K_{sp} and ionic concentration.***

Ans. ***Relationship between KSP and ionic concentration:***

(1) If K_{sp} is equal to the ionic concentration, then it will be a saturated solution.

(2) If K_{sp} is less than ionic concentration then it will be a supersaturated solution and salt will appear in the form of precipitates.

(3) If K_{sp} is greater than ionic concentration then it will an unsaturated solution i.e. more solute can be dissolved.

Q.23 ***What are the applications of solubility product (K_{sp}) ?***

Ans. The following are the applications of solubility product (K_{sp}):

(i) It is used to predict the precipitation of a saturated solution.

(ii) Solubility product is used for the purification of common salt.

(iii) K_{sp} is used for salting out soap.

(iv) K_{sp} is used to calculate solubility.

Q.24 ***Define common ion effect. How does it decreases the solubility of electrolytes.***

Karachi Board: 2009, 2010, 2011, 2015

Ans.

Definition: The phenomenon in which the degree of ionization of a less soluble electrolyte is suppressed by the addition of a highly soluble electrolyte containing a common ion and the concentration of unionized species increases, which may comes out as a precipitate is called common ion effect.

e.g., Consider the dissociation of an electrolyte AB:

$$AB \longrightarrow A^- + B^+$$

$$K \text{ (dissociation constant)} = \frac{[A^-][B^+]}{[AB]}$$

If now another electrolyte yielding the A^- or B^+ ions be added to the above solution. It will result in the increase of concentration (AB).

Decrease in Solubility: Suppression of ionization resulted by common ion causes to decrease the solubility of the electrolyte.

Q.25 ***Write down the applications of common ion effect with suitable examples.***

Ans. ***Karachi Board: 2010***

The following are the examples of common ion effect:

(1) Purification of sodium chloride:

HCl gas is passed through saturated solution of NaCl in which ionized and unionized NaCl is at equilibrium, ionization takes place as under:

$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$HCl_{(aq)} \rightleftharpoons H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

HCl causes to increase the concentration of Cl^- ions (common ion). According to Le-Chatelier's principle, Cl^- ion will react with Na^+ ions to from precipitates of pure NaCl.

- ***Precipitation of basic radicals of group II:***

Basic radicals of group II and IV are precipitated as their sulphides. For this purpose H_2S gas passed through their solution. Solubility product of sulphides of group II are smallest than those of group IV. It means smaller amount of ions are required for the precipitation of basic radicals of group II as compared to those of group IV. For this purpose HCl is added before passing H_2S. Ionization takes place as given below:

$$H_2S_{(aq)} \rightleftharpoons 2H^{+}_{(aq)} + S^{2-}_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

HCl causes to increase the concentration of H^+ ions (common ion) which according to Le-Chatelier's principle, suppress the ionization of H_2S to such an extent that sulphides of group II only precipitate out.

- ***Precipitation of Basic radicals of group III:***

Basic radicals of group III are precipitated as their hydroxides. For this purpose NH_4OH is added to their solution. But before its addition NH_4Cl is added. Ionization takes place as given below:

$$NH_4OH_{(aq)} \rightleftharpoons NH^{+}_{4\,(aq)} + OH^{-}_{(aq)}$$

$$NH_4Cl_{(aq)} \longrightarrow NH^{+}_{4\,(aq)} + Cl^{-}_{(aq)}$$

NH_4Cl causes to increase concentration of NH_4^+ ions (common ion) which according to Le-Chatelier's principle, suppress the ionization of NH_4OH to such an extent that hydroxides of group III only form precipitate which the hydroxides of next group do not from precipitate.

- ***Precipitation of sulphides of group IV:***

The sulphides of this group are precipitated by H_2S gas in the presence of NH_4OH.

The OH^- ions of NH_4OH combines with H^+ of H_2S to from H_2O.

$$H^{+} + OH^{-} \longrightarrow H_2O$$

The removal of H^+ ions form the product side results in the increase of concentration of sulphide ions S^{-2} which is enough to exceed the solubility product for the precipitation of CuS, NiS, and ZnS etc.

Solved Problems of Textbook

Determination of Equilibrium Constant

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.*

Solution:

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

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

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

or $0.1 - x = 0.033$ moles

or $x = 0.1 - 0.033 = 0.067$ moles

Therefore 0.067 mole of 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
Concentration at equilibrium state	0.033	0.033	0.067	0.067
	$\frac{0.033}{v}$	$\frac{0.033}{v}$	$\frac{0.067}{v}$	$\frac{0.067}{v}$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{0.067}{v} \times \frac{0.067}{v}}{\frac{0.033}{v} \times \frac{0.033}{v}} = \frac{0.067 \times 0.67}{0.033 \times 0.033}$$

$$K_c = 4.0 \quad \textbf{Ans.}$$

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?*

Solution:

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

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 (ethyl acetate 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	0.05 + n
Concentration at equilibrium state:	$\frac{0.06 - n}{v}$	$\frac{0.2 - n}{v}$	$\frac{0.0125 + n}{v}$	$\frac{0.05 + n}{v}$

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

$$K_c = \frac{\frac{(0.0125 + x)}{v}\frac{(0.05 + x)}{v}}{\frac{0.06 + x}{v}\frac{0.05 + x}{v}}$$

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

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:

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

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

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

Application of the Law of Equilibrium

Example 4: ***The K_c for the dissociation of hydrogen iodide at 365°C is 1.3×10^{-2}. If there are 0.5 moles/dm³ hydrogen, 1.5 moles/dm³ iodine and 5 moles/dm³ hydrogen iodide, predict the direction in which the reaction moves so as to achieve the equilibrium.***

Solution: ***Karachi Board: 2019***

The dissociation of hydrogen iodide is represented by the equation,

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \qquad K_C = 1.3\times10^{-2}$$

According to the law of mass action:

$$K_{initial} = \frac{[H_2]_{initial}\,[I_2]_{initial}}{[HI]^2_{initial}} = \frac{(0.5)\,(1.5)}{(5)^2} = \frac{0.75}{25} = 3\times10^{-2}$$

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.***

Solution:

According to the law of mass action:

$$K_{initial} = \frac{[H_2]_{initial}\,[I_2]_{initial}}{[HI]^2_{initial}} = \frac{0.2\times12}{(15)^2} = \frac{2.4}{225} = 0.0106$$

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.

Calculation of solubility product from the solubility

Example 6: ***The solubility of AgCl is 1.4×10^{-3} g / dm³ at 25°C. Molecular mass of AgCl is 143.5. Calculate its solubility product.***

Solution:

Data:

Solubility of $AgCl$ = 1.4×10^{-3} g / dm³

Molecular mass of $AgCl$ = 143.5

$$\text{molarity} = \frac{1.4\times10^{-3}}{143.5} = 0.98\times10^{-5} \text{ mole dm}^{-3}$$

Since the concentration of Ag^+ is 0.98×10^{-5} moles dm^{-3}.

The concentration of the Cl^- is also 0.98×10^{-5} moles dm^{-3}.

$K_{sp} = [Ag^+]\,[Cl^-] = (0.98\times10^{-5} \text{ moles dm}^{-3})\quad(0.98\times10^{-3} \text{ moles dm}^{-3})$

$K_{sp} = 0.96\times10^{-10}$

$K_{sp} = 9.6\times10^{-11} \text{ moles}^2 \text{ dm}^{-6}$ **Ans.**

Calculation of solubility from solubility product

Example 7: ***The solubility product of lead iodie (PbI_2) at 25°C is 1.00×10^{-9} mol^3 dm^{-9}. Calculate solubility of PbI_2 at 25°C.***

Solution:

$$\underset{\text{undissolved}}{PbI_{2(s)}} \rightleftharpoons \underset{\text{dissolved}}{Pb^{2+}_{(aq)} + 2I^-_{(aq)}}$$

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

If x moles per dm^3 of PbI_2 dissolve (i.e. ionize), then

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

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

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 dm^3 is converted into g / dm^3 (Chemical units into physical unit of concentration) as follows:

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

$\therefore$ Moles in gm = Moles × molecular mass

= $0.63 \times 10^{-3} \times 461$

= 0.00063×461

= 0.29g

Solubility of PbI_2 at 25°C = 0.29 g / dm^3 **Ans.**

Example 8: ***Should $PbCrO_4$ precipitate from a solution prepared by mixing $100cm^3$ of 2.5×10^{-4} M $Pb(NO_3)_2$ and $300cm^3$ of 1.5×10^{-5} M K_2CrO_4? (K_{sp} of $PbCrO_4 = 1.8 \times 10^{-14}$)***

Solution:

The equation for the equilibrium is:

$$\underset{\text{undissolved}}{PbCrO_{4(s)}} \rightleftharpoons \underset{\text{dissolved}}{Pb^{2+}_{(aq)} + CrO_4^{2-}_{(aq)}}$$

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

Total volume of the solution = 100 cm^3 + 300 cm^3 = 400 cm^3. This volume contains the equivalent of 100 cm^3 $Pb(NO_3)_2$ and 300 cm^3 of K_2CrO_4 the concentration of each ion is calculated as:

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

$$[CrO_4^{2-}] = \left(\frac{300\ cm^3\ K_2CrO_4}{400\ cm^3\ Total\ solution}\right) \times 1.5 \times 10^{-4}\ M = 1.125 \times 10^{-4}\ M$$

The ionic product of $PbCrO_4$ is:

$$[Pb^{2+}]\ [CrO_4^{2-}] = (6.25 \times 10^{-5})\ (1.125 \times 10^{-4}) = 7.03 \times 10^{-13}$$

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

Scientific Reasons

Q.01 ***Equilibrium constant is the quantitative measurement of the extent of the reaction.***

Ans. Greater the value of K_c, greater would be the extent of the reaction or vice versa. If K_c is very large then the reaction will proceed in forward direction to a very large extent to produce maximum amount of product. If K_c is very small the reaction will proceed in backward direction to a very small extent to produce minimum amount of the product. This explanation indicates that K_c is the quantitative measurement of extent of chemical reaction.

Q.02 ***The ratio of concentration of reactants and the product at equilibrium stage is independent of the direction form where it is started.***

Ans. Consider the following reaction which is at equilibrium:

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

Whether the reaction is started from A and B to form C and D or it is started form C and D to form A and B. The following value of K_c will remain the same.

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

This indicates that the reactants and products at equilibrium stage is independent of the direction from where it is started.

Q.03 ***Why it is necessary to mention the physical states of reactant and product in a thermochemical reaction?***

Ans.

- To Consider the latent heats of substances, it is essential to indicates their physical states.
- No information about the physical states of matter will lead to wrong calculation of energy changes.
- All reactions are carried out with specific physical states of reactants and if is not present in that physical states then no reaction will take place.

Q.04 ***Le-Chateliers's principle says that solid ice at 0°C can be melted by applying pressure and without supply of heat from outside.***

Ans. Following equilibrium is established between ice and water at 0°C:

$$\underset{\text{Ice occupies more volume}}{\text{Ice}} \longleftrightarrow \underset{\text{Water occupies less volume}}{\text{Water}}$$

Increase in pressure decreases the volume which favours the conversion of ice into water according to Le-Chatelier's principle. This is why ice melts by applying pressure only without supply of heat from outside.

Differences

Q.01 ***What is the difference between the following:***
(i) Solubility and Solubility Product
(ii) Reversible Reactions and Irreversible Reactions

S. No.	*Solubility*	*Solubility Product*
1.	Solubility is defined as the maximum amount of solute required to form a saturated solution at a particular temperature in 100gm of solvent.	Solubility product is defined as the product of molar concentration of ions in a saturated solution of a sparingly soluble at a particular temperature.
2.	It increases with the rise in temperature.	It also increases with temperature but has a definite value at particular temperature.
3.	It decreases due to common ion effect.	It is not affected by common ion effect.
4.	Its unit is gm / dm^3	Its uint may be mole/dm^3, $mole^2$ / dm^6 etc.

S. No.	*Reversible Reactions*	*Irreversible Reactions*
1.	These reactions do not proceed to completion.	These reaction proceed to completion.
2.	It is represented by arrows with opposite heads. ($\rightleftharpoons$).	It is represented by one arrow with single head ($\longrightarrow$)
3.	Reaction products can react to form the original reactant.	Reaction products cannot react to form the original reactants.
4.	These reactions take place in both directions.	These reactions take place only in one direction.
5.	Law of mass action is applied to reversible reaction.	Law of mass action cannot be applied to irreversible reaction.
6.	Le-Chatelier's principle, and common ion effect are applied to reversible reaction	Le-Chatelier's principle, and common ion Effect cannot be applied to irreversible reaction.

Solved Problems From Past Papers

Problem 1: ***Calculate the solubility product of $PbCrO_4$ when the solubility of $PbCrO_4$ is 1.0×10^{-3} gm / dm^3.*** ***Karachi Board: 2014***

Solution:

Solubility of $PbCrO_4$ = 1.0×10^{-3} g / dm^3

Solubility product = K_{sp} = ?

Molecular mass of $PbCrO_4$ = 327

Hence, solubility in terms of molarity is:

$$\text{Molarity} = \frac{1.0 \times 10^{-3}}{327} = 3.05 \times 10^{-6} \text{ mol / dm}^3$$

Now $PbCrO_4 \rightleftharpoons [Pb^{+2}]\ [CrO_4^{-2}]$

Concentration of Pb^{+2} = 3.05×10^{-6} mol / dm^3

Concentration of CrO_4^{-2} = 3.05×10^{-6} mol / dm^3

$K_{sp\ PbCrO_4} = [Pb^{+2}]\ [CrO_4^{-2}]$

$K_{sp\ PbCrO_4} = (3.05 \times 10^{-6}) \times (3.05 \times 10^{-6})$

$K_{sp} = 9.30 \times 10^{-12}$ mol^2 / dm^6 **Ans.**

Problem 2: *5.88 moles of nitrogen and 16.2 moles oxygen are mixed and heated at 2000°C unit. The equilibrium is established. 11.28 moles of nitric oxide is formed. Calculate the value of equilibrium constant.*

$$N_2 + O_2 \rightleftharpoons 2NO$$

Solution:

$N_2 + O_2 \rightleftharpoons 2NO$

No. of moles of N_2 = 5.88 moles

No of moles of O_2 = 16.2 moles

No. of moles of NO = 11.25 moles

K_c = ?

$$K_c = \frac{[NO]}{[N_2]\ [O_2]}$$

$$K_c = \frac{[11.28]}{[5.88]\ [16.2]} = 1.335$$

K_c = 1.335 **Ans.**

Problem 3: *The solubility of AgCl at 25°C is 1.40×10^{-3} g / dm³. Its molecular mass is 143.5. Calculate the:*

- *molarity of AgCl Solution*
- *solubility product of AgCl*

Karachi Board: 2013

Solution:

For solution see example no. 6 on page 210.

Problem 4: *The equilibrium constant expression for a gaseous equilibrium is*

$$K_C = \frac{[NO]^4\ [H_2O]^6}{[NH_3]^4\ [O_2]^5}$$

From this write equation for the reaction.

Solution: ***Karachi Board: 2012***

Equation the reaction:

$$K_c = \frac{[NO]^4\ [H_2O]^6}{[NH_3]^4\ [O_2]^5}$$

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

Problem 5: *The solubility of calcium oxalate (CaC_2O_4) is 0.0016 gm/dm³ at 25°C. Find the solubility product of calcium oxalate.*

$$CaC_2O_4 \rightleftharpoons Ca^{+2} + C_2O_4^{-2}$$

Solution: ***Karachi Board: 2012***

Solubility of CaC_2O_4 = 0.0016 gm / dm³

Solubility product of CaC_2O_4 = K_{sp} = ?

Molecular mass of CaC_2O_4 = 128

Equation:

$$CaC_2O_4 \rightleftharpoons Ca^{2+} + C_2O_4^{2-}$$

$$K_{sp} = [Ca^{2+}]\ [C_2O_4^{2-}]$$

$$[Ca^{2+}] = \frac{\text{mass}}{(\text{molecular mass})}$$

$$[Ca^{2+}] = \frac{0.0016}{128}$$

$$[Ca^{2+}] = 1.25 \times 10^{-5} \text{ mole / dm}^3$$

$$[C_2O_4^{2-}] = \frac{\text{mass}}{(\text{molecular mass})}$$

$$[C_2O_4^{2-}] = \frac{0.0016}{128}$$

$$[C_2O_4^{2-}] = 1.25 \times 10^{-5} \text{ mole / dm}^3$$

We know that,

$$K_{sp} = [Ca^{2+}]\ [C_2O_4^{2-}]$$

$$K_{sp} = (1.25 \times 10^{-5})\ (1.25 \times 10^{-5})$$

$$K_{sp} = 1.5625 \times 10^{-10} \text{ mole / dm}^6$$ **Ans.**

Problem 6: ***3 moles of H_2 and 4 moles of I_2 were heated in a sealed tube at a given temperature at which K_c is 50. If the volume of the tube is dm³, determine the composition of the equilibrium.***

$$H_2 + I_2 \rightleftharpoons 2HI$$

Solution: ***Karachi Board: 2013***

$[H_2]$ = 3 moles/dm³
$[I_2]$ = 4 moles/dm³
K_c = 50
V = 1 dm³

Composition of Equilibrium (Composition at Equilibrium):

$[H_2]$ = ?
$[I_2]$ = ?
$[HI]$ = ?
K_c = 50

	H_2	+	I_2	$\rightleftharpoons$	2HI
Initial Concentration	3 mole dm³		4 mole dm³		(0)
Used	-x		-x		
Concentration at equilibrium	(3 - x)		(4 - x)		2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$50 = \frac{(2x)^2}{(3-x)(4-x)}$$

$$\Rightarrow 50(3-x)(4-x) = 4x^2$$
$$\Rightarrow (150-50x)(4-x) = 4x^2$$
$$\Rightarrow 600-150x-200x+50x^2 = 4x^2$$
$$\Rightarrow 46x^2-350x+600 = 0$$
$$\Rightarrow ax^2+bx+c=0$$

Here $a = 46$, $b = -350$, $c = 600$

By using quadratic formula:

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

$$x = \frac{-(-350) \pm \sqrt{(350)^2-4\times 46\times 600}}{2\times 46}$$

$$x = \frac{350 \pm \sqrt{12100}}{92}$$

$$x = \frac{350 \pm 110}{92}$$

$$x = \frac{350+110}{92} = 5 \quad \text{(it is not correct as concentration)}$$

$$x = \frac{350-110}{92} = 2.60$$

Hence $x = 2.60$

Therefore composition at equilibrium are:

$[H_2] = (3-x) = 3-2.6 = 0.4$ moles/dm^3
$[I_2] = (4-x) = 4-2.6 = 1.4$ moles/dm^3
$[HI] = (2x) = 2(2.6) = 5.2$ moles/dm^3

Problem 7: *The K_C for the reaction $2\ HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ is 1.3×10^{-2}. If there are 0.5 moles / dm³ H_2, 1.5 mol / dm³ I_2 and 5 moles / dm³ HI. Predict the direction in which the reaction moves so as to achieve the equilibrium.*

Solution: *Karachi Board: 2010*

Data:

$K_c = 1.3 \times 10^{-2} = 0.013$

$[H_2] = 0.5$ moles / dm³

$[I_2] = 1.5$ moles / dm³

$[HI] = 5$ moles / dm³

direction = ?

Reaction: $2HI \rightleftharpoons H_2 + I_2$

$$Kc = \frac{[H_2]\,[I_2]}{[HI]^2}$$

$$Kc = \frac{(0.5)\,(1.5)}{(5)^2} = \frac{0.75}{25} = 0.03$$

$K_c = 0.03$

Since the calculated K_c is greater than the given value, the reaction will move towards left. **Ans.**

Problem 8: *K_C for the reaction $CH_3OOH + C_2H_5OH \rightleftharpoons CH_3COO_2H_5 + H_2O$ at room temperature is 4. Calculate the equilibrium concentration when 1.66 moles of CH_3COOH and 2.17 moles of C_2H_5OH are allowed to come to equilibrium.*

Solution: *Karachi Board: 2010*

$K_c = 4$

Initially:

$[CH_3COOH] = 1.66$ moles

$[C_2H_5OH] = 2.17$ moles

Reaction: $CH_3COOH_2 + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH_2]\,[C_2H_5OH]}$$

$$4 = \frac{(x)\,(x)}{(1.66 - x)\,(2.17 - x)}$$

$$4 = \frac{x^2}{3.66 - 1.66x - 2.17x + x^2}$$

$$4(3.60 - 1.66x - 2.17x + x^2) = x^2$$

$$4(3.60 - 3.83x + x^2) = x^2$$

$$14.4 - 15.32x + 4x^2 = x^2$$

$$3x^2 - 15.32x + 14.4 = 0$$

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

$a = 3 \qquad b = -15.32 \qquad c = 14.4$

$$x = \frac{-(-15.32) \pm \sqrt{(-15.32)^2 - 4(3)(14.4)}}{2(3)}$$

$$x = \frac{15.32 \pm \sqrt{234.7 - 172.8}}{6}$$

$$x = \frac{15.32 \pm \sqrt{61.9}}{6}$$

$$x = \frac{15.32 + 7.86}{6} \quad \text{or} \quad \frac{15.32 + 7.86}{6}$$

$x = 3.86$ or 1.24

As 3.86 is greater then initial concentration

$\therefore$ 1.24 moles / dm^3 is the correct value

$x = 1.24$ moles / dm^3 **Ans.**

Problem 9: ***Write the solubility product (K_{sp}) expressions of the following sparingly soluble salts along with their units:***
(i) $CaCO_3$ (ii) $Mg(OH)_2$

Solution: **K_c Expression:** ***Karachi Board: 2010***

(i) For $CaCO_3$

$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$

$K_{sp} = [Ca^{+2}][CO_3^{-2}]$

Unit: $K_{sp} = mol^2\ dm^{-6}$

(ii) For $Mg(OH)_2$

$Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^-$

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

Unit: $K_{sp} = mol^3\ dm^{-9}$

Problem 10: ***When the equilibrium was attained for the reaction $A + B \rightleftharpoons 2C$, the concentration of [A] = [B] was 4 moles / dm^3 and that of [C] was 6 moles / dm^3. Calculate K_c and the initial concentration of A and B.***

Solution: ***Karachi Board: 2009***

K_c for the reaction:

$$A + B \rightleftharpoons 2C$$

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

$$K_c = \frac{[6]^2}{[4][4]} = \frac{36}{16}$$

$K_c = 2.25$

6 moles of C are produced from 3 moles of A and 3 moles of B. The initial concentration of A and B was $A = B = 4 + 3 = 7$ moles / dm^3.

Problem 11: *The given reaction is $PbI_2 \rightleftharpoons Pb^{+2} + 2I^-$. At 25°C the solubility of $PbI_2 = 0.63 \times 10^{-3}$ mol / dm³. Find the value of K_{sp} and express its unit.*

Solution: *Karachi Board: 2009*

$$PbI_2 \rightleftharpoons Pb^{+2} + 2I^-$$

$K_{sp} = [Pb^{+2}]\ [I^-]^2$

$[Pb^{+2}] = 0.63 \times 10^{-3}$ mol/dm³

$[I^-] = 0.63 \times 10^{-3} \times 2 = 1.26 \times 10^{-3}$ mol / dm³

$K_{sp} = [Pb^{+2}]\ [I^-]^2$

$K_{sp} = [0.63 \times 10^{-3}]\ [1.26 \times 10^{-3}]^2$

$K_{sp} = 1.00018 \times 10^{-9}$ mol³ / dm⁹ **Ans.**

Problem 12: *In a reaction $A + B \rightleftharpoons 2C$, 7 mol / dm³ of A and 7 moles / dm³ of B were mixed and allowed to attain equilibrium. If $K_c = 2.25$, find out concentration of A, B & C equilibrium state.*

Solution: *Karachi Board: 2008*

	A	+	B	⇌	2C
Initially:	7 moles		7 moles		Nil moles
At equilibrium:	(7x) moles		(7 - x) moles		2x moles

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

$$2.25 = \frac{(2x)^2}{(7-x)\ (7-x)}$$

$$2.25 = \frac{4x^2}{49 - 7x - 7x + x^2}$$

$$2.25 = \frac{4x^2}{49 - 14x + x^2}$$

$$2.25\ (49 - 14x + x^2) = 4x^2$$

$$110.25 - 31.5x + 2.25x^2 - 4x^2 = 0$$

$$110.25 - 31.5x - 1.75x^2 = 0$$

or $$1.75x^2 + 31.5x - 10.25 = 0$$

Solving by quadratic formula:

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

$$x = \frac{-(31.5) \pm \sqrt{(31.5)^2 - 4\ (1.75)\ (-11.025)}}{2\ (1.75)}$$

$$x = \frac{-31.5 \pm \sqrt{992.25 + 771.75}}{3.5}$$

$$x = \frac{-31.5 \pm \sqrt{1764}}{3.5}$$

$$x = \frac{-31.5 \pm 42}{3.5}$$

$$x = \frac{-31.5 + 42}{3.5} \quad \text{or} \quad \frac{-31.5 - 42}{3.5}$$

$x = 3 \qquad x = -21$

$[A] = 7 - x$
$= 7 - 3$
$= 4$ moles

$[B] = 7 - x$
$= 7 - 3$
$= 4$ moles

$[C] = 2x$
$= 2(7)$
$= 14$ moles

Problem 13: ***The solubility of AgCl at 25°C is 1.4×10^{-3} g/dm³. What is the solubility product? (Atomic mass of Ag = 108 and Cl = 35.5)***

Solution:

Solubility $= 1.4 \times 10^{-3}$ gm / dm³

$K_{sp} = ?$

$AgCl \rightleftharpoons Ag^+ + Cl^-$

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

$[Ag^+] = \frac{1.43 \times 10^{-3}}{143.5} = 0.98 \times 10^{-5}$ mol / dm³

$[Cl^-] = \frac{1.43 \times 10^{-3}}{143.5} = 0.98 \times 10^{-5}$ mol / dm³

$K_{sp} = [Ag^+]\ [Cl^-]$
$= [0.98 \times 10^{-5}]\ [0.98 \times 10^{-5}]$
$K_{sp} = 9.6 \times 10^{-11}$ mol² dm⁻⁶ **Ans.**

Problem 14: ***Find the K_{sp} of $CaCO_3$, the solubility of $CaCO_3$ is 0.001 gm / dm³.***
$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{-2}$

Solution: ***Karachi Board: 2009***

Solubility of $CaCO_3$ = 0.001 gm / dm³
Solubility product = K_{sp} = ?
Molecular mass of $CaCO_3$ = 100 amu

$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$

$K_{sp} = [Ca^{+2}]\ [CO_3^{-2}]$

$$[Ca^{2+}] = \frac{\text{mass}}{\text{molecular mass}} = \frac{0.001}{100}$$

$$= 1 \times 10^{-5} \text{ mol / dm}^3$$

$$[CO_3^{-2}] = \frac{\text{mass}}{\text{molecular mass}} = \frac{0.001}{100} = 1 \times 10^{-5} \text{ mol / dm}^3$$

$$K_{sp} = [Ca^{+2}]\ [CO_3^{-2}]$$

$$K_{sp} = [1 \times 10^{-5}] \times [1 \times 10^{-5}]$$

$$K_{sp} = 1 \times 10^{-5} \text{ mol}^2 / \text{dm}^6$$ **Ans.**

Problem 15: ***The equilibrium constant for the reaction $N_2 + O_2 \rightleftharpoons 2NO$ at 2000°C is 0.1. Calculate the equilibrium concentration of the reactant and product when initial concentration of N_2 and O_2 are 10 moles / dm³ ?***

Solution: ***Karachi Board: 2006***

Data:

K_c	=	0.1
Initial concentration of N_2	=	10 mol / dm³
Initial concentration of O_2	=	10 mol / dm³
Equilibrium concentration of reactant	=	?
Equilibrium concentration of product	=	?

Calculation:

	N_2	+	O_2	$\rightleftharpoons$	2NO
	10 mol / dm³		10 mol / dm³		Nil
At equilibrium:	$(10 - x)$		$(10 - x)$		$(10 - x)$

$$K_c = \frac{[NO]^2}{[N_2]\ [O_2]}$$

$$K_c = \frac{(2x)^2}{(10 - x)\ (10 - x)}$$

$$K_c = \frac{4x^2}{100 - 10x - 10x - x^2}$$

$$0.1 = \frac{4x^2}{100 - 20x + x^2}$$

$$0.1\ (100 - 20x + x^2) = 4x^2$$

$$10 - 2x + 0.1\ x^2 = 4x^2$$

$$4x^2 - 0.1x^2 + 2x - 10 = 0$$

$$3.99x^2 + 2x - 10 = 0$$

$$\frac{3.99x^2 + 2x - 10}{3.99} = 0$$

$$x^2 + 0.5x - 2.56 = 0$$

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

We know that: $a = 1, \quad b = 0.5, \quad c = -2.56$

$$x = \frac{-(0.5) \pm \sqrt{(0.5)^2 - 4(1)(-2.56)}}{2(1)}$$

$$x = \frac{-(0.5) \pm \sqrt{0.25 + 10}}{2}$$

$$x = \frac{-0.5 \pm \sqrt{10.25}}{2}$$

$$x = \frac{-0.5 + 3.2}{2}$$

$$x = \frac{-0.5 + 3.2}{2} \quad \text{and} \quad x = \frac{-0.5 - 3.2}{2}$$

$$x = 1.35 \qquad x = 1.85$$

Equilibrium concentration of N_2 = $10 - x$ = $10 - 1.35$ = 8.65 mol / dm^3
Equilibrium concentration of O_2 = $10 - x$ = $10 - 1.35$ = 8.65 mol / dm^3
Equilibrium concentration of product = $2x$ = 2×1.35 = 2.7 mol / dm^3

Problem 16: ***Will $PbCrO_4$ precipitate from a solution prepared by mixing 200 cm^3 of 2.5×10^{-4} M. $Pb(NO_3)_2$ and 600 cm^3 of 1.5×10^{-5} M K_2CrO_4? (K_{sp} of $PbCrO_4 = 1.8 \times 10^{-14}$)***

Karachi Board: 2005

Solution:

Data:

Volume of $Pb(NO_3)_2$ = 200 cm^3
Volume of K_2CrO_4 = 600 cm^3
Total Volume = 800 cm^3

Concentration of $Pb(NO_3)_2$ = 2.5×10^{-4} M
Concentration of K_2CrO_4 = 1.5×10^{-5} M

Calculation:

$$[Pb^{+2}] = \frac{200}{800} \times 2.5 \times 10^{-4}$$

$$= 6.25 \times 10^{-5} \text{ mol / dm}^3$$

$$[CrO_4^{-2}] = \frac{600}{800} \times 1.5 \times 10^{-5}$$

$$= 1.125 \times 10^{-5} \text{ mol / dm}^3$$

Ionic product = $[Pb^{+}]\,[CrO_4^{-2}]$

$$= (6.25 \times 10^{-5})(1.125 \times 10^{-5})$$

$$= 7.03 \times 10^{-13} \text{ mol}^2 / \text{dm}^3$$

Ionic product > K_{sp}
Therefore, precipitate will form.

Problem 17: ***What is the ionic concentration of Ag^+ and CrO_4^{-2} in a saturated solution of Ag_2CrO_4 at 25°C ? K_{sp} of Ag_2CrO_4 is 1.9×10^{-12} mole^3 / dm^9.***

Solution: *Karachi Board: 2015*

Ag_2CrO_4 dissolves in water as follows:

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

$K_{sp} = [2x][x]$

$K_{sp} = [Ag^+]^2 [CrO_4^{-2}]$

$K_{sp} = (2x)^2 (x) = 4x^3$

$1.9 \times 10^{-12} = 4x^3.$

$$x^3 = \frac{1.9 \times 10^{-12}}{4} = 4.75 \times 10^{-13}$$

$$x = \sqrt[3]{4.75 \times 10^{-13}} = 7.8 \times 10^{-5} \text{ mol / dm}^3$$

$[CrO_4^{-2}] = x = 7.8 \times 10^{-5}$ mol / dm^3

$[Ag^+] = 2x = 2(7.8 \times 10^{-5}) = 1.56 \times 10^{-4}$ mol / dm^3

ionic concentration $= [Ag^+][CrO_4^{-2}]$

ionic concentration $= (7.8 \times 10^{-5})(1.56\times10^{-4}) = 1.2 \times 10^{-8}$ mol^2 / dm^6 **Ans.**

Problem 18: ***In the reaction $H_2 + I_2 \rightleftharpoons 2HI$, when equilibrium was attained, concentrations were $[H_2] = [I_2] = [HI] = 4$ moles / dm^3. Calculate the equilibrium constant and the initial concentration of H_2 and I_2.***

Solution:

$$H_2 + I_2 \rightleftharpoons 2HI$$

[4] [4] [4] at equilibrium

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{[4]^2}{[4][4]} = \frac{16}{16} = 1$$

$[2HI] = 4$

$$[HI] = \frac{4}{2} = 2 \text{ mol}$$

	H_2 +	I_2 $\rightleftharpoons$	2HI
initial concentration	[4+2]	[4+2]	Nil
initial concentration	[6]	[6]	Nil

initial concentration $[H_2] = [I_2] = 6$ mol / dm^3 **Ans.**

Problem 19: ***The solubility of $Mg(OH)_2$ at 25°C is 4.6×10^{-3} gm / 100cm³. What is the solubilty product of $Mg(OH)_2$?***

Solution: *Karachi Board: 2016*

Data:

Solubility = 4.6×10^{-3} gm/100cm³

Molecular mass of $Mg(OH)_2$ = 58 a.m.u.

We know that:

$$\text{Moles} = \frac{\text{Solubility}}{\text{Molecular mass}}$$

$$\text{Moles} = \frac{4.6 \times 10^{-3}}{58} = 7.9 \times 10^{-5} \text{ moles / dm}^3$$

$$Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^-$$

$$K_{sp} = [7.9 \times 10^{-5}] [2 \times 7.9 \times 10^{-5}]^2$$
$$K_{sp} = [7.9 \times 10^{-5}] [1.58 \times 10^{-4}]^2$$
$$K_{sp} = [7.9 \times 10^{-5}] [2.50 \times 10^{-8}]$$
$$K_{sp} = 1.975 \times 10^{-12} \text{ mol}^3 / \text{dm}^9$$ **Ans.**

Problem 20: ***For the reaction: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ the equilibrium mixture contains 0.25 M nitrogen and 0.15 M hydrogen gas at 25°C. Calculate the concentration of NH_3, given $K_c = 9.6$. The volume of the container is 1 dm³.***

Solution: *Karachi Board: 2016*

	$N_{2(g)}$	+	$3H_{2(g)}$	$\rightleftharpoons$	$2NH_{3(g)}$
at equilibrium:	[0.25]		[0.15]		[x]

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

$$9.6 = \frac{[x]^2}{[0.25] [0.15]^3}$$

$$x^2 = (9.6) (0.25) (0.15)^3$$
$$x^2 = (9.6) (0.25) (3.375 \times 10^{-3})$$
$$x^2 = 8.1 \times 10^{-3}$$

$$x = \sqrt{8.1 \times 10^{-3}}$$

$$x = 0.09$$
$$[NH_3] = 0.09 \text{ M}$$ **Ans.**

Problem 21: ***Phosphorus pentachloride decomposes in a gas phase reaction at 25°C as follows:*** $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$
An equilibrium mixture in a 5.0 litre container is found to have 3.84gm PCl_5, 9.14gm PCl_3 and 2.84gm of Cl_2.

Solution: ***Karachi Board: 2017***

PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
3.84 gm		9.14 gm		2.84 gm
$\frac{3.84}{208.5}$		$\frac{9.14}{137.5}$		$\frac{2.84}{71}$
0.018 mol		0.066 mol		0.04
$\left[\frac{0.018}{5}\right]$		$\left[\frac{0.066}{5}\right]$		$\left[\frac{0.04}{5}\right]$
3.6×10^{-3} M		0.0132 M		8×10^{-3} M

$$K_c = \frac{[PCl_3]\ [Cl_2]}{[PCl_5]}$$

$$K_c = \frac{[0.0132]\ [8 \times 10^{-3}]}{[3.6 \times 10^{-3}]}$$

$$K_c = \frac{1.056 \times 10^{-4}}{3.6 \times 10^{-3}}$$

$$K_c = 0.03$$ **Ans.**

Problem 22: ***The concentration of Ag^+ ions is 1×10^{-6} M in AgBr solution. Find the minimum concentration of Br- ions necessary to cause precipitation of AgBr (K_{sp} of AgBr = 4×10^{-13} M^2)***

Solution: ***Karachi Board: 2017***

$$AgBr \rightleftharpoons Ag^+ + Br^-$$

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

Ionic concentration $-$ $[Ag^+]\ [Br^-]$

Ionic concentration $=$ $[Ag^+]\ [Br^-]$

Ionic concentration $=$ $[Ag^+]\ [Br^-]$

If $K_{sp} = 4 \times 10^{-13}\ M^2$

$1 \times 10^{-12} > 4 \times 10^{-13}$

Therefore,

$[Br^-] = 1 \times 10^{-6}$ mol / dm^3

Solution of Textbook Progress Test - 6

Q.01 ***What are reversible and irreversible changes? Describe an experiment to demonstrate a reversible change.***

Ans. See Q 1, 2 and 3 on page 196 and 197.

Q.02 ***(a) State and explain the law of equilibrium. Describe its application.***
(b) What do you understand by K_c and K_p ? Describe their relationship.

Ans. (a) See Q 6 and Q 11 on page 197 and 200.
(b) K_c is called equilibrium constant.
K_p is the equilibrium constant for a gaseous reaction.
For relationship between K_c and K_p, see Q 8 on page 198.

Q.03 ***What is meant by solubility product and the common ion effect? Discuss the application of common ion effect in the qualitative salt analysis.***

Ans. See Q. 20, 24 and 25 on page no 205, 206 and 207.

Q.04 ***How is the balance of chemical equilibrium in influenced? Explain giving examples.***

Ans. See Q 12 & for examples see Q 13, 14, 15, 16 & 17 on page 201, 202, 203 and 204.

Q.05 ***For the gaseous equilibrium $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$; $\Delta H = 87.9$ KJ/mol, explain the effect upon the material distribution of (a) increased temperature (b) increased pressure (c) high concentration of Cl_2 (d) higher concentration of PCl_5 (e) presence of a catalyst.***

Ans.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad \Delta H = 87.9 \text{ KJ/mol}$$

(a) Increased in temperature:

As above reaction is endothermic. By absorbing heat the equilibrium will disturb and it will move in the forward direction till the equilibrium is established

$$PCl_{5(g)} \xrightarrow{\text{heat}} PCl_{3(g)} + Cl_{2(g)}$$

(b) Increased pressure:

Product favour in decrease of volume, but by increasing pressure the equilibrium will disturbs and the reaction will move in backward direction.

$$PCl_{5(g)} \xrightarrow{\text{pressure}} PCl_{3(g)} + Cl_{2(g)}$$

(c) Higher concentration of Cl_2:

According to Le-Chatelier's principle, increase in concentration of Cl_2 will shift the equilibrium to left i.e., more & more PCl_5 will formed.

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

(d) Higher concentration of PCl_5:

If concentration of PCl_5 is increased K_c decreases and to keep K_c constant, the concentration of PCl_3 and Cl_2 increases, we get high yield of product.

(e) Presence of a Catalyst:

Catalyst has no effect on the equilibrium position. It increases the rates of both forward and backward reactions. It reduces the time to attain the state of equilibrium.

Q.06 ***A quantity of PCl_5 was heated in a 12 dm^3 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.

Solution:

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
no. of moles:	0.21		0.32		0.32
Molar concentration at equilibrium	$\frac{0.21}{12}$		$\frac{0.32}{12}$		$\frac{0.32}{12}$

According to the law of mass action:

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\left[\frac{0.32}{12}\right]\left[\frac{0.32}{12}\right]}{\left[\frac{0.21}{12}\right]} = \frac{0.32}{12} \times \frac{0.32}{12} \times \frac{0.32}{12} = 0.041$$

$K_c = 0.041$ **Ans.**

Q.07 ***Consider the following equilibrium:***

(i)	$3O_{2(g)}$	$\rightleftharpoons$	$2O_{3(g)}$	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***
(iv)	$CH_2 = CH_2 + H_2$	$\rightleftharpoons$	$CH_3 - CH_3$	ΔH	= ***negative***

(a) Write the equilibrium constant expression.

(b) In which direction will each equilibrium change as the temperature is raised?

(c) Which of the equilibrium will not be affected by change in total pressure?

Solution:

(i) (a) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$ ΔH = positive

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

(b) On raising temperature the equilibrium will shift to forward direction.

(c) Pressure will effect the equilibrium state.

(ii) (a) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ ΔH = negative

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

(b) On increasing the temperature the equilibrium will shift in backward direction as it is an exothermic reaction.

(c) The pressure will effect the equilibrium state.

(iii) (a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ ΔH = positive

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

(b) On increasing the temperature the equilibrium will shift to the right as it is an endothermic reaction.

(c) The pressure has no effect on equilibrium as the volume of reactants and product are same.

(iv) (a) $CH_2 = CH_2 + H_2 \rightleftharpoons CH_3 - CH_3$ ΔH = Negative

$$K_c = \frac{[CH_3 - CH_3]}{[CH_2 = CH_2][H_2]}$$

(b) This is exothermic reaction. Increase in temperature will shift the equilibrium to backward direction.

(c) Equilibrium will be affected if there is change in pressure.

Q.08 ***One mole of HI is introduced in to 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.***

Solution:

	$2HI_{(g)} \longrightarrow$	$H_{2(g)}$	+ $I_{2(g)}$
Initial concentration:	1 mole		
At equilibrium:	{1 - (0.1 + 0.1)}	0.1	0.1
	1 - 0.2 = 0.8	0.1 mole	0.1 mole

According to the law of mass action:

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.1)(0.1)}{(0.8)^2} = \frac{0.01}{0.64}$$

K_c = 0.0156 **Ans.**

Chemical Equilibrium

Q.09 ***What effect on the position of equilibrium $CaCO_3 \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ for which $\Delta H = +176\ KJ/mol$, 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.

Ans. $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

(a) ***Adding $CaCO_{3(s)}$:*** The equilibrium state will shift to forward direction.
(b) ***Adding CaO:*** The equilibrium state will shift to backward direction.
(c) No effect on equilibrium state as all the reactant & products are not in gaseous state.
(d) ***Removing CO_2 :*** The equilibrium state will shift to forward direction till the equilibrium is re-established.

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

Ans. See Q 12, 18 and 19 on page 201, and 204.

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

Ans. *(i)* See Q 2 on page 197.
(ii) **Dynamic equilibrium:** The reaction proceeds in both forward and backward direction but with equal rates, as the motion of each reactions is not ceased hence it is called "Dynamic equilibrium". Thus all chemical equilibrium are considered to be dynamic in nature.
(iii) See Q 8 on page 198.

Q.12 ***(a) 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. What is the equilibrium constant K_c?***

Solution:

Consider the equation:

	CH_3COOH	+ C_2H_5OH	⟶ $CH_3COOC_2H_5$	+ H_2O
Initial concentration:	1 mole		0	0
Concentration at equilibrium	$1-\frac{2}{3}$	$1-\frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
	$\frac{1}{3}$ mole	$\frac{1}{3}$ mole	$\frac{1}{3}$ mole	$\frac{1}{3}$ mole

At equilibrium: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

According to the low of mass action:

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

$$K_c = \frac{\frac{2}{3} \times \frac{2}{3}}{\frac{1}{3} \times \frac{1}{3}} = \frac{2}{3} \times \frac{2}{3} \times \frac{3}{1} \times \frac{3}{1} = 4$$

Value of K_c = 4 **Ans.**

(b) ***How many moles of ester are formed at equilibrium when 3 moles of alcohol are mixed with 1 mole of acid? All the substances are liquids at room temperature. (K_c = 4)***

Solution:

If the amount of ester present at equilibrium = x, the equation is:

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

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial concentration:	1 mole	3 mole	0	0
Concentration at equilibrium:	(1 - x)	(3 - x)	x	x

Now,

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

$$4 = \frac{x}{1-x} \times \frac{x}{3-x} = \frac{x^2}{(1-x)(3-x)} = \frac{x^2}{(1-x)(3-x)} = \frac{x^2}{(1-x)(3-x^2)}$$

$$x^2 = 4(3 - 4x + x^2) = 12 - 16x + 4x^2$$

$$4x^2 - 16x + 12 - x^2 = 0$$

$$3x^2 - 16x + 12 = 0$$

Now by quadratic equation:

$$a = 3, \quad b = -16, \quad c = 12$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{16 \pm \sqrt{(-16)^2 - 4(3)(12)}}{2(3)} = \frac{-16 \pm \sqrt{256 - 144}}{6}$$

$$= \frac{+16 \pm \sqrt{112}}{6} = \frac{+16 \pm 10.583}{6}$$

$$x = \frac{16 + 10.583}{6} = \frac{26.583}{6} = 4.4305 \text{ moles} \quad \text{..... (a)}$$

$$x = \frac{16 - 10.583}{6} = \frac{5.417}{6} = 0.9028 \text{ moles} \quad \text{..... (b)}$$

The lower value (b) is correct = 0.9028 moles **Ans.**

Q.13 ***$PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Calculate the number 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 = 0.0147 for dissociation.***

Solution:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

	PCl_5	PCl_3	Cl_2
Initial concentration	1	0	0
At equilibrium	(1-x)	x	x
Molar concentration	$\frac{1-x}{10}$	$\frac{x}{10}$	$\frac{x}{10}$

According to the Law of Mass Action

$$K_c = \frac{[PCl_5]\,[Cl_2]}{[PCl_3]}$$

$$= \frac{\frac{x}{10} \times \frac{x}{10}}{\frac{1-x}{10}} = \frac{x}{10} \times \frac{x}{10} \times \frac{10}{1-x} = \frac{x^2}{10(1-x)}$$

or $$0.041 = \frac{x^2}{10 - 10x}$$

or $$x^2 = 0.041(10 - 10x)$$

or $$x^2 = 0.41 - 0.41x$$

$$x^2 + 0.41x - 0.41 = 0$$

Solve by using quadratic formula:

$$x = \frac{-b \pm \sqrt{(b)^2 - 4(a)(c)}}{2a} = \frac{-0.41 \pm \sqrt{(0.41)^2 - 4(1)(-0.41)}}{2a}$$

$$x = \frac{-0.41 \pm \sqrt{0.1681 + 1.64}}{2} = \frac{-0.41 \pm \sqrt{1.808}}{2} = \frac{-0.41 \pm 1.3446}{2}$$

$$x = \frac{-0.41 - 1.3446}{2} = \frac{-1.7546}{2} = -0.887 \text{ moles} \ldots\ldots\ldots\ldots \text{a}$$

$$x = \frac{-0.41 + 1.3446}{2} = \frac{0.9346}{2} = 0.467 \text{ moles} \ldots\ldots\ldots\ldots \text{b}$$

Because the value 0.467 is positive therefore it is the correct number of moles of chlorine at equilibrium. **Ans.**

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

Ans. Equilibrium constant (K_c) is a value that expresses how far the reaction proceeds before reaching equilibrium. A small number means that the equilibrium is towards the reactants side while a large number means that the equilibrium is towards the products side.

e.g., $A + B \rightleftharpoons C + D$

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

For determination of equilibrium constant

See Q 9 on page 199.

(b) To determine the value of K_c for the reaction

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

1 mole of CH_3COOH and 1 mole of C_2H_5OH in 1 dm^3 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 K_c.

Solution:

Consider the equation:

	CH_3COOH	+	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	+	H_2O
Initial Concentration.	1 mole		1 mole		0		0
Concentration at equilibrium	(1-0.667)		(1-0.667)		0.667		0.667
or	= 0.333		= 0.333		0.667		0.667

According to the law of mass action:

$$K_c = \frac{[\text{ester}]\ [\text{water}]}{[\text{acid}]\ [\text{alcohol}]}$$

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

$$K_c = \frac{(0.667)\ (0.667)}{(0.333)\ (0.333)} = \frac{0.4449}{0.1109} = 4$$

Value of K_c = 4 **Ans.**

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

Ans. For a chemical system the above statement is wrong as the chemical equilibrium is dynamic i.e. it is an equilibrium involving the constant interchange of particles in motion as it involves the balancing of two reactions occurring simultaneously.

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

Ans. See Q 20 and Q 23 on page 205 and 206.

(b) What is the solubility of lead chromate in moles / dm^3 at 25°C. K_{sp} for $PbCrO_4$ = 2.8 × 10^{-13} mole / dm^3.

Solution:

Lead chromate ionizes as:

$$PbCrO_4 \rightleftharpoons Pb^{2+} + CrO_4^{-2}$$

Let the solubility of lead chromate = x

Now apply the formula of solubility product:

$$K_{sp} = [Pb^{2+}]\ [CrO_4^{-2}]$$

Therefore $2.8 \times 10^{-13} = [x]\ [x]$

$$x^2 = 2.8 \times 10^{-13}$$

$$x = \sqrt{2.8 \times 10^{-13}}$$

$$x = 5.29 \times 10^{-7}$$

These solubility of $PbCrO_4$ is 5.29×10^{-7} mole / dm^3 **Ans.**

Q.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.***

Solution:

Molarity of $CdCl_2$ = 0.01M pH – 9

K_{sp} of $Cd(OH)_2$ = 2.5×10^{-14} mole³ / dm⁶

Now,

	$Cd(OH)_2$	$\rightleftharpoons$	Cd^{2+}	+	$2OH^-$
	1 mole		1 mole		2 mole
	0.01 mole/dm³		0.01		mole/dm³

Here the concentration of Cd^{2+} is 0.01 mole/dm³

or the concentration of Cd^{2+} = 10^{-2} mole/dm³

now the concentration of OH^- will be

$$pH + POH = 14$$
$$pOH = 14 - pH$$
$$pOH = 14 - 9$$
$$pOH = 5 \quad [OH^-] = 10^{-5} M$$

$$Cd(OH)_2 \rightleftharpoons Cd^{2+} + 2OH^-$$

Ionic product – $[10^{-2}]\ [2 \times 10^{-5}]^2$

= $10^{-2} \times 4 \times 10^{-10}$

Thus ionic product = 4×10^{-12} mole³ / dm⁹

Since the ionic product of Cd (OH)₂ is greater than its solubility product (2.5×10^{-14}) thus Cd(OH)² will precipitate out form 0.01M solution. **Ans.**

(b) i - The solubility of $Mg(OH)_2$ at 25°C is 0.00764 g / dm³. What is the solubility product of $Mg(OH)_2$?

Solution:

Solubility of $Mg(OH)_2$ = 0.00764 gm / dm³ at 25°C

Molecular weight of $Mg(OH)_2$ = 58

Moles of $Mg(OH)_2$ = $\frac{0.00764}{58}$ = 0.0001317 mole

Or Moles of $Mg(OH)_2$ = 1.317×10^{-4}

Now, $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$[Mg^{2+}]$ – 1.31×10^{-4}

$[OH^-]$ = $2\ (1.31 \times 10^{-4})$

K_{sp} = $(1.31 \times 10^{-4})\ (2.62 \times 10^{-4})^2$

∴ K_{sp} = $1.31 \times 10^{-4} \times 6.937 \times 10^{-8}$

= 9.1×10^{-12} mole³ / dm⁹ **Ans.**

(b) ii - Should AgCl precipitate from a solution prepared by mixing 400ml of 0.1M NaCl and 600 ml of 0.03 M $AgNO_3$? (K_{sp} of AgCl = 1.6×10^{-10} moles / dm^3) **Karachi Board: 2018**

Solution:

Molarity of NaCl solution	=	0.1 M
Volume of NaCl solution	=	400 ml
Molarity of $AgNO_3$	=	0.03 M
Volume of $AgNO_3$	=	600 ml
Total volume after mixing them	=	400 + 600 = 1000 ml

Now the concentration of silver ion (Ag^+ ion)

$vol \times M_1 = vol \times M_2$

Before mixing *After mixing*

$600 \times 0.03 = 1000 \times M_2$

$$M_2 = \frac{(600 \times 0.03)}{1000} = 0.018$$

New concentration of chloride ion (Cl^- ion)

$vol \times M_1 = vol \times M_2$

$400 \times 0.1 = 1000 \times M_2$

$$M_2 = \frac{(400 \times 0.1)}{1000} = 0.04$$

Now consider $AgCl \rightleftharpoons Ag^+ + Cl^-$

Ionic product = $[0.018]\ [0.04]$

= 0.00072 or 7.2×10^{-4}

Because the value of ionic product = (7.2×10^{-4}) of AgCl is greater than its solubility product (1.6×10^{-10}) therefore by mixing the two solutions precipitate of AgCl will formed. **Ans.**