

## CHAPTER

## 7

## Equilibrium

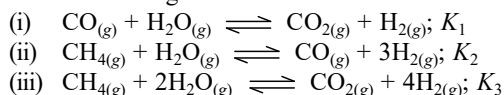
- An aqueous solution contains 0.10 M  $\text{H}_2\text{S}$  and 0.20 M  $\text{HCl}$ . If the equilibrium constants for the formation of  $\text{HS}^-$  from  $\text{H}_2\text{S}$  is  $1.0 \times 10^{-7}$  and that  $\text{S}^{2-}$  from  $\text{HS}^-$  ions is  $1.2 \times 10^{-13}$  then the concentration of  $\text{S}^{2-}$  ions in aqueous solution is  
(a)  $5 \times 10^{-8}$  (b)  $3 \times 10^{-20}$   
(c)  $6 \times 10^{-21}$  (d)  $5 \times 10^{-19}$  (2018)
- An aqueous solution contains an unknown concentration of  $\text{Ba}^{2+}$ . When 50 mL of a 1 M solution of  $\text{Na}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  just begins to precipitate. The final volume is 500 mL. The solubility product of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ . What is the original concentration of  $\text{Ba}^{2+}$ ?  
(a)  $5 \times 10^{-9}$  M (b)  $2 \times 10^{-9}$  M  
(c)  $1.1 \times 10^{-9}$  M (d)  $1.0 \times 10^{-10}$  M (2018)
- Which of the following are Lewis acids?  
(a)  $\text{PH}_3$  and  $\text{BCl}_3$  (b)  $\text{AlCl}_3$  and  $\text{SiCl}_4$   
(c)  $\text{PH}_3$  and  $\text{SiCl}_4$  (d)  $\text{BCl}_3$  and  $\text{AlCl}_3$  (2018)
- Which of the following salts is the most basic in aqueous solution?  
(a)  $\text{Al}(\text{CN})_3$  (b)  $\text{CH}_3\text{COOK}$   
(c)  $\text{FeCl}_3$  (d)  $\text{Pb}(\text{CH}_3\text{COO})_2$  (2018)
- In which of the following reactions, an increase in the volume of the container will favour the formation of products?  
(a)  $2\text{NO}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{O}_{2(g)}$  (b)  $3\text{O}_{2(g)} \rightleftharpoons 2\text{O}_{3(g)}$   
(c)  $\text{H}_{2(g)} + \text{I}_{2(g)} \rightleftharpoons 2\text{HI}_{(g)}$   
(d)  $4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightleftharpoons 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(l)}$  (Online 2018)
- The minimum volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution ( $K_{sp}$  of  $\text{PbCl}_2 = 3.2 \times 10^{-8}$ ; atomic mass of  $\text{Pb} = 207$  u) is  
(a) 0.36 L (b) 0.18 L (c) 17.98 L (d) 1.798 L (Online 2018)
- Which of the following is a Lewis acid?  
(a)  $\text{NaH}$  (b)  $\text{NF}_3$  (c)  $\text{PH}_3$  (d)  $\text{B}(\text{CH}_3)_3$  (Online 2018)
- Following four solutions are prepared by mixing different volumes of  $\text{NaOH}$  and  $\text{HCl}$  of different concentrations, pH of which one of them will be equal to 1?  
(a)  $75 \text{ mL } \frac{\text{M}}{5} \text{ HCl} + 25 \text{ mL } \frac{\text{M}}{5} \text{ NaOH}$   
(b)  $100 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 100 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$   
(c)  $55 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 45 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$   
(d)  $60 \text{ mL } \frac{\text{M}}{10} \text{ HCl} + 40 \text{ mL } \frac{\text{M}}{10} \text{ NaOH}$  (Online 2018)
- At a certain temperature in a 5 L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction,  
$$\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$$
  
At equilibrium, if one mole of  $\text{CO}$  is present then equilibrium constant ( $K_c$ ) for the reaction is  
(a) 4 (b) 3 (c) 2 (d) 2.5 (Online 2018)
- At 320 K, a gas  $A_2$  is 20% dissociated to  $A_{(g)}$ . The standard free energy change at 320 K and 1 atm in  $\text{J mol}^{-1}$  is approximately  
( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $\ln 2 = 0.693$ ;  $\ln 3 = 1.098$ )  
(a) 4281 (b) 4763 (c) 2068 (d) 1844 (Online 2018)
- The gas phase reaction,  $2\text{NO}_{2(g)} \rightarrow \text{N}_2\text{O}_{4(g)}$  is an exothermic reaction. The decomposition of  $\text{N}_2\text{O}_4$ , in equilibrium mixture of  $\text{NO}_{2(g)}$  and  $\text{N}_2\text{O}_{4(g)}$ , can be increased by  
(a) addition of an inert gas at constant volume  
(b) increasing the pressure  
(c) lowering the temperature  
(d) addition of an inert gas at constant pressure. (Online 2018)
- $\text{p}K_a$  of a weak acid ( $\text{HA}$ ) and  $\text{p}K_b$  of a weak base ( $\text{BOH}$ ) are 3.2 and 3.4 respectively. The pH of their salt ( $\text{AB}$ ) solution is  
(a) 7.0 (b) 1.0 (c) 7.2 (d) 6.9 (2017)
- Addition of sodium hydroxide solution to a weak acid ( $\text{HA}$ ) results in a buffer of pH 6. If ionisation constant of  $\text{HA}$  is  $10^{-5}$ , the ratio of salt to acid concentration in the buffer solution will be  
(a) 5 : 4 (b) 1 : 10 (c) 4 : 5 (d) 10 : 1 (Online 2017)
- 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M  $\text{HCl}$ . If  $\text{p}K_b$  of ammonia solution is 4.75, the pH of the mixture will be  
(a) 4.75 (b) 3.75 (c) 9.25 (d) 8.25 (Online 2017)
- The equilibrium constant at 298 K for a reaction,  $A + B \rightleftharpoons C + D$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of  $D$  (in  $\text{mol L}^{-1}$ ) will be  
(a) 0.182 (b) 0.818 (c) 1.818 (d) 1.182 (2016)

16. A solid  $XY$  kept in an evacuated sealed container undergoes decomposition to form a mixture of gases  $X$  and  $Y$  at temperature  $T$ . The equilibrium pressure is 10 bar in this vessel.  $K_p$  for this reaction is  
(a) 25 (b) 100 (c) 10 (d) 5  
(Online 2016)
17. The standard Gibbs energy change at 300 K for the reaction  $2A \rightleftharpoons B + C$  is 2494.2 J. At a given time, the composition of the reaction mixture is  $gW = \frac{6}{7} \lg Xi = 7 \text{ m.p } gYi = \frac{6}{7} 3$ . The reaction proceeds in the [ $R = 8.314 \text{ J/K/mol}$ ,  $e = 2.718$ ]  
(a) forward direction because  $Q < K_c$   
(b) reverse direction because  $Q < K_c$   
(c) forward direction because  $Q > K_c$   
(d) reverse direction because  $Q > K_c$ . (2015)
18. Gaseous  $N_2O_4$  dissociates into gaseous  $NO_2$  according to the reaction,  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ . At 300 K and 1 atm pressure, the degree of dissociation of  $N_2O_4$  is 0.2. If one mole of  $N_2O_4$  gas is contained in a vessel, then the density of the equilibrium mixture is  
(a) 1.56 g/L (b) 3.11 g/L  
(c) 4.56 g/L (d) 6.22 g/L (Online 2015)
19. For the equilibrium,  $A_{(g)} \rightleftharpoons B_{(g)}$ ,  $\Delta H$  is  $-40 \text{ kJ/mol}$ . If the ratio of the activation energies of the forward ( $E_f$ ) and reverse ( $E_b$ ) reactions is then  
(a)  $E_f = 60 \text{ kJ/mol}$ ;  $E_b = 100 \text{ kJ/mol}$   
(b)  $E_f = 30 \text{ kJ/mol}$ ;  $E_b = 70 \text{ kJ/mol}$   
(c)  $E_f = 80 \text{ kJ/mol}$ ;  $E_b = 120 \text{ kJ/mol}$   
(d)  $E_f = 70 \text{ kJ/mol}$ ;  $E_b = 30 \text{ kJ/mol}$ . (Online 2015)
20. The increase of pressure on ice  $\rightleftharpoons$  water system at constant temperature will lead to  
(a) no effect on that equilibrium  
(b) a decrease in the entropy of the system  
(c) a shift of the equilibrium in the forward direction  
(d) an increase in the Gibbs energy of the system.  
(Online 2015)
21. For the reaction,  $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ , if  $K_p = K_c(RT)^x$  where the symbols have usual meaning then the value of  $x$  is (assuming ideality)  
(a) 1 (b) -1 (c)  $-\frac{1}{2}$  (d)  $\frac{1}{2}$  (2014)
22. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?  
(a) 9.0 L (b) 0.1 L (c) 0.9 L (d) 2.0 L  
(2013)
23. The equilibrium constant ( $K_c$ ) for the reaction  $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$  at temperature  $T$  is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction,  $NO_{(g)} \rightarrow \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$  at the same temperature is  
(a)  $2.5 \times 10^2$  (b)  $4 \times 10^{-4}$   
(c) 50.0 (d) 0.02 (2012)
24. The pH of a 0.1 molar solution of the acid  $HQ$  is 3. The value of the ionization constant,  $K_a$  of this acid is  
(a)  $1 \times 10^{-3}$  (b)  $1 \times 10^{-5}$   
(c)  $1 \times 10^{-7}$  (d)  $3 \times 10^{-1}$  (2012)
25. A vessel at 1000 K contains  $CO_2$  with a pressure of 0.5 atm. Some of the  $CO_2$  is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of  $K$  is  
(a) 1.8 atm (b) 3 atm  
(c) 0.3 atm (d) 0.18 atm (2011)
26. At  $25^\circ\text{C}$ , the solubility product of  $Mg(OH)_2$  is  $1.0 \times 10^{-11}$ . At which pH, will  $Mg^{2+}$  ions start precipitating in the form of  $Mg(OH)_2$  from a solution of 0.001 M  $Mg^{2+}$  ions?  
(a) 8 (b) 9 (c) 10 (d) 11  
(2010)
27. Three reactions involving  $H_2PO_4^-$  are given below:  
(i)  $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$   
(ii)  $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$   
(iii)  $H_2PO_4^- + OH^- \longrightarrow H_3PO_4 + O^{2-}$   
In which of the above does  $H_2PO_4^-$  act as an acid?  
(a) (i) only (b) (ii) only  
(c) (i) and (ii) (d) (iii) only (2010)
28. Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as  $120 \text{ g mol}^{-1}$ ) to be added to 1 litre of 0.05M solution of silver nitrate to start the precipitation of AgBr is  
(a)  $5.0 \times 10^{-8} \text{ g}$  (b)  $1.2 \times 10^{-10} \text{ g}$   
(c)  $1.2 \times 10^{-9} \text{ g}$  (d)  $6.2 \times 10^{-5} \text{ g}$  (2010)
29. In aqueous solution the ionisation constants for carbonic acid are  
 $K_1 = 4.2 \times 10^{-7}$  and  $K_2 = 4.8 \times 10^{-11}$   
Select the correct statement for a saturated 0.034M solution of the carbonic acid.  
(a) The concentration of  $H^+$  is double that of  $CO_3^{2-}$ .  
(b) The concentration of  $CO_3^{2-}$  is 0.034 M.  
(c) The concentration of  $CO_3^{2-}$  is greater than that of  $HCO_3^-$ .  
(d) The concentration of  $H^+$  and  $HCO_3^-$  are approximately equal. (2010)
30. The correct order of increasing basicity of the given conjugate bases ( $R = CH_3$ ) is  
(a)  $RCOO^- < HC \equiv C^- < NH_2^- < R^-$   
(b)  $RCOO^- < HC \equiv C^- < R^- < NH_2^-$   
(c)  $R^- < HC \equiv C^- < RCOO^- < NH_2^-$   
(d)  $RCOO^- < NH_2^- < HC \equiv C^- < R^-$  (2010)
31. Solid  $Ba(NO_3)_2$  is gradually dissolved in a  $1.0 \times 10^{-4} \text{ M}$   $Na_2CO_3$  solution. At what concentration of  $Ba^{2+}$  will a precipitate begin to form? ( $K_{sp}$  for  $BaCO_3 = 5.1 \times 10^{-9}$ )  
(a)  $4.1 \times 10^{-5} \text{ M}$  (b)  $5.1 \times 10^{-5} \text{ M}$   
(c)  $8.1 \times 10^{-8} \text{ M}$  (d)  $8.1 \times 10^{-7} \text{ M}$  (2009)
32. Four species are listed below :  
(i)  $HCO_3^-$  (ii)  $H_3O^+$   
(iii)  $HSO_4^-$  (iv)  $HSO_3F$   
Which one of the following is the correct sequence of their acid strength?

- (a)  $\text{iii} < \text{i} < \text{iv} < \text{ii}$  (b)  $\text{iv} < \text{ii} < \text{iii} < \text{i}$   
(c)  $\text{ii} < \text{iii} < \text{i} < \text{iv}$  (d)  $\text{i} < \text{iii} < \text{ii} < \text{iv}$  (2008)

33. The  $\text{p}K_a$  of a weak acid, (HA), is 4.80. The  $\text{p}K_b$  of a weak base, BOH is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be  
(a) 9.22 (b) 9.58 (c) 4.79 (d) 7.01 (2008)

34. For the following three reactions (i), (ii) and (iii), equilibrium constants are given

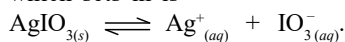


Which of the following relation is correct?

- (a)  $K_3 \cdot K_2^3 = K_1^2$  (b)  $K_1\sqrt{K_2} = K_3$   
(c)  $K_2 K_3 = K_1$  (d)  $K_3 = K_1 K_2$  (2008)

35. The equilibrium constants  $K_{p1}$  and  $K_{p2}$  for the reactions  $X \rightleftharpoons 2Y$  and  $Z \rightleftharpoons P + Q$ , respectively are in the ratio of 1 : 9. If degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is  
(a) 1 : 9 (b) 1 : 36 (c) 1 : 1 (d) 1 : 3 (2008)

36. In a saturated solution of the sparingly soluble strong electrolyte  $\text{AgIO}_3$  (molecular mass = 283) the equilibrium which sets in is



If the solubility product constant  $K_{sp}$  of  $\text{AgIO}_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $\text{AgIO}_3$  contained in 100 mL of its saturated solution?

- (a)  $1.0 \times 10^{-4}$  g (b)  $28.3 \times 10^{-2}$  g  
(c)  $2.83 \times 10^{-3}$  g (d)  $1.0 \times 10^{-7}$  g (2007)

37. The  $\text{p}K_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is  
(a) 7.0 (b) 4.5 (c) 2.5 (d) 9.5 (2007)

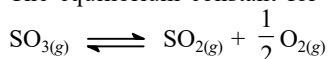
38. The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be  
(a)  $0.2 \times 10^5$  (b)  $5.0 \times 10^{-5}$   
(c)  $5.0 \times 10^{15}$  (d)  $5.0 \times 10^{-15}$  (2007)

39. Given the data at 25°C,  
 $\text{Ag} + \text{I}^- \rightarrow \text{AgI} + e^-; E^\circ = 0.152 \text{ V}$   
 $\text{Ag} \rightarrow \text{Ag}^+ + e^-; E^\circ = -0.800 \text{ V}$   
What is the value of  $\log K_{sp}$  for AgI?

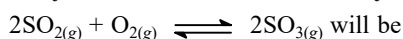
$$\left( 2.303 \frac{RT}{F} = 0.059 \text{ V} \right)$$

- (a) -8.12 (b) +8.612 (c) -37.83 (d) -16.13 (2006)

40. The equilibrium constant for the reaction,

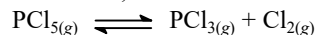


is  $K_c = 4.9 \times 10^{-2}$ . The value of  $K_c$  for the reaction



- (a) 416 (b)  $2.40 \times 10^{-3}$   
(c)  $9.8 \times 10^{-2}$  (d)  $4.9 \times 10^{-2}$  (2006)

41. Phosphorus pentachloride dissociates as follows in a closed reaction vessel,



If total pressure at equilibrium of the reaction mixture is  $P$  and degree of dissociation of  $\text{PCl}_5$  is  $x$ , the partial pressure of  $\text{PCl}_3$  will be

- (a)  $\left( \frac{x}{x+1} \right) P$  (b)  $\left( \frac{2x}{1-x} \right) P$  (c)  $\left( \frac{x}{x-1} \right) P$  (d)  $\left( \frac{x}{1-x} \right) P$  (2006)

42. An amount of solid  $\text{NH}_4\text{HS}$  is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm. pressure. Ammonium hydrogen sulphide decomposes to yield  $\text{NH}_3$  and  $\text{H}_2\text{S}$  gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for  $\text{NH}_4\text{HS}$  decomposition at this temperature is  
(a) 0.30 (b) 0.18 (c) 0.17 (d) 0.11 (2005)

43. Among the following acids which has the lowest  $\text{p}K_a$  value?

- (a)  $\text{CH}_3\text{COOH}$  (b)  $(\text{CH}_3)_2\text{CH}-\text{COOH}$   
(c)  $\text{HCOOH}$  (d)  $\text{CH}_3\text{CH}_2\text{COOH}$  (2005)

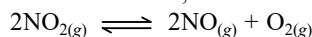
44. What is the conjugate base of  $\text{OH}^-$ ?

- (a)  $\text{O}_2$  (b)  $\text{H}_2\text{O}$  (c)  $\text{O}^-$  (d)  $\text{O}^{2-}$  (2005)

45. Hydrogen ion concentration in mol/L in a solution of  $\text{pH} = 5.4$  will be

- (a)  $3.98 \times 10^8$  (b)  $3.88 \times 10^6$   
(c)  $3.68 \times 10^{-6}$  (d)  $3.98 \times 10^{-6}$  (2005)

46. For the reaction,

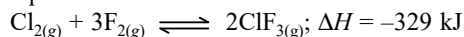


( $K_c = 1.8 \times 10^{-6}$  at  $184^\circ\text{C}$ ,  $R = 0.0831 \text{ kJ}/(\text{mol}\cdot\text{K})$ ).

When  $K_p$  and  $K_c$  are compared at  $184^\circ\text{C}$  it is found that

- (a)  $K_p$  is greater than  $K_c$  (b)  $K_p$  is less than  $K_c$   
(c)  $K_p = K_c$   
(d) whether  $K_p$  is greater than, less than or equal to  $K_c$  depends upon the total gas pressure. (2005)

47. The exothermic formation of  $\text{ClF}_3$  is represented by the equation:



Which of the following will increase the quantity of  $\text{ClF}_3$  in an equilibrium mixture of  $\text{Cl}_2$ ,  $\text{F}_2$  and  $\text{ClF}_3$ ?

- (a) Increasing the temperature  
(b) Removing  $\text{Cl}_2$   
(c) Increasing the volume of the container  
(d) Adding  $\text{F}_2$  (2005)

48. The solubility product of a salt having general formula  $\text{MX}_2$ , in water is  $4 \times 10^{-12}$ . The concentration of  $\text{M}^{2+}$  ions in the aqueous solution of the salt is

- (a)  $2.0 \times 10^{-6} \text{ M}$  (b)  $1.0 \times 10^{-4} \text{ M}$   
(c)  $1.6 \times 10^{-4} \text{ M}$  (d)  $4.0 \times 10^{-10} \text{ M}$  (2005)

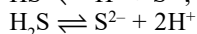
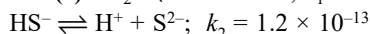
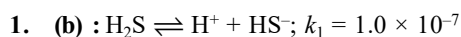
49. Consider an endothermic reaction  $X \rightarrow Y$  with the activation energies  $E_b$  and  $E_f$  for the backward and forward reactions, respectively. In general

- (a)  $E_b < E_f$  (b)  $E_b > E_f$   
 (c)  $E_b = E_f$   
 (d) there is no definite relation between  $E_b$  and  $E_f$ . (2005)
50. The molar solubility (in mol L<sup>-1</sup>) of a sparingly soluble salt  $MX_4$  is  $s$ . The corresponding solubility product is  $K_{sp}$ .  $s$  is given in terms of  $K_{sp}$  by the relation  
 (a)  $s = (K_{sp}/128)^{1/4}$  (b)  $s = (128K_{sp})^{1/4}$   
 (c)  $s = (256K_{sp})^{1/5}$  (d)  $s = (K_{sp}/256)^{1/5}$  (2004)
51. The equilibrium constant for the reaction,  
 $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$   
 at temperature  $T$  is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction :  
 $NO_{(g)} \rightleftharpoons \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$  at the same temperature is  
 (a)  $2.5 \times 10^2$  (b) 50  
 (c)  $4 \times 10^{-4}$  (d) 0.02 (2004)
52. For the reaction,  $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ , the  $K_p/K_c$  is equal to  
 (a)  $1/RT$  (b)  $RT$  (c)  $\sqrt{RT}$  (d) 1.0 (2004)
53. What is the equilibrium expression for the reaction  
 $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$ ?  
 (a)  $K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$  (b)  $K_c = \frac{[P_4O_{10}]}{5[P_4][O_2]}$   
 (c)  $K_c = [O_2]^5$  (d)  $K_c = \frac{1}{[O_2]^5}$  (2004)
54. The conjugate base of  $H_2PO_4^-$  is  
 (a)  $PO_4^{3-}$  (b)  $P_2O_5$  (c)  $H_3PO_4$  (d)  $HPO_4^{2-}$  (2004)
55. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value  
 (a) slightly lower than that of rain water without thunderstorm  
 (b) slightly higher than that when the thunderstorm is not there  
 (c) uninfluenced by occurrence of thunderstorm  
 (d) which depends on the amount of dust in air. (2003)
56. Which one of the following statements is not true?  
 (a) The conjugate base of  $H_2PO_4^-$  is  $HPO_4^{2-}$ .  
 (b)  $pH + pOH = 14$  for all aqueous solutions.  
 (c) The pH of  $1 \times 10^{-8}$  M HCl is 8.  
 (d) 96,500 coulombs of electricity when passed through a  $CuSO_4$  solution deposits 1 gram equivalent of copper at the cathode. (2003)
57. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_c$  is  
 (a)  $\Delta G = RT \ln K_c$  (b)  $-\Delta G = RT \ln K_c$   
 (c)  $\Delta G^\circ = RT \ln K_c$  (d)  $-\Delta G^\circ = RT \ln K_c$  (2003)
58. The solubility in water of a sparingly soluble salt  $AB_2$  is  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>. Its solubility product will be  
 (a)  $4 \times 10^{-15}$  (b)  $4 \times 10^{-10}$   
 (c)  $1 \times 10^{-15}$  (d)  $1 \times 10^{-10}$  (2003)
59. For the reaction equilibrium,  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$   
 the concentrations of  $N_2O_4$  and  $NO_2$  at equilibrium are  $4.8 \times 10^{-2}$  and  $1.2 \times 10^{-2}$  mol L<sup>-1</sup> respectively. The value of  $K_c$  for the reaction is  
 (a)  $3.3 \times 10^2$  mol L<sup>-1</sup> (b)  $3 \times 10^{-1}$  mol L<sup>-1</sup>  
 (c)  $3 \times 10^{-3}$  mol L<sup>-1</sup> (d)  $3 \times 10^3$  mol L<sup>-1</sup> (2003)
60. Consider the reaction equilibrium:  
 $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ ;  $\Delta H^\circ = -198$  kJ.  
 On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is  
 (a) lowering of temperature as well as pressure  
 (b) increasing temperature as well as pressure  
 (c) lowering the temperature and increasing the pressure  
 (d) any value of temperature and pressure. (2003)
61. In which of the following reactions, increase in the volume at constant temperature does not affect the number of moles at equilibrium?  
 (a)  $2NH_3 \rightarrow N_2 + 3H_2$  (b)  $C_{(g)} + (1/2)O_{2(g)} \rightarrow CO_{(g)}$   
 (c)  $H_{2(g)} + O_{2(g)} \rightarrow H_2O_{2(g)}$  (d) None of these. (2002)
62. Change in volume of the system does not alter the number of moles in which of the following equilibria?  
 (a)  $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$   
 (b)  $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$   
 (c)  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$   
 (d)  $SO_2Cl_{2(g)} \rightleftharpoons SO_{2(g)} + Cl_{2(g)}$  (2002)
63. For the reaction  
 $CO_{(g)} + (1/2)O_{2(g)} \rightleftharpoons CO_{2(g)}$ ,  $K_p/K_c$  is  
 (a)  $RT$  (b)  $(RT)^{-1}$  (c)  $(RT)^{-1/2}$  (d)  $(RT)^{1/2}$  (2002)
64. Let the solubility of an aqueous solution of  $Mg(OH)_2$  be  $x$  then its  $K_{sp}$  is  
 (a)  $4x^3$  (b)  $108x^5$  (c)  $27x^4$  (d)  $9x$  (2002)
65. Species acting as both Bronsted acid and base is  
 (a)  $(HSO_4)^-$  (b)  $Na_2CO_3$   
 (c)  $NH_3$  (d)  $OH^-$  (2002)
66. 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is  
 (a) not a buffer solution with  $pH < 7$   
 (b) not a buffer solution with  $pH > 7$   
 (c) a buffer solution with  $pH < 7$   
 (d) a buffer solution with  $pH > 7$ . (2002)

### ANSWER KEY

- |         |         |         |         |         |         |         |         |         |         |         |         |
|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (c)  | 3. (d)  | 4. (b)  | 5. (a)  | 6. (b)  | 7. (d)  | 8. (a)  | 9. (d)  | 10. (a) | 11. (d) | 12. (d) |
| 13. (d) | 14. (c) | 15. (c) | 16. (a) | 17. (d) | 18. (b) | 19. (c) | 20. (c) | 21. (c) | 22. (a) | 23. (c) | 24. (b) |
| 25. (a) | 26. (c) | 27. (b) | 28. (c) | 29. (d) | 30. (a) | 31. (b) | 32. (d) | 33. (d) | 34. (d) | 35. (b) | 36. (c) |
| 37. (d) | 38. (d) | 39. (d) | 40. (a) | 41. (a) | 42. (d) | 43. (b) | 44. (d) | 45. (d) | 46. (a) | 47. (d) | 48. (b) |
| 49. (a) | 50. (d) | 51. (b) | 52. (a) | 53. (d) | 54. (d) | 55. (a) | 56. (c) | 57. (d) | 58. (c) | 59. (c) | 60. (c) |
| 61. (d) | 62. (a) | 63. (c) | 64. (a) | 65. (a) | 66. (a) |         |         |         |         |         |         |

# Explanations



$$K = k_1 \times k_2 = 1.0 \times 10^{-7} \times 1.2 \times 10^{-13} = 1.2 \times 10^{-20}$$

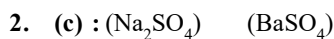
$$K = \frac{[\text{S}^{2-}][\text{H}^+]^2}{[\text{H}_2\text{S}]} = 1.2 \times 10^{-20}; [\text{S}^{2-}] = \frac{1.2 \times 10^{-20} \times [\text{H}_2\text{S}]}{[\text{H}^+]^2}$$

$$[\text{H}_2\text{S}] = 0.1 \text{ M}$$

$$[\text{HCl}] = 0.2 \text{ M}$$

As HCl is stronger acid so,  $[\text{H}^+] = 0.2 \text{ M}$

$$[\text{S}^{2-}] = \frac{1.2 \times 10^{-20} \times 0.1}{(0.2)^2} = 3 \times 10^{-20} \text{ M}$$



$$\frac{M_1 V_1}{1 \text{ M} \times 50} = \frac{M_2 V_2}{M_2 \times 500}$$

$$M_2 = \frac{50}{500} = \frac{1}{10}$$

For just precipitation,  $Q_{sp} = K_{sp}$ ;  $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_{sp}(\text{BaSO}_4)$

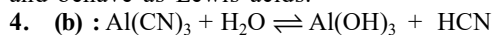
$$\text{Ba}^{2+} \times \frac{1}{10} = 10^{-10} \Rightarrow \text{Ba}^{2+} = 10^{-9} \text{ M in } 500 \text{ mL}$$

Initially,  $[\text{Ba}^{2+}]$  in original solution (450 mL)

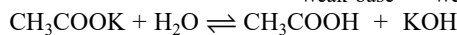
$$M_1 \times 450 = 10^{-9} \times 500$$

$$M_1 = \frac{500 \times 10^{-9}}{450} = 1.1 \times 10^{-9} \text{ M}$$

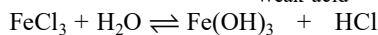
3. (d) : The compound which can accept a pair of electrons is known as Lewis acid.  $\text{BCl}_3$  and  $\text{AlCl}_3$  have vacant orbitals and their octet is not complete thus these can accept electron pairs and behave as Lewis acids.



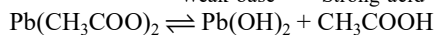
Weak base      Weak acid



Weak acid      Strong base



Weak base      Strong acid

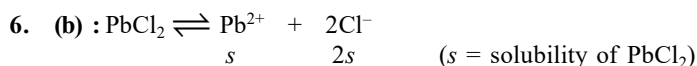


Weak base      Weak acid

Hence, for the  $\text{CH}_3\text{COOK}$ , nature of solution is basic.

5. (a) : According to Boyle's law : Pressure  $\propto \frac{1}{\text{Volume}}$

*i.e.*, when volume of the container is increased, the pressure decreases. To undo the effect of decreased pressure, the reaction will move in a direction where pressure increases *i.e.*, towards the greater moles of gaseous substances. This is in accordance with Le Chatelier's principle.



$s \qquad \qquad 2s \qquad \qquad (s = \text{solubility of } \text{PbCl}_2)$

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

$$3.2 \times 10^{-8} = s \times (2s)^2 = 4s^3 \Rightarrow s = 2 \times 10^{-3} \text{ M}$$

$$\text{Solubility} = \frac{n_{\text{PbCl}_2}}{\text{Volume (in L)}}$$

$$s = \frac{0.1}{278} \times \frac{1}{V} = 2 \times 10^{-3} \Rightarrow V = \frac{0.1}{278} \times \frac{10^3}{2} = 0.1798 \approx 0.18 \text{ L}$$

7. (d)



(a) 25 mL NaOH will react with 25 mL HCl

Total volume of solution = 75 + 25 = 100 mL

$$\text{Millimoles of HCl left} = \frac{75}{5} - \frac{25}{5} = 10$$

$$\text{Concentration of HCl} = \frac{\text{Millimoles}}{\text{Volume}} = \frac{10}{100} = 0.1 \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log[0.1] = 1$$

(b) This will be a neutral solution *i.e.*, pH = 7

$$(c) \text{ Millimoles of HCl left} = \frac{55}{10} - \frac{45}{10} = 5.5 - 4.5 = 1$$

$$\text{Concentration of HCl} = \frac{1}{100} = 0.01 \text{ M}$$

$$\therefore \text{pH} = 2$$

$$(d) \text{ Millimoles of HCl left} = \frac{60}{10} - \frac{40}{10} = 6 - 4 = 2$$

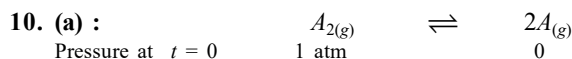
$$\text{Concentration of HCl} = \frac{2}{100} = 0.02 \text{ M}$$

$$\therefore \text{pH} = 1.69$$



Initial moles	2	3	0
At equil.	1	2	1

$$K_c = \frac{[\text{COCl}_2]}{[\text{CO}][\text{Cl}_2]} = \frac{\frac{1}{5}}{\left(\frac{1}{5}\right)\left(\frac{2}{5}\right)} = \frac{5}{2} = 2.5$$



Pressure at  $t = 0$

1 atm

0

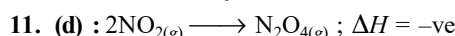
At eq.

$$1 - \frac{20}{100} = 0.8 \text{ atm}$$

$$2 \times \frac{20}{100} = 0.4 \text{ atm}$$

$$\text{Equilibrium constant, } K_p = \frac{(P_A)^2}{P_{A_2}} = \frac{(0.4)^2}{0.8} = 0.2$$

$$\Delta G^\circ = -2.303 RT \log K_p = -2.303 \times 8.314 \times 320 \log 0.2 = 4282.64 \text{ J mol}^{-1}$$



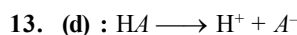
According to Le-Chatelier's principle, when inert gas is added at constant pressure, the total volume increases which leads to decrease in molar concentration of reactant and product. Thus, the reaction moves towards backward direction and decomposition of  $\text{N}_2\text{O}_4$  increases. Addition of inert gas at constant volume does not affect equilibrium.

On increasing the pressure, the reaction moves towards forward direction (lesser moles).

On lowering temperature, the reaction moves to forward direction as it is an exothermic reaction.

12. (d) : pH of a salt of a weak acid and a weak base is given by :

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b) = 7 + \frac{1}{2} (3.2 - 3.4) = 6.9$$

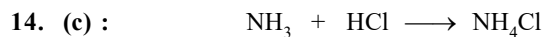


$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 10^{-5}; \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$6 = -\log[10^{-5}] + \log \frac{[\text{Salt}]}{[\text{Acid}]} \Rightarrow 6 = 5 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = \text{Antilog } 1 = 10$$

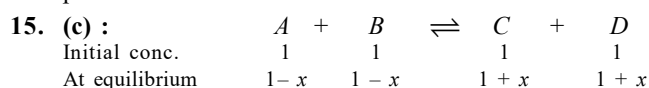
$$[\text{Salt}] : [\text{Acid}] = 10 : 1$$



Initial	$\frac{50 \times 0.2}{1000}$	$\frac{25 \times 0.2}{1000}$	
After reaction :	= 10	= 5	0
Buffer solution :	5	0	5

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]} = 4.75$$

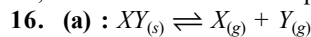
$$\text{pH} = 14 - 4.75 = 9.25$$



$$V \left\{ \frac{1}{1} = \frac{gY_i g_i}{gW_i g_i} \Rightarrow 655 = \frac{-6 + \frac{7}{6}}{-6 - \frac{7}{6}} \Rightarrow 65 = \frac{6 + \frac{7}{6}}{6 - \frac{7}{6}} \right.$$

$$10 - 10x = 1 + x \Rightarrow 9 = 11x \Rightarrow x = 0.818$$

$$\text{So, concentration of D at equilibrium} = 1 + 0.818 = 1.818 \text{ M}$$

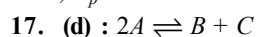


$$K_p = (p_X)(p_Y)$$

$$p_X = x_X \times P_{\text{Total}} = \frac{1}{2} \times 10 = 5 \text{ bar}$$

$$\text{Similarly, } p_Y = \frac{1}{2} \times 10 = 5 \text{ bar}$$

$$\text{Now, } K_p = 5 \times 5 = 25$$



$$\text{Given : } T = 300 \text{ K, } \Delta G^\circ = 2494.2 \text{ J, } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

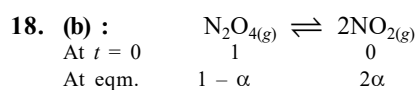
$$\Delta G^\circ = -2.303 RT \log K_c$$

$$2494.2 = -2.303 \times 8.314 \times 300 \times \log K_c$$

$$\log K_c = \text{antilog} (-0.4342) \Rightarrow K_c = 0.3679$$

$$n = \frac{gX_i gY_i}{gW_i^7} = \frac{7 \times \frac{6}{7}}{\left(\frac{6}{7}\right)^7} = 9$$

Here,  $Q_c > K_c$  thus, the reaction will proceed in the backward direction.



where  $\alpha$  is degree of dissociation.

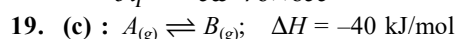
$$\text{Mol. wt. of mixture } (M_{\text{mix.}}) = \frac{-6 - \alpha \times j}{-6 + \alpha} \times \frac{V_7 W_9 + 7\alpha \times j}{V W_7}$$

$$= \frac{-6 - 53 \times 7 + 7 \times 53 \times 9}{-6 + 53} = < 3;$$

Now, as per ideal gas equation,  $PV = nRT$

$$PM_{\text{mix.}} = dRT$$

$$\therefore \frac{nj}{oq} = \frac{6 \times < 3}{53 \times 7 \times 855} = 836 \text{ s4}$$

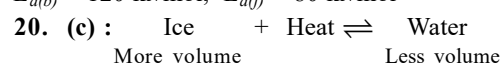


$$\frac{b}{b} = \frac{7}{8}$$

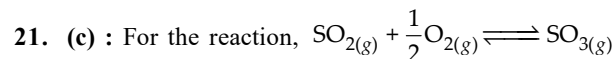
We know that,  $E_{a(f)} - E_{a(b)} = \Delta H$

$$E_{a(f)} - E_{a(b)} = -40 \Rightarrow \frac{7}{8}b - b = -95$$

$$E_{a(b)} = 120 \text{ kJ/mol, } E_{a(f)} = 80 \text{ kJ/mol}$$



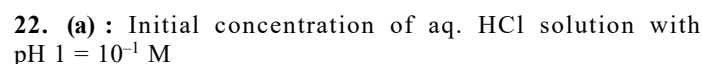
On increasing the pressure on this system in equilibrium, the equilibrium tends to shift in a direction in which volume decreases, i.e., in the forward direction.



$$\text{Using formula, } K_p = K_c(RT)^{\Delta n_g}$$

$$\text{where, } \Delta n_g = \text{no. of products}_{(g)} - \text{no. of reactants}_{(g)}$$

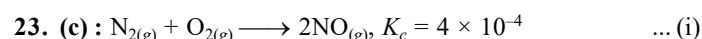
$$= 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2} = x$$



$$\text{Final concentration of this solution after dilution} = 10^{-2} \text{ M}$$

$$MV = M_1(V_1 + V_2) \Rightarrow 10^{-1} \times 1 = 10^{-2} (1 + V_2)$$

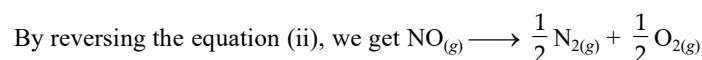
$$\frac{0.1}{0.01} = 1 + V_2 \Rightarrow 10 = 1 + V_2 \Rightarrow V_2 = 9 \text{ L}$$



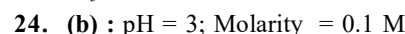
By multiplying the equation (i) by  $\frac{1}{2}$



$$K'_c = \sqrt{K_c} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2}$$



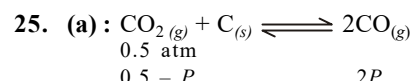
$$K''_c = \frac{1}{K'_c} = \frac{1}{2 \times 10^{-2}} = 50.0$$



$$[\text{H}^+] = \sqrt{K_a C}$$

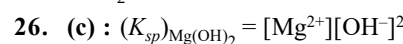
$$\text{H}^+ = 10^{-\text{pH}} = 10^{-3}$$

$$10^{-3} = \sqrt{K_a \times 0.1} \Rightarrow 10^{-6} = K_a \times 0.1 \Rightarrow K_a = 10^{-5}$$



$$\text{Total pressure} = 0.5 - P + 2P = 0.8 \Rightarrow P = 0.3$$

$$K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(2P)^2}{(0.5 - P)} = \frac{(0.6)^2}{(0.5 - 0.3)} = 1.8 \text{ atm}$$

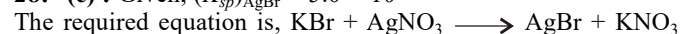
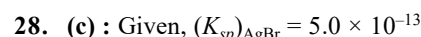


$$1 \times 10^{-11} = [0.001][\text{OH}^-]^2 \Rightarrow [\text{OH}^-]^2 = \frac{10^{-11}}{10^{-3}} = 10^{-8} \Rightarrow [\text{OH}^-] = 10^{-4}$$

$$\text{pOH} = 4$$

$$\text{Thus, pH} = 14 - 4 = 10$$

27. (b) : In equation (ii),  $\text{H}_2\text{PO}_4^-$  acts as a proton donor and thus, acts as an acid.



$$\text{Given, } [\text{AgNO}_3] = 0.05 \text{ M; } [\text{Ag}^+] = [\text{NO}_3^-] = 0.05 \text{ M}$$

$$\therefore [\text{Ag}^+][\text{Br}^-] = (K_{sp})_{\text{AgBr}}$$

$$\Rightarrow 0.05 \times [\text{Br}^-] = 5 \times 10^{-13} \Rightarrow [\text{Br}^-] = \frac{5 \times 10^{-13}}{5 \times 10^{-2}} = 1 \times 10^{-11} \text{ M}$$

$$\therefore [K^+] = [Br^-] = [KBr] \Rightarrow [KBr] = 1 \times 10^{-11} \text{ M}$$

$$\text{Molarity} = \frac{n_{KBr}}{V_{\text{Solution}}(\text{L})}$$

$$1 \times 10^{-11} = \frac{w_{KBr} / 120}{1} \quad (\text{Mol. wt. of KBr} = 120)$$

$$\Rightarrow w_{KBr} = 1 \times 10^{-11} \times 120 = 120 \times 10^{-11} = 1.2 \times 10^{-9} \text{ g}$$

$$29. \text{ (d) : } H_2CO_3 \rightleftharpoons H^+ + HCO_3^-; K_1 = 4.2 \times 10^{-7}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}; K_2 = 4.8 \times 10^{-11}$$

$\therefore K_1 \gg K_2$ , so  $H_2CO_3$  ionises more than  $HCO_3^-$  and hence, contribution of  $H^+$  is mostly due to ionisation of carbonic acid, thus the concentrations of  $H^+$  and  $HCO_3^-$  are approximately equal.

30. (a) : The order of acidity can be explained on the basis of the acidity of the acids of the given conjugate base. Stronger is the acid, weaker is the conjugate base. Since  $RCOOH$  is the strongest acid amongst all,  $RCOO^-$  is the weakest base. Due to  $sp$  hybridised carbon, acetylene is also acidic and hence a weak base but stronger than  $RCOO^-$ . As  $sp^3$  carbon is less electronegative than  $sp^3$  nitrogen,  $R^-$  is more basic than  $NH_2^-$ .

$$31. \text{ (b) : } K_{sp} \text{ for } BaCO_3 = [Ba^{2+}][CO_3^{2-}]$$

$$\text{given, } [CO_3^{2-}] = 1 \times 10^{-4} \text{ M} \quad (\text{from } Na_2CO_3)$$

$$K_{sp} = 5.1 \times 10^{-9}$$

$$\therefore 5.1 \times 10^{-9} = [Ba^{2+}] \times [10^{-4}] \Rightarrow [Ba^{2+}] = 5.1 \times 10^{-5} \text{ M}$$

Thus, when  $[Ba^{2+}] = 5.1 \times 10^{-5} \text{ M}$ ,  $BaCO_3$  precipitate will begin to form.

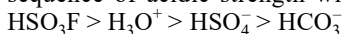
32. (d) :  $HSO_3F$  is the super acid. Its acidic strength is greater than any given species. The  $pK_a$  value of other species are given below :

$$HCO_3^- \rightarrow 10.25$$

$$H_3O^+ \rightarrow -1.74$$

$$HSO_4^- \rightarrow 1.92$$

Lesser the  $pK_a$  value, higher will be its acidic strength. Hence sequence of acidic strength will be

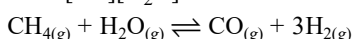


$$33. \text{ (d) : Given that } pK_a = 4.8 \text{ and } pK_b = 4.78$$

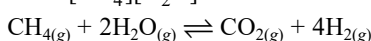
$$\therefore pH = 7 + 1/2 (pK_a - pK_b) = 7 + 1/2 (4.80 - 4.78) = 7.01$$

$$34. \text{ (d) : } CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

$$K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \dots(i)$$



$$K_2 = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \quad \dots(ii)$$



$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} \quad \dots(iv)$$

From equations (i), (ii) and (iii) ;  $K_3 = K_1 \times K_2$

$$35. \text{ (b) : } X \rightleftharpoons 2Y; \quad Z \rightleftharpoons P + Q$$

$$\begin{array}{cccccc} \text{Initial mol.} & 1 & 0 & 1 & 0 & 0 \\ \text{At equilibrium} & 1 - \alpha & 2\alpha & 1 - \alpha & \alpha & \alpha \end{array}$$

$$K_{p_1} = \frac{p_Y^2}{p_X} = \frac{\left(\frac{2\alpha}{1+\alpha} p_1\right)^2}{\left(\frac{1-\alpha}{1+\alpha} p_1\right)}$$

$$K_{p_2} = \frac{p_P p_Q}{p_Z} = \frac{\left(\frac{\alpha}{1+\alpha} p_2\right) \left(\frac{\alpha}{1+\alpha} p_2\right)}{\left(\frac{1-\alpha}{1+\alpha} p_2\right)}$$

$$\Rightarrow K_{p_1} = \frac{4\alpha^2 p_1}{1-\alpha^2} \quad \dots(i) \Rightarrow K_{p_2} = \frac{\alpha^2 p_2}{1-\alpha^2} \quad \dots(ii)$$

$$\text{Given is } \frac{K_{p_1}}{K_{p_2}} = \frac{1}{9} \quad \dots(iii)$$

Substituting values of from equation (i) and (ii) into (iii), we get

$$\frac{\frac{4\alpha^2 p_1}{1-\alpha^2}}{\frac{\alpha^2 p_2}{1-\alpha^2}} = \frac{1}{9} \Rightarrow \frac{4 p_1}{p_2} = \frac{1}{9} \Rightarrow \frac{p_1}{p_2} = \frac{1}{36}$$

$$36. \text{ (c) : } AgIO_3 \rightleftharpoons Ag^+ + IO_3^- \quad [S = \text{Solubility}]$$

$$K_{sp} = S^2 \Rightarrow S^2 = 1.0 \times 10^{-8}$$

$$S = 1.0 \times 10^{-4} \text{ mol/L}$$

$$= 1.0 \times 10^{-4} \times 283 \text{ g/L} = \frac{1.0 \times 10^{-4} \times 283}{1000} \text{ g/L}$$

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ g/100mL}$$

$$= 28.3 \times 10^{-4} \text{ g/100 mL} = 2.83 \times 10^{-3} \text{ g/100 mL}$$

$$37. \text{ (d) : For acidic buffer, } pH = pK_a + \log \frac{[A^-]}{[HA]}$$

When the acid is 50% ionised,  $[A^-] = [HA]$

$$pH = pK_a + \log 1 \Rightarrow pH = pK_a$$

$$\text{Given } pK_a = 4.5; pH = 4.5$$

$$\therefore pOH = 14 - 4.5 = 9.5$$

$$38. \text{ (d) : } H_2A \rightleftharpoons H^+ + HA^-;$$

$$K_1 = \frac{[H^+][HA^-]}{[H_2A]} = 1 \times 10^{-5}$$

$$HA^- \rightleftharpoons H^+ + A^{2-}; K_2 = 5 \times 10^{-10} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

$$K = \frac{[H^+]^2[A^{2-}]}{[H_2A]} = K_1 \times K_2 = 1 \times 10^{-5} \times 5 \times 10^{-10} = 5 \times 10^{-15}$$

$$39. \text{ (d) : } AgI_{(s)} + e^- \rightarrow Ag_{(s)} + I^-, E^\circ = -0.152 \text{ V}$$

$$Ag_{(s)} \rightarrow Ag^+ + e^-, E^\circ = -0.800 \text{ V}$$

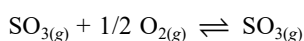
$$AgI_{(s)} \rightarrow Ag^+ + I^-, E^\circ = -0.952 \text{ V}$$

$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K \Rightarrow -0.952 = \frac{0.059}{1} \log K_{sp}$$

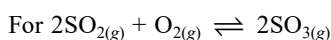
$$\text{or, } \log K_{sp} = -\frac{0.952}{0.059} = -16.135$$

$$40. \text{ (a) : } SO_{3(g)} \rightleftharpoons SO_{2(g)} + 1/2 O_{2(g)}$$

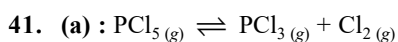
$$\frac{[SO_2][O_2]^{1/2}}{[SO_3]} = K_c = 4.9 \times 10^{-2} \quad \dots(i)$$



$$\frac{[SO_3]}{[SO_2][O_2]^{1/2}} = K'_c = \frac{1}{4.9 \times 10^{-2}} \quad \dots(ii)$$



$$\frac{[SO_3]^2}{[SO_2]^2 [O_2]} = K_c'^2 = \frac{1}{4.9 \times 4.9 \times 10^{-4}} = \frac{10000}{24.01} = 416.49$$



$$\begin{array}{ccccc} t = 0 & 1 & 0 & 0 \\ t_{eq} & 1-x & x & x \end{array}$$

Total number of moles =  $1 - x + x + x = 1 + x$

Thus partial pressure of  $\text{PCl}_3 = \left( \frac{x}{1+x} \right) P$



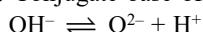
$$\begin{array}{ccccc} \text{Initial pressure} & 0 & 0.5 & 0 \\ \text{At equi.} & 0 & 0.5+x & x \end{array}$$

Total pressure =  $0.5 + 2x = 0.84 \Rightarrow x = 0.17 \text{ atm}$

$K_p = p_{\text{NH}_3} \times p_{\text{H}_2\text{S}} = (0.5 + 0.17)(0.17) = 0.11 \text{ atm}^2$

43. (b) : Higher the  $\text{p}K_a$  value, weaker is the acid. Hence, strongest acid has lowest  $\text{p}K_a$  value.

44. (d) : Conjugate base of  $\text{OH}^-$  is  $\text{O}^{2-}$ .



45. (d) :  $\text{pH} = -\log[\text{H}^+]$

$$[\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-5.4) = 3.98 \times 10^{-6}$$

46. (a) :  $K_p = K_c (RT)^{\Delta n}$  ;  $\Delta n = 3 - 2 = 1$

$$K_p = K_c (0.0831 \times 457)^1$$

$$\therefore K_p > K_c$$

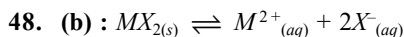
47. (d) :  $\text{Cl}_{2(g)} + 3\text{F}_{2(g)} \rightleftharpoons 2\text{ClF}_{3(g)}$  ;  $\Delta H = -329 \text{ kJ}$

Favourable conditions:

(i) As the reaction is exothermic, hence decrease in temperature will favour the forward reaction.

(ii) Addition of reactants or removal of product will favour the forward reaction.

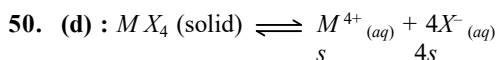
(iii) Here  $\Delta n = 2 - 4 = -2$  (i.e., -ve) hence decrease in volume or increase in pressure will favour the forward reaction.



$$\begin{array}{c} s \qquad \qquad 2s \\ K_{sp} = s \cdot (2s)^2 = 4s^3 \Rightarrow 4 \times 10^{-12} = 4s^3 \Rightarrow s^3 = 1 \times 10^{-12} \\ \Rightarrow s = 1 \times 10^{-4} \text{ M} \Rightarrow [\text{M}^{2+}] = 1 \times 10^{-4} \text{ M} \end{array}$$

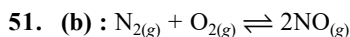
49. (a) : For endothermic reaction,  $\Delta H = +ve$

$$\Rightarrow \Delta H = E_f - E_b, \text{ it means } E_b < E_f$$

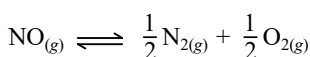


$$\text{Solubility product, } K_{sp} = s \times (4s)^4 = 256 s^5.$$

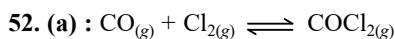
$$\therefore s = \sqrt[5]{\frac{K_{sp}}{256}} = \left( \frac{K_{sp}}{256} \right)^{1/5}$$



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 4 \times 10^{-4}$$

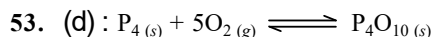


$$K'_c = \frac{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}{[\text{NO}]} = \frac{1}{\sqrt{K_c}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = \frac{100}{2} = 50$$



$$\Delta n = 1 - 2 = -1$$

$$K_p = K_c (RT)^{\Delta n} \Rightarrow \frac{K_p}{K_c} = (RT)^{-1} = \frac{1}{RT}$$



$$K_c = \frac{[\text{P}_4\text{O}_{10(s)}]}{[\text{P}_{4(s)}][\text{O}_{2(g)}]^5}$$

We know that concentration of a solid component is always taken as unity.

$$K_c = \frac{1}{[\text{O}_2]^5}$$

54. (d) : Conjugate base is formed by the removal of  $\text{H}^+$  from acid.  $\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} + \text{H}^+$

55. (a) : Due to thunderstorm, temperature increases. As temperature increases,  $[\text{H}^+]$  also increases, hence pH decreases.

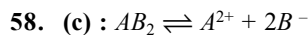
56. (c) : pH of an acid cannot exceed 7. Here we should also consider  $[\text{H}^+]$  that comes from  $\text{H}_2\text{O}$ .

$$\begin{aligned} \text{Now } [\text{H}^+] &= [\text{H}^+]_{\text{from HCl}} + [\text{H}^+]_{\text{from H}_2\text{O}} \\ &= 10^{-8} + 10^{-7} = 10^{-8} + 10 \times 10^{-8} = 11 \times 10^{-8} \\ \therefore \text{pH} &= -\log(11 \times 10^{-8}) = 6.9587 \end{aligned}$$

57. (d) :  $\Delta G = \Delta G^\circ + 2.303 RT \log K_c$

At equilibrium,  $\Delta G = 0$

$$\Delta G^\circ = -2.303 RT \log K_c$$



$$S = 1.0 \times 10^{-5} \text{ mol L}^{-1}$$

$$K_{sp} = [\text{A}^{2+}][\text{B}^-]^2 = 1.0 \times 10^{-5} \times (1.0 \times 10^{-5})^2 = 1.0 \times 10^{-15}$$

59. (c) :  $[\text{N}_2\text{O}_4] = 4.8 \times 10^{-2} \text{ mol L}^{-1}$  ;  $[\text{NO}_2] = 1.2 \times 10^{-2} \text{ mol L}^{-1}$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{1.2 \times 10^{-2} \times 1.2 \times 10^{-2}}{4.8 \times 10^{-2}} = 0.3 \times 10^{-2} = 3 \times 10^{-3} \text{ mol L}^{-1}$$

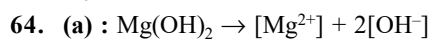
60. (c) : The conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is an exothermic reaction, hence decrease the temperature will favour the forward reaction. There is also a decrease in volume or moles in product side. Thus the reaction is favoured by low temperature and high pressure. (Le Chatelier's principle).

61. (d) : For those reactions, where  $\Delta n = 0$ , increase in volume at constant temperature does not affect the number of moles at equilibrium.

62. (a) : In this reaction the ratio of number of moles of reactants to products is same i.e. 2 : 2, hence change in volume will not alter the number of moles.

$$63. (c) : K_p = K_c (RT)^{\Delta n} ; \Delta n = 1 - \left( 1 + \frac{1}{2} \right) = 1 - \frac{3}{2} = -\frac{1}{2}$$

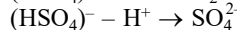
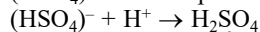
$$\therefore \frac{K_p}{K_c} = (RT)^{-1/2}$$



$$\begin{array}{c} x \qquad \qquad 2x \\ K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 \Rightarrow K_{sp} = (x) \times (2x)^2 = x \times 4x^2 = 4x^3 \end{array}$$

65. (a) : According to Bronsted-Lowry concept, a Bronsted acid is a substance which can donate a proton to any other substance and a Bronsted base is a substance which can accept a proton from any other substance.

$(\text{HSO}_4)^-$  can accept and donate a proton.



66. (a) :  $\text{HCl}$  is a strong acid and its salt do not form buffer solution. As the resultant solution is acidic, hence pH is less than 7.

