Chapter - Equilibrium

Topic-1: Chemical Equilibrium

1 MCQs with One Correct Answer

1. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order – **[2008S]**
   (a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$
   (c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

2. The Haber's process for the formation of NH_3 at 298 K is $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = -46.0$ kJ; Which of the following is the correct statement **[2006 - 3M, –1]**
   (a) The condition for equilibrium is
   $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$
   where G is Gibb's free energy per mole of the gaseous species measured at that partial pressure.
   (b) On adding N_2, the equilibrium will shift to forward direction because according to IInd law of thermodynamics, the entropy must increase in the direction of spontaneous reaction
   (c) The catalyst will increase the rate of forward reaction by 2 times and that of backward reaction by 1.5 times
   (d) None of these

3. Consider the following equilibrium in a closed container **[2002S]**
   $$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
   At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
   (a) neither K_p nor α changes
   (b) both K_p and α change
   (c) K_p changes, but α does not change
   (d) K_p does not change, but α changes

4. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_p = (4x^2P)/(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true? **[2001S]**
   (a) K_p increases with increase of P
   (b) K_p increases with increase of x
   (c) K_p increases with decrease of x
   (d) K_p remains constant with change in P and x

5. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_S) with its solubility (S) is **[2001S]**
   (a) $L_S = S^{p+q}.p^p.q^q$ (b) $L_S = S^{p+q}.p^q.q^p$
   (c) $L_S = S^{pq}.p^p.q^q$ (d) $L_S = S^{pq}.(pq)^{p+q}$

6. When two reactants, A & B are mixed to give products C & D, the reaction quotient Q, at the initial stages of the reaction **[2000S]**
   (a) is zero (b) decreases with time
   (c) is independent of time (d) increases with time

7. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500 °C, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_c, with concentration in mole litre^{-1}, is **[2000S]**
   (a) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (b) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$
   (c) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{2}}$ (d) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

8. For the chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by **[1999 - 2 Marks]**
   (a) temperature and pressure
   (b) temperature only
   (c) pressure only
   (d) temperature, pressure and catalyst

9. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25 °C) is **[1990 - 1 Mark]**
   (a) $Mg(OH)_2$ (b) $Ca(OH)_2$
   (c) $Ba(OH)_2$ (d) $Be(OH)_2$

10. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with **[1988 - 1 Mark]**
    (a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
    (b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
    (c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
    (d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

11. An example of a reversible reaction is : **[1985 - 1 Mark]**
(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$
(b) $AgNO_3(aq) + HCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$
(c) $2Na(s) + H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$
(d) $KNO_3(aq) + NaCl(aq) \rightarrow KCl(aq) + NaNO_3(aq)$

12. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium: **[1984 - 1 Mark]**
(a) K_p does not change significantly with pressure.
(b) α does not change with pressure.
(c) concentration of NH_3 does not change with pressure.
(d) concentration of hydrogen is less than that of nitrogen.

13. A liquid is in equilibrium with its vapour at its boiling point. On the average, the molecules in the two phases have equal : **[1984 - 1 Mark]**
(a) inter-molecular forces (b) potential energy
(c) total energy (d) kinetic energy

14. The precipitate of **[1982 - 1 Mark]**
$CaF_2(K_{sp} = 1.7 \times 10^{-10})$
is obtained when equal volumes of the following are mixed
(a) $10^{-4}M\ Ca^{2+} + 10^{-4}M\ F^-$ (b) $10^{-2}M\ Ca^{2+} + 10^{-3}M\ F^-$
(c) $10^{-5}M\ Ca^{2+} + 10^{-3}M\ F^-$ (d) $10^{-3}M\ Ca^{2+} + 10^{-5}M\ F^-$

15. For the reaction : **[1981 - 1 Mark]**
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
the equilibrium constant K_p changes with
(a) total pressure
(b) catalyst
(c) the amounts of H_2 and I_2 present
(d) temperature

16. The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if **[1981 - 1 Mark]**
(a) temperature is increased and pressure is kept constant
(b) temperature is reduced and pressure is increased
(c) both temperature and pressure are increased
(d) both temperature and pressure are reduced

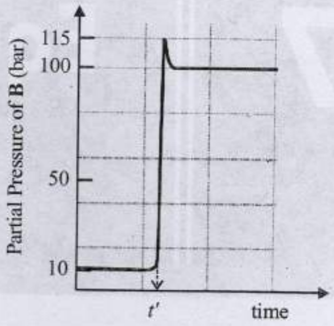
17. Molten sodium chloride conducts electricity due to the presence of **[1981 - 1 Mark]**
(a) free electrons
(b) free ions
(c) free molecules
(d) atoms of sodium and chlorine

2 Integer Value Answer

18. In 1 L saturated solution of AgCl [$K_{sp}(AgCl) = 1.6 \times 10^{-10}$], 0.1 mol of CuCl [$K_{sp}(CuCl) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. The value of "x" is **[2011]**

3 Numeric / New Stem Based Questions

19. Consider the reaction $A \rightleftharpoons B$ at 1000 K. At time t', the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of **A** was maintained at 1 bar. Given below is the plot of the partial pressure of **B** with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? **[Adv. 2020]**



20. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}. **[Adv. 2019]**
$$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$$
When equal volumes of 0.06 M Fe^{2+}(aq) and 0.2 M S^{2-}(aq) solutions are mixed, the equilibrium concentration of Fe^{2+}(aq) is found to be $Y \times 10^{-17}$ M. The value of Y is

21. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? **[1993 - 3 Marks]**
K_{sp} for $MS = 6.0 \times 10^{-21}$; concentration of saturated $H_2S = 0.1$ M
$K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S.

22. The equilibrium constant of the reaction
$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$
at 100 °C is 50. If a one litre flask, containing one mole of A_2 is connected to a two litre flask, containing two mole of B_2, how many mole of AB will be formed at 373 °C? **[1985 - 4 Marks]**

4 Fill in the Blanks

23. A ten-fold increase in pressure on the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium results in .... in K_P. **[1996 - 1 Mark]**

24. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by........ **[1994 - 1 Mark]**

5 True / False

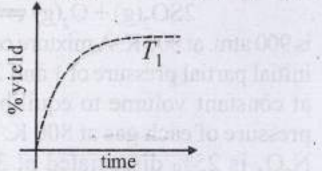
25. Solubility of sodium hydroxide increases with increase in temperature. **[1985 - ½ Mark]**

26. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **[1984 - 1 Mark]**

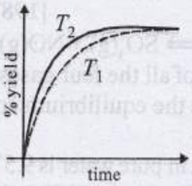
27. If equilibrium constant for the reaction $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $1/K$. **[1984 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

28. The % yield of ammonia as a function of time in the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \Delta H < 0$ at (P, T_1) is given below



If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by **[Adv. 2015]**

(a)


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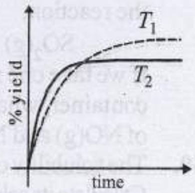

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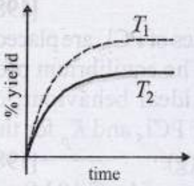

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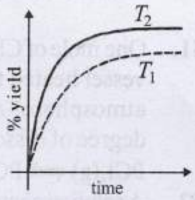


29. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions **[Adv. 2013]**

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. For this equilibrium, the correct statement(s) is (are)

(a) ΔH is dependent on T
(b) K is independent of the initial amount of $CaCO_3$
(c) K is dependent on the pressure of CO_2 at a given T
(d) ΔH is independent of catalyst, if any

30. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is **[Adv. 2013]**

(a) 1.1×10^{-11} (b) 1.1×10^{-10}
(c) 1.1×10^{-12} (d) 1.1×10^{-9}

31. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by **[1998 - 2 Marks]**

(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of the container
(d) increasing the amount of CO(g).

32. For the reaction : **[1991 - 1 Mark]**

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

The forward reaction at constant temperature is favoured by

(a) introducing an inert gas at constant volume
(b) introducing an inert gas at constant pressure
(c) increasing the volume of the container
(d) introducing PCl_5 at constant volume

33. The equilibrium : **[1989 - 1 Mark]**

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

is attained at 25 °C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct?

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 do not change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) More SO_2Cl_2 is formed.

34. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium. **[1986 - 1 Mark]**

(a) addition of $NaNO_2$ favours reverse reaction
(b) addition of $NaNO_3$ favours forward reaction
(c) increasing temperature favours forward reaction
(d) increasing pressure favours reverse reaction

35. For the gas phase reaction : **[1984 - 1 Mark]**

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \ (\Delta H = -32.7 \text{ kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) increasing the temperature
(b) decreasing the pressure
(c) removing some H_2
(d) adding some C_2H_6

9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

36. **Statement -1** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-2 At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[2008]**

37. **Statement-1** The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.

Statement-2 When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change. **[1991 - 2 Marks]**

10 Subjective Problems

38. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27° C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate K_c and K_p for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ? **[1999 - 7 Marks]**

39. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of $AgCl = 1.8 \times 10^{-10}$ at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia. **[1998 - 5 Marks]**

40. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl ($K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}$). **[1997 - 5 Marks]**

41. For the reaction

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

the equilibrium costant, at 25°C, is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$. **[1994 - 3 Marks]**

42. At temperature T, a compound AB_2 (g) dissociates according to the reaction **[1994 - 4 Marks]**

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation x which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, P.

43. 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K along with a catalyst so that the following reaction can take place :

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Hydrogen is introduced until the total pressure of the system is 8.5 atmosphere at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place. **[1993 - 5 Marks]**

44. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated? **[1992 - 4 Marks]**

45. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} $mol^3\ L^{-3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached : **[1991 - 4 Marks]**

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

46. For the reaction : $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constant, K_p and K_c. **[1990 - 5 Marks]**

47. The equilibrium constant K_p of the reaction :

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

is 900 atm. at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm. respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. **[1989 - 3 Marks]**

48. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C. **[1988 - 4 Marks]**

49. At a certain temperature equilibrium constant (K_c) is 16 for the reaction. **[1987 - 5 Marks]**

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO(g) and $NO_2(g)$?

50. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $Mg(NO_3)_2$ solution. **[1986 - 5 Marks]**

51. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. **[1984 - 6 Marks]**

52. A solution contains a mixture of Ag (0.10 M) and Hg_2^{++} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated? [K_{sp} : $AgI = 8.5 \times 10^{-17}$; $Hg_2I_2 = 2.5 \times 10^{-26}$] **[1984 - 4 Marks]**

53. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction **[1981 - 4 Marks]**

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

calculate the equilibrium constant (K_c) in concentration units. What will be the value of K_c for the following equilibrium ?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(ag)$$

Topic-2: Ionic Equilibrium

1 MCQs with One Correct Answer

1. On decreasing the pH from 7 to 2, the solubility of a sparingly soluble salt (MX) of a weak acid (HX) increased from 10^{-4} mol L^{-1} to 10^{-3} mol L^{-1}. The pK_a of HX is **[Adv. 2023]**

(a) 3 (b) 4 (c) 5 (d) 2

2. 2.5 mL of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25° C) is titrated (2/15) M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) **[2008S]**

(a) 3.7×10^{-14} M (b) 3.2×10^{-7} M
(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

3. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution? **[2005S]**

(a) 8×10^{-2} M (b) 8×10^{-11} M
(c) 1.6×10^{-11} M (d) 8×10^{-5} M

4. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is **[2004S]**
(a) 25% (b) 50% (c) 75% (d) 85%

5. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is **[2004S]**
(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

6. The set with correct order of acidity is **[2001S]**
(a) $HClO < HClO_2 < HClO_3 < HClO_4$
(b) $HClO_4 < HClO_3 < HClO_2 < HClO$
(c) $HClO < HClO_4 < HClO_3 < HClO_2$
(d) $HClO_4 < HClO_2 < HClO_3 < HClO$

7. The pH of 0.1 M solution of the following salts increases in the order. **[1999 - 2 Marks]**
(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

8. The following acids have been arranged in the order of decreasing acid strength. Identify the correct order.
ClOH (I), BrOH (II), IOH (III) **[1996 - 1 Mark]**
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

9. Which one is more acidic in aqueous solution. **[1995S]**
(a) $NiCl_2$ (b) $FeCl_3$ (c) $AlCl_3$ (d) $BeCl_2$

10. The degree of dissociation of water at 25°C is $1.9 \times 10^{-7}\%$ and density is 1.0 g cm^{-3}. The ionic constant for water is :
(a) 1.0×10^{-10} (b) 1.0×10^{-14} **[1995S]**
(c) 1.0×10^{-16} (d) 1.0×10^{-8}

11. Which of the following solutions will have pH close to 1.0? **[1992 - 1 Mark]**
(a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH
(b) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH
(c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH
(d) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH

12. The following equilibrium is established when hydrogen chloride is dissolved in acetic acid.

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

The set that characterises the conjugate acid-base pairs is **[1992 - 1 Mark]**
(a) (HCl, CH_3COOH) and $(CH_2COOH_2^+, Cl^-)$
(b) $(HCl, CH_3COOH_2^+)$ and (CH_3COOH, Cl^-)
(c) $(CH_3COOH_2^+, HCl)$ and (Cl^-, CH_3COOH)
(d) (HCl, Cl^-) and $(CH_3COOH_2^+, CH_3COOH)$

13. The reaction which proceeds in the forward direction is
(a) $Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$ **[1991 - 1 Mark]**
(b) $NH_3 + H_2O + NaCl \rightarrow NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 \rightarrow SnCl_2 + 2HgCl_2$
(d) $2CuI + I_2 + 4K^+ \rightarrow 2Cu^{2+} + 4KI$

14. Which one of the following is the strongest acid? **[1989 - 1 Mark]**
(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

15. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be **[1988 - 1 Mark]**
(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach.

16. The compound whose 0.1 M solution is basic is : **[1986 - 1 Mark]**
(a) ammonium acetate (b) ammonium chloride
(c) ammonium sulphate (d) sodium acetate

17. The compound insoluble in acetic acid is : **[1986 - 1 Mark]**
(a) calcium oxide (b) calcium carbonate
(c) calcium oxalate (d) calcium hydroxide

18. The compound that is not a Lewis acid is : **[1985 - 1 Mark]**
(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$

19. The conjugate acid of NH_2^- is : **[1985 - 1 Mark]**
(a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4

20. The best indicator for detection of end point in titration of a weak acid and a strong base is : **[1985 - 1 Mark]**
(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenolphthalein (8 to 9.6)

21. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is : **[1984 - 1 Mark]**
(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 1.0×10^{10} (d) 1.0×10^{14}

22. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is:
(a) 4 (b) 7 **[1984 - 1 Mark]**
(c) 10 (d) 14

23. At 90°C, pure water has $[H_3O^+]$ 10^{-6} mole $litre^{-1}$. What is the value of K_w at 90°C? **[1981 - 1 Mark]**
(a) 10^{-6} (b) 10^{-12} (c) 10^{-14} (d) 10^{-8}

24. Of the given anions, the strongest Bronsted base is **[1981 - 1 Mark]**
(a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

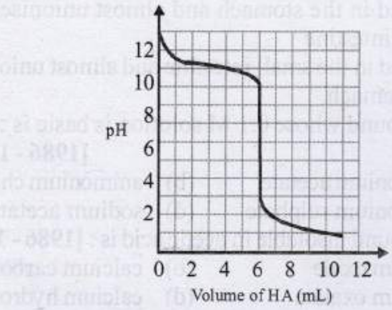
25. The pH of a 10^{-8} molar solution of HCl in water is
(a) 8 (b) –8 **[1981 - 1 Mark]**
(c) between 7 and 8 (d) between 6 and 7

26. An acidic buffer solution can be prepared by mixing the solutions of **[1981 - 1 Mark]**
(a) ammonium acetate and acetic acid
(b) ammonium chloride and ammonioum hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide.

2 Integer Value Answer

27. Concentration of H_2SO_4 and Na_2SO_4 in a solution is 1 M and 1.8×10^{-2} M, respectively. Molar solubility of $PbSO_4$ in the same solution is $X \times 10^{-Y}$ M (expressed in scientific notation). The value of Y is ________.
[Given: Solubility product of $PbSO_4$ $(K_{sp}) = 1.6 \times 10^{-8}$. For H_2SO_4, K_{a1} is very large and $K_{a2} = 1.2 \times 10^{-2}$] **[Adv. 2022]**

28. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + HA \rightarrow BH^+ + A^-$. **[Adv. 2020]**



29. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3 and LiCN **[2010]**

30. The total number of diprotic acids among the following is: H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_3BO_3, H_3PO_2, H_2CrO_4 and H_2SO_3. **[2010]**

31. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of a 0.01 M solution of its sodium salt is **[2009 - 2 Marks]**

32. 0.1 M NaOH is titrated with 0.1 M *HA* till the end point; K_a for *HA* is 5.6×10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point. **[2004 - 2 Marks]**

33. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a = 1.0 \times 10^{-5}$)? **[1997 - 2 Marks]**

3 Numeric / New Stem Based Questions

34. A solution is prepared by mixing 0.01 mol each of H_2CO_3, $NaHCO_3$, Na_2CO_3, and NaOH in 100 mL of water. *p*H of the resulting solution is ______.
[Given: pK_{a_1} and pK_{a_2} of H_2CO_3 are 6.37 and 10.32, respectively; log 2 = 0.30] **[Adv. 2022]**

35. An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S. What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS?
Use K_{sp} (ZnS) = 1.25×10^{-22} and overall dissociation constant of H_2S, $K_{NET} = K_1K_2 = 1 \times 10^{-21}$. **[Adv. 2020]**

36. The solubility of a salt of weak acid (***AB***) at pH 3 is $Y \times 10^{-3}$ mol L^{-1}. The value of *Y* is ______. **[Adv. 2018]**
(Given that the value of solubility product of ***AB*** (K_{sp}) = 2×10^{-10} and the value of ionization constant of ***HB*** (K_a) = 1×10^{-8})

37. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **[2000 - 5 Marks]**

38. What will be the resultant pH when 200mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ? **[1998 - 2 Marks]**

39. What is the pH of a 0.50 M aqueous NaCN solution? pK_b of CN^- is 4.70. **[1996 - 2 Marks]**

40. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.
(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.) **[1995 - 2 Marks]**

41. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4 ? K_a for H_2CO_3 in blood is 7.8×10^{-7}. **[1993 - 2 Marks]**

4 Fill in the Blanks

42. In the reaction $I^- + I_2 \rightarrow I_3^-$, the Lewis acid is .... **[1997 - 1 Mark]**

43. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .... **[1984 - 1 Mark]**

44. The conjugate base of HSO_4^- in aqueous solution is .... **[1982 - 1 Mark]**

5 True / False

45. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **[1982 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

46. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (*HA*, 1M) is 1/100th of that of a strong acid (*HX*, 1M), at 25°C. The K_a of *HA* is **[Adv. 2013]**
(a) 1×10^{-4}
(b) 1×10^{-5}
(c) 1×10^{-6}
(d) 1×10^{-3}

47. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are) **[2010]**
(a) HNO_3 and CH_3COOH
(b) KOH and CH_3COONa
(c) HNO_3 and CH_3COONa
(d) CH_3COOH and CH_3COONa

48. A buffer solution can be prepared from a mixture of **[1999 - 3 Marks]**
(a) sodium acetate and acetic acid in water
(b) sodium acetate and hydrochloric acid in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

49. Which of the following statements(s) is (are) correct? **[1998 - 2 Marks]**
(a) The pH of 1.0×10^{-8} M solution of HCl is 8
(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(c) Autoprotolysis constant of water increases with temperature
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = (1/2) pK_a.

7 Match the Following

50. Dilution processes of different aqueous solutions, with water, are given in LIST-I. The effects of dilution of the solutions on $[H^+]$ are given in LIST-II.
(Note: Degree of dissociation (α) of weak acid and weak base is $<< 1$; degree of hydrolysis of salt $<<1$; $[H^+]$ represents the concentration of H^+ ions) **[Adv. 2018]**

	LIST-I		LIST-II
P.	(10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1.	the value of $[H^+]$ does not change on dilution
Q.	(20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2.	the value of $[H^+]$ changes to half of its initial value on dilution
R.	(20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3.	the value of $[H^+]$ changes to two times of its initial value on dilution
S.	10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	4.	the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
		5.	the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST-I with one or more effect(s) in LIST-II. The correct option is

(a) P-4; Q-2 ; R-3; S-1 (b) P-4 ; Q-3 ; R-2; S-3
(c) P-1 ; Q-4 ; R-5; S-3 (d) P-1 ; Q-5 ; R-4 ; S-1

8 Comprehension/Passage Based Questions

PASSAGE-I

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation:

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G°$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{\text{equilibrium}}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.
(Given $R = 0.083$ L bar K^{-1} mol^{-1}) **[Adv. 2016]**

51. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is

(a) $\dfrac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (b) $\dfrac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(c) $\dfrac{4\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ (d) $\dfrac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

52. The INCORRECT statement among the following, for this reaction, is
(a) Decrease in the total pressure will result in formation of more moles of gaseous X
(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously
(c) $\beta_{\text{equilibrium}} = 0.7$
(d) $K_C < 1$

PASSAGE-II

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6 °C was measured. (Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1}) **[Adv. 2015]**

53. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt.2 is
(a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4

54. The pH of the solution after Expt. 2 is
(a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

9 Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

55. **Statement -1** HNO_3 is a stronger acid than HNO_2
Statement -2 In HNO_3 there are two nitrogen-to-oxygen bonds whereas in HNO_2 there is only one. **[1998 - 2 Marks]**

10 Subjective Problems

56. Arrange the following oxides in the decreasing order of Bronsted basicity :
$BaO, SO_3, CO_2, Cl_2O_7, B_2O_3$ **[2004 - 2 Marks]**

57. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.
(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.
(ii) If 6 g of NaOH is added to the above solution, determine the final pH.
[Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}]. **[2002 - 5 Marks]**

58. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8. **[1999 - 4 Marks]**

59. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25 °C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25 °C is 3.4×10^{10} L mol^{-1}s^{-1}. Calculate the rate constant for proton transfer from water to NH_3. **[1996 - 3 Marks]**

60. Increasing basicity order : H_2O, OH^-, CH_3OH, CH_3O^- **[1992 - 1 Mark]**

61. A 40.0 mL solution of weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. **[1991 - 6 Marks]**

62. What is the pH of 1.0 M solution of acetic acid? To what volume must one liter of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given : $K_a = 1.8 \times 10^{-5}$. **[1990 - 4 Marks]**

63. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mole/L of ammonium chloride and 0.05 mole/L of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution:

$K_b[NH_4OH] = 1.80 \times 10^{-5}$ **[1989- 3 Marks]**
$K_{sp}[Mg(OH)_2] = 6 \times 10^{-10}$
$K_{sp}[Al(OH)_3] = 6 \times 10^{-32}$

64. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 gram formula weight of NaCN? K dissociation (HCN) $= 4.1 \times 10^{-10}$. **[1988 - 4 Marks]**

65. What is the pH of the solution when 0.20 mole of hydrochloric acid is added to one litre of a solution containing. **[1987 - 5 Marks]**

(i) 1 M each of acetic acid and acetate ion?
(ii) 0.1 M each of acetic acid and acetate ion?

Assume the total volume is one litre.

K_a for acetic acid $= 1.8 \times 10^{-5}$.

66. Increasing acid strength : $HClO_3$, $HClO_4$, $HClO_2$, $HClO$ **[1986 - 1 Mark]**

67. The $[H^+]$ in 0.2 M solution of formic acid is 6.4×10^{-3} mole litre^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre^{-1}. What wil be pH of this solution? K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75. **[1985 - 3 Marks]**

68. Increasing bond length : F_2, N_2, Cl_2, O_2 **[1985 - 1 Mark]**

69. The dissociation constant of a weak acid HA is 4.9×10^{-8}. After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7. **[1983 - 2 Marks]**

70. Twenty mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid to give 70 mL of the solution. What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8×10^{-5}. **[1982 - 3 Marks]**

71. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at 25°C $= 1.34 \times 10^{-5}$. **[1981 - 4 Marks]**

72. A solution contains Na_2CO_3 and $NaHCO_3$. 10 mL of solution requires 2.5 mL of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5 mL of 0.2 M H_2SO_4 was required. Calculate the amount of Na_2CO_3 and $NaHCO_3$ in one litre of the solution. **[1979]**

Answer Key

Topic-1 : Chemical Equilibrium

1.	(d)	**2.**	(a)	**3.**	(d)	**4.**	(d)	**5.**	(a)	**6.**	(d)	**7.**	(d)	**8.**	(a)	**9.**	(d)	**10.**	(a)
11.	(d)	**12.**	(a)	**13.**	(d)	**14.**	(b)	**15.**	(d)	**16.**	(b)	**17.**	(b)	**18.**	(7)	**19.**	(0.25)	**20.**	(8.93)
21.	(0.983)	**22.**	(1.886)	**23.**	(no change)	**24.**	($K_p = K_c(RT)^{\Delta n}$)	**25.**	(True)	**26.**	(True)	**27.**	(False)	**28.**	(b)				
29.	(a, b, d)	**30.**	(b)	**31.**	(d)	**32.**	(b,c,d)	**33.**	(a)	**34.**	(c, d)	**35.**	(a, b, c, d)	**36.**	(d)	**37.**	(d)		

Topic-2 : Ionic Equilibrium

1.	(b)	**2.**	(d)	**3.**	(b)	**4.**	(c)	**5.**	(b)	**6.**	(a)	**7.**	(b)	**8.**	(a)	**9.**	(c)	**10.**	(b)
11.	(d)	**12.**	(d)	**13.**	(a)	**14.**	(a)	**15.**	(d)	**16.**	(d)	**17.**	(c)	**18.**	(N)	**19.**	(a)	**20.**	(d)
21.	(c)	**22.**	(a)	**23.**	(b)	**24.**	(a)	**25.**	(d)	**26.**	(a)	**27.**	(6)	**28.**	(3)	**29.**	(3)	**30.**	(6)
31.	(8)	**32.**	(9)	**33.**	(2)	**34.**	(10.02)	**35.**	(0.20)	**36.**	(4.47)	**37.**	(4.86)	**38.**	(11.30)			**39.**	(11.5)
40.	(6.5)	**41.**	(78.36)	**42.**	(I_2)	**43.**	(amphoteric)			**44.**	(SO_4^{2-})	**45.**	False	**46.**	(a)	**47.**	(c, d)	**48.**	(a, c)
49.	(b, c)	**50.**	(d)	**51.**	(b)	**52.**	(c)	**53.**	(a)	**54.**	(b)	**55.**	(c)						

Hints & Solutions

Topic-1: Chemical Equilibrium

1. **(d)** $MX \longrightarrow \underset{s}{M^+} + \underset{s}{X^-}$ (Where *s* is the solubility)

Then $K_{sp} = s^2$ or $s = \sqrt{K_{sp}}$

Similarly for $MX_2 \longrightarrow \underset{s}{M^{2+}} + \underset{2s}{2X^-}$

$$K_{sp} = s \times (2s)^2 = 4s^3 \quad \text{or} \quad s = \left[\frac{K_{sp}}{4}\right]^{\frac{1}{3}}$$

and for $M_3X \longrightarrow \underset{3s}{3M^+} + \underset{s}{X^{-3}}$

$$K_{sp} = (3s)^3 \times s = 27s^4 \quad \text{or} \quad s = \left[\frac{K_{sp}}{27}\right]^{\frac{1}{4}}$$

From the given values of K_{sp} for MX, MX_2 and M_3X, we can find the solubilities of those salts at temperature, *T*.

Solubility of $MX = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$

$$\text{Solubility of } MX_2 = \left[\frac{3.2 \times 10^{-14}}{4}\right]^{\frac{1}{3}} \text{ or } \left[\frac{32}{4} \times 10^{-15}\right]^{\frac{1}{3}}$$

$$= \left[8 \times 10^{-15}\right]^{\frac{1}{3}} \text{ or } 2 \times 10^{-5}$$

$$\text{Solubility of } M_3X = \left[\frac{2.7 \times 10^{-15}}{27}\right]^{\frac{1}{4}} = \left[10^{-16}\right]^{\frac{1}{4}} \text{ or } 10^{-4}$$

Thus, the solubilities are in the order $MX > M_3X > MX_2$ *i.e.* the correct answer is (d).

2. **(a)** In a reversible reaction, catalyst speeds up both the forward and backward reactions to the same extent, so (c) is wrong. At equilibrium,

$$\Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

$$\Rightarrow 2G_{NH_3} - (G_{N_2} + 3G_{H_2}) = 0$$

$$\text{or } 2G_{NH_3} = G_{N_2} + 3G_{H_2}$$

On adding N_2, reaction will move to forward direction because of Le-Chatelier's principle.

3. **(d)** At constant temperature K_p or K_c remains constant.

For the equilibria :

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$\Delta n = 1$

Since, temperature is constant so K_c or K_p will remain constant. Further, since volume is halved, the pressure will be doubled so α will decrease so as to maintain the constancy of K_c or K_p.

From Le-Chatelier's principle reaction will move backwards.

4. **(d)** At constant temperature, K_p remains constant. With change of pressure, *x* will change in such a way that K_p remains a constant.

5. **(a)** $A_pB_q(s) \rightleftharpoons \underset{pS}{pA^{+q}} + \underset{qS}{qB^{-p}}$

$$L_S = (pS)^p.(qS)^q = p^p.q^q.S^{(p+q)}$$

6. **(d)** At initial stage of reaction, concentration of each product will increase and hence, *Q* will increase.

7. **(d)** $K_p = K_c \cdot (RT)^{\Delta n}$

$$\Delta n = 2 - 4 = -2; \quad K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}},$$

(*R* in $L.atm.K^{-1} mole^{-1}$).

8. **(a)** The given reaction will be exothermic in nature due to the formation of three *X* - *Y* bonds from the gaseous atoms. The reaction is also accompanied with the decrease in the gaseous species (*i.e.* Δn is negative). Hence, the reaction will be affected by both temperature and pressure. The use of catalyst does not affect the equilibrium concentrations of the species in the chemical reaction.

9. **(d)** In case of alkaline earth hydroxides solubility increases on moving down the group. $Be(OH)_2$ has lowest solubility and hence, lowest solubility product.

10. **(a)** For a precipitation to occur

Solubility product < Ionic product

Given $K_{sp} = 1.8 \times 10^{-10}$

Calculating ionic products in each

$$\text{Ionic product} = [Ag^+][Cl^-] = \frac{10^{-4}}{2} \times \frac{10^{-4}}{2} = 2.5 \times 10^{-9}$$

which is greater than K_{sp} (1.8×10^{-10}).

11. **(d)** As all the reactants and products are present in aqueous form in (d), so it is a reversible reaction. In others, either solid or gas is generated, which is insoluble or volatile and hence, makes the reaction unidirectional.

12. **(a)** Statement (a) is correct and the rest statements are wrong. K_p depends only on temperature, hence at constant temp. K_p will not change.

13. **(d)** Liquid $\xrightleftharpoons{\text{b.p.}}$ Vapour at equilibrium

(a) Inter-molecular forces are more in liquid phase than that in gas phase.

(b) Due to difference in inter-molecular forces, the potential energy is different.

(c) Due to difference in potential energy, the total energy of the molecules are different.

(d) Kinetic energy depends on temperature only. Hence, both the molecules of liquid and solid have same kinetic energy.

14. **(b)** For precipitation to occur, ionic product > solubility products

Given, $K_{sp}CaF_2 = 1.7 \times 10^{-10}$

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

Ionic product of $CaF_2 = [Ca^{2+}][F^-]^2$

Calculate I.P. in each case

(a) I.P. of $CaF_2 = (10^{-4}) \times (10^{-4})^2 = 10^{-12}$

(b) I.P. of $CaF_2 = (10^{-2}) \times (10^{-3})^2 = 10^{-8}$

(c) I.P. of $CaF_2 = (10^{-5}) \times (10^{-3})^2 = 10^{-11}$

(d) I.P. of $CaF_2 = (10^{-3}) \times (10^{-5})^2 = 10^{-13}$

$\because$ I.P > solubility in choice (b) only.

$\therefore$ ppt of CaF_2 is obtained in case of choice (b) only.

15. **(d)** Only temperature affects the equilibrium constant.

16. **(b)**

(i) According is Le-Chateliers principle, exothermic, reactions are favoured at low temperature.

(ii) According to Le-Chateliers principle, the reaction in which $n < 0$, are favoured at high pressure.

Given $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{Heat}$

$\because$ It is exothermic reaction

$\therefore$ Yield of SO_3 is maximum at low temperature

$n = 2 - 3 = -1$ or $n < 0$

$\therefore$ Yield of SO_3 is maximum at high pressure.

17. **(b)** In molten state, the cations and anions become free and flow of current is due to migration of these ions in opposite directions in the electric field.

18. **(7)** Let the solubility of AgCl is x mol litre^{-1} and that of CuCl is y mol litre^{-1}

$$\underset{}{AgCl} \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$

$$CuCl \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$$

$\therefore$ K_{sp} of AgCl = $[Ag^+][Cl^-]$

$1.6 \times 10^{-10} = x(x+y)$ ...(i)

Similarly, K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x+y)$ ...(ii)

On solving, (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7}$ $\therefore$ $x = 7$

19. **(0.25)** $A \rightleftharpoons B$

$$K_{eq} = \frac{P_B}{P_A}$$

$$K_{1000k} = \frac{10}{1} = 10;\ K_{2000k} = \frac{100}{1} = 100$$

$$\text{Now, } \frac{\Delta G^\circ_{1000k}}{\Delta G^\circ_{2000k}} = \frac{(-RT\ln k_{eq})_{1000k}}{(-RT\ln k_{eq})_{2000k}} = \frac{1000 \times \ln 10}{2000 \times \ln 100} = 0.25$$

20. **(8.93)** $Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)\ (K_c = 1.6 \times 10^{17})$

$t = 0$ 0.03M 0.1 M

At equilibrium $(0.03 - x)$ $(0.1 - x)$

Since,

$K_c >> 10^3;\ 0.03 - x = 0\ \therefore\ x = 0.03$ and $0.1 - x = 0.07$

$$K_c = \frac{1}{(0.07) \times [Fe^{2+}]} = 1.6 \times 10^{17} \text{ (conc. of solid is taken as 1)}$$

$$[Fe^{2+}] = \frac{1}{0.07 \times 1.6} \times 10^{-17} = \frac{250}{28} \times 10^{-17}$$

$$= 8.93 \times 10^{-17} \qquad \text{(i)}$$

comparing (i) with given value in question we get, $Y = 8.93$.

21. **(0.983)**

$H_2S \rightleftharpoons H^+ + HS^-$ $\therefore K_1 = \dfrac{[H^+][HS^-]}{[H_2S]}$

Further, $HS^- \rightleftharpoons H^+ + S^{2-}$ $\therefore K_2 = \dfrac{[H^+][S^{2-}]}{[HS^-]}$

Dissociation constant of H_2S, $K = K_1 \times K_2$

i.e. $K = 1 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$

Now we know that

$K_{sp} = [M^{2+}][S^{2-}] \Rightarrow 6 \times 10^{-21} = 0.05 \times [S^{2-}]$

$$[S^{2-}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}$$

Substituting the various values in the following relation

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$1.3 \times 10^{-20} = \frac{[H^+]^2[1.2 \times 10^{-19}]}{0.1} \quad \because [H_2S] = 0.1\,M$$

$$[H^+]^2 = \frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}$$

$$[H^+] = \sqrt{\frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}} = 1.04 \times 10^{-1}$$

$pH = -\log[H^+]$; $pH = -\log(1.04 \times 10^{-1})$

$= 1.0 - \log 1.04 = 1.0 - 0.017 = \mathbf{0.983}$

22. **(1.886)**

$$\begin{array}{llll} & A_2(g) & + \; B_2(g) & \rightleftharpoons 2AB(g) \\ \text{At start} & 1 & 2 & 0 \\ \text{At equ.} & 1-x & 2-x & 2x \end{array}$$

$$\therefore [A_2]=\frac{1-x}{3}, [B_2]=\frac{2-x}{3}, [AB]=\frac{2x}{3}$$

$$\therefore K=\frac{(2x/3)^2}{[(1-x)/3][(2-x)/3]}=50$$

On solving we get, $23x^2-75x+50=0; x=2.317$ or 0.943
The value 2.317 is inadmissable because initial concentration of reactants is 2 moles and so $x=0.943$

$\therefore$ Moles of AB formed $= 2 \times 0.943 =$ **1.886**

23. **No change;** (K_p of an equilibrium reaction is independent of the pressure of the system.)

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

Here Δn = No. of moles of gaseous products – no. of moles of gaseous reactants

R = gas constant, and T = absolute temperature.

25. **True :** Overal disolution of NaOH is exothermic but near saturation point, the change in dissolution enthalpy is positive. Hence, from the definition of solubility, it will increase with increase in temperature.

26. **True :** Lower the pressure, lower will be boiling point. More liquid will vapourise and temperature decreases.

27. **False :** K for $A_2 + B_2 \rightleftharpoons 2AB$ is $\dfrac{[AB]^2}{[A_2][B_2]}$

K' for $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$ is $\dfrac{[A_2]^{1/2}[B_2]^{1/2}}{[AB]}$

or $\quad (K')^2 = \dfrac{[A_2][B_2]}{[AB]^2} = \dfrac{1}{K} \quad \therefore \quad K' = \sqrt{\dfrac{1}{K}}$

28. **(b)** Initially, on increasing temperature, rate of reaction will increase, so % yield will also increase with time. But at equilibrium, % yield at high temperature (T_2) would be less than at T_1 as reaction is exothermic so the graph is represented by option (b).

29. **(a, b, d)**

(a) $\Delta H = C_{P(rxn)}\Delta T$

Hence, enthalpy depends on temperature.

(b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad K_p = P_{CO_2}$

(c) K_{eq} depends only on temperature and not on Pressure.

(d) Enthalpy of reaction is independent of the catalyst. Catalyst changes activation energy.

30. **(b)** $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

$K_{sp} = 1.1 \times 10^{-12} = [Ag^+]^2 [CrO_4^{-2}]$

$1.1 \times 10^{-12} = [0.1]^2 [s]; \; s = 1.1 \times 10^{-10}$

31. **(d)** $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

$$K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

A catalyst simply helps in attaining the equilibrium earlier. Addition of inert gas has no effect on a reaction because in it, $\Delta n = 0$.

This equilibrium is not based upon volume because in it, $\Delta n = 0$.

On increasing the amount of CO, K_C should decrease but it is constant at constant temperature, so for maintaining the constant value of K_C, the amount of CO_2 increases.

32. **(b, c, d)**

(b) Introducing an inert gas at constant pressure will increase the volume. As a result, concentration of reactants and products will decrease. Thus, the reaction will move in forward direction to increase the concentration.

(c) Increasing the volume of container, will move the reaction in forward direction.

(d) Introducing PCl_5 at constant volume will favour the forward direction to decrease the concentration of PCl_5.

33. **(a)** At constant volume, concentrations do not change.

34. **(c, d)** $2NaNO_3(s) \rightleftharpoons 2NaNO_2(s) + O_2(g)$

According to Le-Chatelier principle, an increase in pressure always favours the reaction, where volume or moles decrease (*i.e.* reverse direction). As heat is added, *i.e.* reaction is endothermic and is supported in forward direction with increase in temperature. $NaNO_3$ and $NaNO_2$ both are solid. Thus, they will not effect the position of equilibrium.

35. **(a, b, c, d)** The reaction is exothermic, hence increasing temperature will favour backward reaction (*i.e.* conc. of C_2H_4 increases). Removing H_2 and adding C_2H_6 favours backward reaction. By decreasing the pressure, reaction will move towards preparing more moles, *i.e.*, backward reaction.

36. **(d)** We know that for every chemical reaction at equilibrium, change in Gibbs free energy ($\Delta G = 0$) is zero. However, charge in standard Gibbs free energy ($\Delta G°$) may or may not be zero. Thus, statement 1 is False.

For a spontaneous reaction, at constant temperature and pressure, the reaction proceeds in the direction in which ΔG is < 0, *i.e.*, in the direction of decreasing Gibbs energy (G). So, statement 2 is True.

37. **(d)** Statement-1 is clearly wrong in context to Le-Chateliers principle, which states that "increase in temperature shifts the equilibrium in the forward direction of those reactions which proceed with absorption of heat (**endothermic reactions**), and in the backward direction of those reactions which proceed with the evolution of heat (**exothermic reactions**)."

Statement -2 is clearly true again according to Le-chatelier principle.

38.

$$\begin{array}{llll} & NH_4HS(s) & \rightleftharpoons NH_3(g) & + \; H_2S(g) \\ \text{Initial moles} & \frac{3.06}{51} & 0 & 0 \\ \text{Moles at eq.} & \frac{3.06}{51}\times\frac{70}{100} & \frac{3.06}{51}\times\frac{30}{100} & \frac{3.06}{51}\times\frac{30}{100} \end{array}$$

Given $V = 2$ litre, $T = 300$ K, $\Delta n = 2 - 0 = 2$

$$\therefore K_c = [NH_3][H_2S] = \frac{3.06\times 30}{51\times 100\times 2}\times\frac{3.06\times 30}{51\times 100\times 2}$$
$$= \mathbf{8.1 \times 10^{-5}\ mol^2\ litre^{-2}}$$

$$\text{Also } K_p = K_c(RT)^{\Delta n} = 8.1\times 10^{-5}(0.082\times 300)^2$$
$$= \mathbf{4.90 \times 10^{-2}\ atm^2}$$

Addition of more NH_4HS on this equilibrium will cause no effect because concentration of NH_4HS is not involved in formula of K_p or K_c.

39. For AgCl; $AgCl \rightleftharpoons Ag^+ + Cl^-$

$\therefore K_{sp} = [Ag^+][Cl^-]$ .....(i)

Again it is given that

$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3\,;\, K_c = 6.2 \times 10^{-8}$

or $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$;

$$K_f = \frac{1}{6.2\times10^{-8}} = \frac{10^8}{6.2}$$

$$\therefore K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \text{ or } [Ag^+] = \frac{[Ag(NH_3)_2]^+}{K_f[(NH_3)_2]}$$

Since the formation constant of the complex is very high, most of the $[Ag^+]$ which dissolves must be converted into complex and each Ag^+ dissolved also requires dissolution of Cl^-.

$\therefore [Cl^-] = [Ag(NH_3)_2]^+$ and let it be c M

Equation (i) becomes

$$K_{sp} = \frac{[Ag(NH_3)_2]^+}{K_f[NH_3]^2} \times c \Rightarrow K_{sp} = \frac{c}{K_f[1]^2} \times c$$

$$\Rightarrow \quad c^2 = K_{sp} \times K_f[1]^2 = 1.8\times10^{-10} \times \frac{10^8}{6.2} \times (1)^2$$

$$\Rightarrow \quad c^2 = \frac{1.8\times10^{-2}}{6.2} = 0.2903 \times 10^{-2}$$

or $c = 0.538 \times 10^{-1} = \mathbf{0.0538\ M}$

40. The concerned chemical reaction is

$$2AgCl + Na_2CO_3 \longrightarrow Ag_2CO_3 + 2NaCl$$

Calculation of $[Ag^+]$ left in the solution :

$K_{sp}(Ag_2CO_3) = [Ag^+]^2[CO_3^{2-}]$

$$[Ag^+] = \sqrt{\frac{8.2\times10^{-12}}{1.5}} = 2.34\times10^{-6}\text{ M}$$

Concentration of Cl^- left $= 0.0026$ g/L

$$= \frac{0.0026}{35.5}\text{ mol/L} = 7.33\times10^{-5}\text{ M}$$

$\therefore K_{sp}(AgCl) = [Ag^+][Cl^-] = (2.34\times10^{-6})(7.33\times10^{-5})$

$= \mathbf{1.71 \times 10^{-10}}$

41. Consider common ion effect

Conc. of Ag^+ ions = Conc. of $AgNO_3 = 0.03$ M

Most of these Ag^+ ions will be present in the form of $[Ag(CN)_2]^-$.

0.03 M $AgNO_3$ requires 2×0.03 M

$= 0.06$ M CN^- to form $[Ag(CN)_2]^-$

$\therefore$ Conc. of free CN^- at equilibrium will be $0.1 - 0.06 = 0.04$ M

$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$

$$\therefore K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]}\,;\, 4.0\times10^{-9} = \frac{[Ag^+][0.04]^2}{0.03}$$

$$[Ag^+] = \frac{4.0\times10^{-19}\times0.03}{(0.04)^2} = \mathbf{7.5\times10^{-18}\ M}$$

42.

$$\begin{array}{lccc} & 2AB_2(g) & \rightleftharpoons\ 2AB(g) & +\ B_2(g) \\ \text{Initial mole} & 1 & 0 & 0 \\ \text{Moles at equb} & 1-x & x & \frac{x}{2} \end{array}$$

Total moles at equb. $= 1 - x + x + \frac{x}{2} = 1 + \frac{x}{2} = \frac{2+x}{2}$

$$p_{AB_2} = \frac{(1-x)}{(2+x)/2}P = \frac{2(1-x)}{(2+x)}P$$

$$p_{AB} = \frac{x}{(2+x)/2}P = \frac{2x}{(2+x)}P$$

$$p_{B_2} = \frac{x/2}{(2+x)/2}P = \frac{x}{(2+x)}P$$

$$\therefore K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2} = \frac{\left[\frac{2x}{(2+x)}P\right]^2\left[\frac{x}{(2+x)}P\right]}{\left[\frac{2(1-x)}{(2+x)}P\right]^2}$$

$$= \frac{x^3P}{(2+x)(1-x)^2}$$

$$K_p \approx \frac{x^3}{2}P \quad \text{or} \quad x = \left[\frac{2K_p}{P}\right]^{1/3}$$

43. (i)

$$\begin{array}{lccc} & CO(g) & +\ 2H_2(g) & \rightleftharpoons\ CH_3OH(g) \\ \text{Moles at start} & 0.15 & a & 0 \\ \text{Moles at equb.} & (0.15-x) & (a-2x) & 0.08 \\ \text{or} & (0.15-0.08) & (a-0.16) & 0.08 \end{array}$$

$\therefore$ Total moles at equb. $= 0.15 - 0.08 + a - 0.16 + 0.08$

$= a - 0.01$

Total moles at equilibrium can also be calculated from the following relation,

$$n = \frac{PV}{RT} = \frac{8.5\times2.5}{0.0821\times750} = 0.345$$

$\therefore 0.345 = a - 0.01$ or $a = 0.355$

Thus, Moles of CO at equilibrium $= 0.15 - 0.08 = 0.07$

Moles of H_2 at equilibrium $= 0.355 - 0.16 = 0.195$

Moles of CH_3OH at equilibrium $= 0.08$

Substituting the values in the relation,

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.08/2.5}{(0.195/2.5)^2\times(0.07/2.5)}$$

$= \mathbf{187.85\ mole^{-2}\ litre^2}$ $[\because V = 2.5\text{ L}]$

Calculation of K_p

$K_p = K_c(RT)^{\Delta n} = 187.85 \times (0.0821 \times 750)^{-2} = \mathbf{0.05\ atm^{-2}}$

$[\because \Delta n = -2]$

(ii) *Calculation of final pressure when there is no reaction*

Moles of CO $= 0.15$; Moles of $H_2 = 0.355$

$\therefore$ Total moles $= 0.15 + 0.355 = 0.505$

$PV = nRT$

$P \times 2.5 = 0.505 \times 0.0821 \times 750 \Rightarrow P = \mathbf{12.438\ atm.}$

44. Let the solubility of $Ca(OH)_2$ in pure water $= S$ moles/litre

$$\begin{array}{ccc} Ca(OH)_2 \rightleftharpoons & Ca^{2+} & +\ 2OH^- \\ & S & 2S \end{array}$$

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

$4.42 \times 10^{-5} = S \times (2S)^2$; $4.42 \times 10^{-5} = 4S^3$

$S = 2.224 \times 10^{-2} = 0.0223$ moles litre^{-1}

$\therefore$ No. of moles of Ca^{2+} ions in 500 mL. of solution = λ

$$= \frac{0.0223 \times 500}{1000} = 0.01115$$

Now when 500 mL of saturated solution is mixed with 500 mL of 0.4M NaOH, the resultant volume is 1000 mL. The molarity of OH^- ions in the resultant solution would therefore be 0.2 M.

$$\therefore [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 0.001105 \text{ M}$$

Thus, No. of moles of Ca^{2+} or $Ca(OH)_2$ precipitated

$= 0.01115 - 0.001105 = 0.010045$

Mass of $Ca(OH)_2$ precipitated

$= 0.010045 \times 74 = 0.7433$ g $=$ **743.3 mg**

[mole wt. of $Ca(OH)_2 = 74$]

45.

	Ag_2CO_3 +	$K_2C_2O_4$	$\rightarrow$ $Ag_2C_2O_4$ +	K_2CO_3
Moles at start	Excess	0.1520	0	0
Moles after reaction		0.1520–0.0358 = 0.1162	0.0358	0.0358

Molar concentration of $K_2C_2O_4$ or $C_2O_4^{2-}$ left unreacted

$$= \frac{0.1162}{0.5} = 0.2324 \text{ moles L}^{-1} \qquad [\because 500 \text{ mL} = 0.5 \text{ L}]$$

$[K_2CO_3] = [CO_3^{2-}]$ at equilibrium

$$= \frac{0.0358}{0.5} = 0.07156 \text{ moles L}^{-1}$$

Given that K_{sp} for $Ag_2C_2O_4 = 1.29 \times 10^{-11}$ mol^3 L^{-3} at 25°C

So, $[Ag^+]^2[C_2O_4^{2-}] = 1.29 \times 10^{-11}$

or $[Ag^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$

$$\text{Hence } [Ag^+]^2 = \frac{1.29}{0.2324} \times 10^{-11}$$

Then K_{sp} for Ag_2CO_3

$$= [Ag^+]^2[CO_3^{2-}] = \frac{1.29 \times 10^{-11}}{0.2324} \times 0.0716$$

$= \mathbf{3.974 \times 10^{-12}}$ **mol^3 L^{-3}**

46. Let the total number of moles of all gases at equilibrium point $= n$

$P = 4.92$ atm. $\qquad V = 5$L

$R = 0.0821$ atm. L mol^{-1} K^{-1} $\qquad T = 273 + 327 = 600$K

By applying the formula $\qquad PV = nRT$

$$n = \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.5 \text{ moles}$$

(i) *Calculation of the number of moles of the individual gases at equilibrium point.*

No. of moles of CH_3OH formed $= 0.1$ (Given)

$\therefore$ No. of moles of CO (also) $= 0.1$

[$\because$ moles of CO = moles of CH_3OH formed]

Hence, No. of moles of $H_2 = 0.5 - (0.1 + 0.1) = 0.3$

$\therefore$ Molar concentration of various species will be

$$[CH_3OH] = [CO] = \frac{0.1}{5} = 0.02; [H_2] = \frac{0.3}{5} = 0.06$$

$$\therefore K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.02}{0.02 \times (0.06)^2} = \mathbf{277.78 \text{ mol}^{-2} \text{ L}^2}$$

(ii) *Calculation of K_p.* We know that

$K_p = K_c \times (RT)^{\Delta n} = 277.78 \times (0.0821 \times 600)^{-2}$

$(\Delta n = 1 - 3 = -2)$

$$= \frac{277.78}{2426.54} = \mathbf{0.1144 \text{ atm}^{-2}}$$

47. Since the reaction is carried out at constant volume, change in partial pressure of a species will be directly proportional to the change in its amount. Hence, we can write

	$2SO_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2SO_3(g)$
Initial pressure	0	2 atm	1 atm
Equb. pressure	$2x$	2 atm + x	1 atm − $2x$

Where $2x$ is the change in partial pressure of SO_3 at equilibrium.

Substituting the expression of partial pressure in the expression. For K_p, we get

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2(p_{O_2})} \text{ or } 900 \text{ atm}^{-1} = \frac{(1 \text{ atm} - 2x)^2}{(2x)^2(2 \text{ atm} + x)}$$

Assuming x is very small as compared to 1

$$900 \text{ atm}^{-1} = \frac{1 \text{ atm}^2}{(4x^2)\text{atm}^2 (2 \text{ atm})}$$

On usual calculations, $x = 0.0118$ atm

Thus, $p_{SO_2} = 2x = 2 \times 0.0118$ atm $=$ **0.0236 atm**

$p_{O_2} = 2$ atm $+ x = 2 + 0.0118 =$ **2.0118 atm**

$p_{SO_3} = 1$ atm $- 2x = 1 - 0.0236 =$ **0.9764 atm**

48. (i)

	N_2O_4 $\rightleftharpoons$	$2NO_2$
Before dissociation	1	0
After dissociation	$1 - \alpha$	2α

$\therefore$ Total moles $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$\therefore K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \times P\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times P\right)}$$

where P is total pressure

$$K_p = \frac{\left(\frac{2 \times 0.25 \times 1}{1 + 0.25}\right)^2}{\left(\frac{1 - 0.25}{1 + 0.25} \times 1\right)} = \mathbf{0.266 \text{ atm}} \quad [\because \alpha = 0.25]$$

$$\text{(ii)} \quad K_p = \frac{4\alpha^2 P^2 \times (1+\alpha)}{(1+\alpha)^2 (1-\alpha) \times P} = \frac{4\alpha^2 P}{(1+\alpha)(1-\alpha)}$$

$$0.266 = \frac{4\alpha^2 \times 0.1}{1 - \alpha^2} \Rightarrow \alpha = 0.63$$

$\therefore$ Percentage dissociation $=$ **63 %**

49. Initial concentration of each gas = 1 mole

Let the No. of moles of NO_2 reacted at equilibrium $= x$

Then,	$SO_2(g)$ +	$NO_2(g)$ $\rightleftharpoons$	$SO_3(g)$ +	$NO_2(g)$
At equilibrium	$(1-x)$	$(1-x)$	$(1+x)$	$(1+x)$

$$\text{Now we know that, } \frac{[SO_3][NO]}{[SO_2][NO_2]} = K_c$$

or $\frac{\{(1+x)/V\}\{(1+x)/V\}}{\{(1-x)/V\}\{(1-x)/V\}}=16$ or $\frac{(1+x)^2}{(1-x)^2}=16$ ($\because V=1\text{L}$)

or $\frac{1+x}{1-x}=4$ or $1+x=4-4x$ or $5x=3, x=\frac{3}{5}=0.6$

$\therefore$ Thus, the concentration of NO at equilibrium $=1+x=1+0.6=$ **1.6 moles**

Concentration of NO_2 at equilibrium $=1-x=1-0.6=$ **0.4 moles**

50. Solubility of $Mg(OH)_2$ in water

$$S=9.57\times10^{-3}\text{ g/litre}=\frac{9.57\times10^{-3}}{58}=1.65\times10^{-4}\text{ mole/litre}$$

[$\because$ Molar mass for $Mg(OH)_2=58$]

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

$K_{sp}=(S)(2S)^2=4S^3=4(1.65\times10^{-4})^3=1.8\times10^{-11}$ approx.

Calculation of solubility of $Mg(OH)_2$, say, x, in $Mg(NO_3)_2$

or $[Mg^{2+}]=x+0.02; [OH^-]=x$

$K_{sp}=[Mg^{2+}][2OH^-]^2$ or $1.8\times10^{-11}=(x+0.02)(2x)^2$

Neglecting x in comparison to 0.02 (common ion effect)

$$\Rightarrow 4x^2=\frac{1.8\times10^{-11}}{0.02}=9\times10^{-10} \text{ or } 2x=3\times10^{-5}$$

$x=1.5\times10^{-5}$ moles/litres

$=1.5\times58\times10^{-5}=$ **8.7×10^{-4} g/litre.**

51. Let x be the degree of dissociation of $PCl_5(g)$, then

$$\begin{array}{llccc} & PCl_5(g) & \rightleftharpoons & PCl_3(g) & + & Cl_2(g) \\ \text{Initial} & 3 & & 0 & & 1 \\ \text{At equilibrium} & 3(1-x) & & 3x & & 1+3x \end{array}$$

$\therefore$ Total number of moles at equilibrium

$=3(1-x)+3x+1+3x=3(1+x)+1$

Using the gas equation : $PV=nRT$

$$\therefore n=\frac{PV}{RT}$$

Here, $P=2.05$ atm., $V=100$ litres, $R=0.082$ atm/deg., $T=273+227=500\text{ K}$

$$\therefore \quad n=\frac{2.05\times100}{0.082\times500}=5 \quad \therefore 3(1+x)+1=5$$

Hence perecentage dissociation of $PCl_5=0.333\times100=$ **33.3%**

Calculation of K_p for the reaction :

$$K_p=\frac{[PCl_3][Cl_2]}{[PCl_5]}=\frac{\left[\frac{3xP}{3(1+x)+1}\right]\left[\frac{(1+3x)P}{3(1+x)+1}\right]}{\left[\frac{3(1-x)}{3(1+x)+1}P\right]}$$

$$=\frac{3x(3x+1)}{4+3x}\times\frac{P}{3(1-x)}$$

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

Substituting, $x=1/3$ and $P=2.05$ atm., we get

$$K_p=\frac{\frac{1}{3}\left(3\times\frac{1}{3}+1\right)\times2.05}{\left(4+3\times\frac{1}{3}\right)\left(1-\frac{1}{3}\right)}=\frac{4.1}{10}=\mathbf{0.41}$$

52. For precipitation to occur ionic product $>K_{sp}$.

Mixture solution contains 0.1 M Ag^+ and 0.1 M Hg_2^{2+}.

K_{sp} of $Hg_2I_2=2.5\times10^{-26}$ is much smaller than K_{sp} of AgI which is 8.5×10^{-17}.

$[I^-]$ concentration needed to precipitate Hg_2I_2 is calculated as :

$Hg_2I_2 \rightleftharpoons Hg_2^{2+}+2I^-$

$$[I^-]=\sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}}=\sqrt{\frac{2.5\times10^{-26}}{0.1}}=\mathbf{5.0\times10^{-13}\ M}$$

Similarly, $[I^-]$ concentration needed to precipitate AgI is :

$AgI \rightleftharpoons Ag^++I^-$

$$[I^-]=\frac{K_{sp}}{[Ag^+]}=\frac{8.5\times10^{-17}}{0.1}=8.5\times10^{-16}\text{ M}$$

Since $[I^-]$ concentration needed to ppt. AgI is smaller than that needed to ppt. Hg_2I_2, AgI is completely precipitated first. AgI starts precipitation with $[I^-]=8.5\times10^{-16}$ M. However, Hg_2I_2 starts precipitating with AgI only when molar concentration of I^- reaches **5.0×10^{-13} M.**

$[Ag^+]$ left when Hg_2I_2 begins to ppt. is given by

$$\frac{K_{sp}\text{ of AgI}}{[I^-]_{Hg_2I_2}}=\frac{8.5\times10^{-17}}{5.0\times10^{-13}}=1.7\times10^{-4}\text{ M}$$

Thus % $[Ag^+]$ left unprecipitated $=\frac{1.7\times10^{-4}}{0.1}\times100=0.17\%$

Hence % Ag^+ precipitated = **99.83%**

53.

$$\begin{array}{lccccc} \text{Initial moles} & 1 & & 3 & & 0 \\ & N_2(g) & + & 3H_2(g) & \rightleftharpoons & 2NH_3(g) \\ \text{Eq. moles} & 1-0.0025 & & 3-0.0075 & & 2\times0.0025 \\ \text{Eq. conc.} & \frac{1-0.0025}{4} & & \frac{3-0.0075}{4} & & \frac{2\times0.0025}{4} \end{array}$$

Now we know that $K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}$

Since 0.0025 and 0.0075 are very small, 1–0.0025 and 3–0.0075 may be taken as 1 and 3 respectively.

Substitute the various values

$$K_c=\frac{\left(\frac{2\times0.0025}{4}\right)^2}{\left[\frac{1}{4}\right]\left[\frac{3}{4}\right]^3}=\frac{0.0025\times0.0025}{4}\times\frac{4\times4\times4\times4}{3\times3\times3}$$

$$=\mathbf{1.48\times10^{-5}\ litre^2\ mol^{-2}}$$

For the equilibrium, $\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

$$K_c'=\frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}}=\sqrt{K_c}$$

$$=\sqrt{(1.48\times10^{-5}\text{ litre}^2\text{ mol}^{-2})}=\mathbf{3.82\times10^{-3}\ litre\ mol^{-1}}$$

Topic-2: Ionic Equilibrium

1. **(b)** Let the solubility of MX at PH 7 = s

$$\underset{}{MX(s)} \rightleftharpoons \underset{s}{M^+} + \underset{s}{X^-}$$

$$K_{sp} = s^2 \qquad \text{....(1)}$$

Let the solubility of MX at pH = 2 = s_1

$$MX(s) \rightleftharpoons \underset{s_1}{M^+} + \underset{s_1}{X^-}$$

$$\begin{array}{ccccc} X^- & + & H^+ & \rightarrow & HX \\ s_1 & & 10^{-2} & & \\ - & & 10^{-2} & & s_1 \end{array}$$

$$\frac{1}{K_a} = \frac{[HX]}{[X^-];[H^+]} = \frac{s_1}{[X^-] \times 10^{-2}}$$

$$\frac{{s_1}^2}{10^{-2}} = \frac{K_{sp}}{K_a} \qquad \text{....(2)}$$

Divide equation (2) by equation (1)

$$\frac{{s_1}^2}{s^2 \times 10^{-2}} = \frac{K_{sp}}{K_a} \times \frac{1}{K_{sp}};$$

$$\frac{10^{-3}}{(10^{-4})^2 \times 10^{-2}} = \frac{1}{K_a}$$

$$K_a = 10^{-4} \Rightarrow pK_a = 4$$

2. **(d)** Let the weak manoacidic base be BOH, then the reaction that occurs during titration is $BOH + HCl \rightarrow BCl + H_2O$

Equilibrium : $\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{C.h}{BOH} + \underset{C.h}{H^+}$

Using the normality equation, $\underset{(acid)}{N_1V_1} = \underset{(base)}{N_2V_2}$

Substituting various given values, we get

$$\frac{2}{15} \times V_1 = 2.5 \times \frac{2}{5} \text{ or } V_1 = 2.5 \times \frac{2}{5} \times \frac{15}{2} = 2.5 \times 3 = 7.5 \text{ mL}$$

Then the concentration of BCl in resulting solution is given by

$$[BCl] = \frac{\frac{2}{15} \times 2.5}{10} = \frac{2}{10} \text{ or } 0.1 \text{ M}$$

Since $K_h = \frac{K_w}{K_b}$ $\therefore K_h = \frac{1 \times 10^{-14}}{1 \times 10^{-12}} = 10^{-2}$

Thus $K_h = \frac{0.1h^2}{(1-h)}$ or $10^{-2} = \frac{0.1h^2}{(1-h)}$

or $10^{-2} - 10^{-2}h = 0.1h^2$ or $0.1h^2 + 10^{-2}h - 10^{-2} = 0$

(Solving this quadratic equation for h, we get)

$$h = \frac{-10^{-2} \pm \sqrt{(10^{-2})^2 + 4 \times 10^{-1} \times 10^{-2}}}{2 \times 0.1}$$

$$\left[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}\right] = \frac{-10^{-2} \pm \sqrt{10^{-4} + 4 \times 10^{-3}}}{2 \times 0.1}$$

$$= \frac{-0.01 \pm \sqrt{.0001 + 0.004}}{0.2} = \frac{-0.01 \pm \sqrt{0.0041}}{0.2}$$

$$= \frac{-0.01 \pm 0.64}{0.2} = \frac{0.54}{0.2} \text{ [Neglecting the negative term]}$$

$= 0.27$

$\therefore [H^+] = C.h = 0.1 \times 0.27 = 2.7 \times 10^{-2}$ M

3. **(b)** For basic buffer pH is more than 7.

$$\begin{array}{lccccc} & CH_3NH_2 & + & HCl & \longrightarrow & CH_3NH_3^+Cl^- \\ \text{Initial moles} & 0.1 & & 0.08 & & 0 \\ \text{Moles after mixing} & 0.02 & & 0 & & 0.08 \end{array}$$

As it is a basic buffer solution.

$$pOH = pK_b + \log \frac{0.08}{0.02} = -\log 5 \times 10^{-4} + \log 4$$

$$= 3.30 + 0.602 = 3.902$$

$pH = 14 - 3.902 = 10.09; [H^+] = 7.99 \times 10^{-11} \approx 8 \times 10^{-11}$ M

4. **(c)** For isotonic solutions, osmotic pressure is same.

$$\underset{(0.004-x)}{Na_2SO_4} \rightleftharpoons \underset{2x}{2Na^+} + \underset{x}{SO_4^{2-}}$$

Since both solutions are isotonic,
therefore, $0.004 + 2x = 0.01$; $x = 3 \times 10^{-3}$

$$\therefore \text{ \% Dissociation } = \frac{3 \times 10^{-3}}{0.004} \times 100 = 75\%$$

5. **(b)** $h = \sqrt{\frac{K_w}{K_a \times c}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4}$;

Hence, % hydrolysis = $10^{-4} \times 100 = 0.01$

6. **(a)** For oxyacids containing similar central atom, the acid strength increases with the increase in the number of oxygen atom attached to the central atom and not attached to any other atom.

Higher the oxidation number of the central atom, higher is the acidity of the species. Thus, acidity follows the order

$$\begin{array}{lccccccc} \text{Oxi. No. of Cl} & HClO & < & HClO_2 & < & HClO_3 & < & HClO_4 \\ & +1 & & +3 & & +5 & & +7 \end{array}$$

7. **(b)** The characteristics of the given solutions are:

NaCl – neutral solution

NH_4Cl – slightly acidic due to the following reaction

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

NaCN – slightly alkaline due to the following reaction

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

HCl – highly acidic

The pH of the solution will follow the order highly acidic < slightly acidic < neutral < slightly alkaline *i.e.*

$HCl < NH_4Cl < NaCl < NaCN$

8. **(a)** Among oxyacids of the same type formed by different elements, acidic nature increases with increasing electronegativity. In general, the strength of oxyacids decreases as we go down the family in the periodic table.

HOCl (I) > HOBr (II) > HOI (III)

9. **(c)** Salts of weak base and strong acid get hydrolysed in aqueous solution forming an acidic solution.

$$\underset{\text{(weak)}}{AlCl_3} + 3H_2O \longrightarrow \underset{\text{(strong)}}{Al(OH)_3} + \underset{\text{(acidic)}}{3HCl}$$

10. **(b)**

$$\underset{(1-\alpha)\,c}{H_2O} \rightleftharpoons \underset{\alpha\,c}{H^+} + \underset{\alpha\,c}{OH^-}$$

$\alpha = 1.9 \times 10^{-7}$; Density of water $= \dfrac{1.0\text{ gm}}{\text{cm}^3}$

$\therefore c = \dfrac{1}{18} \times 1000 = 55.56$ moles/l

$\therefore [H^+] = 55.56 \times 1.9 \times 10^{-9} = 1.055 \times 10^{-7}$

$[\because 1.9 \times 10^{-}\% = 1.9 \times 10^{-9}]$

$\therefore K_w = [H^+][OH^-] = (1.055 \times 10^{-7})^2 = 1.0 \times 10^{-14}$

11. **(d)** (a) It is not correct answer because 100 ml M/10 HCl will completely neutralise 100 ml M/10 NaOH and the solution will be neutral.

(b) After neutralisation resultant solution will be acidic due to presence of excess of HCl.

(c) After netralisation resultant solution will be basic due to presence of excess of NaOH.

(d) M. eq. of HCl = 75 N/5 = 15 Meq

M.eq. of NaOH $= 25 \times \dfrac{1}{5} = 5$ Meq

$\therefore$ M. eq. of HCl left = 10 $\quad \therefore [HCl] = \dfrac{10}{100} = M/10$

$\therefore pH = -\log [H^+] = -\log\left[\dfrac{1}{10}\right] = 1$

12. **(d)** Since HCl is stronger than CH_3COOH hence acts as acid. On the other hand Cl^- is a stronger base than $CH_3COOH_2^+$ and is the conjugate base of HCl.

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{CH_3COOH} \rightleftharpoons \underset{\text{base}_1}{Cl^-} + \underset{\text{acid}_2}{CH_3COOH_2^+}$$

13. **(a)** Due to hydrolysis of $FeCl_3$, backward reaction will not take place.

$$FeCl_3 + 6H_2O \longrightarrow [Fe(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)$$

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \longrightarrow [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

14. **(a)**

(i) Higher the electronegatively of central atom, higher will be the acidic strength.

(ii) In case of same atom, higher the value of oxidation state of the metal, higher will be its acidic strength.

The electronegativity of Cl > S.

Oxidation no. of Cl in $ClO_3(OH) = +7$

Oxidation no. of Cl in $ClO_2(OH) = +5$

Oxidation no. of S in $SO(OH)_2 = +4$

Oxidation no. of S in $SO_2(OH)_2 = +6$

$\therefore ClO_3(OH)$ is the strongest acid.

15. **(d)** In acidic medium, weak acids are unionized due to common ion effect and they are completely ionised in alkaline medium.

Aspirin (or acetyl salicylic acid) is unionised in stomach (where pH is 2-3) and is completely ionised in small intestine (when pH is 8).

16. **(d)** (a) is a neutral solution due to both cationic and anionic hydrolysis ($K_a = K_b = 1.8 \times 10^{-5}$); (b) is acidic solution due to cationic hydrolysis; (c) is acidic solution due to cationic hydrolysis; (d) is basic solution due to anionic hydrolysis.

17. **(c)** CaO, $CaCO_3$ and $Ca(OH)_2$ dissolve in CH_3COOH due to formation of $(CH_3COO)_2Ca$. But CaC_2O_4 does not dissolve as CH_3COO^- is a stronger conjugate base than $C_2O_4^{2-}$.

18. **(N)** Electron acceptors or elements having incomplete octet are Lewis acids.

(i) BF_3 (B has 6 e^- in valance shell), $AlCl_3$ (Al has 6 electrons in valance shell), $BeCl_2$ (Be has 4 e^- in valance shell) are electron defecient compounds and hence Lewis acids.

(ii) $SnCl_4$ has complete octet but due to empty *d*-orbitals, it can accept electron pair and can be considered as a Lewis acid.

19. **(a)** Base + $H^+ \rightarrow$ (conjugate acid)

NH_2^- (base) + $H^+ \rightarrow NH_3$ (conjugate acid)

20. **(d)** The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis. So an indicator giving colour in basic medium will be suitable.

Phenolphthalein is a good indicator if the base is strong because strong base immediately changes the pH at end point.

21. **(c)** The equilibrium constant for the nuetralization of a weak acid with a strong base is given by

$$K = K_a / K_w = \frac{1.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 1.0 \times 10^{10}$$

22. **(a)** For a basic buffer, $pH = 14 - pK_b - \log \dfrac{[\text{salt}]}{[\text{base}]}$

$$pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]} = 14 - (-\log 10^{-10}) - \log 1$$

$\Rightarrow pH = 4$

23. **(b)** For pure water, $[H_3O^+] = [OH^-]$

$\Rightarrow K_w = 10^{-6} \times 10^{-6} = 10^{-12}$

24. **(a)**

(i) Lower the oxidation state of central atom, weaker will be oxy acid.

(ii) Weaker the acid, stronger will be its conjugate base.

Oxidation state of Cl in HClO is + 1, in $HClO_2$ is + 3, in $HClO_3$ is + 5, and in $HClO_4$ is + 7

$\therefore$ HClO is the weakest acid and so its conjugate base ClO^- is the strongest Bronsted base.

25. **(d)** (i) pH of acid cannot be more than 7.

(ii) While calculating pH in such case, consider contribution of $[H^+]$ from water also.

Molar conc. of HCl = 10^{-8}. (given)

$\therefore$ pH = 8. But this cannot be possible as pH of an acidic solution can not be more than 7. So, we have to consider $[H^+]$ coming from H_2O.

Total $[H^+] = [H^+]_{HCl} + [H^+]_{H_2O}$

Ionisation of H_2O : $H_2O \rightleftharpoons H^+ + OH^-$

$K_w = 10^{-14} = [H^+][OH^-]$

Let x be the conc. of $[H^+]$ from H_2O

or $[H^+] = x = [OH^-]$ $\quad [\because [H^+] = [OH^-]$ in water$]$

$\therefore 10^{-14} = (x + 10^{-8})(x)$ or $x = 9.5 \times 10^{-8}$ M

[For quadratic equation $x = \dfrac{-b \pm \sqrt{4ac}}{2a}$]

$\therefore$ Total $[H^+] = 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8}$ or pH $= -\log(10.5 \times 10^{-8}) = \mathbf{6.98}$

It is between 6 and 7.

Trick : pH of acidic solution cannot be more than 7. Thus, only option (d) is possible.

26. **(a)** Acidic buffer is mixture of weak acid and its salt with common anion.

(a) $CH_3COOH + CH_3COONH_4$ is acidic buffer.

(b) $NH_4Cl + NH_4OH$ is basic buffer.

(c) $H_2SO_4 + Na_2SO_4$ is not buffer because both the compounds are strong electrolytes.

(d) NaCl + NaOH is not buffer solution because both compounds are strong electrolytes.

27. **(6)** $H_2SO_4(aq) \longrightarrow \underset{1M}{H^+(aq)} + \underset{1M}{HSO_4^-(aq)}$

(as K_{a_1} is very large)

$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + \underset{0.018\,M}{SO_4^{2-}(aq)}$

(as Na_2SO_4 is a salt)

Now, due to common ion effect, dissociation of HSO_4^- will be suppressed.

$\underset{1M}{HSO_4^-(aq)} \rightleftharpoons \underset{1M}{H^+(aq)} + \underset{0.018\,M}{SO_4^{2-}(aq)}$ (at start)

$$Q_C = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} \Rightarrow Q_C = \frac{1 \times 0.018}{1} = 0.018$$

$K_C = K_{a_2} = 1.2 \times 10^{-2} = 0.012$

Thus, $Q_C > K_C$ and the reaction will move in backward direction.

$\underset{(1+x)}{HSO_4^-(aq)} \rightleftharpoons \underset{(1-x)}{H^+(aq)} + \underset{(0.018-x)}{SO_4^{2-}(aq)}$

$$K_{a_2} = \frac{(1-x)(0.018-x)}{(1+x)} = 0.012$$

Assuming x to be very small, $1 - x \approx 1$ and $1 + x \approx 1$.

$\Rightarrow 0.018 - x = 0.012 \Rightarrow x = 0.006$

$[SO_4^{2-}] = 0.018 - x = 0.012$ mol/L

$PbSO_4(s) \rightleftharpoons \underset{\substack{0 \\ S}}{Pb^{2+}(aq)} + \underset{\substack{0.012 \\ S+0.012}}{SO_4^{2-}(aq)}$

$K_{sp} = S(S + 0.012)$

Since, S is very small, $S + 0.012 \approx 0.012$

$\Rightarrow 1.6 \times 10^{-8} = S \times 0.012$

$\Rightarrow S = 1.33 \times 10^{-6} = X \times 10^{-Y} \Rightarrow Y = 6.$

28. **(3)** $B + HA \longrightarrow BH^+ + A^-$

Volume of HA used till equivalence point = 6 mL

At half of equivalence point, solution will be basic buffer with B and BH^+

$$\therefore \quad pOH = pK_b + \log\frac{[BH^+]}{[B]}$$

At half equivalence point $[BH^+] = [B]$

$\therefore$ $pOH = pK_b = 14 - 11 = 3$

29. **(3)** KCN, K_2CO_3 and LiCN are the salts of weak acid and strong base. So, their aqueous solutions turns red litmus paper blue.

30. **(6)** Diprotic acids are H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4 and H_2SO_3.

31. **(8)** pH of sodium salt of weak acid

$$= \frac{1}{2}(pK_w + pK_a + \log C) = \frac{1}{2}(14 + 4 - 2) = 8$$

32. **(9)** $HA + NaOH \longrightarrow NaA + H_2O$

At the end point, the solution contains only NaA whose concentration is 0.1/2 = 0.05 M

Since, the salt NaA is formed by strong alkali (NaOH) and weak acid HA (indicated by its low K_a value), its pH can be evaluated by the following relation.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$$= \frac{1}{2}(14 + 5.3010 + (-1.3010)) = 9$$

33. **(2)** Given $K_a = 1 \times 10^{-5}$ $\therefore pK_a = 5$

The two conditions when colour indicator will be visible are derived by

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

(i) $pH = 5 + \log 10 = 6$

(ii) $pH = 5 + \log 0.1 = 4$

Thus, minimum change in pH = 2

34. **(10.02)** H_2CO_3 is a weak dibasic acid. Since NaOH is a strong acid H_2CO_3 reacts completely as a monobasic acid.

$H_2CO_3 \underset{pK_{a_1} = 6.37}{\rightleftharpoons} H^+ + HCO_3^-$; $\quad HCO_3^- \underset{pK_{a_2} = 10.32}{\rightleftharpoons} H^+ + CO_3^{2-}$

$$\begin{array}{llll} & H_2CO_3 + NaOH & \longrightarrow & NaHCO_3 + H_2O \\ \text{Initial :} & 0.01\ \text{mol} \quad 0.01\ \text{mol} & & \\ \text{After mixing :} & - \quad - & & 0.01\ \text{mol} \end{array}$$

Final components in mixture :

$NaHCO_3 = 0.01\ \text{mol} + 0.01\ \text{mol} = 0.02\ \text{mol}$

$Na_2CO_3 = 0.01\ \text{mol}$

Now, $\underset{\text{Acid}}{HCO_3^-} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugated base}}{CO_3^{2-}}$

Applying Henderson – Hasselbalch equation,

$$pH = pK_{a_2} + \log\frac{\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = 10.32 + \log\frac{0.01/0.1}{0.02/0.1}$$

$$= 10.32 + \log\frac{1}{2} = 10.32 - 0.3 = 10.02$$

35. **(0.20)** $ZnS(s) \rightleftharpoons Zn^{2+}(aq) + S^{2-}(aq)$

$[S^{2-}]_{max}$ to prevent precipitation is given by

$$[S^{2-}]_{max} = \frac{1.25\times10^{-22}}{0.05} = 2.5\times10^{-21}\ M$$

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

$$K_1 \cdot K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$K_{Net} = 10^{-21} = \frac{[H^+]^2 \times 2.5\times10^{-21}}{0.1}$$

$$[H^+]^2 = \frac{1}{25} \Rightarrow [H^+] = \frac{1}{5}\ M = 0.2\ M$$

36. **(4.47)** $S = \sqrt{K_{sp}\left(\frac{[H^+]}{K_a}+1\right)} = \sqrt{20\times10^{-10}\left(\frac{10^{-3}}{10^{-8}}+1\right)}$

$$\simeq \sqrt{2\times10^{-5}} = 4.47\times10^{-3}\ M$$

Alternate solution :

Let the solubility of salt AB be x.

$$AB \rightleftharpoons \underset{x}{A^+} + \underset{x-y}{B^-}$$

$$K_{sp} = 2\times10^{-10} = x(x-y) \qquad \text{..... (i)}$$

Association constant of weak acid HA,

$$K_a' = 1/K_a = 10^8$$

$$\underset{10^{-3}}{H^+} + \underset{x-y}{B^-} \rightleftharpoons \underset{y}{HB}$$

Let concentration of HB at equilibrium be y. It is given that pH of solution is 3 which means $[H^+] = 10^{-3}$

$$10^8 = \frac{y}{10^{-3}\times(x-y)} \qquad \text{..... (ii)}$$

$$\Rightarrow y = \frac{x}{1+10^{-5}}$$

Putting value of y in equation (i) :

$$x\left(x - \frac{x}{1+10^{-5}}\right) = 2\times10^{-10}$$

$$\Rightarrow x^2 = 2\times10^{-5} + 2\times10^{-10} \Rightarrow x^2 \approx 2\times10^{-5}$$

$$\Rightarrow x = \sqrt{20\times10^{-6}} \Rightarrow x = 4.47\times10^{-3}$$

Hence, $Y = 4.47$

37. **(4.86)** Amount of SO_2 in atmosphere $= \frac{10}{10^6} = 10\times10^{-6}$

Molar concentration of SO_2 present in water

$=$ Amount of SO_2 × Solubility of SO_2 in water

$= 10\times10^{-6}\times1.3653\ \text{mole}\ L^{-1} = 1.3653\times10^{-5}\ M$

Writing the concerned chemical equation

$$\begin{array}{llll} & H_2SO_3 & \longrightarrow & H^+ \quad + \quad HSO_3^- \\ \text{Initial conc.} & 1.3653\times10^{-5} & & 0 \qquad\quad 0 \\ \text{Molar conc. at equb.} & 1.3653\times10^{-5}-x & & x \qquad\quad x \end{array}$$

Therefore $K_a = \frac{x^2}{(1.3653\times10^{-5}-x)}$

$$\Rightarrow 10^{-1.92} = \frac{x^2}{(1.3653\times10^{-5}-x)}$$

$(pK_a = 1.92, \therefore K_a = 10^{-1.92})$

$$\Rightarrow 1.2\times10^{-2} = \frac{x^2}{(1.3653\times10^{-5}-x)}$$

$x^2 = 1.2\times10^{-2}(1.3653\times10^{-5}-x)$

On solving, $x = 1.364\times10^{-5}$

Therefore, $pH = -\log(1.364\times10^{-5}) = \mathbf{4.865}$

38. **(11.30)**

$$\begin{array}{lllll} & HCl & + NaOH & \longrightarrow NaCl & + \ H_2O \\ \text{Meq. before reaction} & 200\times10^{2-} & 300\times10^{2-} & & \\ \text{Meq. after reaction} & 0 & 100\times10^{2-} & 200\times10^{2-} & 200\times10^{2-} \end{array}$$

pH of HCl = 2, pH of NaOH = 12

$\therefore [HCl] = 10^{-2}\ M, \therefore [NaOH] = 10^{-2}\ M$

$$\therefore [OH^-] = \frac{100\times10^{-2}}{500} = 2\times10^{-3} \text{ or } p[OH] = -\log(2\times10^{-1})$$

$\therefore pOH = 2.6989;\ \therefore pH = 14 - 2.6989 = \mathbf{11.3010}$

39. **(11.5)** $pK_b = 4.70,\ \therefore K_b = 10^{-4.7}$

Now we know that, $[OH^-] = \sqrt{K_b\times c}$

$$\therefore [OH^-] = \sqrt{10^{-4.7}\times0.5} = 3.158\times10^{-3}\ M$$

Now we know that, $pOH = -\log[OH^-]$

$pOH = -\log 3.158\times10^{-3} = 2.5$ or, $pH = 14 - 2.5 = \mathbf{11.5}$

40. **(6.5)** For ammonium formate which is a salt of weak acid with weak base, we know that

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b] = \frac{1}{2}[14 + 3.8 - 4.8] = \mathbf{6.5}$$

41. **(78.36)** Volume of blood = 10 mL (given)

$[H_2CO_3]$ in blood = 2 M (given)

$[NaHCO_3]$ to be added = 5 M (given)

Let volume of $NaHCO_3$ added in 10 mL blood = V mL

$$\therefore [H_2CO_3] \text{ in blood mixture} = \frac{2\times 10}{(V+10)}$$

$$[NaHCO_3] \text{ in blood mixture} = \frac{5\times V}{(V+10)}$$

$$\therefore pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$$\text{or } 7.4 = -\log 7.8\times 10^{-7} + \log\frac{5V/(V+10)}{20/(V+10)} \quad \therefore \mathbf{V = 78.36\ mL}$$

42. I_2. $\because$ electron acceptors are Lewis acids.

43. **amphoteric;** because amphoteric substances show properties of both acids and basic.

$$\underset{\text{(amphoteric)}}{Al_2O_3} + \underset{\text{(acid)}}{6HF} \longrightarrow 2AlF_3 + 3H_2O \quad [Al^{3+}3F^-]$$

$$\underset{\text{(amphoteric)}}{Al_2O_3} + \underset{\text{(base)}}{2NaOH} + 3H_2O \longrightarrow 2NaAl(OH)_4$$

$$[Na^+[Al(OH)_4]^-]$$

44. SO_4^{2-} ; Conjugate base = Acid – H^+

$\therefore$ Conjugate base of HSO_4^- is SO_4^{2-}

45. **False :** $AlCl_3$ is a Lewis acid (although they do not have a proton, aprotic) because it accepts electrons (octet being incomplete).

46. **(a)** As ester hydrolysis is first order with respect $[H^+]$.

$R_{HA} = K[H^+]_{HA}[\text{ester}]$

$R_{HX} = K[H^+]_{HX}[\text{ester}]$

$$\therefore \frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}};\quad \frac{1}{100} = [H^+]_{HA} = 0.01$$

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ 1-0.01 & & 0.01 & & 0.01 \\ \approx 1 & & & & \end{array}$$

$$K_a = \frac{0.01\times 0.01}{1} = 10^{-4}$$

47. **(c, d)** Any solution of a weak acid and its salt with strong base acts as an acidic buffer solution.

If volume of HNO_3 solution added is less as compared to that of CH_3COONa solution, it results in the formation of an acidic buffer solution.

$$\begin{array}{llll} CH_3COONa + & HNO_3 \longrightarrow & CH_3COOH & + NaNO_3 \\ \text{Excess} & \text{limiting} & & \\ & \text{reagent} & & \\ MV & MV' & - & - \\ M(V-V') & 0 & MV' & MV' \quad (V' < V) \end{array}$$

48. **(a, c)** A buffer solution is prepared by mixing a weak acid/base with salt of its conjugate base/acid.

49. **(b, c)** (a) pH of 1×10^{-8} M is below 7 because it is an acid.

(b) $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$

(c) $H_2O + H_2O \rightleftharpoons OH^- + H_3O^+$

K (Auto protolysis constant of water *i.e.* ionic product of water) increases with temperature.

(d) For half neutralisation of a weak acid by a strong base,

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

$[Salt] = [Acid]$, $\therefore pH = pK_a$

50. **(d) P – 1; Q – 5; R – 4; S – 1**

$$\begin{array}{lllll} \text{(P)} & NaOH & + \ CH_3COOH & \longrightarrow CH_3COONa + H_2O \\ \text{m mole} & 10\times 0.1 & \ 20\times 0.1 & \\ & = 1\ \text{m.mol} & \ = 2\ \text{m.mol} & \end{array}$$

$\therefore$ Solution contains 1 m. mol CH_3COOH & 1 m.mol CH_3COONa in 30 mL solution.

It is a Buffer solution. Hence, pH does not change with dilution.

$$\begin{array}{lllll} \text{(Q)} & NaOH & + \ CH_3COOH & \longrightarrow CH_3COONa + H_2O \\ \text{m mole} & 20\times 0.1 & \ 20\times 0.1 & \\ & = 2\ \text{m.mol} & \ = 2\ \text{m.mol} & \end{array}$$

$\therefore$ Solution contains 2 m. mol of CH_3COONa in 40 mL solution (salt of weak acid and strong base)

For salts of weak acid and strong base : $[H^+]_{\text{initial}} = \sqrt{\dfrac{K_wK_a}{C}}$

On dilution upto 80 mL, new conc. will be $= \dfrac{C}{2}$

$$\therefore [H^+]_{\text{new}} = \sqrt{\frac{K_wK_a}{C/2}} = [H^+]_{\text{initial}} \times \sqrt{2}$$

$$\begin{array}{lllll} \text{(R)} & HCl & + \ NH_3 & \longrightarrow & NH_4Cl \\ \text{m mole} & 20\times 0.1 & \ 20\times 0.1 & & \\ & = 2\text{m.mol} & \ = 2\ \text{m.mol} & & \end{array}$$

$\therefore$ Solution contains 2 m. mol of NH_4Cl in 40 mL solution (salt of strong acid and weak base)

For salts of strong acid and weak base, $[H^+]_{\text{initial}} = \sqrt{\dfrac{K_wC}{K_b}}$

On dilution upto 80 mL, new conc. will be $= \dfrac{C}{2}$.

$$\therefore [H^+]_{\text{new}} = \sqrt{\frac{K_wC}{K_b2}} = \frac{[H^+]_{\text{initial}}}{\sqrt{2}}$$

(S) $Ni(OH)_2(s) \longrightarrow Ni^{2+} + 2OH^-$

$\because$ it is sparingly soluble salt

$\therefore$ On dilution $[OH^-]$ conc. in saturated solution of $Ni(OH)_2$ remains constant

$\therefore [H^+]_{\text{new}} = [H^+]_{\text{initial}}$

51. **(b)**

$$\begin{array}{llcl} & X_2(g) & \rightleftharpoons & 2X(g) \\ \text{Initial mole :} & 1 & & 0 \\ \text{moles at equilibrium :} & \left(1-\dfrac{\beta_{eqbm}}{2}\right) & & \beta_{eqbm} \\ \text{Partial pressure :} & \dfrac{1-\dfrac{\beta_{eqbm}}{2}}{\left(1+\dfrac{\beta_{eqbm}}{2}\right)}\times P & & \dfrac{\beta_{eqbm}}{\left(1+\dfrac{\beta_{eqbm}}{2}\right)}P \end{array}$$

$$\therefore\ K_p = \frac{(P_x)^2}{P_{x_2}} = \frac{\beta_{eqbm}^2 P}{\left(1 - \frac{\beta_{eqbm}^2}{4}\right)} \Rightarrow K_p = \frac{4\beta_{eqbm}^2 P}{\left(4 - \beta_{eqbm}^2\right)}$$

Since, $P = 2$ bar So, $\boxed{K_p = \frac{8\beta_{eqbm}^2}{\left(4 - \beta_{eqbm}^2\right)}}$

52. **(c)**

(a) Correct statement.

As on decrease in pressure, reactions moves in direction where no. of gaseous molecules increase.

(b) Correct statement

At the start of reaction, $Q_P < K_P$ so dissociation of X_2 take place spontaneousely. $\Delta G0° > 0$ but at start $\Delta G << 0$.

(c) Incorrect statement as

$$K_P = \frac{8\beta_{eq}^2}{4 - \beta_{eq}^2} = \frac{8 \times (0.7)^2}{4 - (0.7)^2} > 1$$

at equilibrium, $\Delta G° = -RT \ln K_P$

If $K_P > 1$, then $\Delta G°$ is negative.

But it is given that, $\Delta G°$ is positive.

(d) $K_P < 1$ and $K_P = K_C (RT)^{\Delta n}$; $\Delta n = 1$

$$\Rightarrow K_C = \frac{K_P}{RT} \Rightarrow K_C < 1;\ RT > 1$$

53. **(a)** Let the heat capacity of insulated beaker be C.

Mass of aqueous content in expt. 1 = (100 + 100) × 1 = 200 g

$\Rightarrow$ ± Total heat capacity = (C + 200 × 4.2) J/K

Moles of acid, base neutralised in expt.

1 = 0.1 × 1 = 0.1

$\Rightarrow$ Heat released in expt. 1 = 0.1 × 57 = 5.7 kJ = 5.7 × 1000 J

$\Rightarrow$ 5.7 × 1000 = (C + 200 × 4.2) × Δ T.

5.7 × 1000 = (C + 200 × 4.2) × 5.7

$\Rightarrow$ (C + 200 × 4.2) = 1000

In second experiment, $n_{CH_3COOH} = 0.2$, $n_{NaOH} = 0.1$

Total mass of aqueous content = 200 g

$\Rightarrow$ Total heat capacity = (C + 200 × 4.2) = 1000

$\Rightarrow$ Heat released = 1000 × 5.6 = 5600 J.

Overall, only 0.1 mol of CH_3COOH undergo neutralization.

$$\Rightarrow \Delta H_{neutralization} \text{ of } CH_3COOH = \frac{-5600}{0.1}$$

$= -56000$ J/mol $= -56$ KJ/mol.

$\Rightarrow \Delta H_{dissociation}$ of $CH_3COOH = 57 - 56 = 1$ kJ/mol

54. **(b)** Final solution contain 0.1 mole of CH_3COOH and CH_3COONa each.

Hence, it is a buffer solution.

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 5 - \log 2 + \log\frac{0.1}{0.1} = 4.7$$

55. **(c)** Among oxyacids, the acidic character increases with increase in oxidation state of the central atom.

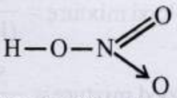
O.S. of N in $HNO_3 = +5$

O.S. of N in $HNO_2 = +3$

Thus, HNO_3 is stronger acid than HNO_2. Hence, assertion is correct.

Structure of HNO_2 : H—O—N═O;

Structure of HNO_3 :



The statement-1 is true but the statement-2 is wrong as can be clearly seen from the above structures.

56. $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

Oxide basicity decreases in a period but increases in a group.

57. (*i*) The volume being doubled by mixing the two solutions, the molarity of each component will be halved *i.e.* $[CH_3COOH] = 0.1$ M, $[HCl] = 0.1$ M.

HCl being a strong acid will remain completely ionised and hence H^+ ion concentration furnished by it will be 0.1 M. This would exert common ion effect on the dissociation of acetic acid, (a weak acid).

	$CH_3COOH \rightleftharpoons$	CH_3COO^- +	H^+
At start	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha + 0.1$

$$K_a = \frac{C\alpha(C\alpha + 0.1)}{C(1-\alpha)} = \frac{C\alpha^2 + 0.1\alpha}{(1-\alpha)}$$

Since α is very very small, $C\alpha^2$ can be neglected and $(1 - \alpha)$ can be taken as unity

$$\therefore K_a = 0.1\,\alpha \text{ or } \alpha = \frac{K_a}{0.1} = \frac{1.75 \times 10^{-5}}{0.1} = \mathbf{1.75 \times 10^{-4}}$$

$[H^+]_{Total} = 0.1 + C\alpha$, $C\alpha$ is negligible as compared to 0.1.

$\therefore [H^+]_{Total} = 0.1$ $\therefore$ **pH = 1**

(*ii*) $6\text{g NaOH} = \frac{6}{40} = 0.15\text{mol}$

0.1 mole of NaOH will be consumed by 0.1 mole of HCl.

Thus, 0.05 mole of NaOH will react with acetic acid according to the equation.

	CH_3COOH +	$NaOH \rightarrow$	CH_3COONa +	H_2O
Initial moles	0.1 mol	0.05 mol	0	0
At equilibrium	0.05 mol	0 mol	0.05 mol	0.05mol

Thus, solution of acetic acid and sodium acetate will become acidic buffer. So, pH of the buffer will be

$$pH = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} = -\log\left(1.75 \times 10^{-5}\right) + \log 1 = \mathbf{4.75}$$

58.

	$Pb(OH)_2 \rightleftharpoons$	Pb^{2+} +	$2OH^-$
(given)	6.7×10^{-6}M	6.7×10^{-6}M	$2 \times 6.7 \times 10^{-6}$M

$$\therefore K_{sp} = [Pb^{2+}][OH^-]^2 = (6.7 \times 10^{-6})(2 \times 6.7 \times 10^{-6})^2$$

$$= 1.203 \times 10^{-15}$$

The buffer solution pH = 8 (given)

$\therefore$ pOH = 6 or $[OH^-] = 10^{-6}$

Thus, in this buffer we have, $[Pb^{2+}][OH^-]^2 = 1.203 \times 10^{-15}$

or $[Pb^{2+}] \times [10^{-6}]^2 = 1.203 \times 10^{-15}$

$\therefore [Pb^{2+}] = \mathbf{1.203 \times 10^{-3}\ mol\ litre^{-1}}$

59. $$\underset{\text{(water)}}{NH_4^+(aq)+H_2O(l)} \rightleftharpoons NH_4OH(aq)+H^+(aq);$$

$$K_a = 5.6\times10^{-10}$$

$$\underset{\text{(acid)}}{NH_4^+(aq)} + \underset{\text{(base)}}{\bar{O}H\,(aq)} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} \underset{\text{(conj. base)}}{NH_3(aq)} + \underset{\text{(conj. acid)}}{H_2O\,(l)};$$

$$K_f = 3.4\times10^{10}$$

$$\underset{\text{(base)}}{NH_3(aq)} + \underset{\text{(water)}}{H_2O\,(l)} \underset{K_r}{\overset{K_f}{\rightleftharpoons}} NH_4^+(aq)+\bar{O}H(aq);\ K_r = ?$$

For above reaction, the dissociation constant base, $K_b(NH_3) = K_r/K_f$

$$\Rightarrow \quad \frac{K_w}{K_a(NH_4^+)} = \frac{K_r}{K_f} \Rightarrow \frac{1\times10^{-14}}{5.6\times10^{-10}} = \frac{K_r}{3.4\times10^{10}}$$

$$\Rightarrow \quad K_r = 6.07\times10^5.$$

60. $H_2O < CH_3-\ddot{\underset{\cdot\cdot}{O}}H < {}^-OH < {}^-OCH_3$

Weaker the base, stronger is its conjugate acids

$H_3O^+ > CH_3\overset{+}{O}H_2 > H_2O > CH_3OH$ (Decreasing acidic order of the conjugate bases.)

NOTE: Acidic order in aqueous medium: $CH_3OH > H_2O > C_2H_5OH$.

61. **Case I.** Write the concerned chemical reaction

	BOH +	HCl $\longrightarrow$	BCl +	H_2O
Moles before reaction	x	$0.1\times5=0.5$	0	0
Moles after reaction	$(x-0.5)$	0	0.5	0.5
∴ Molar concentration	$\frac{x-0.5}{V}$		$\frac{0.5}{V}$	$\frac{0.5}{V}$

Since, the solution represents a basic buffer, following Hendersen equation can be applied.

$$pOH = -\log K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$14-10.04 = -\log K_b + \log\frac{0.5}{(x-0.5)} \qquad ...(i)$$

Case II.

	BOH +	HCl $\longrightarrow$	BCl +	H_2O
Moles at start	x	$0.1\times20=2$	0	0
Moles after adding 20 ml. of 0.1N HCl	$(x-2)$	0	2	2
∴ Molar concentration	$\frac{x-2}{V_1}$	0	$\frac{2}{V_1}$	$\frac{2}{V_1}$

Again the solution is acting as basic buffer

$$\therefore pOH = -\log K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$14-9.14 = -\log K_b + \log\frac{2}{(x-2)} \qquad ...(ii)$$

Subtracting (i) by (ii):

$$0.9 = \log\left\{\left(\frac{2}{x-2}\right)\times\left(\frac{x-0.5}{0.5}\right)\right\}$$

$$\Rightarrow \quad \log 8 = \log\left\{\frac{4(x-0.5)}{(x-2)}\right\} \Rightarrow x = 3.5$$

Substituting this value in eq. (ii) :

$$4.86 = -\log K_b + \log\left(\frac{2}{3.5-2}\right)$$

$$\Rightarrow \quad \log K_b = -4.735 \Rightarrow \log K_b = 1.84\times10^{-5}.$$

62. **Case I.**

	CH_3COOH $\rightleftharpoons$	CH_3COO^- +	H^+
At start	1	0	0
At equib.	$1-\alpha$	α	α

$$[H^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$$

$$\therefore [H^+] = \sqrt{1.8\times10^{-5}\times1} = 4.24\times10^{-3}\,M$$

Thus $pH = -\log[H^+] = -\log 4.24\times10^{-3} = \mathbf{2.3724}$

Case II. pH after dilution $= 2\times$ original pH

$= 2\times2.3724 = 4.7448$

Let conc. after dilution $= c_1$

and degree of dissociation $= \alpha_1$

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

$4.7448 = -\log[H^+]$

$[H^+] = 1.8\times10^{-5} = c_1\alpha_1 \ \therefore c_1\alpha_1 = 1.8\times10^{-5}$

Dissociation constant

$$\text{Since } K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{(c_1\alpha_1)(c_1\alpha_1)}{c_1[1-\alpha_1]} = \frac{c_1\alpha^2}{(1-\alpha_1)}$$

$$1.8\times10^{-5} = \frac{1.8\times10^{-5}\times\alpha_1}{1-\alpha_1} \quad \therefore \alpha_1 = 0.5$$

Substituting the value of α_1 in the following relation

$c_1\alpha_1 = [H^+];\ c_1\times0.5 = 1.8\times10^{-5}$

$$c_1 = \frac{1.8\times10^{-5}}{0.5} = 3.6\times10^{-5}\,M$$

The number of moles of CH_3COOH before and after dilution will be same

∴ Mole of CH_3COOH before dilution = Mole of CH_3COOH after dilute $\quad (\because \text{Mole} = M\times V_{\text{in litre}})$

$1\times1 = 3.6\times10^{-5}\times V \Rightarrow V = \mathbf{2.78\times10^4}$ **litres**

63. p(OH) for basic buffer $= pK_b + \log\left(\frac{\text{Salt}}{\text{Base}}\right)$

We know that

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} \quad \text{or} \quad -\log 1.8\times10^{-5} + \log\frac{0.25}{0.05}$$

$pOH = 5 - \log 1.8 + \log 5 = 5.6989 - 0.2552$

$-\log[OH^-] = 5.4437;\ \log[OH^-] = -5.4437$

$[OH^-] = 3.5999\times10^{-6}$ [Taking antilog]

K_{sp} for $Mg(OH)_2 = [Mg^{2+}][OH^-]^2$

$6\times10^{-10} = [Mg^{2+}][3.5999\times10^{-6}]^2$

$$[Mg^{2+}] = \frac{6\times10^{-10}}{12.9598\times10^{-12}} = 0.4629\times10^{2}$$

$= \mathbf{46.29}$ **mole ion/L**

K_{sp} for $Al(OH)_3 = [Al^{3+}][OH^-]^3$

$6\times10^{-32} = [Al^{3+}](3.5999\times10^{-6})^3$

$$[Al^{3+}] = \frac{6\times10^{-32}}{(3.5999\times10^{-6})^3} = \mathbf{1.286\times10^{-15}}\ \textbf{mol ion/L}$$

64. $pH = pK_a + \log\left(\frac{Salt}{Acid}\right)$

If x moles of HCl are added then they will combine with NaCN to form x moles of very weak acid HCN.

$$\begin{array}{lcccc} & NaCN & +\ HCl & \rightarrow NaCl & +\ HCN \\ \text{At equilibrium :} & (0.01-x) & x & x & x \end{array}$$

For an acidic buffer,

$$pH = -\log K_a + \log\frac{[Salt]}{[Acid]}$$

$$\therefore\ 8.5 = -\log 4.1\times10^{-10} + \log\left(\frac{0.01-x}{x}\right)$$

$x = 8.85\times10^{-3}$ M $= \mathbf{8.85\times10^{-3}}$ **moles of HCl**

65. (i) Amount of HCl added = 0.20 mole

$[H^+] = 0.2$ g litre^{-1}

Added H^+ ions will combine with the acetate ions forming acetic acid with the result, concentration of acetate ions will decrease while that of acetic acid will increase.

$$\begin{array}{lcccc} & CH_3COO^- & +\ HCl & \longrightarrow CH_3COOH & +\ Cl^- \\ \text{before reaction} & 1 & 0.2 & 1 & 0 \\ \text{after reaction} & 0.8 & 0 & 1.2 & 0.2 \end{array}$$

$\therefore$ Concentration of acetate ions after adding 0.20 mole of HCl.

$[CH_3COO^-] = 1.0 - 0.2 = 0.8$ mole

Similarly, concentration of acetic acid,

$[CH_3COOH] = 1.0 + 0.2 = 1.2$ mole

$$\text{Now, } pH = -\log K_a + \log\frac{[Salt]}{[Acid]} = -\log 1.8\times10^{-5} + \log\frac{0.8}{1.2}$$

$pH = 4.7447 + 0.3010 - 0.4771 = \mathbf{4.5686}$

(ii) Amount of HCl added = 0.20 mole

Out of 0.2 mole of $[H^+]$ added, 0.1 mole will combine with 0.1 mole of CH_3COO^- forming 0.1 mole of CH_3COOH.

$$\begin{array}{lcccc} & CH_3COO^- & +\ H^+ & \rightarrow CH_3COOH & +\ Cl^- \\ \text{before reaction} & 0.1 & 0.2 & 0.1 & 0 \\ \text{after reaction} & 0 & 0.1 & 0.2 & 0.1 \end{array}$$

$\therefore$ Total concentration of acetic acid $[CH_3COOH]$ $= 0.1 + 0.1 = 0.2$ mole

In presence of $[H^+]$, CH_3COOH will not ionize. Therefore, pH of the solution will be due to the presence of H^+ of HCl, *i.e.* $0.2 - 0.1 = 0.1$ mole HCl

$pH = -\log[H^+] = -\log[0.1] = \mathbf{1}$

66. Among oxyacids of the same element, acidic nature increases with its oxidation number, *e.g.*,

$$\begin{array}{lccccccc} & HOCl & < & HOClO & < & HOClO_2 & < & HOClO_3 \\ \text{O.N. of Cl} & +1 & & +3 & & +5 & & +7 \end{array}$$

67. For acidic buffer $pH = -\log K_a + \log\frac{[Salt]}{[Acid]}$

Calculation of concentration of HCOOH.

Here, $c = 0.2$ M; $[H^+] = 6.4\times10^{-3}$

$$[H^+] = c\alpha \text{ or } \alpha = \frac{[H^+]}{c} \Rightarrow \alpha = \frac{6.4\times10^{-3}}{0.2} = 3.2\times10^{-2}$$

Since the degree of dissociation is very low (3.2×10^{-2}), it can be neglected and hence [HCOOH] can be taken as 0.2 M.

Calculation of concentration of $HCOO^-$, $[HCOO^-]$

It can be obtained in the following manner :

$$\begin{array}{lcccc} & HCOONa & \rightleftharpoons HCOO^- & + & Na^+ \\ \text{At start} & 1 & 0 & & 0 \\ \text{At equb.} & 0.25 & 0.75 & & 0.75 \end{array}$$

$\therefore [HCOO^-] = 0.75$

$$\text{For acidic buffer } pH = -\log K_a + \log\frac{[Salt]}{[acid]}$$

$$= -\log 2.4\times10^{-4} + \log\frac{0.75}{0.20} = \mathbf{4.19}$$

68. $N_2 < O_2 < F_2 < Cl_2$

i.e., $N\equiv N < O=O < F-F < Cl-Cl$

As the number of bonds increases the bond length decreases.

So $N_2 < O_2 <$ halogens. Among F_2 and Cl_2, bond length of Cl_2 will be higher because of higher atomic radii.

69. (i) From the dissociation of weak acid HA, $HA \rightleftharpoons H^+ + A^-$

It α is the degree of ionization of the acid HA, then $[H^+] = 0.1\ \alpha$ [$\because$ the acid is decimolar]

$[A^-] = 0.1\ \alpha$; $[HA] = 0.1\ (1-\alpha)$

$$\text{Therefore, } K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.1\alpha\times0.1\alpha}{0.1(1-\alpha)}$$

$$= \frac{0.1\alpha\times0.1\alpha}{0.1} \quad \text{(since acid is weak, } 1-\alpha = 1)$$

$K_a = 0.1\ \alpha^2$ or $4.9\times10^{-8} = 0.1\ \alpha^2$

$$\text{or } \alpha^2 = \frac{4.9\times10^{-8}}{0.1} \text{ or } \alpha = 7\times10^{-4}$$

$\therefore$ Percentage ionization $= 100\times7\times10^{-4} = \mathbf{7\times10^{-2}\%}$

(ii) Calculation of pH

$[H^+] = 0.1\alpha = 0.1\times7\times10^{-4}$ mole/litre $= 7\times10^{-5}$ mole/litre

Now since $pH = -\log[H^+] = -\log[7\times10^{-5}]$

$= 5 - \log 7 = 5 - 0.8451 = \mathbf{4.1549}$

(iii) Concentration of OH^- in decimolar solution

$[H^+] = 7\times10^{-5}$ mole per litre

Now, $K_w = [H^+][OH^-]$ or $1.0\times10^{-14} = 7\times10^{-5}\times[OH^-]$

$$\therefore [OH^-] = \frac{1\times10^{-14}}{7\times10^{-5}} = \mathbf{1.43\times10^{-10}}\ \textbf{mole per litre}$$

70. (i) Find the moles of each species after reaction.

(ii) $\text{pH} = -\log K_a + \log\left[\dfrac{\text{salt}}{\text{Acid}}\right]$

Given, NaOH 0.2 M, 20 mL; CH_3COOH 0.2 M, 50 mL

$K_a = 1.8 \times 10^{-5}$

V of 0.2M NaOH required to make $pH = 4.74 = ?$

From the chemical reaction

$$\underset{50\text{ mL}}{CH_3COOH} + \underset{20\text{ mL}}{NaOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{70\text{ mL}}$$

It is evident that 70 mL of the product will contain

(i) 30 mL of 0.2 M unused CH_3COOH
[unused $CH_3COOH = 50 - 20 = 30$ mL]

(ii) 20 mL of CH_3COONa.

$\therefore$ No. of moles of CH_3COOH in solution

$$= \frac{0.2}{1000} \times 30 = 0.006 \text{ mole}$$

Similarly, No. of moles of CH_3COONa solution

$$= \frac{0.2}{1000} \times 20 = 0.004 \text{ moles}$$

$$\text{pH} = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

Substituting the values of the various values

$$\text{pH} = -\log 1.8 \times 10^{-5} + \log\frac{0.004}{0.006}$$

$$= 4.7447 - 0.1761 = \mathbf{4.5686}$$

Calculation of the additional volume of 0.2 M NaOH required to make pH of solution 4.74.

$$\text{pH} = -\log K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \log\frac{[\text{Salt}]}{[\text{Acid}]} = 0.0047 \quad \text{or} \quad \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{1.011}$$

Let x mL. be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralise x mL of 0.2 M CH_3COOH and produce x mL of 0.2 M sodium acetate. The resulting solution $(70 + x)$ mL will now contain

(i) $(30 - x)$ mL of 0.2 M acetic acid.

(ii) $(20 + x)$ mL of 0.2 M sodium acetate.

Number of moles of acetic acid in $(70 + x)$ mL. solution

$$= \frac{0.2}{1000} \times (30 - x) = 2 \times 10^{-4}(30 - x)$$

Number of moles of CH_3COONa in $(70 + x)$ mL. solution

$$= \frac{0.2}{1000} \times (20 + x) = 2 \times 10^{-4}(20 + x)$$

Therefore, $\dfrac{[\text{Salt}]}{[\text{Acid}]} = \dfrac{2 \times 10^{-4}(20 + x)}{2 \times 10^{-4}(30 - x)} = \dfrac{20 + x}{30 - x}$

or $1.001x + x = 30 - 20.22$; $2.011x = 9.78$ or $x = 4.86$

Therefore, the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74 is **4.86 mL.**

71. Suppose the number of moles of sodium propionate $= x$

Then $\text{pH} = \text{p}K_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log\left(\frac{x}{0.02}\right)$$

$x = 0.7536 \times 0.02 = \mathbf{1.5072 \times 10^{-2}}$ **mol**

$$\underset{0.01\text{ mole}}{HCl} \rightleftharpoons \underset{0.01\text{ mole}}{H^+} + Cl^-$$

When 0.01 mole of HCl is added, there is $(0.01 + 0.02)$ M of propionic acid and $(0.015 - 0.010)$ M of propionate. Therefore,

$$\text{pH} = -\log(1.34 \times 10^{-5}) + \log\frac{0.005}{0.03} = \mathbf{4.09}$$

The pH of a 0.010 molar HCl solution $= -\log 10^{-2} = \mathbf{2}$

72. Phenolphthalein indicates half neutralization.

$$Na_2CO_3 + H^+ \longrightarrow NaHCO_3 + Na^+ \qquad \text{...(i)}$$

Methyl orange indicates complete neutralisation

$$NaHCO_3 + H^+ \longrightarrow Na^+ + H_2O + CO_2 \qquad \text{...(ii)}$$

$\therefore$ Volume of 0.1M H_2SO_4 required for complete neutralisation $= 2 \times 2.5 = 5.0$ mL

0.1 M $H_2SO_4 \equiv$ 0.2 N H_2SO_4

[For H_2SO_4 molarity $= 2 \times$ normality]

($\because$ Mol. wt. of $H_2SO_4 = 98$, and eq. wt. of $H_2SO_4 = 49$)

$\therefore$ 0.2 M $H_2SO_4 \equiv$ 0.4 NH_2SO_4

N_1 = normality of Na_2CO_3,

V_1 = volume of Na_2CO_3 = 10 mL,

N_2 = normality of H_2SO_4 = 0.2,

V_2 = volume of H_2SO_4 = 5.0 mL

$$\therefore N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 5 \;\therefore N_1 = \frac{0.2 \times 5}{10} = 0.1\text{ N}$$

$$\therefore \text{Eq. wt. of } Na_2CO_3 = \frac{1}{2} \times \text{molecular weight} = \frac{106}{2} = 53$$

Strength of $Na_2CO_3 = 53 \times 0.1 = \mathbf{5.3}$ **g/L**

[$\because$ strength = normality × Eq. wt]

For neutralization with methyl orange, volume of 0.2 M H_2SO_4 used = 2.5 mL = 2.5 mL of 0.4 N H_2SO_4
= 5 mL of 0.2 N H_2SO_4 [$\because N_1V_1 = N_2V_2$]

From 5 mL of 0.2 N H_2SO_4, 2.5 mL is used for neutralising $NaHCO_3$ formed during first half neutralization Na_2CO_3.

$\therefore$ Volume of 0.2N H_2SO_4 used for neutralisation of $NaHCO_3$ present in original solution $= 5.0 - 2.5 = 2.5$ mL

$\therefore N_1V_1 = N_2V_2$

where N_1 = Normality of $NaHCO_3$,

N_2 = Normality of H_2SO_4 = 0.2,

V_1 = Volume of $NaHCO_3$ = 10 mL, V_2 = Volume of H_2SO_4 = 2.5 mL

$N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 2.5$

$$N_1 = \frac{0.2 \times 2.5}{10} = 0.05\text{ N}$$

Eq. wt. of $NaHCO_3 = 84$

$\therefore$ Strength of $NaHCO_3 = 84 \times 0.05 = \mathbf{4.2}$ **g/L**