6

Chemical and Ionic Equilibrium

Topic 1 Chemical Equilibrium

Objective Questions I (Only one correct option)

1. The incorrect match in the following is **(2019 Main, 12 April II)**

(a) $G \quad 0, K \quad 1$ (b) $G \quad 0, K \quad 1$
(c) $G \quad 0, K \quad 1$ (d) $G \quad 0, K \quad 1$

2. In which one of the following equilibria, $K_p \quad K_c$? **(2019 Main, 12 April II)**

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$
(b) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
(c) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

3. For the reaction,

$2SO_2(g) \quad O_2(g) \qquad 2SO_3(g), \quad H \qquad 57.2 \text{ kJ mol}^{\;1}$ and $K_c \quad 1.7 \quad 10^{16}$. Which of the following statement is incorrect? **(2019 Main, 10 April II)**

(a) The equilibrium constant decreases as the temperature increases
(b) The addition of inert gas at constant volume will not affect the equilibrium constant
(c) The equilibrium will shift in forward direction as the pressure increases
(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required

4. For the following reactions, equilibrium constants are given :

$$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 \quad 10^{52}$$
$$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 \quad 10^{129}$$

The equilibrium constant for the reaction,

$2SO(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is **(2019 Main, 8 April II)**

(a) 10^{25} (b) 10^{77} (c) 10^{154} (d) 10^{181}

5. In a chemical reaction, $A \quad 2B \overset{K}{\rightleftharpoons} 2C \quad D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is **(2019 Main, 12 Jan I)**

(a) $\frac{1}{4}$ (b) 16 (c) 1 (d) 4

6. Two solids dissociate as follows:

$$A(s) \rightleftharpoons B(g) \quad C(g); \; K_{p_1} \quad x \text{ atm}^2$$
$$D(s) \rightleftharpoons C(g) \quad E(g); \; K_{p_2} \quad y \text{ atm}^2$$

The total pressure when both the solids dissociate simultaneously is **(2019 Main, 12 Jan I)**

(a) $\sqrt{x \quad y}$ atm (b) $x^2 \quad y^2$ atm
(c) $(x \quad y)$ atm (d) $2(\sqrt{x \quad y})$ atm

7. Consider the reaction,

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

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{\text{total}}$ at equilibrium) **(2019 Main, 11 Jan I)**

(a) $\frac{3^{3/2} K_p^{1/2} P^2}{4}$ (b) $\frac{3^{3/2} K_p^{1/2} P^2}{16}$
(c) $\frac{K_p^{\;1/2} P^2}{16}$ (d) $\frac{K_p^{\;1/2} P^2}{4}$

8. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327 C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327 C is ($R = 0.082 \text{ atm mol}^{\;1} \text{K}^{\;1}$, molar mass of S $\quad 32 \text{ g mol}^{\;1}$, molar mass of N $\quad 14 \text{ g mol}^{\;1}$) **(2019 Main, 10 Jan II)**

(a) $0.242 \quad 10^{\;4} \text{ atm}^2$ (b) 0.242 atm^2
(c) $4.9 \quad 10^{\;3} \text{ atm}^2$ (d) $1 \quad 10^{\;4} \text{ atm}^2$

9. The values of $\frac{K_p}{K_C}$ for the following reactions at 300 K are, respectively (At 300 K, $RT \quad 24.62 \text{ dm}^3 \text{ atm mol}^{\;1}$)

$$N_2(g) \quad O_2(g) \rightleftharpoons 2NO(g)$$
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$$

(2019 Main, 10 Jan I)

(a) 1, 24.62 dm^3 atm mol ^{1}, 606.0 dm^6 atm^2 mol ^{2}
(b) 1, 24.62 dm^3 atm mol ^{1}, 1.65   10 ^{3} dm ^{6} atm ^{2} mol^2
(c) 24.62 dm^3 atm mol ^{1}, 606.0 dm^6 atm ^{2} mol^2, 1.65   10 ^{3} dm ^{6} atm ^{2} mol^2
(d) 1, 4.1   10 ^{2} dm ^{3}atm ^{1} mol, 606 dm^6 atm^2 mol ^{2}

10 Consider the following reversible chemical reactions,

$$A_2(g) \quad B_2(g) \overset{K_1}{\rightleftharpoons} 2AB(g) \qquad \ldots\text{(i)}$$

$$6AB(g) \overset{K_2}{\rightleftharpoons} 3A_2(g) \quad 3B_2(g) \qquad \ldots\text{(ii)}$$

The relation between K_1 and K_2 is **(2019 Main, 9 Jan II)**

(a) $K_2 \quad K_1^3$ (b) $K_1K_2 \quad 3$
(c) $K_2 = K_1 \;^{3}$ (d) $K_1K_2 \quad \frac{1}{3}$

11. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS   from H_2S is 1.0   10 ^{7} and that of S^2 from HS   ions is 1.2   10 ^{13} then the concentration of S^2 ions in aqueous solution is : **(2018 Main)**

(a) 5   10 ^{8} (b) 3   10 ^{20}
(c) 6   10 ^{21} (d) 5   10 ^{19}

12. The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentrations of all the four species were 1 M each, then equilibrium concentration of D (in mol L ^{1}) will be **(2016 Main)**

(a) 0.818 (b) 1.818
(c) 1.182 (d) 0.182

13. The standard Gibbs energy change at 300 K for the reaction, $2A \rightleftharpoons B \quad C$ is 2494. 2 J. At a given time, the composition of the reaction mixture is $[A] \quad \frac{1}{2}, [B] \quad 2$ and $[C] \quad \frac{1}{2}$. The reaction proceeds in the

(R 8.314 JK / mol, e = 2.718) **(2015, Main)**

(a) forward direction because $Q \quad K_c$
(b) reverse direction because $Q \quad K_c$
(c) forward direction because $Q \quad K_c$
(d) reverse direction because $Q \quad K_c$

14. For the reaction, $SO_2(g) \quad \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

if $K_p \quad K_C(RT)^x$ where, the symbols have usual meaning, then the value of x is (assuming ideality) **(2014 Main)**

(a)   1 (b) $\frac{1}{2}$ (c) $\frac{1}{2}$ (d) 1

15. The species present in solution when CO_2 is dissolved in water are **(2006 Main)**

(a) CO_2, H_2CO_3, HCO_3, CO_3^2
(b) H_2CO_3, CO_3^2
(c) HCO_3, CO_3^2
(d) CO_2, H_2CO_3

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

Which is correct statement if N_2 is added at equilibrium condition? **(2006, 3M)**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics, the entropy must increases in the direction of spontaneous reaction
(b) The condition for equilibrium is $G(N_2) + 3G(H_2) = 2G(NH_3)$ where, G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward reactions to the same extent
(c) The catalyst will increase the rate of forward reaction by   and that of backward reaction by
(d) Catalyst will not alter the rate of either of the reaction

17. $Ag \quad NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $K_1 \quad 3.5 \quad 10^{3}$

$[Ag(NH_3)] \quad NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 \quad 1.7 \quad 10^{3}$

then the formation constant of $[Ag(NH_3)_2]$ is **(2006, 3M)**

(a) 6.08   10 ^{6} (b) 6.08 10^6
(c) 6.08   10 ^{9} (d) None of these

18. Consider the following equilibrium in a closed container

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

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation ( )? **(2002, 3M)**

(a) Neither K_p nor   changes
(b) Both K_p and   change
(c) K_p changes but   does not change
(d) K_p does not change but   changes

19. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction, $N_2O_4 \rightleftharpoons 2NO_2$, is expressed by $K_p \quad \frac{4x^2p}{(1 \quad x^2)}$, where, p pressure, x extent of decomposition. Which one of the following statement is true? **(2001, 1M)**

(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

20. When two reactants, A and B are mixed to give products, C and D, the reaction quotient, (Q) at the initial stages of the reaction **(2000)**

(a) is zero
(b) decreases with time
(c) is independent of time
(d) increases with time

21. For the reversible reaction,

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

at 500 C, the value of K_p is $1.44 \quad 10^{-5}$ when partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol/L is **(2000, S, 1M)**

(a) $\dfrac{1.44 \quad 10^{\ 5}}{(0.082 \quad 500)^{\ 2}}$ (b) $\dfrac{1.44 \quad 10^{\ 5}}{(8.314 \quad 773)^{\ 2}}$

(c) $\dfrac{1.44 \quad 10^{\ 5}}{(0.082 \quad 773)^{2}}$ (d) $\dfrac{1.44 \quad 10^{-5}}{(0.082 \quad 773)^{\ 2}}$

22. For the chemical reaction,

$$3X(g) + Y(g) \rightleftharpoons X_3Y(g)$$

the amount of X_3Y at equilibrium is affected by **(1999, 2M)**

(a) temperature and pressure

(b) temperature only

(c) pressure only

(d) temperature, pressure and catalyst

23. 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)**

(a) adding a suitable catalyst

(b) adding an inert gas

(c) decreasing the volume of the container

(d) increasing the amount of CO(g)

24. One mole of $N_2O_4(g)$ at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of $N_2O_4(g)$ decomposes to $NO_2(g)$. The resultant pressure is **(1996, 1M)**

(a) 1.2 atm (b) 2.4 atm (c) 2.0 atm (d) 1.0 atm

25. An example of a reversible reaction is **(1985, 1M)**

(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \quad PbI_2(s) + 2NaNO_3(aq)$

(b) $AgNO_3(aq) + HCl(aq) \quad AgCl(s) + HNO_3(aq)$

(c) $2Na(s) + 2H_2O(l) = 2NaOH(aq) + H_2(g)$

(d) $KNO_3(aq) + NaCl(aq) \quad KCl(aq) \quad NaNO_3(aq)$

26. Pure ammonia is placed in a vessel at a temperature where its dissociation constant ( ) is appreciable. At equilibrium,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$ **(1984, 1M)**

(a) K_p does not change significantly with pressure

(b) 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

27. For the reaction, $H_2(g) \quad I_2(g) \rightleftharpoons 2HI(g)$

the equilibrium constant K_p changes with **(1981, 1M)**

(a) total pressure

(b) catalyst

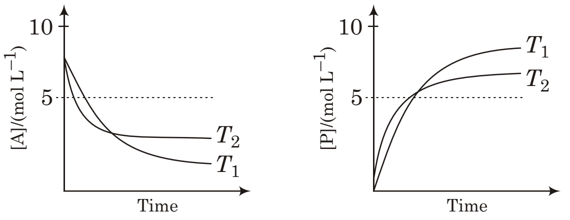
(c) the amount of H_2 and I_2 present

(d) temperature

Objective Questions II

(One or more than one correct option)

28. For a reaction, $A \rightleftharpoons P$, the plots of $[A]$ and $[P]$ with time at temperatures T_1 and T_2 are given below.



If $T_2 \quad T_1$, the correct statement(s) is are

(Assume $H^{\ominus}$ and $S^{\ominus}$ are independent of temperature and ratio of ln K at T_1 to ln K at T_2 is greater than T_2 / T_1. Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.) **(2018 Adv.)**

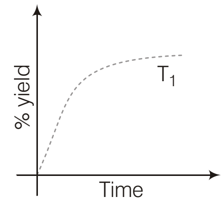
(a) $H^{\ominus} \quad 0, \ S^{\ominus} \quad 0$ (b) $G^{\ominus} \quad 0, \ H^{\ominus} \quad 0$

(c) $G^{\ominus} \quad 0, \ S^{\ominus} \quad 0$ (d) $G^{\ominus} \quad 0, \ S^{\ominus} \quad 0$

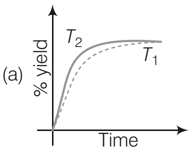
29. The % yield of ammonia as a function of time in the reaction,

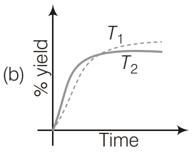
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad H < 0$ **(2015 adv.)**

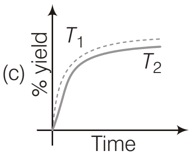
at (p, T_1) is given below.

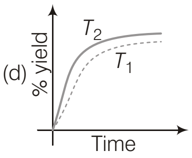


If this reaction is conducted at (p, T_1), with $T_2 > T_1$ the % yield by of ammonia as a function of time is represented by









30. The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a (HA) is **(2013 Adv.)**

(a) $1 \quad 10^{\ 4}$ (b) $1 \quad 10^{\ 5}$

(c) $1 \quad 10^{\ 6}$ (d) $1 \quad 10^{\ 3}$

31. The equilibrium $2\,Cu^{I} \rightleftharpoons Cu^{0} + Cu^{II}$ in aqueous medium at 25 C shifts towards the left in the presence of **(2011)**

(a) NO_3 (b) Cl (c) SCN (d) CN

32. For the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ the forward reaction at constant temperature is favoured by **(1991, 1M)**

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

33. The equilibrium $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25 C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct? **(1989, 1M)**

(a) Concentration of SO_2, Cl_2 and SO_2Cl_2 change
(b) More chlorine is formed
(c) Concentration of SO_2 is reduced
(d) None of the above

34. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left behind. At equilibrium, **(1986, 1M)**

(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,

$$C_2H_4 + H_2 \rightleftharpoons C_2H_6 \qquad (\quad H \qquad 32.7 \text{ kcal})$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by **(1984, 1M)**

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

Fill in the Blanks

36. For a gaseous reaction $2B \qquad A$, the equilibrium constant K_p is …… to/than K_c. **(1997 C, 1M)**

37. 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, 1M)**

38. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are related by ...... **(1994, 1M)**

True/False

39. The rate of an exothermic reaction increases with increasing temperature. **(1993, 1M)**

40. Catalyst makes a reaction more exothermic. **(1987, 1M)**

41. 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 $\frac{1}{K}$. **(1984, 1M)**

42. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **(1984, 1M)**

Subjective Questions

43. (a) In the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ when 5 moles of each are taken, the temperature is kept at 298 K the total pressure was found to be 20 bar. Given that

$$G_f(N_2O_4) \quad 100\text{kJ}, \quad G_f(NO_2) \quad 50 \text{ kJ}$$

(i) Find G of the reaction.
(ii) The direction of the reaction in which the equilibrium shifts.

(b) A graph is plotted for a real gas which follows van der Waals' equation with pV_m taken on Y-axis and p on X-axis. Find the intercept of the line where V_m is molar volume. **(2004, 4M)**

44. When 3.06 g of solid NH_4SH 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_4SH is introduced into the flask? **(1999, 7M)**

45. (a) The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atm (relative atomic mass of P 31.0 and Cl 35.5).

(b) Given, $[Ag(NH_3)_2^+] \rightleftharpoons Ag^+ + 2NH_3$,

$K_c \quad 6.2 \quad 10^{8}$ and K_{sp} of AgCl

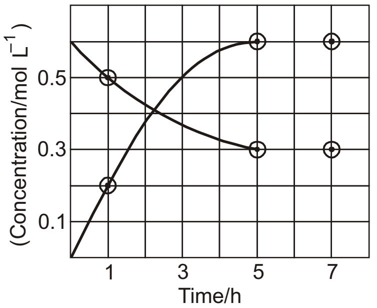
$1.8 \quad 10^{10}$ at 298 K.

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, 3M+5M)**

46. The progress of reaction,

$$A \rightleftharpoons nB$$

with time, is represented in fig. use given below.



Determine :

(i) the value of n
(ii) the equilibrium constant, K and
(iii) the initial rate of conversion of A. **(1994, 3M)**

47. 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 atm 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, 5M)**

48. 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, 5M)**

49. 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 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, 3M)**

50. 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 atm and 37 C. **(1988, 4M)**

51. At a certain temperature, equilibrium constant (K_c) is 16 for the reaction;

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

If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO and NO_2? **(1987, 5M)**

52. 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 moles of B_2, how many moles of AB will be formed at 373 K? **(1985, 4M)**

53. One mole of N_2 and 3 moles of PCl_5 are placed in a 100 L vessel heated to 227°C. The equilibrium pressure is 2.05 atm. 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, 6M)**

54. One mole of nitrogen is mixed with three moles of hydrogen in a four litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

$$N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g), \text{ then}$$

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

$$\frac{1}{2}N_2(g) \quad \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$ **(1981, 4M)**

Passage Based Questions

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, $_rG$, 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 . Thus, $_{\text{equilibrium}}$ 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, $R \quad 0.083$ L bar $K^{\ 1}$ mol ^{1})

55. The equilibrium constant K_p for this reaction at 298 K, in terms of $_{\text{equilibrium}}$ is **(2016 Adv.)**

(a) $\dfrac{8\ ^{2}_{\text{equilibrium}}}{2\quad_{\text{equilibrium}}}$ (b) $\dfrac{8\ ^{2}_{\text{equilibrium}}}{4\quad^{2}_{\text{equilibrium}}}$

(c) $\dfrac{4\ ^{2}_{\text{equilibrium}}}{2\quad_{\text{equilibrium}}}$ (d) $\dfrac{4\ ^{2}_{\text{equilibrium}}}{4\quad^{2}_{\text{equilibrium}}}$

56. The incorrect statement among the following for this reaction, is **(2016 Adv.)**

(a) Decrease in the total pressure will result in the formation of more moles of gaseous X

(b) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(c) $_{\text{equilibrium}} \quad 0.7$

(d) $K_C \quad 1$

Topic 2 Ionic Equilibrium

Objective Questions I (Only one correct option)

1. The molar solubility of Cd $(OH)_2$ is $1.84 \quad 10^{\ 5}$m in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH 12 is **(2019 Main, 12 April II)**

(a) $1.84 \quad 10^{\ 9}$ M (b) $\dfrac{2.49}{1.84} \quad 10^{\ 9}$ M

(c) $6.23 \quad 10^{\ 11}$ M (d) $2.49 \quad 10^{\ 10}$ M

2. What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3 \quad 2.4 \quad 10^{\ 24}$ **(2019 Main, 12 April II)**

(a) $3 \quad 10^{\ 19}$

(b) $12 \quad 10^{\ 21}$

(c) $3 \quad 10^{\ 22}$

(d) $12 \quad 10^{\ 23}$

3. The pH of a 0.02 M NH_4Cl solution will be [Given $K_b(NH_4OH) \quad 10^{5}$ and $\log 2 \quad 0.301$] **(2019 Main, 10 April II)**

(a) 4.65 (b) 2.65 (c) 5.35 (d) 4.35

4. Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

II. Ionic product of water is temperature dependent.

III. A monobasic acid with $K_a \quad 10^{5}$ has a pH 5. The degree of dissociation of this acid is 50%.

IV. The Le-Chatelier's principle is not applicable to common-ion effect.

The correct statements are **(2019 Main, 10 April I)**

(a) I, II and IV (b) II and III

(c) I and II (d) I, II and III

5. If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct? **(2019 Main, 8 April I)**

(a) $S \quad {\frac{K_{sp}}{144}}^{1/6}$ (b) $S \quad {\frac{K_{sp}}{6912}}^{1/7}$

(c) $S \quad {\frac{K_{sp}}{929}}^{1/9}$ (d) $S \quad {\frac{K_{sp}}{216}}^{1/7}$

6. If K_{sp} of Ag_2CO_3 is $8 \quad 10^{12}$, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is **(2019 Main, 12 Jan II)**

(a) $8 \quad 10^{12}$ M (b) $8 \quad 10^{13}$ M

(c) $8 \quad 10^{10}$ M (d) $8 \quad 10^{11}$ M

7. 20 mL of 0.1 M H_2SO_4 solution is added to 30 mL of 0.2 M NH_4OH solution. The pH of the resultant mixture is [pK_b of $NH_4OH = 4.7$] **(2019 Main, 9 Jan I)**

(a) 9.3 (b) 5.0 (c) 9.0 (d) 5.2

8. An aqueous solution contains an unknown concentration of Ba^{2} . When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is $1 \quad 10^{10}$. What is the original concentration of Ba^{2} ? **(2018 Main)**

(a) $5 \quad 10^{9}$ M (b) $2 \quad 10^{9}$ M

(c) $1.1 \quad 10^{9}$ M (d) $1.0 \quad 10^{10}$ M

9. Which of the following are Lewis acids? **(2018 Main)**

(a) PH_3 and BCl_3 (b) $AlCl_3$ and $SiCl_4$

(c) PH_3 and $SiCl_4$ (d) BCl_3 and $AlCl_3$

10. Which of the following salts is the most basic in aqueous solution? **(2018 Main)**

(a) $Al(CN)_3$ (b) CH_3COOK

(c) $FeCl_3$ (d) $Pb(CH_3COO)_2$

11. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is **(2017 Main)**

(a) 7.2 (b) 6.9 (c) 7.0 (d) 1.0

12. How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(2013 Main)**

(a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L

13. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are $4.0 \quad 10^{8}$, $3.2 \quad 10^{14}$ and $2.7 \quad 10^{15}$, respectively. Solubilities (mol dm^{3}) of the salts at temperature 'T' are in the order **(2008, 3M)**

(a) $MX \quad MX_2 \quad M_3X$ (b) $M_3X \quad MX_2 \quad MX$

(c) $MX_2 \quad M_3X \quad MX$ (d) $MX \quad M_3X \quad MX_2$

14. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \quad 10^{12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \quad 10^{14}$ at 25°C) **(2008, 3M)**

(a) $3.7 \quad 10^{13}$ M (b) $3.2 \quad 10^{7}$ M

(c) $3.2 \quad 10^{2}$ M (d) $2.7 \quad 10^{2}$ M

15. CH_3NH_2 (0.1 mole, $K_b \quad 5 \quad 10^{4}$) is added to 0.08 mole of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is **(2005, 1M)**

(a) $1.6 \quad 10^{11}$ (b) $8 \quad 10^{11}$

(c) $5 \quad 10^{5}$ (d) $8 \quad 10^{2}$

16. HX is a weak acid ($K_a \quad 10^{5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is **(2004, 1M)**

(a) 0.01% (b) 0.0001%

(c) 0.1% (d) 0.5%

17. A solution which is 10^{3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{15}, 10^{23}, 10^{20} and 10^{54} respectively, which one will precipitate first? **(2003, 1M)**

(a) FeS (b) MgS (c) HgS (d) ZnS

18. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium. **(2002)**

(a) CuS > ZnS > Na_2S (b) ZnS > Na_2S > CuS

(c) Na_2S > CuS > ZnS (d) Na_2S > ZnS > CuS

19. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is **(2001, 1M)**

(a) $L_s \quad S^{p+q} \quad p^p \quad q^q$ (b) $L_s \quad S^{p+q} \quad p^q \quad q^p$

(c) $L_s \quad S^{pq} \quad p^p \quad q^q$ (d) $L_s \quad S^{pq} \quad (p.q)^{(p \quad q)}$

20. The pH of 0.1 M solution of the following salts increases in the order **(1999, 2M)**

(a) NaCl < NH_4Cl < NaCN < HCl

(b) HCl < NH_4Cl < NaCl < NaCN

(c) NaCN < NH_4Cl < NaCl < HCl

(d) HCl < NaCl < NaCN < NH_4Cl

21. Which of the following solutions will have pH close to 1.0 ? **(1992, 1M)**

(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

22. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25 C) is **(1990, 1M)**

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$ (c) $Ba(OH)_2$ (d) $Be(OH)_2$

23. Which of the following is the strongest acid? **(1989, 1M)**

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$
(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

24. When equal volumes of the following solutions are mixed, precipitation of AgCl (K_{sp} 1.8 10^{10}) will occur only with **(1988, 1M)**

(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)

25. The pK_a of acetyl salicylic 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, 1M)**

(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

26. The compound that is not a Lewis acid is **(1985, 1M)**

(a) BF_3 (b) $AlCl_3$ (c) $BeCl_2$ (d) $SnCl_4$

27. The conjugate acid of NH_2^- is **(1985, 1M)**

(a) NH_3 (b) NH_2OH (c) NH_4^+ (d) N_2H_4

28. The best indicator for detection of end point in titration of a weak acid and a strong base is **(1985, 1M)**

(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)

29. 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, 1M)**

(a) 1.0 10^{4} (b) 1.0 10^{10}
(c) 1.0 10^{10} (d) 1.0 10^{14}

30. 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 **(1984, 1M)**

(a) 4 (b) 7
(c) 10 (d) 14

31. The precipitate of CaF_2, (K_{sp} 1.7 10^{10}) is obtained, when equal volumes of which of the following are mixed? **(1982, 1M)**

(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

32. An acidic buffer solution can be prepared by mixing the solution of **(1981, 1M)**

(a) acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

33. Of the given anions, the strongest base is **(1981, 1M)**

(a) ClO (b) ClO_2
(c) ClO_3 (d) ClO_4

34. At 90°C, pure water has $[H_3O\ ]$ as 10^{6} mol L^{1}. What is the value of K_w at 90°C ? **(1981, 1M)**

(a) 10^{6} (b) 10^{12} (c) 10^{14} (d) 10^{8}

35. The pH of 10^{8} M solution of HCl in water is **(1981, 1M)**

(a) 8 (b) 8
(c) between 7 and 8 (d) between 6 and 7

Objective Questions II

(One or more than one correct option)

36. 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

(a) 1.1 10^{11} (b) 1.1 10^{10}
(c) 1.1 10^{12} (d) 1.1 10^{9} **(2013 Adv.)**

37. 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

38. A buffer solution can be prepared from a mixture of **(1999, 3M)**

(a) sodium acetate and acetic acid in water
(b) sodium acetate and HCl in water
(c) ammonia and ammonium chloride in water
(d) ammonia and sodium hydroxide in water

39. Which of the following statement(s) is (are) correct?

(a) The pH of $1.0 \quad 10^{\ 8}$ M solution of HCl is 8 **(1998, 2M)**

(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 $pH = \frac{1}{2}\ pK_a$

Numerical Value Based Question

40. The solubility of a salt of weak acid (AB) at pH 3 is $Y \quad 10^{\ 3}$ mol $L^{\ 1}$. The value of Y is__ (Given that the value of solubility product of AB $(K_{sp}) \quad 2 \quad 10^{\ 10}$ and the value of ionisation constant of HB $(K_a) \quad 1 \quad 10^{\ 8}$ **(2018 Adv.)**

Matrix Match Type

41. Dilution processes of different aqueous solutions, with water, are given in List-I. The effects of dilution of the solution on $[H\ \ ]$ are given in List-II.

Note Degree of dissociation ( ) of weak acid and weak base is 1; degree of hydrolysis of salt 1; $[H\ \ ]$ represents the concentration of H ions

	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 0.1M 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 exces 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 **(2018 Adv.)**

(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

Fill in the Blanks

42. In the reaction, $I \quad + I_2 \qquad I_3$, the Lewis acid is .... **(1997, 1M)**

43. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy. **(1987, 1M)**

44. 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, 1M)**

45. The conjugate base of HSO_4^- in aqueous solution is …… **(1982, 1M)**

True/False

46. The following species are in increasing order of their acidic property : ZnO, Na_2O_2, P_2O_5, MgO. **(1985, 1/2M)**

47. Solubility of sodium hydroxide increases with increase in temperature. **(1985, 1/2M)**

48. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(1982, 1M)**

Integer Answer Type Questions

49. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\,^0_X \qquad \,^0_Y$, the difference in their pK_a values, pK_a (HX) pK_a (HY), is (consider degree of ionisation of both acids to be <<1). **(2015 Adv.)**

50. In 1 L saturated solution of AgCl $[K_{sp}(AgCl) \quad 1.6 \quad 10^{\ 10}]$, 0.1 mole of CuCl $[K_{sp}(CuCl) = 1.0 \quad 10^{\ 6}]$ is added. The resultant concentration of Ag in the solution is $1.6 \quad 10^{\ x}$. The value of 'x' is **(2011)**

51. 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
LiCN			

(2010)

Subjective Questions

52. The dissociation constant of a substituted benzoic acid at 25°C is $1.0 \quad 10^{\ 4}$. The pH of 0.01 M solution of its sodium salt is **(2009)**

53. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point. Given, K_a (HA) = $5 \quad 10^{\ 6}$ and 1. **(2004)**

54. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 250°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 (assuming there is no change in volume on mixing, K_a of acetic acid is $1.75 \quad 10^{5}$ mol/L. **(1984, 1M)**

55. 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 mol/L and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(2000, 5M)**

56. The solubility of $Pb(OH)_2$ in water is $6.7 \quad 10^{6}$ M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH 8. **(1999, 4M)**

57. (a) Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+$ (saturated. Ag_2CrO_4 solution.) || Ag^+ (0.1 M) | Ag is 0.164 V at 298 K. **(1998, 6M)**

(b) What will be the resultant pH when 200 mL of an aqueous solution of HCl (pH 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH 12.0)? **(1998, 6M)**

58. 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^- ions per litre. Calculate the solubility product of AgCl. $[K_{sp} (Ag_2CO_3) \quad 8.2 \quad 10^{12}]$ **(1997, 5M)**

59. 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? ($K_a \quad 1.0 \quad 10^{5}$) **(1997, 2M)**

60. The ionisation constant of NH_4^+ in water is $5.6 \quad 10^{10}$ 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 $3.4 \quad 10^{10}$ L/mol/s. Calculate the rate constant per proton transfer from water to NH_3. **(1996, 3M)**

61. What is the pH of a 0.50 M aqueous NaCN solution? (pK_b of CN 4.70). **(1996, 2M)**

62. 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, 2M)**

63. For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ \quad 2CN$

The equilibrium constant, at 25 C, is $4.0 \quad 10^{19}$. Calculate the silver ion concentration in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$. **(1994, 3M)**

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

65. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.4? (K_a for H_2CO_3 in blood is $7.8 \quad 10^{7}$) **(1993, 2M)**

66. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25 C is $4.42 \quad 10^{5}$. 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, 4M)**

67. A 40 mL solution of a 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 the addition of 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. **(1991, 6M)**

68. The solubility product of $Ag_2C_2O_4$ at 25 C is $1.29 \quad 10^{11} mol^3L^{3}$. 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

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

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. **(1991, 4M)**

69. What is the pH of a 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given, $K_a \quad 1.8 \quad 10^{5}$ **(1990, 4M)**

70. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution.

$$K_b[NH_4OH] \quad 1.8 \quad 10^{5}$$

$$K_{sp}[Mg(OH)_2] \quad 8.9 \quad 10^{12}$$

$$K_{sp}[Al(OH)_3] \quad 6 \quad 10^{32}$$

(1989, 3M)

71. 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 g formula weight of NaCN?

$K_{HCN} \quad 4.1 \quad 10^{10}$ **(1988, 4M)**

72. What is the pH of the solution when 0.20 mole of HCl is added to one litre of a solution containing
(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 $1.8 \quad 10^{5}$. **(1987, 5M)**

73. The solubility of $Mg(OH)_2$ in pure water is $9.57 \quad 10^{3}$ g/L. Calculate its solubility (in g/L) in 0.02 M $Mg(NO_3)_2$ solution. **(1986, 5M)**

74. The concentration of hydrogen ions in a 0.20 M solution of formic acid is $6.4 \quad 10^{3}$ mol/L. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre.

What will be the pH of this solution? The dissociation constant of formic acid is $2.4 \quad 10^{4}$ and the degree of dissociation of sodium formate is 0.75. **(1985, 3M)**

75. 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? **(1984, 4M)**
K_{sp} : AgI $8.5 \quad 10^{17}$, $HgI_2 \quad 2.5 \quad 10^{26}$

76. The dissociation constant of a weak acid H*A* is $4.9 \quad 10^{8}$. After making the necessary approximations, calculate
(i) pH
(ii) OH concentration in a decimolar solution of the acid. (Water has a pH of 7). **(1983, 2M)**

77. Give reason for the statement that "the pH of an aqueous solution of sodium acetate is more than seven". **(1982, 1M)**

78. 20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid solution 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.
(Ionisation constant of $CH_3COOH \quad 1.8 \quad 10^{5}$). **(1982, 3M)**

79. How many moles of sodium propionate should be added to 1 L 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 moles of HCl are dissolved in the above buffer solution? Compare the last pH value with the pH of 0.010 M HCl solution. Dissociation constant of propionic acid, K_a at 25°C is $1.34 \quad 10^{5}$. **(1981, 4M)**

Answers

Topic 1

1. (d) **2.** (a) **3.** (d) **4.** (a)
5. (d) **6.** (d) **7.** (b) **8.** (b)
9. (b) **10.** (c) **11.** (b) **12.** (b)
13. (b) **14.** (b) **15.** (a) **16.** (b)
17. (a) **18.** (d) **19.** (d) **20.** (d)
21. (d) **22.** (a) **23.** (d) **24.** (b)
25. (d) **26.** (a) **27.** (d) **28.** (a,c)
29. (b) **30.** (a) **31.** (b, c, d) **32.** (c, d, e)
33. (d) **34.** (c, d) **35.** (a, b, c, d) **36.** smaller
37. no change **38.** $K_p \quad K_c(RT)^{n}$ **39.** T
40. F **41.** F **42.** T **46.** (1.2)
52. (1.86) **53.** (0.33) **55.** (b) **56.** (c)

Topic 2

1. (d) **2.** (c) **3.** (c) **4.** (d)
5. (b) **6.** (c) **7.** (a) **8.** (c)
9. (d) **10.** (b) **11.** (b) **12.** (d)
13. (d) **14.** (d) **15.** (b) **16.** (a)
17. (c) **18.** (d) **19.** (a) **20.** (b)
21. (d) **22.** (d) **23.** (a) **24.** (a)
25. (d) **26.** (c) **27.** (a) **28.** (d)
29. (c) **30.** (a) **31.** (b) **32.** (a)
33. (a) **34.** (b) **35.** (d) **36.** (b)
37. (c, d) **38.** (a, b, c) **39.** (b, c) **40.** (4.47)
41. (d) **42.** I_2 **43.** hydration
44. amphoteric **45.** SO_4^2 **46.** F **47.** F
48. F **49.** (3) **50.** $(1.6 \quad 10^{7})$ **52.** (8)
53. (9) **55.** (4.86) **56.** $(1.2 \quad 10^{3}$ M)
58. $(2 \quad 10^{8})$ **61.** (11.5) **62.** (6.50) **64.** (1)
65. (80) **67.** $(1.8 \quad 10^{5})$ **68.** $(9.67 \quad 10^{11})$ **69.** $(27.78 \quad 10^{3})$
71. (0.177) **72.** $(8.7 \quad 10^{4}$ gL$^{1})$ **74.** (4.20)
75. (99.83) **77.** (>7)

Hints & Solutions

Topic 1 Chemical Equilibrium

1. The incorrect match is $G \quad 0, K \quad 1$.

For an ideal gas $G \quad RT \ln K$.

$$\ln K \quad \frac{G}{RT} \quad \text{and} \quad K \quad e^{\;G\;/RT}$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $G \quad 0, - \; G\;/RT$ ve and $e^{\;G\;/RT} \quad 1$ and hence, $K \quad 1$. It means that the reaction occur spontaneously in the forward direction or products predominate over reactants.

(ii) If $G \quad 0; \quad G\;/RT$ ve and $e^{\;G/RT} \quad 1$ and hence, $K \quad 1$. It means that the reaction is non-spontaneous in forward direction (i.e. product side) but spontaneous in reverse direction (i.e. reactants predominate over products or the reaction occurs rarely).

(iii) When $K \quad 1$, then $G \quad 0$. This situation generally occur at equilibrium.

2.

> **Key Idea** The relationship between K_p and K_c is
>
> $$K_p \quad K_c(RT)^{\;n_g}$$
>
> where, $n_g \quad n_{\text{products}} \quad n_{\text{reactants}}$
>
> If $n_g \quad 0$ then $K_p \quad K_c$
>
> If n_g ve then $K_p \quad K_c$
>
> If n_g ve then $K_p \quad K_c$

Consider the following equilibria reactions

(a) $2C(s) \quad O_2(g) \rightleftharpoons 2CO(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad (1) \quad 1$

$n_g \quad 0$ So, $K_p \quad K_c$

(b) $2HI(g) \rightleftharpoons H_2(g) \quad I_2(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

(c) $NO_2(g) \quad SO_2(g) \rightleftharpoons NO(g) \quad SO_3(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

(d) $2NO(g) \rightleftharpoons N_2(g) \quad O_2(g)$

$n_g \quad n_{\text{product}} \quad n_{\text{reactant}} \quad 2 \quad 2 \quad 0$

$n_g \quad 0$ So, $K_p \quad K_c$

3. The explanation of given statements are as follows:

(a) For the given equilibrium, H is negative, so the equilibrium constant will decrease with increase in temperature and the equilibrium will shift in the backward direction.

Thus, statement (a) is correct.

(b) When inert gas is added at constant volume and constant temperature, an equilibrium remains undisturbed.

Thus, statement (b) is correct.

(c) For the equilibrium,

$$n_g \quad 2 \quad (2 \quad 1) \quad 1, \text{ i.e. } (\;\text{ve})$$

So, increase in pressure will shift the equilibrium in the forward direction.

Thus, statement (c) is correct.

(d) The reaction takes place in the presence of a catalyst which is $V_2O_5(s)$ in contact process or $NO(g)$ in chamber process.

Thus, statement (d) is incorrect.

4. $S + O_2 \rightleftharpoons SO_2, K_1$

$$SO_2 \rightleftharpoons S + O_2, K_1 \quad \frac{1}{K_1}$$

$$\text{or, } 2SO_2 \rightleftharpoons 2S + 2O_2, K_1 \quad (K_1\;)^2 \quad \frac{1}{K_1^2} \qquad \ldots\text{(i)}$$

$$2S + 3O_2 \rightleftharpoons 2SO_3, K_2 \qquad \ldots\text{(ii)}$$

Now, [(i) (ii)] gives

$$2SO_2 + O_2 \rightleftharpoons 2SO_3, K_3$$

The value of equilibrium constant,

$$K_3 \quad K_2 \quad K_1 \quad K_2 \quad \frac{1}{K_1^2}$$

$$10^{129} \quad \frac{1}{(10^{52})^2} \quad 10^{129 \quad 104} \quad 10^{25}$$

5. For the given chemical reaction,

$$\begin{array}{lcccc} & A & + \;2B & \rightleftharpoons \;2C & + \;D \\ \text{At, } t=0 & a_0 & 1.5a_0 & 0 & 0 \\ t \quad t_{\text{eq}} & a_0 \quad x & 1.5a_0 \quad 2x & 2x & x \end{array}$$

[x degree of dissociation]

Given, at equilibrium.

$$[A] = [B]$$

$$a_0 \quad x \quad 1.5a_0 \quad 2x$$

$$x \quad 0.5a_0$$

$[A] \quad a_0 \quad x \quad a_0 \quad 0.5a_0 \quad 0.5a_0$

$[B] \quad 1.5a_0 \quad 2x \quad 1.5a_0 \quad 2 \quad 0.5a_0 \quad 0.5a_0$

$[C] \quad 2x \quad 2 \quad 0.5a_0 \quad a_0$

$[D] \quad x \quad 0.5a_0$

$$\text{Now,} \qquad K \quad \frac{[C]^2[D]}{[A]\,[B]^2}$$

Now, substituting the values in above equation, we get

$$K \quad \frac{(a_0)^2 \quad (0.5a_0)}{(0.5a_0) \quad (0.5a_0)} \quad 4$$

6. The equilibrium reaction for the dissociation of two solids is given as:

$$A(s) \rightleftharpoons B(g) + C(g)$$

$$\text{At equilibrium} \qquad p_1 \qquad p_1 \;\; p_2$$

$$K_{p_1} = x \quad p_B \quad p_C = p_1(p_1 + p_2) \qquad \ldots\text{(i)}$$

Similarly, $D(s) \rightleftharpoons C(g) + E(g)$

At equilibrium $\quad p_1 + p_2 \quad p_2$

$$K_{p_2} = y = p_C \quad p_E = (p_1 + p_2)p_2 \qquad \ldots\text{(ii)}$$

On adding Eq. (i) and (ii), we get.

$$K_{p_1} + K_{p_2} = x \quad y \quad p_1(p_1 + p_2) + p_2(p_1 + p_2)$$
$$(p_1 + p_2)^2$$

or $\sqrt{x \quad y} \quad p_1 \quad p_2$ $\qquad \ldots$(iii)

Now, total pressure is given as

$$p_T = p_B + p_C + p_E$$
$$= p_1 + (p_1 + p_2) + p_2$$
$$= 2\,(p_1 + p_2) \qquad \ldots\text{(iv)}$$

On substituting the value of $p_1 + p_2$ from Eq. (iii) to Eq. (iv), we get

$$p_T = 2\sqrt{x \quad y}$$

7. $N_2(g) \quad 3H_2(g) \rightleftharpoons 2NH_3(g)$

At equilibrium: $p_{N_2} \quad P, \quad p_{H_2} \quad 3P, \quad p_{NH_3} \quad 2P$

$$p_{(\text{total})} \quad p_{N_2} \quad p_{H_2} \quad p_{NH_3} \sim p_{N_2} \quad p_{H_2}$$
$$[\because P_{(\text{total})} \quad p_{NH_3}]$$
$$p \quad 3p \quad 4p$$

Now, $\quad K_p \quad \frac{p^2_{NH_3}}{p_{N_2} \quad p^3_{H_2}} \quad \frac{p^2_{NH_3}}{p \quad (3p)^3}$

$$\frac{p^2_{NH_3}}{27 \quad p^4} \quad \frac{p^2_{NH_3}}{27 \quad \frac{P}{4}^{4}} \qquad [\because P \quad 4p]$$

$$K_p \quad \frac{p^2_{NH_3} \quad 4^4}{3^2 \quad 3 \quad P^4}$$

$$p^2_{NH_3} \quad \frac{3^2 \quad 3 \quad P^4 \quad K_p}{4^4}$$

$$p_{NH_3} \quad \frac{3 \quad 3^{1/2} \quad P^2 \quad K_p^{1/2}}{4^2} \quad \frac{3^{3/2} \quad P^2 \quad K_p^{1/2}}{16}$$

8. Molar mass of $NH_4SH \quad 18 \quad 33 \quad 51\,\text{g mol}^{\ 1}$

Number of moles of NH_4SH introduced in the vessel

$$\frac{\text{Weight}}{\text{Molar mass}} \quad \frac{5\ 1}{51} \quad 0.1\,\text{mol}$$

	$NH_4SH(s) \rightleftharpoons$	$NH_3(g)$	$H_2S(g)$
Number of moles at $t \quad 0$	0.1	0	0
At $t \quad t_{eq}$	0.1(1 0.03)	30% of 0.1 0.03	30% of 0.1 0.03
Active mass (mol L ^{1})		$\frac{0.03}{3}$ 0.01	$\frac{0.03}{3}$ 0.01

$$K_C \quad \frac{[NH_3][H_2S]}{[NH_4HS(s)]} \quad \frac{0.01 \quad 0.01}{1} \quad 10^{\ 4}\,(\text{mol L}^{\ 1})^2$$

$$K_p \quad K_C(RT)^{\ n_g}$$

[where, $n_g \quad n_{\text{product}} \quad n_{\text{reactant}}$] 2 0 2

$$K_p \quad K_C(RT)^2$$
$$10^{\ 4} \quad [0.082 \quad (273 \quad 327)]^2\ \text{atm}^2$$
$$0.242\ \text{atm}^2$$

9. We know that, the relationship between K_p and K_C of a chemical equilibrium state (reaction) is

$$K_p \quad K_C(RT)^{\ n_g} \qquad \frac{K_p}{K_C} \quad (RT)^{\ n_g}$$

where, $\quad n_g \quad n_{\text{Products}} \quad n_{\text{Reactants}}$

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

$$(RT)^{2 \ \ (1 \ \ 1)} \quad (RT)^0 \quad 1$$

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

$$(RT)^{2 \ \ 1} \quad RT \quad 24.62\,\text{dm}^3\,\text{atm}\,\text{mol}^{\ 1}$$

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

$$(RT)^{2 \ \ (3 \ \ 1)} \quad (RT)^{\ 2}$$
$$\frac{1}{(24.62\ \text{dm}^3\ \text{atm mol}^{\ 1})^2}$$
$$1.649 \quad 10^{\ 3}\ \text{dm}^{-6}\ \text{atm}^{\ 2}\ \text{mol}^2$$

10. (i) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g); \qquad K_1 \quad \frac{[AB]^2}{[A_2][B_2]}$

(ii) $6AB(g) \rightleftharpoons 3A_2(g) \quad 3B_2(g);$

$$K_2 \quad \frac{[A_2]^3[B_2]^3}{[AB]^6} \quad \frac{1}{\frac{[AB]^2}{[A_2][B_2]}^{\ 3}} \quad \frac{1}{K_1^3},$$

$$K_2 \quad K_1^{\ 3}$$

11. Given $[H_2S] \quad 0.10\,\text{M}$

$[HCl] \quad 0.20\,\text{M}$ So, $[H \ ] \quad 0.20\,\text{M}$

$H_2S \rightleftharpoons H^+ + HS \ , K_1 \quad 1.0 \quad 10^{\ 7}$

$HS \ \rightleftharpoons H^+ + S^2 \ , K_2 \quad 1.2 \quad 10^{\ 13}$

It means for,

$$H_2S \rightleftharpoons 2H^+ + S^2$$
$$K \quad K_1 \quad K_2 \quad 1.0 \quad 10^{\ 7} \quad 1.2 \quad 10^{\ 13}$$
$$1.2 \quad 10^{\ 20}$$

Now $\quad [S^2 \ ] \quad \frac{K \quad [H_2S]}{[H \ ]^2}$ [according to the final equation]

$$\frac{1.2 \quad 10^{\ 20} \quad 0.1\ \text{M}}{(0.2\text{M})^2}$$
$$\frac{1.2 \quad 10^{\ 20} \quad 1 \quad 10^{\ 1}\ \text{M}}{4 \quad 10^{\ 2}\text{M}}$$
$$3 \quad 10^{\ 20}\text{M}$$

12.

	A	+	B	$\rightleftharpoons$	C	+	D
Initially at $t \quad 0$	1		1		1		1
At equilibrium	$1 \quad x$		$1 \quad x$		$1 \quad x$		$1 \quad x$

$$K_{eq} \quad \frac{[C][D]}{[A][B]} \quad \frac{(1 \quad x)(1 \quad x)}{(1 \quad x)(1 \quad x)} \quad \frac{(1 \quad x)^2}{(1 \quad x)^2}$$

or $\quad 100 \quad \frac{1 \quad x}{1 \quad x}^{2} \quad$ or $\quad 10 \quad \frac{1 \quad x}{1 \quad x}$

or $\quad 10 \quad 10x \quad 1 \quad x$

$$10 \quad 1 \quad x \quad 10x$$
$$9 \quad 11x$$
$$x \quad \frac{9}{11} \quad 0.818$$
$$[D] \quad 1 \quad x \quad 1 \quad 0.818 \quad 1.818$$

13. Given, $G \quad 2494.2\ \text{J}$

$$Q \quad \frac{[B][C]}{[A]^2} \quad \frac{2 \quad \frac{1}{2}}{\frac{1}{2}^{\ 2}} \quad 4$$

We know, $G \quad G \quad RT \ln Q$

$$2494.2 \quad 8.314 \quad 300 \ln\ 4$$

$$28747.27\ \text{J} \ (+\ \text{ve value})$$

Also, we have $G \quad RT \ln \frac{Q}{K}$

If G is positive, $Q \quad K$

Therefore, reaction shifts in reverse direction.

14. For the given reaction, $n_g = n_P \quad n_R$

where, n_P number of moles of products

n_R number of moles of reactants

$$K_p = K_c(RT)^{n_g}$$

$$n_g \quad \frac{1}{2}$$

15. When CO_2 is dissolved in water, following equilibria are established:

$$H_2O + CO_2 \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3$$
$$HCO_3 \rightleftharpoons H^+ + CO_3^2$$

Therefore, in solution, all of the above mentioned species exist.

16. At equilibrium, $G \quad 0$

$$G(\text{reactants}) \quad G(\text{products})$$
$$G(N_2) + 3G(H_2) \quad 2G(NH_3)$$

A catalyst does not affect either equilibrium composition or equilibrium constant, it just increases rate of both forward and backward reaction but by the same factor.

17. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+] \qquad K_1 \quad 3.5 \quad 10^{\ 3}$

$[Ag(NH_3)^+] + NH_3 \rightleftharpoons [Ag(NH_3)_2^+] \quad K_2 \quad 1.7 \quad 10^{\ 3}$

Adding : $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$

$$K \quad K_1 \quad K_2 \quad 5.95 \quad 10^{\ 6}$$

18.

$$\underset{1}{N_2O_4(g)} \rightleftharpoons \underset{2}{2NO_2(g)} \quad \underset{1+}{\text{Total}}$$

$$p_i : \quad \frac{1}{1}p \qquad \frac{2}{1}p \quad K_p \quad \frac{4^{\ 2}}{1^{\ \ 2}}p$$

At constant temperature, halving the volume will change both p and but K_p remains constant.

19. $\underset{1 \quad x}{N_2O_4} \rightleftharpoons \underset{2x}{2NO_2}, K_p \quad \frac{4x^2 p}{1 \quad x^2}$. K_p is function of temperature only, does not change with either p or x.

20. $A \quad B \rightleftharpoons C \quad D,\ Q \quad \frac{[C][D]}{[A][B]}$

As time passes, amount of products 'C' and 'D' increases, hence Q increases.

21. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad n \quad 2$

$$K_p \quad K_c(RT)^{\ n}$$

$$K_c \quad \frac{K_p}{(RT)^{\ n}} \quad \frac{1.44 \quad 10^{\ 5}}{(0.082 \quad 773)^{\ 2}}$$

22. Both temperature and pressure will change the equilibrium amount of $X_3Y(g)$. Temperature changes the value of equilibrium constant.

23. Adding reactant will drive the reaction in forward direction in order to restore equilibrium. Therefore, addition of CO (g) will increase the equilibrium amount of CO_2.

24. $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$	
At 300 K :	1.0 atm	0	
At 600 K :	2.0 – 0.40	0.80	Total pressure = 2.40 atm

25. In reactions (a), (b) and (c), atleast one of the product is either insoluble precipitate or a gas that drive the reaction continuously to right and do not allow equilibrium to be established. Following is the reversible reaction.

$$KNO_3(aq) + NaCl(aq) \rightleftharpoons KCl(aq) + NaNO_3(aq)$$

26. K_p for a given reversible reaction depends only on temperature.

27. Equilibrium constant of a given reversible reaction depends only on temperature.

28. For the reaction, $A \rightleftharpoons P$

Given, $T_1 < T_2$

$$\frac{\ln K_1}{\ln K_2} \quad \frac{T_2}{T_1} \qquad \text{...(i)}$$

It shows, On increasing the temperature, K decreases so reaction is exothermic i.e., $H^\circ \quad 0$

Besides, graph shows $K > 1$

So $G^\circ < 0$

Now from equation (i)

$$T_1 \ln K_1 > T_2 \ln K_2$$
$$G^\circ_1 > \quad G^\circ_2$$

Likewise $(\quad H^\circ + T_1 \quad S^\circ) \quad (\quad H^\circ + T_2 \quad S^\circ)$

or simply $T_1 \quad S^\circ > T_2 \quad S^\circ$

So, $(T_2 \quad T_1) \quad S \quad 0$

$$S^\circ < 0$$

In other words, increase of G with increase in temperature is possible only when $S \quad 0$. Hence, options (a) and (c) are correct.

29. Since, the reaction is exothermic, there will be less ammonia at equilibrium and higher temperature. However, rate of reaction increases with rise in temperature, NH_3 will be formed at faster rate in the initial stage when the temperature is high.

30. **PLAN** $RCOOR \quad H_2O \overset{H}{\quad} RCOOH \quad R\ OH$

Acid hydrolysis of ester is follows first order kinetics.

For same concentration of ester in each case, rate is dependent on [H] from acid.

$$\text{Rate} \quad k[RCOOR\ ]$$

Also for weak acid, $HA \rightleftharpoons H \quad A$

$$K_a \quad \frac{[\mathrm{H}\ \ ][A\ \ ]}{[\mathrm{H}A]}$$

$$(\mathrm{Rate})_{\mathrm{H}A} \quad k[\mathrm{H}\ \ ]_{\mathrm{H}A}$$

$$(\mathrm{Rate})_{\mathrm{H}X} \quad k[\mathrm{H}\ \ ]_{\mathrm{H}X}$$

$$(\mathrm{Rate})_{\mathrm{H}X} \quad 100(\mathrm{Rate})_{\mathrm{H}A}$$

Also in strong acid, $[\mathrm{H}\ \ ] \quad [\mathrm{H}X] \quad 1\,\mathrm{M}$

$$\frac{(\mathrm{Rate})_{\mathrm{H}X}}{(\mathrm{Rate})_{\mathrm{H}A}} \quad 100 \quad \frac{[\mathrm{H}\ \ ]_{\mathrm{H}X}}{[\mathrm{H}\ \ ]_{\mathrm{H}A}} \quad \frac{1}{[\mathrm{H}\ \ ]_{\mathrm{H}A}}$$

$$[\mathrm{H}\ \ ]_{\mathrm{H}A} \quad \frac{1}{100}$$

$$\mathrm{H}A \rightleftharpoons \mathrm{H} \quad A$$

$$1 \qquad 0 \quad 0$$

$$(1 \quad x) \qquad x \quad x$$

$$x \quad 0.01$$

$$K_a \quad \frac{[\mathrm{H}\ \ ][A\ \ ]}{[\mathrm{H}A]} \quad \frac{0.01 \quad 0.01}{0.99} \quad 1.01 \quad 10^{\ \ 4}$$

31. Cl , CN and SCN forms precipitate with Cu (I), remove Cu (I) ion from equilibrium and reaction shifts in backward direction according to Le-Chatelier's principle.

32. If inert gas is introduced at constant pressure, volume of container will have to be increased and this will favour the forward reaction. Also adding $PCl_5(g)$ at constant volume will favour forward reaction because $PCl_5(g)$ is a reactant.

33. $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$,

Adding inert gas at constant volume will not affect partial pressure of reactant or products, hence will not affect equilibrium amount of either reactant or products.

34. $NaNO_3(s) \rightleftharpoons NaNO_2(s) + \frac{1}{2}O_2(g), \quad H \quad 0$

$NaNO_3$ and $NaNO_2$ are in solid state, changing their amount has no effect on equilibrium. Increasing temperature will favour forward reaction due to endothermic nature of reaction. Also, increasing pressure will favour backward reaction in which some $O_2(g)$ will combine with $NaNO_2(s)$ forming $NaNO_3$.

35. $C_2H_4 + H_2 \rightleftharpoons C_2H_6, \quad H \quad 32.7$ kcal

The above reaction is exothermic, increasing temperature will favour backward reaction, will increase the amount of C_2H_4. Decreasing pressure will favour reaction in direction containing more molecules (reactant side in the present case). Therefore, decreasing pressure will increase amount of C_2H_4.

Removing H_2, which is a reactant, will favour reaction in backward direction, more C_2H_4 will be formed.

Adding C_2H_6 will favour backward reaction and some of the C_2H_6 will be dehydrogenated to C_2H_4.

36. Smaller : $K_p \quad \frac{K_c}{RT}$

37. changing pressure has no effect on equilibrium constant.

38. $K_p \quad K_c(RT)^{\ \ n}$, where, $n \quad n$ (products) $\quad n$ (reactants)

39. Rate of any reaction increases on rising temperature.

40. Catalyst has no effect on thermodynamics of reaction.

41. It is $\frac{1}{\sqrt{K}}$.

42. Evaporation is an endothermic process.

43. (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$G \quad 2 \ \ G_f\,(NO_2) \quad G_f\,(N_2O_4) = 0$$

Also $\quad G \quad RT \ln K \quad 0, \quad K \quad 1$

Let the reaction shifts in forward direction.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \text{Total}$$

$$5 \quad x \qquad\qquad 5 \quad 2x \qquad 10 \quad x$$

$$p_i{:} \quad \frac{5 \quad x}{10 \quad x} \ \ 20 \qquad \frac{5 \quad 2x}{10 \quad x} \ \ 20$$

$$K \quad \frac{(5 \quad 2x)^2}{(10 \quad x)^2} \quad \frac{10 \quad x}{5 \quad x} \quad 20 \quad 1$$

$$81x^2 \quad 405x \quad 450 \quad 0$$

$$x \quad 1.66 \text{ and } -3.33$$

Both values of x indicates that reaction actually proceeds in backward direction.

(b) $p \quad \frac{a}{Vm^2} \quad (V_m \quad b) \quad RT$

$$p \quad \frac{ap^2}{(pV)^2} \quad \frac{pV}{p} \quad b \quad RT$$

$$[(pV^2)\,p \quad ap^2][(pV) \quad b] \quad p\,(pV)^2\,RT$$

$$p\ [pV^2 \quad ap](pV \quad bp) \quad p\,(pV^2)\,RT$$

But $p \quad 0$

Intercept $\quad RT \qquad (pV)^3 \quad (pV)^2\,RT$

44. (i) Mole of solid NH_4HS taken initially $\quad \frac{3.06}{51} \quad 0.06$

At equilibrium $\ NH_4HS(s) \rightleftharpoons \underset{0.018}{NH_3(g)} + \underset{0.018}{H_2S(g)}$

$$K_c \quad \frac{0.018}{2}^{\ \ 2} \quad 8.1 \quad 10^{\ \ 5}$$

$$p\,(NH_3) = \frac{0.018 \quad 0.082 \quad 300}{2} = 0.22 \text{ atm}$$

$$K_p \quad (0.22)^2 \quad 4.84 \quad 10^{\ \ 2}$$

(ii) Addition of solid NH_4HS will have no effect on equilibrium.

45. (a) $\ \underset{1}{PCl_5(g)} \rightleftharpoons PCl_3(g) + Cl_2(g) \quad \underset{1}{\text{Total moles}}$

Average molar mass $\quad \frac{208.5}{1.4} \quad 148.9$

$$(\text{density}) \quad \frac{pM}{RT} \quad \frac{1 \quad 148.9}{0.082 \quad 400} \quad 4.54 \text{ g/L}$$

(b) $\underset{x}{AgCl(s)} + \underset{1 \quad 2x}{2NH_3(aq)} \rightleftharpoons \underset{x}{[Ag(NH_3)_2^+]} + \underset{x}{Cl}$

$$K \quad \frac{K_{sp}}{K_c} \quad 2.9 \quad 10^{\ \ 3} \quad \frac{x}{1 \quad 2x}^{\ \ 2}$$

$$x \quad 0.049 \text{ M}$$

46. Observing the graph indicates that when 0.20 mole of A is reacted, 0.40 mole of product is formed.

$$\underset{0.20}{A} \rightleftharpoons \underset{0.40}{nB} \qquad n \quad 2$$

At equilibrium, $[A] = 0.30$ M, $[B] = 0.60$ M

$$K_c \quad \frac{[B]^2}{[A]} \quad \frac{0.36}{0.30} \quad 1.2$$

47. $$\underset{0.15-0.08}{\mathrm{CO}\,(g)} + \underset{x \quad 0.16}{2\mathrm{H_2}\,(g)} \rightleftharpoons \underset{0.08}{\mathrm{CH_3OH}(g)}$$

Total moles at equilibrium $x \quad 0.01$

$$x \quad 0.01 \quad \frac{8.5 \quad 2.5}{0.082 \quad 750} \quad 0.34 \qquad x \quad 0.35$$

(i) Partial pressures : $\mathrm{CO} \quad \frac{0.07}{0.34} \quad 8.5$

$$\mathrm{H_2} \quad \frac{0.18}{0.34} \quad 8.5$$

$$\mathrm{CH_3OH} \quad \frac{0.08}{0.34} \quad 8.5$$

$$K_p \quad \frac{0.08}{(0.07)\,(0.18)^2} \quad \frac{0.34}{8.5}^{\;2} \quad 0.056$$

(ii) Concentrations : $[\mathrm{CH_3OH}] = \frac{0.08}{2.5} \quad 0.032$ M

$$[\mathrm{H_2}] = \frac{0.18}{2.5} \quad 0.072 \text{ M}$$

$$[\mathrm{CO}] \quad \frac{0.07}{2.5} \quad 0.028 \text{ M}$$

$$K_c \quad \frac{0.032}{(0.028)\,(0.072)^2} \quad 213.33$$

48. $$\mathrm{CO}\,(g) + 2\mathrm{H_2}\,(g) \rightleftharpoons \mathrm{CH_3OH}(g)$$

Mole : $0.2 - 0.10 \quad x \quad 0.20 \quad 0.10 \quad$ Total moles x

$$x \quad \frac{4.92 \quad 5}{0.082 \quad 600} \quad 0.5$$

moles of $\mathrm{H_2}$ at equilibrium $x \quad 0.2 \quad 0.3$

Partial pressures : $\mathrm{CO} \quad \frac{0.1}{0.5}\,p$, $\mathrm{H_2} \quad \frac{0.3}{0.5}\,p$,

$$\mathrm{CH_3OH} \quad \frac{0.1}{0.5}\,p$$

$$K_p \quad \frac{\frac{p}{5}}{\frac{p}{5} \quad \frac{3}{5}p^{\;2}} \quad \frac{25}{9p^2} \quad \frac{25}{9\,(4.92)^2} \quad 0.11 \text{ atm}^{\;\;2}$$

Concentrations : $[\mathrm{CO}] \quad \frac{0.1}{5}$ M, $[\mathrm{H_2}] \quad \frac{0.3}{5}$ M,

$$[\mathrm{CH_3OH}] \quad \frac{0.1}{5} \text{ M} \quad K_c \quad \frac{(0.1/5)}{(0.1/5)\,(0.3/5)^2} \quad 277.77 \text{ M}^{\;\;2}.$$

49. $$2\mathrm{SO_2}\,(g) + \mathrm{O_2}\,(g) \rightleftharpoons \mathrm{SO_3}\,(g)$$

Initial p_i : $\quad 0 \quad 2 \quad 1$

Equilibrium p_i : $2p \quad 2 \quad p \quad 1 \quad 2p$

$$K_p \quad 900 \quad \frac{(1 \quad 2p)^2}{(2 \quad p)\,(2p)^2} \quad \text{[Ignoring } p \text{ in comparison to 2]}$$

$$p \quad \frac{1}{87} \text{ atm}$$

Partial pressure of $\mathrm{SO_2} \quad 2p \quad \frac{2}{87}$ atm

Partial pressure of $\mathrm{O_2} \quad 2 \quad p \quad 2 \quad \frac{1}{87} \quad \frac{175}{87}$ atm

Partial pressure of $\mathrm{SO_3} \quad 1 \quad 2p \quad 1 \quad 2 \quad \frac{1}{87} \quad \frac{85}{87}$ atm

50. $$\underset{1}{\mathrm{N_2O_4}} \rightleftharpoons \underset{2}{2\mathrm{NO_2}} \qquad \underset{1}{\text{Total}}$$

$$p_i: \quad \frac{1}{1}\,p \qquad \frac{2}{1}\,p$$

$$K_p \quad \frac{4 \quad ^2}{1 \quad \;_2}\,p \quad \frac{4\,(0.25)^2}{1 \quad (0.25)^2} \quad 0.26 \text{ atm}$$

When $p \quad 0.10$ atm

$$0.26 \quad \frac{4 \quad ^2\,(0.1)}{1 \quad \;^2} \qquad 0.62$$

51. $$\underset{1 \quad x}{\mathrm{SO_2}\,(g)} + \underset{1 \quad x}{\mathrm{NO_2}\,(g)} \rightleftharpoons \underset{x}{\mathrm{SO_3}\,(g)} + \underset{x}{\mathrm{NO}\,(g)}$$

$Q_c \quad 1 \quad K_c$, i.e. reaction proceed in forward direction to attain equilibrium.

$$16 \quad \frac{x}{1 \quad x}^{\;2} \qquad x \quad 0.80$$

$[\mathrm{NO}] = 0.80$ M, $[\mathrm{NO_2}] = 0.20$ M

52. $A_2\,(g) \quad B_2(g) \rightleftharpoons 2AB\,(g) \qquad n \quad 0$

$$K \quad \frac{[AB]^2}{[A_2][B_2]} \quad \frac{(n_{AB})^2}{n_{A_2} \quad n_{B_2}} \quad \frac{(2x)^2}{(1 \quad x)\,(2 \quad x)}$$

$$50 \quad \frac{4x^2}{x^2 \quad 3x \quad 2} \qquad 23x^2 \quad 75x \quad 50 \quad 0$$

$$x \quad \frac{75 \quad \sqrt{75^2 \quad 4 \quad 23 \quad 50}}{46} \quad 0.93,\ 2.32$$

2.32 is not acceptable because x cannot be greater than 1.

Mole of $AB \quad 2x \quad 2 \quad 0.93 = 1.86$

53. Total moles of gases at equilibrium $\frac{pV}{RT} \quad \frac{2.05 \quad 100}{0.082 \quad 500} \quad 5.0$

Out of this 5 moles, 1.0 mole is for $\mathrm{N_2}\,(g)$ and remaining 4 moles for $\mathrm{PCl_5}$ and its dissociation products.

$$\underset{3 \quad x}{\mathrm{PCl_5}} \rightleftharpoons \underset{x}{\mathrm{PCl_3}} + \underset{x}{\mathrm{Cl_2}}$$

$$3 \quad x \quad 4 \qquad x \quad 1$$

Degree of dissociation $\frac{1}{3} \quad 0.33$

54. $$\mathrm{N_2} + 3\mathrm{H_2} \rightleftharpoons 2\mathrm{NH_3}$$

Initial : $\quad 1.0 \quad 3.0 \quad 0$

Equilibrium $\quad 1 - 0.25 = 0.75 \quad 3 - 0.75 = 2.25 \quad 0.05$

$$[\mathrm{N_2}] \quad \frac{0.75}{4},\ [\mathrm{H_2}] = \frac{2.25}{4},\ [\mathrm{NH_3}] = \frac{0.50}{4}$$

$$K_c \quad \frac{[NH_3]^2}{[N_2][H_2]^3} \quad \frac{(0.50)^2}{(0.75)\,(2.25)^3} \quad 16$$

$$0.468 \text{ L}^2 \text{ mol}^{\;\;2}$$

Also for : $\frac{1}{2} N_2 \quad \frac{3}{2} H_2 \rightleftharpoons NH_3$

$$K_c \quad \sqrt{K_c} \quad 0.68$$

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

At $t \quad 0$ $\qquad 1 \qquad 0$

At equilibrium $\quad 1 \quad \frac{x}{2} \qquad x \qquad$ (where, $x \quad _{eq}$)

Total moles $\quad 1 \quad \frac{x}{2}$ and Mole fraction, $X_2(g) \quad \dfrac{1 \quad \frac{x}{2}}{1 \quad \frac{x}{2}}$

$X(g) \quad \dfrac{x}{1 \quad \frac{x}{2}}$ and $p \quad 2$ bar

Partial pressure, $p_{X2} \quad \dfrac{1 \quad \frac{x}{2}}{1 \quad \frac{x}{2}} .p$ and $p_X \quad \dfrac{p \quad x}{1 \quad \frac{x}{2}}$

$$K_p \quad p_X^2 / p_{X_2} \quad \frac{\left(px / \left(1 \quad \frac{x}{2}\right)\right)^2}{p\dfrac{(1 \quad x/2)}{1 \quad \frac{x}{2}}}$$

$$\frac{4px^2}{(4 \quad x^2)} \quad \frac{8 \quad ^2_{eq}}{(4 \quad ^2_{eq})}$$

56. (a) $K_p \quad \dfrac{4px^2}{(4 \quad x^2)} \quad px^2 \qquad (\because 4 \qquad x)$

$$x \quad \sqrt{\frac{1}{p}}$$

If p decreases, x increases. Equilibrium is shifted in the forward side. Thus, statement (a) is correct.

(b) At the start of the reaction, $Q \quad 0$ where, Q is the reaction quotient $\quad G \quad G \quad 2.303RT \log Q$

Since, $\quad G \quad 0$, thus $\quad G$ is $\quad$ ve.

Hence, dissociation takes place spontaneously.

Thus, (b) is correct.

(c) If we use $x \quad 0.7$ and $p \quad 2$ bar then $K_p \quad \dfrac{4 \quad 2(0.7)^2}{[4 \quad (0.7)^2]}$

$$1.16 \quad 1$$

Thus, (c) is incorrect.

(d) At equilibrium, $\quad G \quad 0$

$$G \quad 2.303RT \log K_p$$

Since, $\quad G \quad$ ve

Hence, $K_p \quad 1$

$$K_C \quad \frac{K_p}{(RT)}$$

Then $K_C \quad 1$. Thus, (d) is correct.

Topic 2 Ionic Equilibrium

1. **Key Idea** The concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature.

$$A_xB_y \rightleftharpoons xA^{y} \quad yB^{x} \quad K_{sp} \quad [A^{y} \quad]^x [B^{x} \quad]^y$$

Solubility of $Cd(OH)_2\ (S) \quad 1.84 \quad 10^{\;\;5}$ M

Given, pH $\quad 12$ [for $Cd(OH)_2$ in buffer solution]

So, pOH $\quad 2 \qquad (\because$ pH $\quad$ pOH $\quad$ p$K_w)$

$12 \quad$ pOH $\quad 14$

pOH $\quad 14 \quad 12 \quad 2$

$[OH \quad] \quad 10^{\;\;2}$ in buffer solution.

For reaction $Cd(OH)_2 \qquad \underset{S}{Cd^{2}} \quad \underset{S^2}{2OH}$

$$K_{sp} \quad [Cd^{2} \quad][OH \quad]^2$$

$$K_{sp} \quad (S)(2S)^2 \quad 4S^3 \quad 4(1.84 \quad 10^{\;\;5})^3$$

$$K_{sp} \quad 24.9 \quad 10^{\;\;15}$$

$$[Cd^{2} \quad] \quad \frac{K_{sp}}{[OH \quad]^2}$$

$$[Cd^{2} \quad] \quad \frac{24.9 \quad 10^{\;\;15}}{(10^{\;\;2})^2} \quad 24.9 \quad 10^{\;\;15} \quad 10^{\;\;4}$$

$$24.9 \quad 10^{\;\;11} \text{ M}$$

$$[Cd^{2} \quad] \quad 2.49 \quad 10^{\;\;10} \text{ M}$$

The expected solubility of $Cd(OH)_2$ in a buffer solution of pH $\quad 12$ is $2.49 \quad 10^{\;\;10}$ M.

2. **Key Idea** Concentration of substance in a saturated solution is defined as its solubility (S). Its value depends upon the nature of solvent and temperature. For reaction,

$$AB \rightleftharpoons A \qquad B$$

$$K_{sp} \quad [A \quad][B \quad]$$

	$Al(OH)_3 \rightleftharpoons$	Al^{3}	$3OH$
Initially	1	0	0
At equilibrium	$1 \quad S$	S	$3S \quad 0.2$

$$NaOH \qquad \underset{0.2}{Na} \quad \underset{0.2}{OH}$$

K_{sp} of $Al(OH)_3 \quad 2.4 \quad 10^{\;\;24}$ (Given)

$$K_{sp} \quad [Al^{3} \quad][OH \quad]^3$$

$2.4 \quad 10^{\;\;24} \quad [S][3S \quad 0.2]^3 \qquad [\because 0.2 \qquad S]$

$$2.4 \quad 10^{\;\;24} \quad [S][0.008]$$

$$[S] \quad 3 \quad 10^{\;\;22}$$

3. **Key Idea** NH_4Cl is a salt of weak base (NH_4OH) and strong acid (HCl). On hydrolysis, NH_4Cl will produce an acidic solution (pH $\quad 7$) and the expression of pH of the solution is

$$\text{pH} \quad 7 \quad \frac{1}{2}(\text{p}K_b \quad \log C)$$

Given, $K_b(\mathrm{NH_4OH}) \quad 10^{\ 5}$

$$\mathrm{p}K_b \quad \log K_b \quad \log(10^{\ 5}) \quad 5$$

C concentration of salt solution 0.02 M
2 10 ^{2} M

Now, pH 7 $\frac{1}{2}(\mathrm{p}K_b \quad \log C)$

On substituting the given values in above equation, we get

$$7 \quad \frac{1}{2}[5 \quad \log(2 \quad 10^{\ 2})]$$

$$7 \quad \frac{1}{2}[5 \quad \log 2 \quad 2]$$

$$7 \quad \frac{1}{2}[5 \quad 0.301 \quad 2] \quad 7 \quad 1.65 \quad 5.35$$

4. The explanation of given statements are as follows:

In statement (I), millimoles of H 400 0.1 2 80

Millimoles of OH 400 0.1 40 (Limiting reagent)

Millimoles of H left 80 40 40

$$[\mathrm{H}\ \ ] \quad \frac{40}{400 \quad 400} \quad \frac{40}{800}M \quad \frac{1}{20}M$$

$$\mathrm{pH} \quad \log[\mathrm{H}\ \ ] \quad \log\frac{1}{20}$$

$$\log 1 \quad \log 2 \quad \log 10$$

$$0 \quad 0.301 \quad 1$$

$$1.30$$

Hence, the option (a) is correct.

In statement (II), ionic product of $\mathrm{H_2O}$ is temperature dependent.

$$K_w \quad [\mathrm{H}\ \ ][\mathrm{OH}\ \ ] \quad 10^{\ 14}(\mathrm{mol/L})^2 \text{ at } 25^\circ\mathrm{C}$$

With increase in temperature, dissociation of $\mathrm{H_2O}$ units into H and OH ions will also increase. As a result, the value of ionic product, [H] [OH] will be increased. e.g.

Temperature	**K_w (mol/L^2)**
5ºC	0.186 10 ^{14}
25ºC	1.008 10 ^{14}
45ºC	4.074 10 ^{14}

Hence, the option (b) is correct.

In statement (III), for a weak monobasic acid H*A*

$$\underset{(1\quad)C\,\mathrm{M}}{\mathrm{H}A} \rightleftharpoons \underset{C\,\mathrm{M}}{\mathrm{H}} \quad \underset{C\,\mathrm{M}}{A^{\ominus}}$$

pH of the solution is 5, i.e.

$$[\mathrm{H}\ \ ] \quad 10^{\ 5}\,\mathrm{M} \quad C$$

$$K_a \quad \frac{C \quad C}{(1 \quad)C} \quad \frac{10^{\ 5}}{1}$$

$$10^{\ 5} \quad \frac{10^{\ 5}}{1}$$

$$0.5$$

$$\% \quad 50$$

Hence, the option (c) is correct.

In statement (IV), Le-Chatelier's principle is applicable to common ion effect. Because, in presence of common ion (given) by strong electrolyte (say, Na^+A), the product of the concentration terms in RHS increases. For the weaker electrolyte, H*A* (say) the equilibrium shifts to the LHS, $\mathrm{H}A \rightleftharpoons \mathrm{H} \quad A^{\ominus}$.

As a result dissociation of H*A* gets suppressed. Hence, the option (d) is incorrect.

5. **Key Idea** The concentration of a substance in a saturated solution is defined as its solubility(*S*).
For $A_xB_y \rightleftharpoons xA^y \quad yB^x$; $K_{sp} \quad [A^y\ ]^x[B^x\ ]^y$

For, $\mathrm{Zr_3(PO_4)_4}$,

$$\mathrm{Zr_3(PO_4)_4}(s) \rightleftharpoons \underset{3S\mathrm{M}}{3\mathrm{Zr}^4}\ (aq) \quad \underset{4S\mathrm{M}}{4\mathrm{PO}_4^3}\ (aq)$$

$$K_{\mathrm{sp}} \quad [\mathrm{Zr}^4\ ]^3[\mathrm{PO}_4^3\ ]^4$$

$$K_{\mathrm{sp}} \quad (3S)^3(4S)^4 \quad 6912\,S^7 \text{ or } S \quad \left(\frac{K_{\mathrm{sp}}}{6912}\right)^{\frac{1}{7}}$$

Thus, the relation between molar solubility(*S*) and solubility product (K_{sp}) will be

$$S \quad \left(\frac{K_{\mathrm{sp}}}{6912}\right)^{1/7}$$

6. Let the solubility of $\mathrm{Ag_2CO_3}$ is *S*. Now, 0.1 M of $\mathrm{AgNO_3}$ is added to this solution after which let the solubility of $\mathrm{Ag_2CO_3}$ becomes *S* .

$$[\mathrm{Ag}\ \ ] \quad S \quad 0.1 \text{ and } [\mathrm{CO}_3^2\ \ ] \quad S$$

$$K_{\mathrm{sp}} \quad (S \quad 0.1)^2\,(S\ ) \qquad \text{...(i)}$$

Given, $K_{\mathrm{sp}} \quad 8 \quad 10^{\ 12}$

∵ K_{sp} is very small, we neglect *S* against *S* in Eq. (i)

$$K_{\mathrm{sp}} \quad (0.1)^2 S$$

or $8 \quad 10^{\ 12} \quad 0.01\,S$

or $S \quad 8 \quad 10^{\ 12} \quad 10^2 \quad 8 \quad 10^{\ 10}\,\mathrm{M}$

Thus, molar solubility of $\mathrm{Ag_2CO_3}$ in 0.1 M $\mathrm{AgNO_3}$ is 8 10 ^{10} M.

7. The reaction takes place when $\mathrm{H_2SO_4}$ is added to $\mathrm{NH_4OH}$ is as follows :

	$\mathrm{H_2SO_4}$	$\mathrm{2NH_4OH}$	$\mathrm{(NH_4)_2SO_4}$	$\mathrm{2H_2O}$
	Strong acid	Weak base	Salt of strong acid weak base	
Millimoles at *t* 0	20 0.1 2	30 0.2 6	0	
Millimoles at *t* *t*	0	2	2	

So, the resulting solution is a basic buffer $[\mathrm{NH_4OH} \quad \mathrm{(NH_4)_2SO_4}]$.

According to the Henderson's equation,

$$\mathrm{pOH} \quad \mathrm{p}K_b \quad \log\frac{[\mathrm{(NH_4)_2SO_4}]}{[\mathrm{NH_4OH}]}$$

$$4.7 \quad \log\frac{2}{2} \quad 4.7$$

$$\mathrm{pH} \quad 14 \quad \mathrm{pOH} \quad 14 \quad 4.7 \quad 9.3$$

8. Its given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^{2} solution.

So, we can interpret the volume of unknown Ba^{2} solution as 450 mL i.e.

$$\underset{\text{solution}}{\underset{Ba^{2+}}{450\text{mL}}} + \underset{\text{solution}}{\underset{Na_2SO_4}{50\text{mL}}} \quad \underset{\text{solution}}{\underset{BaSO_4}{500\text{mL}}}$$

From this we can calculate the concentration of SO_4^{2} ion in the solution *via*

$$M_1V_1 \quad M_2V_2$$

$$1 \quad 50 \quad M_2 \quad 500$$

(as 1M Na_2SO_4 is taken into consideration)

$$M_2 \quad \frac{1}{10} \quad 0.1\text{M}$$

Now for just precipitation,

Ionic product Solubility product (K_{sp})

i.e. $[Ba^{2+}][SO_4^{2}]$ K_{sp} of $BaSO_4$

Given K_{sp} of $BaSO_4$ $1 \quad 10^{\;10}$

So, $[Ba^{2+}][0.1] \quad 1 \quad 10^{\;10}$

or $[Ba^{2+}] \quad 1 \quad 10^{\;9}$ M

Remember This is the concentration of Ba^{2} ions in final solution. Hence, for calculating the $[Ba^{2+}]$ in original solution we have to use

$$M_1V_1 \quad M_2V_2$$

as $M_1 \quad 450 \quad 10^{\;9} \quad 500$

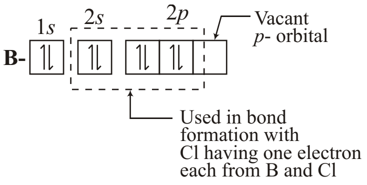
so, $M_1 \quad 1.1 \quad 10^{\;9}$M

9. **Key Idea** Lewis acids are defined as,
"Electron deficient compounds which have the ability to accept atleast one lone pair."

The compound given are

PH_3-Octet complete although P has vacant 3*d*-orbital but does not have the tendency to accept lone pair in it. Hence, it cannot be considered as Lewis acid.

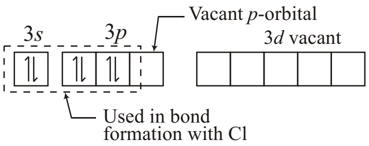
BCl_3-Incomplete octet with following orbital picture.



Hence, vacant *p*-orbital of B can accept one lone pair thus it can be considered as Lewis acid.

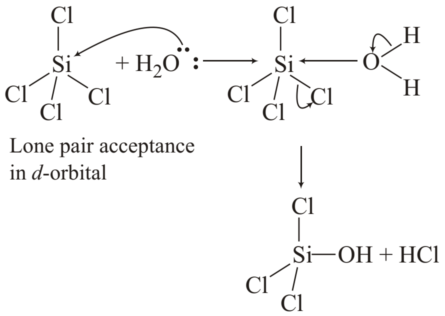
$AlCl_3$-Similar condition is visible in $AlCl_3$ as well i.e.

Al (Valence orbital only)



Hence this compound can also be considered as Lewis acid.

$SiCl_4$ - Although this compound does not have incomplete octet but it shows the tendency to accept lone pair of electrons in its vacant *d*-orbital. This tendency of $SiCl_4$ is visible in following reaction.



Thus, option (b) and (d) both appear as correct but most suitable answer is (d) as the condition of a proper Lewis acid is more well defined in BCl_3 and $AlCl_3$.

10. Among the given salts

$FeCl_3$ is acidic in nature i.e., have acidic solution as it is the salt of weak base and strong acid.

$Al(CN)_3$ and **$Pb(CH_3COO)_2$** are the salts of weak acid and weak base.

CH_3COOK is the salt of strong base and weak acid.

Hence, the solution of CH_3COOK will be most basic because of the following reaction.

$$CH_3COOK + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{(Strong base)}}{KOH}$$

11. For a salt of weak acid and weak base,

$$pH \quad 7 \quad \frac{1}{2}pK_a \quad \frac{1}{2}pK_b$$

Given, $pK_a(HA)$ 3.2, $pK_a(BOH)$ 3.4

$$pH \quad 7+\frac{1}{2}(3.2) \quad \frac{1}{2}(3.4)$$

$$7 \quad 1.6 \quad 1.7 \quad 6.9$$

12. pH 1 $[H \ ]$ $10^{\;1}$ 0.1 M

pH 2 $[H^+]$ $10^{\;2}$ 0.01 M

For dilution of HCl, $M_1V_1 \quad M_2V_2$

$$0.1 \quad 1 \quad 0.01 \quad V_2$$

$$V_2 \quad 10\text{ L}$$

Volume of water to be added 10 1 9 L

13. MX: $K_{sp} \quad S^2 \quad 4 \quad 10^{\;8}$

$S \quad 2 \quad 10^{\;4}$

MX_2: $K_{sp} \quad 4S^3 \quad 3.2 \quad 10^{\;14}$ $S \quad 2 \quad 10^{\;5}$

M_3X: $K_{sp} \quad 27S^4 \quad 2.7 \quad 10^{\;15}$ $S \quad 10^{\;4}$

Order of solubility is $MX \quad M_3X \quad MX_2$

14. mmol of base = 2.5 $\frac{2}{5}$ 1

mmol of acid required to reach the end point = 1

Volume of acid required to reach the end point $\frac{15}{2}$ mL

Total volume at the end point $\frac{15}{2} \quad 2.5 = 10$ mL

Molarity of salt at the end point $\frac{1}{10} \quad 0.10$

$$\underset{C\ (1\qquad)}{B^+} + H_2O \rightleftharpoons \underset{C}{BOH} + \underset{C}{H^+}$$

$$K_h \quad \frac{K_w}{K_b} \quad 10^{\ \ 2}$$

$$K_h \quad 10^{\ \ 2} \quad \frac{C^{\ \ 2}}{1} \quad \frac{0.1^{\ \ 2}}{1}$$

$$10^{\ \ 2} \qquad 1 \quad 0$$

$$\frac{1 \quad \sqrt{1 \quad 40}}{20} \quad 0.27$$

$$[H^+] \quad C \qquad 0.1 \quad 0.27 = 0.027 \text{ M}$$

15.

$$\begin{array}{lcccc} & CH_3NH_2 \ + & HCl & CH_3NH_3^+ \ + & Cl \\ \text{Initial :} & 0.10 & 0.08 & 0 & 0 \\ \text{Final :} & 0.02 & 0 & 0.08 & 0.08 \end{array}$$

$$\text{pOH} \quad \text{p}K_b \quad \log\frac{[CH_3NH_3^+]}{[CH_3NH_2]}$$

$$\log(5 \quad 10^{\ \ 4}) \quad \log\frac{0.08}{0.02} \quad 3.9$$

$$\text{pH} = 14 - \text{pOH} = 10.1$$

$$[H^+] = 8 \quad 10^{\ \ 11}$$

16. $K_h\ (X\ \ ) \quad \frac{K_w}{K_a} \quad \frac{10^{\ \ 14}}{10^{\ \ 5}} \quad 10^{\ \ 9} \qquad\qquad \sqrt{\frac{K_h}{C}} \quad \sqrt{\frac{10^{\ \ 9}}{0.10}} \quad 10^{\ \ 4}$

% hydrolysis $\quad 100 \qquad 0.01$

17. Minimum S^2 concentration would be required for precipitation of least soluble HgS.

For HgS, S^2 required for precipitation is

$$[S^2\ \ ] = \frac{K_{sp}}{[Hg^{2+}]} \quad \frac{10^{\ \ 54}}{10^{\ \ 3}} \quad 10^{\ \ 51} \text{ M}$$

18. Alkali metal salts are usually more soluble than the salts of transition metals. Also, CuS is less soluble than ZnS because of $3d^9$ configuration of Cu^{2+}. Therefore, solubility order is

$$Na_2S > ZnS > CuS$$

19. $A_pB_q \rightleftharpoons \underset{pS}{pA} \quad \underset{qS}{qB}$

$$K_{sp} \quad (pS)^p\ (qS)^q \quad S^{(p \quad q)} \quad p^p \quad q^q$$

20. NaCN is basic salt, has highest pH while HCl has lowest pH. NaCl is neutral salt has pH = 7 while NH_4Cl is acidic salt, has pH less than 7.

pH : HCl < NH_4Cl < NaCl < NaCN

21. $75 \text{ mL} \frac{M}{5}$ HCl $\quad$ 15 mmol HCl

$25 \text{ mL} \frac{M}{5}$ NaOH $\quad$ 5 mmol NaOH

After neutralisation, 10 mmol HCl will be remaining in 100 mL of solution.

Molarity of HCl in the final solution $\frac{10}{100} \quad 0.10$

$$\text{pH} \quad \log[H^+] \quad \log(0.10) = 1$$

22. In case of hydroxides of Group II A, solubility increases down the group. Therefore, $Be(OH)_2$ is least soluble, has lowest value of K_{sp}.

23. $HClO_4$ is the strongest acid among these.

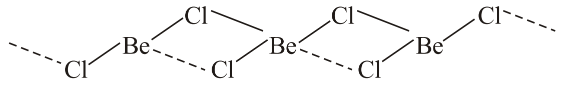
24. For precipitation to occur, $K_{sp} \quad Q_{sp}$.

$$Q_{sp} \quad \frac{10^{\ \ 4}}{2} \quad \frac{10^{\ \ 4}}{2} \quad 2.5 \quad 10^{\ \ 9} \quad K_{sp}$$

Hence, precipitate will be formed in this case. In all other case, $Q_{sp} \quad K_{sp}$ and no precipitation will occur.

25. In stomach, pH is 2-3, i.e. strongly acidic and aspirin will be almost unionised here due to common ion effect. However, pH in small intestine is 8, basic, aspirin will be neutralised here.

26. $BeCl_2$ exist in polymeric forms and has no electron deficiency, not a Lewis acid.



27. $\underset{\text{Base}}{NH_2} + H_2O \rightleftharpoons \underset{\text{Conjugate acid}}{NH_3} + OH$

28. When a weak acid (HX) is titrated against a strong base NaOH, basic salt (NaX) is present at the end point which makes end point slightly basic with pH around 8. Hence, phenolphthalein, that changes its colour in this pH range, would be the best choice of indicator to detect the end point.

29. The reaction of HA with strong base is

$$HA + OH \rightleftharpoons H_2O + A$$

$$K \quad \frac{[A\ \ ]}{[HA][OH\ \ ]} \quad \frac{[H^+]}{[H^+]} \quad \frac{K_a}{K_w} \quad \frac{10^{\ \ 4}}{10^{\ \ 14}} \quad 10^{10}$$

30. $K_a\ (HX) \quad \frac{K_w}{K_b} \quad 10^{\ \ 4}$

$$\text{pH} \quad \text{p}K_a \quad \log\frac{[X\ \ ]}{[HX]}$$

$$\text{p}K_a \quad 4 \qquad\qquad [\because\ [X\ \ ] = [HX]]$$

31. For precipitation reaction, $Q_{IP} \quad K_{sp}$.

$$Q_{IP} \quad [Ca^{2+}][F\ \ ]^2 \quad \frac{10^{\ \ 2}}{2} \quad \frac{10^{\ \ 3}}{2}^{\ \ 2}$$

$$1.25 \quad 10^{\ \ 9} \quad K_{sp}\text{, precipitate will be formed.}$$

32. Acidic buffer is prepared by mixing weak acid with salt of its conjugate base. Therefore, acetic acid and sodium acetate can be used to prepare acidic buffer.

33. The order of acidic strength of conjugate acids is

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

Reverse is the order of basic strength of their conjugate base, i.e. ClO is the strongest base.

34. $K_w \quad [H_3O^+][OH\ ] = 10^{\;6} \quad 10^{\;6} \quad 10^{\;12}$

35. No matter, what is the concentration of HCl, its pH will always be less than 7 at 25°C. In the present case, the solution is very dilute, pH will be between 6 and 7.

36. **PLAN** In presence of common ion (in this case Ag ion) solubility of sparingly soluble salt is decreased.

Let solubility of Ag_2CrO_4 in presence of 0.1 M

$$AgNO_3 \quad x$$

$$Ag_2CrO_4 \rightleftharpoons \underset{2x}{2\,Ag} \qquad \underset{x}{CrO_4^{2}}$$

$$AgNO_3 \rightleftharpoons \underset{0.1}{Ag} \qquad \underset{0.1}{NO_3}$$

Total $[Ag\ ] \quad (2x \quad 0.1)M \quad 0.1\ M$

as $x \quad 0.1$ M

$[CrO_4^{2}\ ] \quad x\,M$

Thus, $[Ag\ ]^2[CrO_4^{2}\ ] \quad K_{sp}$

$(0.1)^2(x) \quad 1.1 \quad 10^{\;12}$

∵ $x \quad 1.1 \quad 10^{\;10}$ M

37. In HNO_3 and CH_3COONa combination, if HNO_3 is present in limiting amount, it will be neutralised completely, leaving behind some excess of CH_3COONa.

$$CH_3COONa + HNO_3 \qquad CH_3COOH + NaNO_3$$

Buffer combination

38. $CH_3COOH + CH_3COONa$ = Buffer solution

$CH_3COONa + HCl \qquad CH_3COOH + NaCl$

If HCl is taken in limited quantity, final solution will have both CH_3COOH and CH_3COONa needed for buffer solution.

Ammonia and ammonium chloride forms basic buffer.

39. pH of $10^{\;8}$ M solution will be between 6 and 7 but never 8. The conjugate base of an acid is formed by removing a proton (H^+) from acid. Therefore, HPO_4^{2} is a conjugate base of H_2PO_4.

$$H_2O \rightleftharpoons H^+ + OH \qquad\qquad H \quad 0$$

Increasing temperature will increase equilibrium constant of the above endothermic reaction.

At the mid-point of titration $\quad pH = pK_a$

40. **Key Idea** Solubility of salt of weak acid (AB) in presence of H ions from buffer solution can be calculated with the help of following formula.

Solubility $\sqrt{K_{sp}\ \dfrac{[H^+]}{k_a} \quad 1}$

Given, pH 3, so $[H^+] \quad 10^{\;3}$

$$K_a \quad 1 \quad 10^{\;8} \qquad\qquad K_{sp} \quad 2 \quad 10^{\;10}$$

after putting the values in above formula

Solubility $\sqrt{2 \quad 10^{\;10}\ \dfrac{10^{\;3}}{10^{\;8}} \quad 1} \quad \sqrt{2 \quad 10^{\;5}} \quad 4.47 \quad 10^{\;3}M$

Hence, the value of y 4.47

41. For *P*, i.e. (10 mL of 0.1 M NaOH 20 mL of 0.1 M acetic acid) is diluted to 60 mL

The correct match is 1, i.e. the value of $[H^+]$ does not change on dilution due to the formation of following buffer.

$$NaOH + CH_3COOH \rightleftharpoons CH_3COO\ \ Na^+ + H_2O$$

	NaOH	CH_3COOH	$CH_3COO\ Na^+$
Initial millimol	1	2	
Final millimol		1	1

Final volume – 30 mL (20 10) in which millimoles of CH_3COOH and $CH_3COO\ \ Na^+$ are counted.

For *Q*, i.e. (20 mL of 0.1 M NaOH 20 mL of 0.1 M CH_3COOH) is diluted to 80 mL

The correct match is 5, i.e. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution.

As per the condition given in *Q* the resultant solution before dilution contain 2 millimoles of $CH_3COO\ Na^+$ in 40 mL solution. Hence, it is the salt of weak acid and strong base. So,

$$[H\ \ ]_{initial} \quad \sqrt{\frac{K_W K_a}{C}}$$

After dilution to 80 mL, the new '*C*' becomes $\dfrac{C}{2}$, So,

$$[H^+]_{new} \quad \sqrt{\frac{K_w K_a}{C/2}} \text{ or } [H^+]_{initial} \quad \sqrt{2}$$

For *R*, i.e. (20 mL of 0.1 M HCl 20 mL of 0.1 M NH_3) is diluted to 80 mL

The correct match is 4, i.e. the value of $[H^+]$ changes to $\dfrac{1}{\sqrt{2}}$ times of its initial value of dilution.

As per the condition given in *R* the resultant solution before dilution contains 2 millimoles of NH_4Cl in 40 mL of solution. Hence, a salt of strong acid and weak base is formed.

For this,

$$[H^+]_{initial} \quad \sqrt{\frac{K_w \quad C}{K_b}}$$

Now on dilution upto 80 mL new conc. becomes $C/2$.

So, $$[H^+]_{new} \quad \sqrt{\frac{K_w \quad \frac{C}{2}}{K_b}}$$

or $$[H^+]_{new} \quad [H\ \ ]_{initial} \quad \frac{1}{\sqrt{2}}$$

For *S*, i.e. 10 mL saturated solution of $Ni(OH)_2$ in equilibrium with excess solid $Ni(OH)_2$ is diluted to 20 mL and solid $Ni(OH)_2$ is still present after dilution.

The correct match is 1.

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+} + 2OH$$

as per the condition given it is a sparingly soluble salt. Hence, on dilution the concentration of OH ions remains constant in saturated solution.

So for this solution,

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

42. $I_2 : \ I \qquad I_2 \ = \ I_3$

43. Hydration energy facilitate solubility.

44. Amphoteric

45. SO_4^{2-} Conjugate base is formed by removing a proton from acid.

46. P_2O_5 is strongest acid and MgO is strongest base.

47. $NaOH + H_2O \qquad NaOH\ (aq); \quad H \quad 0$

48. Lewis acid accept lone pair of electron.

49. Degree of ionisation ($\frac{\wedge \text{m}}{\wedge}$

$$\text{Let} \quad \wedge \text{m}\ (HY) \quad x \qquad \wedge \text{m}\ (HX) \quad \frac{X}{10}$$

$$\frac{\wedge \text{m}\ (HX)}{\wedge \text{m}\ (XY)} \quad \frac{1}{10} \quad \frac{(HX)}{(HY)} \qquad [\because \wedge \quad (HX) \quad \wedge \quad (HY)]$$

$$\text{Also :} \quad K_a(HX) \quad (0.01)[\quad HX)]^2 \qquad \text{...(i)}$$

$$K_a(HY) \quad (0.10)[\quad HY)]^2$$

$$0.10[10 \quad (HX)]^2 \quad 10[\quad (HX)]^2 \qquad \text{... (ii)}$$

$$\frac{K_a(HX)}{K_a(HY)} \quad \frac{0.01}{10} \quad \frac{1}{1000}$$

$$\log K_a(HX) \quad \log K_a(HY) \qquad 3$$

$$\log K_a(HX) \quad [\quad \log K_a(HY)] \quad 3$$

$$pK_a(HX) \quad pK_a(HY) \quad 3$$

50. It is a case of simultaneous solubility of salts with a common ion. Here, solubility product of CuCl is much greater than that of AgCl, it can be assumed that Cl– in solution comes mainly from CuCl.

$$[Cl^-] \qquad \sqrt{K_{sp}(CuCl)} \qquad 10^{-3} M$$

Now, for AgCl, $K_{sp} = 1.6 \times 10^{-10} = [Ag^+]\,[Cl^-]$

$$= [Ag^+] \times 10^{-3}$$

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

51. Basic salts solution will have pH > 7, will change colour of litmus paper red to blue

KCN, K_2CO_3 and LiCN are the only basic salts among these.

52. The hydrolysis reaction is

$$A \ + H_2O \rightleftharpoons AH + OH$$

$$K_h \quad \frac{K_w}{K_a} \quad 10^{\ 10}$$

$$[OH\ ] = \sqrt{K_hC} \quad 10^{\ 6}$$

pOH = 6 and pH 8

53. At the end-point, $[A\ ] = 0.05$

$$K_b\ (A\ ) \quad K_w / K_a \quad 2 \quad 10^{\ 9}$$

$$[OH\ ] = \sqrt{K_bC} \quad \sqrt{2 \quad 10^{\ 9} \quad 0.05} \quad 10^{\ 5}$$

pOH = 5 and pH = 9

54. (i) $CH_3COOH \rightleftharpoons CH_3COO \ + \ H^+$

$C\ (1 \quad) \qquad C \qquad C$

If no HCl is present,

$$[HCl] \quad \frac{0.2}{2} \quad 0.10\ M$$

$$[CH_3COOH] \quad 0.10\ M$$

The major contributor of H^+ in solution is HCl.

$$K_a \quad \frac{C \quad (0.1)}{C\ (1 \quad)} \quad 1.75 \quad 10^{\ 5}$$

$$1.75 \quad 10^{\ 4}$$

(ii) mmol of NaOH added $\frac{6}{40}$ 1000 150

mmol of HCl 500 0.2 = 100

mmol of CH_3COOH 500 0.2 = 100

After neutralisation, mmol of CH_3COOH = 50

mmol of CH_3COONa 50

$$pH \quad pK_a \quad 4.75$$

55. Partial pressure of SO_2 in air $10^{\ 5}$ atm

$$[SO_2]_{aq} \quad 1.3653 \quad 10^{\ 5} \text{mol L}^{\ 1}$$

$\because$ pK_a 1.92 and concentration of H_2SO_3 is very low, it is almost completely ionised as

$$H_2SO_3 \rightleftharpoons H^+ \ + \ HSO_3$$

$$[H^+] = 1.3653 \quad 10^{\ 5}\ M$$

$$pH = -\log(1.3653 \quad 10^{\ 5}) \quad 4.86$$

56. In water, $K_{sp} \quad 4S^3 \quad 4\ (6.7 \quad 10^{\ 6})^3$

$$1.2 \quad 10^{\ 15}$$

In buffer of pH = 8, pOH = 6, $[OH\ ] = 10^{\ 6}$

$$K_{sp} \quad S\ [OH\ ]^2$$

$$S \quad \frac{1.2 \quad 10^{\ 15}}{10^{\ 12}} \quad 1.2 \quad 10^{\ 3}\ M$$

57. (a) $E \quad 0.164 = -\ 0.059 \log \frac{[Ag^+]_{\text{anode}}}{0.10}$

$$[Ag^+]_{\text{anode}} \quad 1.66 \quad 10^{\ 4}\ M$$

$$[CrO_4^2\ ] = \frac{[Ag^+]}{2} \quad 8.3 \quad 10^{\ 5}\ M$$

$$K_{sp} \quad [Ag^+]^2\,[CrO_4^2\ ]$$

$$(1.66 \quad 10^{\ 4})^2\ (8.3 \quad 10^{\ 5})$$

$$2.3 \quad 10^{\ 12}$$

(b) pH of HCl $\ \ 2$

$[H\ \ ]\ \ 10^{\ 2}$ M

Moles of H ions in 200 mL of $10^{\ 2}$ M HCl solution

$$\frac{10^{\ 2}}{1000}\quad 200\quad 2\quad 10^{\ 3}$$

Similarly, pH of NaOH $\ \ 12$

$[H\ \ ]\ \ 10^{\ 12}$ M

or $[OH\ \ ]\ \ 10^{\ 2}$ M $\qquad [\because [H\ \ ][OH\ \ ]\ \ 10^{\ 14}$ m]

Moles of OH ion in 300 mL of $10^{\ 2}$ M NaOH solution

$$\frac{10^{\ 2}}{1000}\quad 300\quad 3\quad 10^{\ 3}$$

Total volume of solution after mixing 500 mL

Moles of OH ion left in 500 mL of solution

$$(3\quad 10^{\ 3})\quad (2\quad 10^{\ 3})\quad 10^{\ 3}$$

Molar concentration of OH ions in the resulting

solution $\dfrac{10^{\ 3}}{500}\quad 1000\quad 2\quad 10^{\ 3}$ M

$$\text{pOH}\qquad \log(2\quad 10^{\ 3})$$
$$\log 2\quad 3\log 10$$
$$0.3\sim 103\quad 2.699$$
$$\text{pH}\quad 14\quad 2.699\quad 11.301$$

58. $2AgCl(s) + CO_3^{2} \rightleftharpoons Ag_2CO_3\,(s)\ +\ 2Cl$

$$K\quad \frac{[Cl\ \ ]^2}{[CO_3^{2}\ \ ]}\quad \frac{[Cl\ \ ]^2}{[CO_3^{2}\ \ ]}\quad \frac{[Ag^+]^2}{[Ag^+]^2}\quad \frac{[K_{sp}\ (AgCl)]^2}{K_{sp}\ (Ag_2CO_3)}$$

$$[Cl\ \ ]\quad \frac{0.0026}{35.5}\text{ M}\quad 7.3\quad 10^{\ 5}\text{ M}$$

The above concentration of Cl indicates that $[CO_3^{2}\ \ ]$ remains almost unchanged.

$$\frac{7.3\quad 10^{\ 5}}{1.5}\quad \frac{[K_{sp}\ (AgCl)]^2}{8.2\quad 10^{\ 12}}$$

$$K_{sp}(AgCl)\quad 2\quad 10^{\ 8}$$

59. $\text{pH}\quad pK_{In}\quad \log 10\quad pK_{In}\quad 1 \qquad \text{When}\ \dfrac{[In\ \ ]}{[HIn]}\quad 10$

$pK_{In}\quad \log(0.1) = pK_{In}\quad {}_1 \qquad \text{When}\ \dfrac{[In\ \ ]}{[HIn]}\quad 0.1$

pH range is $pK_{In}\quad {}_1$ to $pK_{In}\quad {}_1$.

60. $K_a\ (NH_4^+)\quad 5.6\quad 10^{\ 10}$

$$K_b\ (NH_3)\quad K_w/K_a\quad \frac{10^{\ 14}}{5.6\quad 10^{\ 10}}\quad 1.8\quad 10^{\ 5}$$

i.e. $NH_3\quad H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+\quad OH$

$$K\quad \frac{k_1}{k_2}\quad 1.8\quad 10^{\ 5}$$

$$k_1\quad Kk_2\quad 1.8\quad 10^{\ 5}\quad 3.4\quad 10^{10}\quad 6.12\quad 10^{5}$$

61. $CN\quad +\ H_2O \rightleftharpoons HCN\ +\ OH$

$$K_h\quad 2\quad 10^{\ 5}$$

$$[OH\ \ ] = \sqrt{K_hC}\quad \sqrt{2\quad 10^{\ 5}\quad 0.5}\quad \sqrt{10^{\ 5}}$$

pOH 2.5 and pH = 11.5

62. For salts of weak acid and weak base .

$$\text{pH} = 7 + \frac{1}{2}\,(pK_a\quad pK_b)\quad 7\quad \frac{1}{2}\,(3.8\quad 4.8) = 6.50$$

63. $Ag^+ + 2CN \rightleftharpoons Ag(CN)_2$

Initial :	0.03	0.10	0
Equilibrium :	x	0.10 – 0.06	0.03

$$K\quad \frac{1}{4\quad 10^{\ 19}}\quad 2.5\quad 10^{18}$$

$$K\quad 2.5\quad 10^{18}\quad \frac{0.03}{(0.04)^2\ x}$$

$$x\quad 7.50\quad 10^{\ 18}\text{ M } Ag^+$$

64. For H_2S, $\ H_2S \rightleftharpoons 2H^+\ +\ S^{2}$

$$K\quad K_1\quad K_2\quad 1.3\quad 10^{\ 20}$$

Minimum $[S^{2}\ \ ]$ required to begin precipitation of

$$MS = \frac{6\quad 10^{\ 21}}{0.05}\quad 1.2\quad 10^{\ 19}$$

$$K\quad 1.3\quad 10^{\ 20}\quad \frac{[H^+]^2\,[S^{2}\ \ ]}{[H_2S]}\quad [H^+]^2\ \frac{(1.2\quad 10^{\ 19})}{0.10}$$

$$[H^+] = 0.10\text{ M}\qquad \text{pH} = 1$$

65. Mixing H_2CO_3 with $NaHCO_3$ results in buffer solution.

$$\text{pH} = pK_a + \log\frac{[NaHCO_3]}{[H_2CO_3]} = pK_a + \log\frac{n\,(NaHCO_3)}{n\,(H_2CO_3)}$$

$$7.4 = -\log(7.8\quad 10^{\ 7})\quad \log\frac{x}{20}$$

$$x\quad 400\ \text{mmol}$$

$$NaHCO_3 = 5\quad V\qquad V\quad 80\text{ mL}$$

66. $K_{sp}\quad 4S^3\quad 4.42\quad 10^{\ 5}$

$S\quad 0.022$ M

mmol of $Ca(OH)_2$ in 500 mL saturated solution = 11

mmol of NaOH in 500 mL 0.40 M solution = 200

Total mmol of OH = 200 + 2 11 222

$[OH\ \ ] = 0.222$ M

Solubility in presence of NaOH $\ \dfrac{K_{sp}}{[OH\ \ ]^2}$

$$\frac{4.42\quad 10^{\ 5}}{(0.222)^2}\quad 9\quad 10^{\ 4}\text{ M}$$

mmol of Ca^{2+} remaining in solution = 0.9

mmol of $Ca(OH)_2$ precipitated = 10.1

mg of $Ca(OH)_2$ precipitated = 10.1 7.4 = 747.4 mg

67. Let 40 mL of base contain x mmol of BOH.

$$\begin{array}{llll} B\text{OH} + \text{HCl} & & B\text{Cl} + \text{H}_2\text{O} & \\ x \quad 0.5 & & 0.5 & \text{When 5 mL acid is added} \\ x \quad 2 & & 2.0 & \text{When 20 mL of acid is added} \end{array}$$

When pH is 10.04, pOH = 3.96 and when pH is 9.14, pOH is 4.86. Therefore,

$$3.96 \quad \text{p}K_b \quad \log \frac{0.50}{x \quad 0.5} \qquad \ldots\text{(i)}$$

$$3.96 \quad \text{p}K_b \quad \log \frac{2.0}{x \quad 2} \qquad \ldots\text{(ii)}$$

Subtracting Eq. (i) from Eq. (ii) gives

$$0.90 = \log \quad \frac{2}{x \quad 2} \quad \frac{x \quad 0.5}{0.5}$$

$$28 \quad \frac{4\,(x \quad 0.5)}{x \quad 2}$$

$x \quad 3.5$, substituting in equation (i) gives

$$3.96 \quad \text{p}K_b \quad \log \frac{0.5}{3}$$

$$K_b \quad 1.8 \quad 10^{5}$$

68. Initial concentration of $\text{K}_2\text{C}_2\text{O}_4 = \frac{0.152}{0.50} \quad 0.304$ M,

Also for the following equilibrium:

$$\underset{0.304 \quad x}{\text{Ag}_2\text{CO}_3(s) + \text{K}_2\text{C}_2\text{O}_4(aq)} \rightleftharpoons \text{Ag}_2\text{C}_2\text{O}_4(s) + \underset{x}{\text{K}_2\text{CO}_3}$$

$$K \quad \frac{[\text{CO}_3^{2} \;]}{[\text{C}_2\text{O}_4^{2} \;]} \quad \frac{[\text{Ag}^+]^2}{[\text{Ag}^+]^2} \quad \frac{K_{sp}\ (\text{Ag}_2\text{CO}_3)}{K_{sp}\ (\text{Ag}_2\text{C}_2\text{O}_4)}$$

Given, $0.304 - x \quad 0.0358$

$$x \quad 0.2682$$

$$K \quad \frac{0.2682}{0.0358} \quad 7.5$$

$$K_{sp}\ (\text{Ag}_2\text{CO}_3) \quad K \quad K_{sp}\ (\text{Ag}_2\text{C}_2\text{O}_4)$$

$$7.5 \quad 1.29 \quad 10^{11}$$

$$9.675 \quad 10^{11}$$

69. $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO} \quad + \text{H}^+$

When concentration of CH_3COOH is 1.0 M, ‘ ’ is negligible,

$$[\text{H}^+] = \sqrt{K_a C} \quad 4.24 \quad 10^{3} \text{ M}$$

$$\text{pH} \quad \log(4.24 \quad 10^{3}) \quad 2.37$$

Now, let us assume that solution is diluted to a volume where concentration of CH_3COOH (without considering ionisation) is x.

$$\begin{array}{ccccc} \text{CH}_3\text{COOH} & \rightleftharpoons & \text{CH}_3\text{COO} & + & \text{H}^+ \\ x\,(1 \quad) & & x & & x \end{array}$$

$$K_a \quad \frac{x \quad {}^{2}}{1}$$

Also, desired pH $\quad 2 \quad 2.37 = 4.74$

$$[\text{H}^+] = 1.8 \quad 10^{5} \quad x$$

$$K_a \quad 1.8 \quad 10^{5} \quad \frac{1.8 \quad 10^{5}}{1}$$

$$0.5 \text{ and } x \quad 3.6 \quad 10^{5} \text{ M}$$

$$\text{Volume (final)} \quad 1/3.6 \quad 10^{5} \quad 27.78 \quad 10^{3} \text{ L.}$$

70. pOH of buffer solution $\quad \text{p}K_b \quad \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]}$

$$\log(1.8 \quad 10^{5}) \quad \log \frac{0.25}{0.05} \quad 5.44$$

$$[\text{OH} \;] = 3.6 \quad 10^{6} \text{ M}$$

$$[\text{Al}^{3+}] = \frac{K_{sp}}{[\text{OH} \;]^3} \quad \frac{6 \quad 10^{32}}{(3.6 \quad 10^{6})^3} \quad 1.28 \quad 10^{15} \text{ M}$$

$$[\text{Mg}^{2+}] = \frac{K_{sp}}{[\text{OH} \;]^2} \quad \frac{8.9 \quad 10^{12}}{(3.6 \quad 10^{6})^2} \quad 0.68 \text{ M}$$

71. HCN for buffer will be formed by the reaction

$$\text{NaCN} + \text{HCl} \qquad \text{NaCl} + \text{HCN}$$

mmol of NaCN present initially $\quad \frac{0.01}{49} \quad 1000 \quad 0.2$

Let x mmol of HCl is added so that x mmol of NaCN will be neutralised forming x mmol of HCN.

$$\text{pH} \quad \text{p}K_a \quad \log \frac{[\text{NaCN}]}{[\text{HCN}]}$$

$$8.5 \quad \log(4.1 \quad 10^{10}) \quad \log \frac{0.2 \quad x}{x}$$

$$x \quad 0.177 \text{ mmol}$$

72. (i) 0.20 mole HCl will neutralise 0.20 mole CH_3COONa, producing 0.20 mol CH_3COOH. Therefore, in the solution moles of CH_3COOH = 1.20

Moles of CH_3COONa = 0.80

$$\text{pH} \quad \text{p}K_a \quad \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log(1.8 \quad 10^{5}) \quad \log \frac{(0.80)}{(1.20)} = 4.56$$

(ii)

	CH_3COONa +	HCl	CH_3COOH +	NaCl
Initial	0.10	0.20	0	0
Final	0	0.10	0.10	0.10

Now, the solution has 0.2 mole acetic acid and 0.1 mole HCl. Due to presence of HCl, ionisation of CH_3COOH can be ignored (common ion effect) and H^+ in solution is mainly due to HCl.

$$[\text{H}^+] = 0.10$$

$$\text{pH} \quad -\log(0.10) = 1.0$$

73. In pure water, solubility $\quad \frac{9.57}{58} \quad 10^{3}$ M

$$1.65 \quad 10^{4} \text{ M}$$

$$K_{sp} \quad 4S^3 \quad 4\,(1.65 \quad 10^{4})^3 \quad 1.8 \quad 10^{11}$$

In 0.02 M $\text{Mg(NO}_3)_2$;

solubility of $Mg(OH)_2 \quad \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} \quad \frac{1}{2}$

$$1.5 \quad 10^{\ 5} \text{ mol L}^{\ 1}$$

$$1.5 \quad 10^{\ 5} \quad 58 \text{ g L}^{\ 1}$$

$$8.7 \quad 10^{\ 4} \text{ g L}^{\ 1}$$

74. $HCOOH \rightleftharpoons H^+ + HCOO$

$$\underset{1 \quad 0.75}{HCOONa} \rightleftharpoons Na^+ \quad \underset{0.75}{HCOO}$$

In the above buffer solution, the significant source of formate ion (HCOO) is HCOONa. Hence,

$$K_a \quad 2.4 \quad 10^{\ 4}$$

$$\frac{[H^+](0.75)}{[HCOOH]}$$

$$[H^+] \quad \frac{2.4 \quad 10^{\ 4} \quad 0.20}{0.75} \quad 6.4 \quad 10^{\ 5}$$

$$pH \quad -\log(6.4 \quad 10^{\ 5}) \quad 4.20$$

76. K_{sp} (AgI) = 8.5 $10^{\ 17}$ $[Ag^+][I\ ]$

$[I\ ]$ required to start precipitation of AgI

$$\frac{8.5 \quad 10^{\ 17}}{0.10} \quad 8.5 \quad 10^{\ 16} \text{ M}$$

$$K_{sp}\ (HgI_2) \quad 2.5 \quad 10^{\ 26} \quad [Hg^{2+}][I\ ]^2$$

$[I\ ]$ required to start precipitation of HgI_2

$$\sqrt{\frac{2.5 \quad 10^{\ 26}}{0.10}} \quad 5 \quad 10^{\ 13} \text{ M}$$

The above calculation indicates that lower $[I\ ]$ is required for precipitation of AgI. When $[I\ ]$ reaches to 5 $10^{\ 13}$, AgI gets precipitated almost completely.

When HgI_2 starts precipitating,

$$[Ag^+] = \frac{8.5 \quad 10^{\ 17}}{5 \quad 10^{\ 13}} \quad 1.70 \quad 10^{\ 4} \text{ M}$$

$$\%\ Ag^+ \text{ remaining} \quad \frac{1.70 \quad 10^{\ 4} \quad 100}{0.10} \quad 0.17$$

$$\%\ Ag^+ \text{ precipitated} \quad 100 - 0.17 = 99.83$$

76. Molarity (C) 0.10

$$[H^+] = \sqrt{K_a \ C} \quad 7 \quad 10^{\ 5} \text{ M } (\quad \text{is negligible})$$

$$pH = 4.15$$

$$[OH\ ] = \frac{K_w}{[H^+]} \quad \frac{10^{\ 14}}{7 \quad 10^{\ 5}}$$

$$1.43 \quad 10^{\ 10} \text{ M}$$

77. Sodium acetate (CH_3COONa) is a basic salt (salt of strong base and weak acid) therefore, its aqueous solution has pH > 7.

78. mmol of NaOH = 20 0.2 = 4

mmol of acetic acid = 50 0.2 = 10

After neutralisation, buffer solution is formed which contain 6 mmol CH_3COOH and 4 mmol CH_3COONa.

$$pH \quad pK_a \quad \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\log(1.8 \quad 10^{\ 5}) \quad \log\frac{4}{6} \quad 4.56$$

Now, let x mmol of NaOH is further added so that pH of the resulting buffer solution is 4.74.

Now, the buffer solution contains (4 x) mmol CH_3COONa and (6 x) mmol of CH_3COOH.

$$4.74 \quad \log(1.8 \quad 10^{\ 5}) \quad \log\frac{4 \quad x}{6 \quad x}$$

$$\frac{4 \quad x}{6 \quad x} \quad 1$$

$$x \quad 1.0 \text{ mmol} \quad 0.2 \quad V$$

$$V \quad 5.0 \text{ mmol NaOH.}$$

79. For acidic buffer, the Henderson's equation is

$$pH = pK_a \quad \log\frac{(\text{mole of salt})}{(\text{mole of acid})}$$

$$4.75 = -\log(1.34 \quad 10^{\ 5}) \quad \log\frac{x}{0.02}$$

x 0.015 mole of sodium propionate.

Addition of 0.01 mole HCl will increase moles of propionic acid by 0.01 and moles of sodium propionate will decrease by same amount.

New moles of acid = 0.02 + 0.01 = 0.03

New moles of salt = 0.015 – 0.01 = 0.005

$$pH = -\log(1.34 \quad 10^{\ 5}) \quad \log\frac{0.005}{0.030} = 4.09$$

pH of 0.01 HCl = 2, just half of the pH of final buffer solution.