### Unit 7 (EQUILIBRIUM)

**Multiple Choice Questions** 

Single Correct Answer Type

Q1. We know that the relationship between K<sub>c</sub> and K<sub>p</sub> is K<sub>p</sub> = K<sub>c</sub>(RT)<sup> $\Delta$ n</sup> What would be the value of An for the reaction NH<sub>4</sub>C1(s)  $\Leftrightarrow$  NH<sub>3</sub>(g) + HCl(g)? (a) 1 (b) 0.5 (c) 1.5 (d) 2 Sol: (d) The relationship between K<sub>p</sub> and K<sub>c</sub> is K<sub>p</sub> = K<sub>c</sub> (RT)  $\Delta$ n Where  $\Delta$ n = (number of moles of gaseous products) – (number of moles of gaseous reactants) For the reaction, NH<sub>4</sub>C1(s)  $\Leftrightarrow$  NH<sub>3</sub>(g) + HCl(g)  $\Delta$ n = 2 - 0 = 2 Q2. For the reaction H<sub>2</sub>(g) + I<sub>2</sub>(g)  $\rightleftharpoons$ 2HI(g), the standard free energy is  $\Delta$ G° >0 The

equilibrium constant (K) would be (a) K = 0(b)> 1 (c) K=1(d)A:<I Sol: (d)  $\Delta G^{\circ} = -RTIn K. \Delta G^{\circ} > 0$  means  $\Delta G^{\circ}$  is +ve. This can be so only if In K is -ve, i.e., K< 1.

Q3. Which of the following is not a general characteristic of equilibria involving physical processes?

(a) Equilibrium is possible only in a closed system at a given temperature.

(b) All measurable properties of the system remain constant.

(c) All the physical processes stop at equilibrium.

(d) The opposing processes occur at the same rate and there is dynamic but stable condition.

**Sol:** (c) All the physical processes like melting of ice and freezing of water, etc., do not stop at equilibrium.

Q4. PC1<sub>5</sub>, PC1<sub>3</sub> and Cl<sub>2</sub> are at equilibrium at 500 K in a closed container and their concentrations are 0.8 x 10<sup>43</sup> molL<sup>-1</sup>, 1.2 x 10<sup>-3</sup> mol L<sup>1</sup> and 1.2 x 10<sup>-3</sup> mol L<sup>-1</sup> The value of K<sub>c</sub> for the reaction PCl<sub>5</sub>(g)  $\Rightarrow$  PCl<sub>3</sub>(g) + Cl<sub>2</sub>(g) will be

(a) 8 x 10<sup>3</sup> molL<sup>-1</sup>

(b) 1.8 x 10<sup>-3</sup> molL<sup>-1</sup>

(c) 1.8 x 10"<sup>3</sup> molL<sup>-1</sup>

(d) 0.55 x 10<sup>4</sup> molL<sup>-1</sup>

**Sol:** (b)  $PCI_5(g) \rightleftharpoons PCI_3(g) + CI_2(g)$ 

$$K_{\rm C} = \frac{[\rm{PCl}_3][\rm{Cl}_2]}{[\rm{PCl}_5]} = \frac{1.2 \times 10^{-3} \times 1.2 \times 10^{-3}}{0.8 \times 10^{-3}}$$
$$= 1.8 \times 10^{-3} \text{ mol } L^{-1}$$

Q5. Which of the following statements is incorrect?

(a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time.

(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.

(c) On addition of catalyst the equilibrium constant value is not affected.

(d) Equilibrium constant for a reaction with negative AH value decreases as the temperature increases.

**Sol:** (b)Fe<sup>3+</sup>+SCN<sup>-</sup>  $\rightleftharpoons$  FeSCN<sup>2+</sup>(Red)

When oxalic acid is added to a solution containing iron nitrate and potassium thiocyanate, oxalic acid reacts with  $Fe^{3+}$  ions to form a stable complex ion  $[Fe(C_20_4)_3]^{3-}$ , thus, decreasing the concentration of free  $Fe^{3+}$  ions which in mm decreases the intensity of red colour.  $Fe^{3+} + SCN^{-} \rightleftharpoons [Fe(SCN)]^{2+}_{(Red)}$ 

Q6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture, it becomes pink. On the basis of this information mark the correct answer.  $[Co(H_20)_6]^{2+}$  (aq) + 4Cl<sup>-</sup>(aq)  $[CoCl_4]^{2-}$ (aq) + 6H<sub>2</sub>0(l)

(Pink)

(Blue)

(a) $\Delta H > 0$  for the reaction

(b)  $\Delta H < 0$  for the reaction

(c)  $\Delta H = 0$  for the reaction

### (d) The sign of $\Delta H$ cannot be predicted on the basis of this information.

**Sol**:(a) Since the reaction shifts to backward direction on cooling, this means that the backward reaction is exothermic reaction. Therefore, the forward reaction is endothermic reaction and  $\Delta$ H > 0.

Q7. The pH of neutral water at 25°C is 7.0. As the temperature increases, ionization of water increases, however, the concentration of  $H^+$  ions and  $OH^-$  ions are equal. What will be the pH of pure water at 60°C?

(a) Equal to 7.0 (b) Greater than 7.0 (c) Less than 7.0 (d) Equal to zero Sol:(c) At 25°C,  $[H^+] = [OH^-] = 10^{-7}$  and  $K_w = [H^+] [OH^-] = 10^{-14}$ . On heating,  $K_w$  increases, i.e.,  $[H^+] [OH^-] > 10^{-14}$  As  $[H^+] = [OH^-]$ ,  $[H^+]^2 > 10^{-14}$  or  $[H^+] > 10^{-7}$  M or pH < 7.

Q8. The ionization constant of an acid,  $K_a$  is the measure of strength of an acid. The  $K_a$  values of acetic acid, hypochlorous acid and formic acid are  $1.74 \times 10^{-5}$ ,  $3.0 \times 10^{-8}$  and  $1.8 \times 10^{-4}$  Which of the following orders of pH of 0.1 mol dm<sup>-3</sup> solutions of these acids is correct?

(a) acetic acid > hypochlorous acid > formic acid

(b) hypochlorous acid > acetic acid > formic acid

(c) formic acid > hypochlorous acid > acetic acid

(d) formic acid > acetic acid > hypochlorous acid

- Sol. (d)  $[H_3O^+] = \sqrt{K_a \cdot C}$  for the same concentration,  $[H_3O^+] \propto \sqrt{K_a}$ . But  $pH = -\log [H_3O^+]$ Larger the value of  $K_a$ , larger will be  $[H_3O^+]$  and lower will be pH.
- 9.  $K_{a_1}, K_{a_2}$  and  $K_{a_3}$  are the respective ionization constants for the following reactions.

$$H_{2}S \stackrel{\longrightarrow}{\longrightarrow} H^{+} + HS^{-}$$
$$HS^{-} \stackrel{\longrightarrow}{\longrightarrow} H^{+} + S^{2-}$$
$$H_{2}S \stackrel{\longrightarrow}{\longrightarrow} 2H^{+} + S^{2-}$$

The correct relationship between  $K_{a_1}, K_{a_2}$  and  $K_{a_3}$  is

(a)  $K_{a_3} = K_{a_1} \times K_{a_2}$ (b)  $K_{a_3} = K_{a_1} + K_{a_2}$ (c)  $K_{a_3} = K_{a_1} - K_{a_2}$ (d)  $K_{a_3} = K_{a_1}/K_{a_2}$ 

Sol. (a) For the reaction,  $H_2S \rightleftharpoons H^+ + HS^-$ 

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

For the reaction,  $HS^- \iff H^+ + S^{2-}$ 

$$K_{a_2} = \frac{[\mathrm{H}^+][\mathrm{S}^{2^-}]}{[\mathrm{H}\mathrm{S}^-]}$$

When the above two reactions are added, their equilibrium constants are multiplied. Thus

$$K_{a_3} = \frac{[\mathrm{H}^+]^2[\mathrm{S}^{2^-}]}{[\mathrm{H}_2\mathrm{S}]} = K_{a_1} \times K_{a_2}$$

Hence,  $K_{a_3} = K_{a_1} \times K_{a_2}$ 

Q10. Acidity of BF3 can be explained on the basis of which of the following concepts?

(a) Arrhenius concept

(b) Bronsted Lowry concept

(c) Lewis concept

(d) Bronsted Lowry as well as Lewis concept

**Sol:** (c) According to Lewis concept, a positively charged or an electron deficient species acts as Lewis acid.  $BF_3$  is an electron deficient compound with B having 6 electrons only.

Q11. Which of the following will produce a buffer solution when mixed in equal volumes?

(a) 1 mol dm<sup>-3</sup> NH<sub>4</sub>OH and 0.1 mol dm<sup>-3</sup> HC1

(b) 0.05 mol dm<sup>-3</sup> NH<sub>4</sub>OH and 0.1 mol dm<sup>-3</sup> HC1

(c) 1 mol dm<sup>-3</sup> NH<sub>4</sub>OH and 0.05 mol dm<sup>-3</sup> HC1

### (d) 1 mol dm<sup>-3</sup> CH<sub>3</sub>COONa and 0.1 mol dm<sup>-3</sup> NaOH

**Sol:** (c) In (c), all HC1 will be neutralized and NH<sub>4</sub>C1 will be formed. Also some NH<sub>4</sub>OH will be left unneutralized. Thus, the final solution will contain NH<sub>4</sub>OH and NH<sub>4</sub>C1 and hence will form a buffer.

Q12. In which of the following solvents is silver chloride most soluble?

- (a) 0.1 mol dm<sup>-3</sup> AgN0<sub>3</sub> solution
- (b) 0.1 mol dm<sup>-3</sup> HC1 solution
- (c)  $H_20$
- (d) Aqueous ammonia

Sol: (d) Silver chloride forms a soluble complex with aqueous ammonia.

AgCl + 2NH<sub>3</sub>→ [Ag(NH<sub>3</sub>)<sub>2</sub>]Cl

Q13. What will be the value of pH of 0.01 mol dm<sup>-3</sup> CH<sub>3</sub>COOH (K.<sub>A</sub> -74 x 10<sup>-5</sup>)?

(a) 3.4

(b) 3.6

(c) 3.9

(d) 3.0

Sol. (a)  $CH_3COOH + H_2O \implies H_3O^+ + CH_3COO^-$ Initial conc. 0.01 0 0At equilibrium 0.01 - x x x  $K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.01 - x}$ Since x < < 0.01, therefore,  $0.01 - x \approx 0.01$   $\frac{x^2}{0.01} = 1.74 \times 10^{-5}$  $x^2 = 1.74 \times 10^{-7}$  or  $x = 4.2 \times 10^{-4}$ 

$$pH = -log (4.2 \times 10^{-4}) = 3.4$$

Q14.  $K_a$  for  $CH_3COOH$  is 1.8 x  $10^{-5}$  and  $K_b$  for  $NH_4OH$  is 1.8 x  $10^{-5}.$  The pH of ammonium acetate will be

(a) 7.005

(b) 4.75

(c) 7.0

(d) Between 6 and 7

Sol: (c) Ammonium acetate is a salt of weak acid and weak base.

$$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$
$$= \frac{1}{2} [14 - \log(1.8 \times 10^{-5}) + \log(1.8 \times 10^{-5})] = 7.0$$

Q15. Which of the following options will be correct for the stage of half completion of the reaction  $A \rightleftharpoons B$ . (a)  $\Delta G^{\circ} = 0$ 

(a) ΔG° = 0 (b) ΔG° > 0 (c) ΔG° < 0 (d) ΔG° = -RT In 2 Sol: (a) A ⇒B ΔG° = -RT In K At the stage of half completion of reaction [A] = [B], Therefore, K = 1. Thus,  $\Delta G^{\circ} = 0$ .

Q16. On increasing the pressure, in which direction will the gas phase reaction proceed to reestablish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction,

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

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(a) K will remain same

(b) K will decrease

(c) K will increase

#### (d) K will increase initially and decrease when pressure is very high

**Sol:**(a)N<sub>2</sub>(g) +  $3H_2(g) \rightleftharpoons 2NH_3(g)$ 

According to Le Chatelier's principle, at constant temperature, the equilibrium composition will change but K will remain same.

Q17. What will be the correct order of vapour pressure of water, acetone and ether at 30°C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point.

(a) Water < Ether < Acetone

(b) Water < Acetone < Ether

(c) Ether < Acetone < Water

(d) Acetone < Ether < Water

**Sol:** (b) Greater the boiling point, less is the vapour pressure. Hence, the correct order of vapour pressures will be:

water < acetone < ether.

### 18. At 500 K, equilibrium constant, $K_{\rm C}$ , for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \Longrightarrow HI(g)$$

What would be the equilibrium constant  $K_C$  for the reaction 2HI(g)  $\Longrightarrow$  H<sub>2</sub>(g) + I<sub>2</sub>(g)

(a) 
$$0.04$$
 (b)  $0.4$  (c) 25

(d) 2.5

Sol. (a) For the reaction,

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \xrightarrow{} HI(g); K_C = 5$$

For

$$H_2(g) + I_2(g) \implies 2HI(g); K_C = (5)^2 = 25$$

For

2HI(g) 
$$\longrightarrow$$
 H<sub>2</sub>(g) + I<sub>2</sub>(g); K<sub>C</sub> =  $\frac{1}{25}$  = 0.04

Q19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(a) H<sub>2</sub>(g) + I<sub>2</sub>(g) ≓2HI(g) '

(b)  $PCI_5(g) \rightleftharpoons PCI_3(g) + CI_2(g)$ 

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

(d) The equilibrium will remain unaffected in all the three cases.

**Sol:** (d) The equilibrium will remain unaffected in all three cases on addition of small amount of inert gas at constant volume.

Q20. For the reaction  $N_20_4(g) \rightleftharpoons 2N0_2(g)$ , the value of K is 50 at 400 K and 1700 at 500 K. Which of the following options is correct? (a) The reaction is endothermic.

(b) The reaction is exothermic.

# (c) If $NO_2(g)$ and $N_2O_4(g)$ are mixed 400 K at partial pressures 20 bar and 2 bar respectively, more $N_2O_4(g)$ will be formed.

#### (d) The entropy of the system increases.

**Sol:** (a, c, d)

(a) As the value of K increases with increase of temperature and K =  $K_f / K_b$ , this means that  $k_f$  increases, i.e., forward reaction is favoured.

Hence, reaction is endothermic.

(c) At 400 K, 
$$Q = \frac{p_{NO_2}^2}{P_{N_2O_4}} = \frac{(20)^2}{2} = 200$$
. Thus,  $Q > K$ . Equilibrium will

shift backward to form more  $N_2O_4$ .

(d) As reaction is accompanied by increase in the number of moles, entropy increases.

Q21. At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature? .

- (a) Normal melting point
- (b) Equilibrium temperature
- (c) Boiling point
- (d) Freezing point

**Sol:** (a, d) These are normal melting point and freezing point since they are measured at atmospheric pressure.

Q22. The ionization of hydrochloric acid in water is given below:

 $HCl(aq) + H_20(l) \rightleftharpoons H_30^+ (aq) + Cl^-(aq)$ 

Label two conjugate acid-base pairs in this ionization.Sol: HCI (Acid)CI<sup>-</sup> (Conjugate base)

 $H_20$  (Base)  $H_30^+$  (Conjugate acid

Q23. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionization and how is it affected by concentration of sodium chloride?

**Sol:** (i) Sugar being a non-electrolyte does not ionize in water, whereas NaCl ionizes completely in water and produces Na<sup>+</sup> and Cl<sup>-</sup> ions which help in the conduction of electricity. (ii) When concentration of NaCl is increased, more Na<sup>+</sup> and Cl ions will be produced. Hence, conductance increases.

## Q24. $BF_3$ does not have proton but still acts as an acid and reacts with $NH_3$ . Why is it so? What type of bond is formed between the two?

**Sol:**  $BF_3$  is an electron deficient compound. Hence, it acts as Lewis acid.  $NH_3$  has a lone pair of electrons. Hence, acts as Lewis base. A coordinate bond is formed between the two.  $H_3N: \rightarrow BF_3$ 

Q25. Ionization constant of a weak base MOH, is given by the expression



Values of ionization constant of some weak bases at a particular temperature are given below:

Base	Dimethylamine	Urea	Pyridine	Ammonia
	5.4 x 10 <sup>-4</sup>	1.3 x 10 <sup>-14</sup>	1.77 x IO <sup>-9</sup>	1.77 xlO <sup>-5</sup>

## Arrange the bases in decreasing order of the extent of their ionization at equilibrium. Which of the above base is the strongest?

**Sol:** Greater is the ionization constant ( $K_b$ ) of a base, greater is the ionization of the base. Order of extent of ionization at equilibrium is dimethylamine > ammonia > pyridine > urea. Dimethylamine is the strongest base due to maximum value of  $K_b$ .

# Q26. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

### OH<sup>-</sup>, RO<sup>-</sup>, ch<sub>3</sub>coo<sup>-</sup>, cl<sup>-</sup>

Sol: Conjugate acids of given bases are  $H_20$ , ROH,  $CH_3COOH$ , HC1.

Their acidic strength is in the order

HCl > CH<sub>3</sub>COOH > H<sub>2</sub>0 >ROH Hence, basic strength is in the order RO<sup>-</sup> > OH<sup>-</sup> > CH<sub>3</sub>COO<sup>-</sup> > Cl<sup>-</sup>

### Q27. Arrange the following in increasing order of pH. $KN0_3(aq)$ , $CH_3COONa(aq)$ , $NH_4Cl(aq)$ , $C_6H_5COONH_4(aq)$

**Sol:**  $KNO_3$ : salt of strong acid-strong base, solution is neutral, pH = 7. CHjCOONa: salt of weak acid-strong base, solution is basic, pH > 7.

 $NH_4CI$ : salt of strong acid-weak base, solution is acidic, pH < 7.

 $C_6H_5COONH_4$ : both weak put NH<sub>4</sub>OH is slightly stronger than  $C_6H_5COOH$ , pH close to 7 but slightly > 7.

Hence, in order of pH,  $NH_4C1 < C_6H_5COONH_4 > KNO_3 < CH_3COONa$ .

### Q28. The value of $K_{c}$ for the reaction

2HI(g)  $\rightleftharpoons$ H<sub>2</sub>(g) + I<sub>2</sub>(g) is 1 x 10<sup>-4</sup>. At a given time, the composition of reaction mixture is [HI] = 2 x 10<sup>-5</sup> mol, [H<sub>2</sub>] = 1 x 10<sup>-5</sup> mol and [I<sub>2</sub>] = 1 x 10<sup>-5</sup> mol. In which direction will the reaction proceed?

Sol.  $Q = \frac{[H_2][I_2]}{[HI]^2} = \frac{1 \times 10^{-5} \times 1 \times 10^{-5}}{(2 \times 10^{-5})^2}$  $= \frac{1}{4} = 0.25 = 2.5 \times 10^{-1}$ Value of  $K_c = 1 \times 10^{-4}$ Since  $Q > K_c$ , the reaction will proceed in backward direction.

# Q29. On the basis of the equation $pH = -\log [H^+]$ , the pH of $10^{-8}$ mol dm<sup>-3</sup> solution of HC1 should be 8. However, it is observed to be less than 7.0. Explain the reason.

**Sol:** Concentration  $10^{-8}$  mol dm<sup>-3</sup> indicates that the solution is very dilute. So, we cannot neglect the contribution of  $H_30^+$  ions produced from  $H_20$  in the solution. Total  $[H_30^+] = 10^{-8} + 10^{-7}$  M. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.

From calculation, it is found that pH of  $10^{-8}$  mol dm<sup>-3</sup> solution of HC1 is equal to 6.96.

# Q30. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution a 100 times?

**Sol:** pH = 5 i.e.,  $[H^+] = 10^{-5} \text{ mol } L^{-1}$ On dilution by 100 times  $[H^+] = 10^{-7} \text{ mol } L^{-1}$  For a very dilute solution, Total  $[H^+] = [H_30^+ \text{ ions from acid}] + [H_20^+ \text{ ions from water}]$  $= 10^{-7} + 10^{-7}$  pH = -log[H<sup>+</sup>] = -log (2 x 10<sup>-7</sup>) = 7 - log 2 = 7-0.3010 = 6.6990

Q31. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution ( $Q_{sp}$ ) becomes greater than its solubility product. If the solubility of BaS0<sub>4</sub> in water is 8 x 10<sup>-4</sup> mol dm<sup>-3</sup>, calculate its solubility in 0.01 mol dm<sup>-3</sup> of H<sub>2</sub>S0<sub>4</sub>.

Sol. BaSO<sub>4</sub> 
$$\implies$$
 Ba<sup>2+</sup> + SO<sub>4</sub><sup>2-</sup>  
At  $t = 0$  1 0 0  
At equilibrium in water  $1 - S$  S S  
At equilibrium in sulphuric acid  $1 - S$  S  $(S + 0.01)$   
 $K_{sp}$  for BaSO<sub>4</sub> in water = [Ba<sup>2+</sup>] [SO<sub>4</sub><sup>2-</sup>]  
 $= S \times S = S^2$   
 $K_{sp} = (8 \times 10^{-4})^2 = 64 \times 10^{-8}$  ...(i)  
In presence of H<sub>2</sub>SO<sub>4</sub>,  
 $K_{sp} = (S)(S + 0.01)$   
 $K_{sp}$  being constant  
 $(S)(S + 0.01) = 64 \times 10^{-8}$   
 $S^2 + 0.01$  S  $= 64 \times 10^{-8}$   
 $S^2 + 0.01$  S  $= 64 \times 10^{-8} = 0$   
 $\implies$   $S = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$   
 $= \frac{-0.01 \pm \sqrt{10^{-4} + (256 \times 10^{-8})}}{2}$   
 $= \frac{-10^{-2} + (1.012 \times 10^{-2})}{2} = \frac{(-1 + 1.012) \times 10^{-2}}{2}$   
 $= 6 \times 10^{-5}$  mol dm<sup>-3</sup>

Q32. pH of 0.08 mol dm<sup>-3</sup>HOC1 solution is 2.85. Calculate its ionization constant. Sol: pH of HOC1 = 2.85 -pH = log [H<sup>+</sup>] or -2.85 = log [H<sup>+</sup>] => [H<sup>+</sup>] = 1.413 x 10<sup>-3</sup>

Q33. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively.

**Sol:** pH of solution A = 6 [H<sup>+</sup>] = 10<sup>-6</sup>mol L<sup>1</sup> pH of solution B = 4 [H<sup>+</sup>] = 10<sup>-4</sup> molL<sup>-1</sup>

On mixing one litre of each solution Total volume = 1 L + 1 L = 2 LTotal amount of H<sup>+</sup> in 2 L solution formed by mixing solutions A and B =  $10^{-6} + 10^{-4}$  mol

Total 
$$[H^+] = \frac{10^{-4}(1+0.01)}{2} = \frac{1.01 \times 10^{-4}}{2}$$
  
= 5 × 10<sup>-5</sup> mol L<sup>-1</sup>  
pH = -log  $[H^+] = -log (5 × 10^{-5})$   
= -log 5 - (-5 log 10) = -log 5 + 5  
= 5 - log 5 = 5 - 0.6990 = 4.3010 = 4.3

Thus, the pH of resulting solution is 4.3.

Q34. The solubility product of  $AI(OH)_3$  is 2.7 x 10<sup>-11</sup>. Calculate its solubility in g<sup>-</sup>L and also find out pH of this solution. (Atomic mass of A1 = 27 u).

Sol.  
Al(OH)<sub>3</sub> 
$$\implies$$
 Al<sup>3+</sup> + 3OH<sup>-</sup>  
Conc. at t = 0 1 0 0  
Conc. at equilibrium 1 - S S 3S  
 $K_{sp} = [Al^{3+}] [OH^{-}]^3 = (S) (3S)^3 = 27S^4$   
 $S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$   
 $S = 1 \times 10^{-3} \text{ mol } L^{-1}$ 

(i) Solubility of  $Al(OH)_3$ Molar mass of  $Al(OH)_3 = 78 \text{ g}$  $\therefore$  Solubility of  $Al(OH)_3$  in g L<sup>-1</sup> = 1 × 10<sup>-3</sup> × 78 = 78 × 10<sup>-3</sup> = 7.8 × 10<sup>-2</sup> g L<sup>-1</sup>

(ii) *pH of the solution* 

 $S = 1 \times 10^{-3} \text{ mol } \text{L}^{-1}$ [OH<sup>-</sup>] = 3S = 3 × 1 × 10<sup>-3</sup> = 3 × 10<sup>-3</sup> pOH = -log [OH<sup>-</sup>] = -log (3 × 10<sup>-3</sup>) pOH = 3 - log 3 = 3 - 0.4771 = 2.552 pH = 14 - pOH = 14 - 2.522 = 11.4771

Q35. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. ( $K_{sp}$  of PbCl<sub>2</sub> = 3.2 x 10<sup>-8</sup>, atomic mass of Pb = 207 u).

Sol.  
PbCl<sub>2</sub> 
$$\implies$$
 Pb<sup>2+</sup> + 2Cl<sup>-</sup>  
Conc. at  $t = 0$  1 0 0  
Conc. at equilibrium  $1 - S$  S 2S  
 $K_{sp} = [Pb^{2+}] [Cl^{-}]^2 = (S) (2S)^2 = 4S^3$   
 $S^3 = \frac{K_{sp}}{4} = \frac{3.2 \times 10^{-8}}{4} = 8 \times 10^{-9} \text{ mol } L^{-1}$   
 $S = \sqrt[3]{8 \times 10^{-9}} = 2 \times 10^{-3} \text{ mol } L^{-1}$ 

Solubility of  $PbCl_2 = 2 \times 10^{-3} \times 278$  (molar mass of  $PbCl_2$ ) = 556×10<sup>-3</sup> gL<sup>-1</sup> = 0.556 gL<sup>-1</sup>

To get saturated solution, 0.556 g PbCl<sub>2</sub> is dissolved in 1 L water.

0.1 g of PbCl<sub>2</sub> is dissolved in  $\frac{0.1}{0.556} = 0.1798$  L water

To make a saturated solution, 0.1 g PbCl<sub>2</sub> is dissolved in 0.1798  $\approx$  0.2 L water

Q36. A reaction between ammonia and boron trifluoride is given below:

 $:NH_3 + BF_3 \rightarrow H_3N : BF_3$ 

Identify the acid and base in this reaction. Which theory explains it? What is the hybridization of B and N in the reactants?

**Sol**:Although  $BF_3$  does not have a proton but acts as Lewis acid as it is an electron deficient compound. It reacts with  $NH_3$  by accepting the lone pair of electrons from  $NH_3$  and completes its octet. The reaction can be represented by

 $\mathsf{BF}_3 + : \mathsf{NH}_3 {\rightarrow} \mathsf{BF}_3 \leftarrow : \mathsf{NH}_3$ 

Lewis electronic theory of acids and bases can explain it. Boron in  $BF_3$  is  $sp^2$  hybridised, whereas N in  $NH_3$  is  $sp^3$  hybridised.

Q37. Following data is given for the reaction:

### $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta_f H^{\circ} [CaO(s)] = -635.1 \text{ kJ mol}^{-1}$ $\Delta_f H^{\circ} [CO_2(g)] = -393.5 \text{ kJ mol}^{-1}$

 $\Delta_{\rm f}$ H° [CaC0<sub>3</sub>(s)] = -1206.9 kJ mol<sup>-1</sup>

Predict the effect of temperature on the equilibrium constant of the above reaction.

 $\textbf{Sol:} \ \boldsymbol{\Delta}_{r} \mathsf{H}^{\circ} = \boldsymbol{\Delta}_{f} \mathsf{H}^{\circ} \ [\mathsf{CaO}] + \boldsymbol{\Delta}_{f} \mathsf{H}^{\circ} \ [\mathsf{CO}_{2}] - \boldsymbol{\Delta}_{f} \mathsf{H}^{\circ} \ [\mathsf{CaCO}_{3}]$ 

= [-635.1] + [-393.5] - [-1206.9] = 178.3 kJ mol<sup>-1</sup> Thus, the reaction is endothermic. Hence, according to Le Chatelier's principle, on increasing the temperature, the equilibrium will proceed in the forward direction.

Matching Column Type Questions

### Q38. Match the following equilibria with the corresponding condition

Column I		Column II		
(i)	Liquid <b>⇔</b> Vapour	(a)	Saturated solution	
(ii)	Solid <b>⇔</b> Liquid	(b)	Boiling point	
(iii)	Solid <b>⇔</b> Vapour	(c)	Sublimation point	
(iv)	Solute(s) ≓Solute (solution)	(d)	Melting point '	
		(e)	Unsaturated solution	

**Sol:** (i)  $\rightarrow$  (b), (ii)  $\rightarrow$  (d), (iii)  $\rightarrow$  (c), (iv)  $\rightarrow$  (a)

(i) Liquid ≓Vapour equilibrium exists at the boiling point.

(ii) Solid  $\rightleftharpoons$ Liquid equilibrium exists at the melting point.

(iii) Solid  $\rightleftharpoons$  Vapour equilibrium exists at the sublimation point.

(iv) Solute(s) ≓Solute (solution) equilibrium exists in saturated solution.

Q39. For the reaction:  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$  equilibrium constant,

$$K_{\rm C} = \frac{[\rm NH_3]^2}{[\rm N_2][\rm H_2]^3}.$$

Some reactions are written below in Column I and their equilibrium constants in terms of  $K_c$  are written in Column II. Match the following reactions with the corresponding equilibrium constant.

	Column I (Reaction)	(E	Column II (Equilibrium constant)	
(i)	$2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$	(a)	2K <sub>C</sub>	
(ii)	$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$	(b)	$K_{\rm C}^{1/2}$	
(iii)	$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \Longrightarrow NH_3(g)$	(c)	$\frac{1}{K_{\rm C}}$	
		(d)	$K_{\rm C}^2$	

**Sol:** (i)  $\rightarrow$ (d), (ii)  $\rightarrow$  (c), (iii)  $\rightarrow$  (b) ForN<sub>2</sub>(g) + 3H<sub>2</sub>(g) $\rightleftharpoons$ 2NH<sub>3</sub>(g)

$$K_{\rm C} = \frac{[\rm NH_3]^2}{[\rm N_2][\rm H_2]^3}$$
  
(i)  $2\rm N_2(g) + 6\rm H_2(g) \rightleftharpoons 4\rm NH_3(g); \ K_{\rm C}' = K_{\rm C}^2$   
(ii)  $2\rm NH_3(g) \rightleftharpoons \rm N_2(g) + 3\rm H_2(g); \ K_{\rm C}' = \frac{1}{K_{\rm C}}$   
(iii)  $\frac{1}{2}\rm N_2(g) + \frac{3}{2}\rm H_2(g) \rightleftharpoons \rm NH_3(g); \ K_{\rm C}' = K_{\rm C}^{1/2}$ 

Q40. Match standard free energy of the reaction (Column I) with the corresponding equilibrium constant (Column II).

Column I		Column II	
(i)	$\Delta G^{\circ} > 0$	(a)	K > 1
(ii)	$\Delta G^{\circ} < 0$	(b)	<i>K</i> = 1
(iii)	$\Delta G^{\circ} = 0$ .	(c)	K = 0
		(d)	<i>K</i> < 1

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**Sol.** (i)  $\rightarrow$ (d), (ii)  $\rightarrow$  (a), (iii)  $\rightarrow$  (b)

As we know that,  $\Delta G^{\circ} = -\mathbf{R}T \ln K$ 

(i) If  $\Delta G^{\circ} > 0$ , i.e.,  $\Delta G^{\circ}$  is positive, then ln K is negative i.e., K < 1

(ii) If  $\Delta G^{\circ} < 0$ , i.e.,  $\Delta G^{\circ}$  is negative then ln K is positive i.e., K > 1.

(iii) If  $\Delta G^{\circ} = 0$ , ln K = 0, i.e., K = 1