CHEMISTRY (XI)

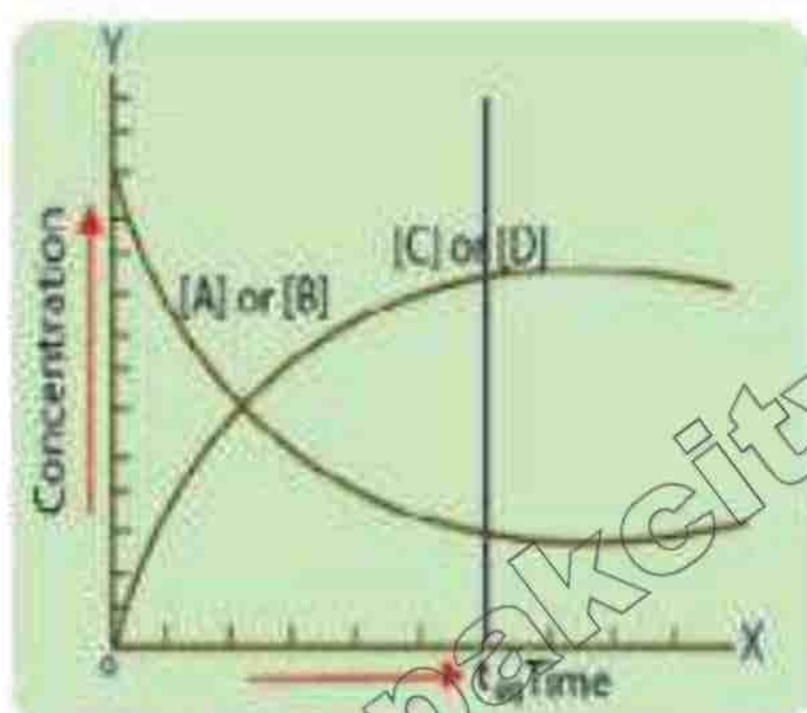
Chapter 8

Chemical Equilibrium

Short Questions

1. What is meant by the stage of chemical equilibrium?

Ans: In reversible chemical reactions two opposing reactions occur. A stage reaches for the reaction when the rates of two opposing reactions are equal. This stage is called stage of chemical equilibrium.



2. Define reversible reaction. Give an example.

Ans: A reversible reaction is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously. For example,

$$H_2 (g) + I_2 (g) \underset{}{\overset{425\ ^oC}{\rightleftharpoons}} 2HI (g)$$

3. Define irreversible reaction. Give an example.

Ans: An irreversible reaction is a reaction that proceeds in one direction only. The products do not react together to form the reactants. For example,

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

4. Justify that chemical equilibrium is dynamic in nature.

Ans: In reversible chemical reactions the molecules of reactants collide and convert into products. At the same time the molecules of the products are converting into reactants. When two opposing forces maintain the equal rates then equilibrium is there and that is dynamic equilibrium in nature.

5. Why the equilibrium constant value has its units for some of the reversible reactions but has no units for some other reactions?

Ans: If the number of moles of reactants and products are equal in a reversible balanced equation then the units are cancelled, and the value of Kc has no units.

$$CH_3COOH\,(aq) + C_2H_5OH\,(aq) \rightleftharpoons CH_3COOC_2H_5\,(aq) + H_2O\,(l)$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} \quad \frac{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]} \quad \text{no units}$$

If the number of moles of reactants and products are unequal, then Kc has net units.

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

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \frac{[\text{moles dm}^{-3}]^2}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]^3} \quad \text{moles}^{-2}\text{dm}^{+6}$$

6. When four types of chemical equilibrium constants for a reaction become equal? How Kp and Kc are related?

Ans: The expressions of equilibrium constants depend upon the concentration units used. Mostly the concentrations are expressed in mole dm^{-3}. Let us consider the following reversible reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{C_C^{\,c}\, C_D^{\,d}}{C_A^{\,a}\, C_B^{\,b}}$$

The square brackets represent the concentration of species in moles dm^{-3}. Anyhow, the capital C is also used for molar concentrations.

If the reactants A, B, and the products C, D of the reaction under consideration are ideal gases, then molar concentration of each gas is proportional to its partial pressure. When the concentrations are expressed in terms of partial pressures, the expression of Kp is

$$K_p = \frac{p_C^{\,c}\, p_D^{\,d}}{p_A^{\,a}\, p_B^{\,b}}$$

Here P_A, P_B, P_C and P_D are partial pressures of A, B, C, D respectively at equilibrium position. As long as the number of moles of products and reactants, which are in the gaseous state, are equal, the values of K_c and K_p remain the same. Otherwise, the following relationship between K_p and K_c can be derived by using Dalton's law of partial pressures.

$$K_p = K_c (RT)^{\Delta n}$$

7. How equilibrium constant helps to determine direction of reaction?

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Ans:

The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium. The value of [product] / [reactants] ratio leads to one of the following three possibilities.

(a) The ratio is less than Kc. This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in the forward direction.

(b) The ratio is greater than Kc. It means that the reverse reaction will occur to attain the equilibrium.

(c) When the ratio is equal to Kc, then the reaction is at equilibrium.

8. How the value of Kc helps to determine extent of reaction?

Ans: (a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.

(b) If the value of Kc is small, it reflects that the reaction does not proceed appreciably in the forward direction.

(c) If the value of Kc is very small, this shows a very little forward reaction.

9. State Le-Chatelier's principle.

Ans: This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

10. What happens to the direction of a reversible reaction when the ratio of the concentrations is less than actual Kc?

Ans: When the ratio of the concentrations for a reversible reaction is less than Kc then it means that the reaction is not at equilibrium stage. It must go to the forward direction to attain the actual value of K_c.

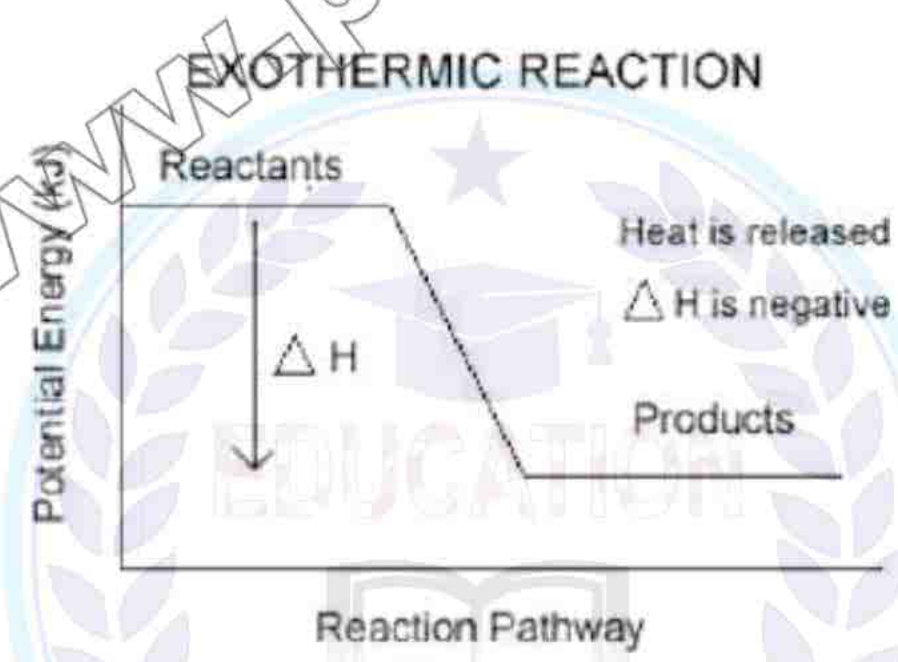
11. The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant. Why?

Ans: Those gaseous phase reversible reactions which happen with changing number of moles are affected by the change of volume at equilibrium stage. Their equilibrium position is disturbed but equilibrium constant is not changed.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

12. Why are the exothermic reactions favored to the forward direction by cooling, but reverse is true for endothermic reactions?

Ans: The amount of heat which is being evolved by the exothermic reaction is taken up by that body which has a cooling effect. So, the reactions move to that direction where there is less energy. The endothermic reactions require extra energy to take place. If the system is cooled it will go to that direction where there is a less energy and that is the backward direction of reaction



13. The change of temperature disturbs the equilibrium position and the equilibrium constant of reaction. Justify.

Ans: All the reversible reactions are disturbed by changing their equilibrium position and equilibrium constant by disturbing the temperature. Actually, change of temperature changes the energy contents of reactants and products.

14. What will be effect of change in pressure on NH_3 and SO_3 synthesis?

Ans:

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

This is a gaseous reaction having less number of moles of products. So this reaction happens with the decrease of volume. The increase of pressure will shift the equilibrium position of reaction to the forward direction and greater amount of ammonia will be produced. Equilibrium constant does not change. In $2SO_2 + O_2 \rightleftharpoons 2SO_3$ same principle is applicable.

15. How does a catalyst affect a reversible reaction?

Ans: A catalyst increases the rate of reaction by lowering the activation energy and giving new path to the reaction. The value of equilibrium constant as well as equilibrium position remains the same. It just increases the rate of both forward and reverse reactions so that the equilibrium is reached earlier.

16. How NaCl can be purified by common ion effect?

Ans: The impure sample of NaCl is dissolved in water to prepare the saturated solution.

$$NaCl\,(s) \rightleftharpoons Na^+\,(aq) + Cl^-\,(aq)$$

If HCl gas is passed in saturated solution of NaCl the Cl^- ions are generated in excess in the solution

$$HCl\,(aq) \rightleftharpoons H^+\,(aq) + Cl^-\,(aq)$$

Due to excess of Cl^- the ionization of NaCl is suppressed and NaCl settles down in the form of precipitate

$$\underset{(ppt)}{NaCl\,(s)} \rightleftharpoons Na^+\,(aq) + Cl^-\,(aq)$$

17. Define common ion effect. Give an example.

Ans: The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect. For example the solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_3\,(s) \rightleftharpoons K^+\,(aq) + ClO_3^-\,(aq)$$

$$KCl\,(aq) \rightleftharpoons K^+\,(aq) + Cl^-\,(aq)$$

18. What is the effect of common ion on solubility?

Ans: The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbSO_4$, which is a sparingly soluble ionic salt.

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

19. Why the ionic product of water increases with the increase of temperature?

Ans: The value of K_w is 0.11×10^{-14} at 0 ⁰ C and is 10^{-14} at 25 ⁰ C. The value increases approximately 10 times when the temperature changes from 0⁰ C to 25 ⁰ C. The reason is that the increase of temperature increases the kinetic energy of the water and possibility of bond breakage increases.

20. What is percentage ionization of acid?

Ans: We can calculate the percentage ionization of weak acid and the formula is as follows:

$$\%\text{ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

21. Define pH and pOH. Give mathematical expression.

Ans: pH is negative log of hydrogen ion concentration.

$$pH = -\log[H^+]$$

pOH is negative log of hydroxide ion concentration

$$pOH = -\log[OH^-]$$

22. Prove that pKw=14 at 25 ⁰ C

Ans:

$$pH = -\log[H^+]$$

and

$$pOH = -\log[OH^-]$$

For neutral water, $pH = -\log 10^{-7} = 7$

$$pOH = -\log 10^{-7} = 7$$

when
$pH = 7, \rightarrow$ solution is neutral
$pH < 7, \rightarrow$ solution is acidic
$pH > 7, \rightarrow$ solution is basic

If we take the negative log of K_w, then it is called pK_w.

$$pK_W = -\log K_W$$
$$= -\log 10^{-14}$$

$$pK_W = 14\log 10$$ Since ($\log 10 = 1$)

$$pK_W = 14 \times 1 = 14 \text{(at 25°C)}$$

23. Calculate ionization constant of acid.

Ans:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Let $K_c[H_2O] = Ka$

K_a is another constant

Hence $Ka = \frac{[H_3O^+][A^-]}{[HA]}$

24. Calculate ionization constant of base.

Ans: Let the base is represented by B. Then

$$B(aq) + H_3O^+ (aq) \rightleftharpoons BH^+ (aq) + OH^- (aq)$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Since, the concentration of H_2O constant, being in large excess

So, $K_c\ [H_2O] = \frac{[BH^+][OH^-]}{[B]}$

Put $K_c[H_2O] = K_b$

Hence $K_b = \frac{[BH^+][OH^-]}{[B]}$

25. Define pK_b and pK_a.

Ans: Negative log of K_a is called pK_a and negative log of K_b is called pK_b

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

26. Define buffers.

Ans: Those solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions. They have a specific constant value of pH and their pH values do not change on dilution and on keeping for a long time. Buffer solutions are mostly prepared by mixing two substances.

27. What are the types of buffers?

Ans: There are two types of buffers:

(i) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of such a buffer.

(ii) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH_4OH and NH_4Cl is one of the best examples of such a basic buffer.

28. Why do we need buffer solutions? OR What are the applications of buffers?

Ans: It is a common experience that the pH of the human blood is maintained at pH 7.35. If it goes to 7.00 or 8.00, a person may die. Sometimes one wants to study a reaction under conditions that would suffer any associated change in the pH of the reaction mixture. So, by suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if a small amount of a strong acid or a strong base is added. Buffers are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

29. Define buffer capacity.

Ans: The buffer capacity of a solution is the capability of a buffer to resist the change of pH.

30. What is Henderson equation?

Ans: For acidic buffer Henderson equation is

$$pH = pKa + \log \frac{[salt]}{[acid]}$$

For basic buffer Henderson equation is

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

31. How acidic buffer works?

Ans: Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa. CH_3COOH, being a weak electrolyte undergoes very little dissociation. When CH_3COONa is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^-

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3COONa(aq) \rightleftharpoons CH3COO^-(aq) + Na^+(aq)$$

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a weak acid will prefer to remain undissociated.

32. How a basic buffer works?

Ans: The buffer solution consisting of NH_4Cl and NH_4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

33. The solubility of glucose in water is increased by increasing the temperature. Explain.

Ans: The solubility of glucose in water involves an endothermic process. The solution has temperature lower than original temperature of solvent. Therefore, according to Le-Chatelier's principle, an increase in temperature will increase the solubility of glucose in solution.

34. Calculate the pH of 10^{-4} moldm^{-3} solution of HCl.

Ans: Mathematically

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log [10^{-4}] \\ &= -(-4)\log [10] \qquad \text{as } \log 10 = 1 \\ &= 4 \end{aligned}$$

35. Calculate the pH of 10^{-4} moldm^{-3} solution of Ba $(OH)_2$.

Ans:

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

$[OH^-] = 2\times10^{-4}\ mol.dm^{-3}$

pOH $= -\log 2\times10^{-4}$
$= 3.69$
pH= 14-pOH
$= 14-3.69$
$= 10.31$

36. Define solubility product. Give an example.

Ans: The solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation.

$$PbCl_2\,(s) + PbCl_2\,(aq) \rightleftharpoons Pb^{2+}\,(aq) + 2Cl^-\,(aq)$$

$$PbCl_2 \qquad K_{sp} = [Pb^{2+}(aq)][Cl^-(aq)]^2$$

37. Mention the applications of solubility product.

Ans: Following are the applications of solubility product:

i. Determination of solubility from K_{sp}

ii. Determination of K_{sp} from solubility

38. How K_{sp} is determined from solubility?

Ans: From the solubility of the compounds, we can calculate K_{sp} of the salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since the quantity of solute is very very small, so 100 g of water solution is 100 mL of solution. The reason is that the density of water is very close to unity. Hence, we get the concentration in moles dm^{-3}. The number of moles of solute dm^{-3} of the solution is calculated by dividing the mass of solute by its molar mass. Then by using the balanced equation, we find the molarity of each ion and then find K_{sp}.

39. How solubility is determined from K_{sp}?

Ans: For the determination of solubility from K_{sp} we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions are determined.

40. What is the effect of common ion on solubility?

Ans: The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

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

Now add Na_2CrO_4 which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So, equilibrium is shifted to the left to keep K_{sp} constant.

41. Write two applications of equilibrium constant?

Ans: Equilibrium constant of reversible reaction is a very informative parameter. It can be used to determine:

i. Direction of reaction before the reversible reaction attains equilibrium.

ii. Extent of reaction in forward and reverse side.

42. Derive solubility product expression for Ag_2CrO_4, $PbCl_2$, $AgCl$?

Ans: The solubility product is the product of the concentrations of ions raised to exponent equal to the co- efficient of the balanced equation.

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

43. How change in volume disturbs the equilibrium position for some of the gas phase reactions but not the equilibrium constant?

Ans: The change in volume disturbs those reactions in which number of moles of reactants and products are different. According to Le-Chatelier's principle, if volume of equilibrium system is decreased at equilibrium position the reaction will move in the direction of decreased number of moles and vice versa. New equilibrium position will be established but the value of K_c ultimately remains constant because it is only permanently affected by temperature change only.

44. Define Lowry-Bronsted concept of acids and bases.

Ans: According to this concept, acids are those species which donate the proton or have a tendency to donate and bases are those species which accept the proton or have a tendency to accept the proton.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

45. Prove by equations that what happens when Na_2CrO_4 is added to saturated solutionof $PbCrO_4$.

Ans:

$$PbCrO_4\,(aq) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}\,(aq)$$

$$Na_2CrO_4(aq) \rightleftharpoons Na^{1+}(aq) + CrO_4^{2-}(aq)$$

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. CrO_4^{2-} is a common ion, it combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

46. Why solid ice at 0•C can be melted by applying pressure without supply of heat from outside.

Ans: When pressure is applied to the broken pieces of ice at 0°C then according to Le-Chatelier's principle the ice moves to that direction where its volume should decrease i.e., towards liquid water. Actually, ice occupies 9% more volume than liquid water.

47. Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Ans: Since rate of forward reaction is directly proportional to molar concentration of reactants, with the passage of time the concentration of reactants decreases and rate of forward reaction decreases also.

48. Reversible reaction attains the position of equilibrium which is dynamic in nature and not static. Explain it.

Ans: At equilibrium state the reaction is not stopped. Only the rate of forward reaction becomes equal to the rate of reverse reaction. Since reaction is in progress in both the directions, therefore, equilibrium is dynamic in nature not static one.

49. Mention the properties of chemical equilibrium.

Ans: The properties of chemical equilibrium are:

i. All reactions cease at equilibrium so that the system becomes stationary.

ii. The forward and reverse reactions are taking place simultaneously at exactly the same rate.

50. What is the justification for the increase of ionic product with temperature?

Ans: The value of ionic product of water (K_w) increases almost 75 times when temperature is increased from 0 °C to 100 °C. The increase in K_w is not regular. This occurs because ionization of water is an endothermic process and with the increase in temperature bonds become weaker and ionization increases.

51. The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant.

Ans: The change in volume disturbs those reactions in which number of moles of reactants and products are different. According to Le-Chatelier's principle if volume of equilibrium mixture is decreased at equilibrium point then the reaction will move in the direction of decreased number of moles and vice versa. New equilibrium position will be established but the value of K_c ultimately remains constant because it is temporarily affected by volume change.

52. When a graph is plotted between time on x-axis and the concentrations of reactants and products on y-axis for a reversible reaction, the curves become parallel to time axis ata certain stage.

(a) At what stage the curves become parallel?

(b) Before the curves become parallel, the steepness of curves falls? Give reasons.

(c) The rate of decreases of concentrations of any of the reactants and rate of increaseof concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Ans:

(a) The curves become parallel at the stage of chemical equilibrium.

(b) The steepness of curves falls before the curves become parallel because rate of reaction decreases at that stage.

(c) The rate of decrease of concentrations of any of the reactants and rate of increase of concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. This is true for some reactions, when concentration of products is different from those of reactants. For example,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

53. Decide the comparative magnitudes of Kc and Kp, for the following reversible reactions.

(i) ***Ammonia synthesis*** ***(ii) Dissociation of PCl_5***

Ans: **(i) Ammonia synthesis:**

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Since $K_p = Kc\,(RT)^{\Delta n}$

Δn = number of moles of products – no of moles of reactants

$\Delta n = 2 - 4 = -2$

As value of Δn is negative so K_p will be lesser than K_c for this reaction.

(ii) Dissociation of PCl_5

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Since $K_p = Kc\,(RT)^{\Delta n}$

Δn = number of moles of products – no of moles of reactants

In this equation

$\Delta n = +1$

As value of Δn is positive so K_p will be greater than K_c for this reaction.