9
Chapter

EQUILIBRIUM-2 (IONIC EQUILIBRIUM)

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. The dissociation constants of a weak acid HA and weak base BOH are 2×10^{-5} and 5×10^{-6} respectively. The equilibrium constant for the neutralization reaction of the two is :
(a) 1.0×10^{-4} (b) 1.0×10^{-10}
(c) 2.5×10^{-1} (d) 1.0×10^{4}

2. At certain temperature K_w for water 4.0×10^{-14}. Which of the following is wrong for pure water at this temperature?
(a) pH = 6.699 ; water is acidic
(b) pH = 6.699 ; water is neutral
(c) pOH = 6.699 ; water is neutral
(d) pH + pOH = 13.398 ; water is neutral

3. If the equilibrium constant of $BOH \rightleftharpoons \overset{+}{B} + \overset{-}{OH}$ at 25ºC is 2.5×10^{-6}, then equilibrium constant for $BOH + H_3\overset{+}{O} \rightleftharpoons \overset{+}{B} + 2H_2O$ at the same temperature is :
(a) 4.0×10^{-9} (b) 2.5×10^{8}
(c) 4.0×10^{9} (d) 2.5×10^{-8}

4. The degree of dissociation of 1.0 *M* weak acid, HA, is 0.5%. If 2 ml of 1.0 *M* HA solution is diluted to 32 ml, the degree of dissociation of the acid and H_3O^+ ion concentration in the resulting solution will be respectively:
(a) 0.02 and 3.125×10^{-4}
(b) 0.02 and 1.25×10^{-3}
(c) 1.25×10^{-3} and 0.02
(d) 0.02 and 8.0×10^{-12}

5. Ionization constants of a weak acid HA and weak base BOH are 3.0×10^{-7} each at 298 K. The percent degree of hydrolysis of their salt at the dilution of 10 L is :
(a) 40 (b) 50
(c) 75 (d) 25

6. pH of a solution obtained on mixing 50 ml of 0.1 *M* NaCN and 50 ml of 0.2 *M* HCl will be (p^{Ka} for HCN = 9.40)
(a) 1.30 (b) 1.00
(c) 9.40 (d) 9.10

7. Which of the following increasing order of pH of 0.1 *M* solution of the compounds (A) $HCOONH_4$, (B) CH_3COONH_4, (C) CH_3COONa and (D) NH_4Cl is correct ?
(a) A < D < B < C (b) D < A < C < B
(c) A < D < C < B (d) D < A < B < C

8. The pH of a weak mono acid base at 80% neutralization with a strong acid in a dilute solution is 7.40. The ionization constant of the base is :
(a) 1.0×10^{-6} (b) 1.6×10^{-7}
(c) 1.0×10^{-5} (d) none of these

9. pH of a solution containing 0.3 *M* HA and 0.1 *M* A^- (K_b for $A^- = 1.0 \times 10^{-5}$) is :
(a) 5 + log 3 (b) 5 – log 3
(c) 9 + log 3 (d) 9 – log 3

10. The pH at the equivalence point of titration of 0.2 *M* NH_3 with 0.2 *M* HCl is : (p^{Kb} of NH_3 = 4.74)
(a) 9.72 (b) 9.87
(c) 5.13 (d) 4.98

11. A weak base BOH is titrated with a strong acid HA. When 10 ml of HA is added, the pH is found to be 9.00 and when 25 ml is added, pH is 8.00. The volume of the acid required to reach the equivalence point
(a) 35 ml (b) 40 ml
(c) 30 ml (d) 50 ml

12. pH of 0.5 *M* $Ba(CN)_2$ solution (pK_b of CN^- = 9.30) is :
(a) 8.35 (b) 3.35
(c) 9.35 (d) 9.50

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ			

13. At the isoelectric pH the ion $H_3\overset{+}{N}CH_2COO^-$, when subjected to electric field, migrates

(a) toward cathode
(b) toward anode
(c) toward both anode and cathode
(d) in neither direction

14. The pH of a solution of a weak base at its half neutralization with a strong acid is 8. K_b for the base is

(a) 1.0×10^{-8} (b) 1.0×10^{-6}
(c) 1.0×10^{-4} (d) none of these

15. On increasing the temperature of pure water

(a) Both pH and pOH increase
(b) both pH and pOH decrease
(c) pH increases and pOH decreases
(d) pH decreases and pOH increases

16. Solubility of CaF_2 in a solution of 0.1 *M* $Ca(NO_3)_2$ is given by

(a) $[Ca^{2+}]$ (b) $[F^-]$
(c) $\frac{1}{2}[F^-]$ (d) $2[NO_3^-]$

17. 1.0 ml of dilute solution of NaOH is added to 100 ml of a buffer of pH 4. The pH of the resulting solution

(a) becomes 7.0
(b) becomes 9.0
(c) becomes 3.0
(d) remains practically unchanged

18. In which of the following cases pH is greater than 7?

(a) 50 ml of 0.1 *M* HCl + 50 ml of 0.1 *M* NaCl
(b) 50 ml of 0.1 *M* H_2SO_4 + 50 ml of 0.2 *M* NaOH
(c) 50 ml of 0.1 *M* CH_3COOH + 50 ml of 0.1 *M* KOH
(d) 50 ml of 0.1 *M* HNO_3 + 50 ml of 0.1 *M* NH_3

19. The solubility product of an electrolyte AB_3 type is 2.7×10^{-19} $(mol\ L^{-1})^4$. The molarity of its saturated solution is

(a) 3.0×10^{-5} (b) 1.0×10^{-5}
(c) $27^{1/4} \times 10^{-5}$ (d) 3.0×10^{-4}

20. K_{sp} of $Mg(OH)_2$ is 4.0×10^{-12}. The number of moles of Mg^{2+} ions in one litre of its saturated solution in 0.1 *M* NaOH is :

(a) 4.0×10^{-10} (b) 1.0×10^{-4}
(c) 2.0×10^{-6} (d) 8.0×10^{-6}

21. K_{sp} of $M(OH)_2$ is 3.2×10^{-11}. The pH of its saturated solution in water is :

(a) 10.30 (b) 10.60
(c) 3.70 (d) 3.40

22. Solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 2.7×10^{-23} and 3.2×10^{-14} respectively. If to a solution of 0.1 *M* each of Al^{3+} and Zn^{2+} ions, NH_4OH is added in increasing amounts which of the following will be precipitated first ?

(a) $Zn(OH)_2$ (b) $Al(OH)_3$
(c) both of them (d) none of them

23. On addition of increasing amount of $AgNO_3$ to 0.1 *M* each of NaCl and NaBr in a solution, what % of Br^- ion gets precipitated when Cl^- ion starts precipitating? K_{sp} (AgCl) $= 1.0 \times 10^{-10}$; K_{sp} (AgBr) $= 1 \times 10^{-13}$

(a) 0.1 (b) 0.01
(c) 99.9 (d) 99.99

24. At certain temperature saturated solution of $Mg(OH)_2$ has a pH of 8.699. K_{sp} of $Mg(OH)_2$ at this temperature is

(a) 8.0×10^{-15} (b) 6.25×16^{-17}
(c) 4.0×10^{-10} (d) 2.0×10^{-10}

25. The ionization constant of an acid-base indicator (a weak acid) is 1.0×10^{-6}. The ionized form of the indicator is red whereas the unionized form is blue. The pH change required to alter the colour of the indicator from 80% blue to 80% red is:

(a) 2.00 (b) 1.40
(c) 1.20 (d) 0.80

26. K_b of an acid-base indicator is 1.0×10^{-9}. The pH at which its 10^{-3} *M* solution shows the colour change

(a) 9.0 (b) 7.0
(c) 5.0 (d) 3.0

27. Which of the following statements is wrong for glycine ?

(a) It behaves as an acid when titrated with a strong base
(b) It behaves as a base when titrated with a strong acid
(c) Its acidic and basic groups ionize equally at isoelectric pH
(d) Its zwitter ion at isoelectric point migrates under the electric field.

MARK YOUR RESPONSE	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ
	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ

28. Mass loss of 1.0000 g of the AgCl ($K_{sp} = 1.0 \times 10^{-10}$) on repeated washing with 10L of water is

(Ag = 108 ; Cl = 35.5)

(a) 1.43×10^{-3} g
(b) 1.0×10^{-4} g
(c) 1.43×10^{-2} g
(d) none

29. K_{sp} of SrF_2 in water is 3.2×10^{-11}. Molarity of F^- ions in its saturated solution of 0.1 *M* NaCl is

(a) 3.2×10^{-9}
(b) 2×10^{-4}
(c) 4×10^{-4}
(d) 6.4×10^{-9}

30. In the precipitation of sulphides of second group of basic radicals, H_2S is passed into the acidified solution with dilute HCl. If the solution is not acidified, then which is the correct statement ?

(a) Only the sulphides of second group get precipitated
(b) Only the sulphides of fourth group get precipitated
(c) Neither of the sulphides of second and fourth groups get precipitated
(d) Sulphides of both the groups get precipitated.

31. In the precipitation of hydroxides in third group of basic radicals, if NaCl and NaOH are used in place of NH_4Cl and NH_4OH, then what happens ?

(a) No precipitation of third group hydroxides
(b) Only the precipitation of third group hydroxides
(c) Precipitation of 3rd group hydroxides alongwith those of higher groups
(d) No precipitation of 3rd group hydroxides but the precipitation of higher group hydroxides.

32. On addition of few drops of concentrated HCl to $BaCl_2$ solution (which is not too dilute), a white precipitate appears. The precipitate is :

(a) $BaSO_4$
(b) $Ba(OH)_2$
(c) Ba(OH)Cl
(d) $BaCl_2$

33. The correct order of increasing solubility of AgCl in (*A*) water, (*B*) 0.1 *M* NaCl, (*C*) 0.1 *M* $BaCl_2$ and (*D*) 0.1 *M* NH_3 is :

(a) $A < B < C < D$
(b) $B < C < A < D$
(c) $C < B < D < A$
(d) $C < B < A < D$

34. Buffer capacity may be defined as the number of moles of a strong acid or a strong base required to be added to one litre of buffer so as to change the molarity of H_3O^+ ion by a factor of

(a) 100
(b) 10 or 1/10
(c) 1/100
(d) unity

35. Which of the following solutions will have pH close to 1.0 ?

(a) 100 ml of 0.1 *M* HCl + 100 ml of 0.1 *M* NaOH
(b) 55 ml of 0.1 *M* HCl + 45 ml of 0.1 *M* NaOH
(c) 75 ml of 0.2 *M* HCl + 25 ml of 0.2 *M* NaOH
(d) 10 ml of 0.1 *M* HCl + 90 ml of 0.1 *M* NaOH

36. A solution of NH_4Cl and NH_3 has pH = 8. Which of the following hydroxides may be precipitated when this solution is mixed with equal volume of 0.2 *M* of metal ion ?

(a) $Mg(OH)_2$ ($K_{sp} = 3.5 \times 10^{-4}$)
(b) $Ca(OH)_2$ ($K_{sp} = 2.1 \times 10^{-5}$)
(c) $Ba(OH)_2$ ($K_{sp} = 1.1 \times 10^{-4}$)
(d) $Fe(OH)_2$ ($K_{sp} = 8.1 \times 10^{-16}$)

37. The pH of a solution containing equimolar amounts of CH_3COOH (p^{Ka} = 4.74 at 25ºC) and sodium acetate at 50ºC is :

(a) 4.74
(b) <4.74
(c) >4.74
(d) none of these

38. pH of $Ba(OH)_2$ solution is 13. Millimoles of $Ba(OH)_2$ present in 10 ml of solution would be

(a) 1.00
(b) 0.50
(c) 10.00
(d) 15.00

39. Which of the following constitutes a set of amphoteric species :

(a) $H_3O^+, H_2PO_4^-, HCO_3^-$
(b) H_2O, HPO_4^{2-}, $H_2PO_2^-$
(c) H_2O, $H_2PO_3^-, HPO_4^{2-}$
(d) $HC_2O_4^-, H_2PO_4^-, SO_4^{2-}$

40. A buffer solution contains 500 ml of 0.2 *M* CH_3COONa and 500 ml of 0.1*M* CH_3COOH. 1 L of water is added to this buffer. pH before and after dilution : (p^{Ka} of CH_3COOH = 4.74)

(a) 5.04, 3.74
(b) 5.04, 5.04
(c) 5.04, 4.89
(d) 9.56, 9.56

41. In order to prepare a buffer of pH 8.26, the amount of $(NH_4)_2SO_4$ required to be mixed with 1L of 0.1*M* NH_3 (p^{Kb} = 4.74) is

(a) 1.0 mole
(b) 10.0 mole
(c) 0.50 mole
(d) 5 mole

MARK YOUR RESPONSE	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ
	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ
	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	

42. Sucrose is hydrolysed into glucose and fructose in presence of H_3O^+ as catalyst

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{[H_3O^+]} C_6H_{12}O_6 + C_6H_{12}O_6$$

Rate of reaction = $k\,[H_3O^+]$ [Sucrose]

The reaction will be fastest in :

(a) 0.2 M HCl (b) 0.2 M H_2SO_4
(c) 0.5 M CH_3COOH (d) 0.5 M $H_2C_2O_4$

43. Which of the following will have highest pH ?

(a) 0.1 M NH_4Br (b) 0.1 M $(NH_4)_2SO_4$
(c) 0.1 M NH_4NO_3 (d) 0.1 M $(NH_4)_3PO_4$

44. Solution of potash alum is acidic in nature. This is due to hydrolysis of

(a) SO_4^{2-} (b) K^+
(c) $Al_2(SO_4)_3$ (d) Al^{3+}

45. K_{sp} of $Ca(OH)_2$ is 4.0×10^{-6}. At what minimum pH, Ca^{2+} ions start precipitating in 0.01 M $CaCl_2$?

(a) $12 - \log 2$ (b) $12 + \log 2$
(c) $2 - \log 2$ (d) $2 + \log 2$

46. One litre of 0.5 M NaCl is electrolysed by passing 9650 coulombs of electricity. The pH of resulting solution is :

(a) 1.00 (b) 7.00
(c) 13.00 (d) none of these

47. Molarity of H_3PO_3 solution is 1.0×10^{-2}. Which of the following is then correct?

(a) $1.0 \times 10^{-2} M = [H_3PO_3] + [H_2PO_3^-] + [HPO_3^{2-}] + [PO_3^{2-}]$

(b) $1.0 \times 10^{-2} M = [H_3PO_3] + [H_2PO_3^-] + [HPO_3^{3-}]$

(c) $1.0 \times 10^{-2} M = [H_2PO_3^-] + [HPO_3^{2-}] + [PO_3^{3-}]$

(d) $1.0 \times 10^{-2} M = [H_3PO_3] + [H_2PO_3^-] + 2[HPO_3^{2-}]$

48. In which of the following, the buffer action ceases to act ?

(a) 100 ml of 0.1 M CH_3COOH + 25 ml of 0.1 M NaOH
(b) 100 ml of 0.1 M CH_3COOH + 50 ml of 0.1 M NaOH
(c) 100 ml of 0.1 M CH_3COOH + 80 ml of 0.1 M NaOH
(d) 100 ml of 0.1 M CH_3COOH + 50 ml of 0.3 M NaOH

49. On addition of 10 ml of 1.0 M HCl, which of the following is no more a buffer solution ?

(a) 100 ml containing 0.2 M NH_3 and NH_4Cl each
(b) 100 ml containing of 0.2 M NH_3 and 0.1 M NH_4Cl
(c) 100 ml containing 0.05 M NH_3 and NH_4Cl each
(d) 100 ml containing 0.15 M NH_3 and NH_4Cl each

50. What can be the maximum possible molarity of Co^{2+} ions in 0.1 M HCl saturated with H_2S ($K_a = 4 \times 10^{-21}$), given that K_{sp} for CoS is 2×10^{-21} and concentration of saturated $H_2S = 0.1\ M$

(a) 1.00 M (b) 0.50 M
(c) 4.48×10^{-11} M (d) 0.10 M

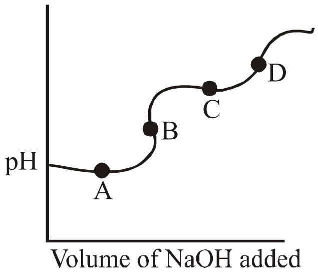
51. For the titration of a weak base with strong acid, the pH at the equivalence point is on the acidic side. It is because of

(a) slight excess of the acid
(b) slight excess of the base
(c) cationic hydrolysis of the salt formed
(d) anionic hydrolysis of the salt formed

52. In the titration of a monoacid weak base with a strong acid, the pH at half of the equivalence point is

(a) pK_b (b) $14 - pK_b$
(c) $7 - pK_b$ (d) $7 + pK_b$

53. For the titration of a dibasic weak acid H_2A $(pK_{a(2)} - pK_{a(1)} \geq 2)$ with a strong base, pH versus volume of the base graph is as shown in the figure. $pK_{a(1)}$ and $pK_{a(3)}$ are equal to the pH values corresponding to the points :



(a) B and D respectively (b) A and B respectively
(c) C and D respectively (d) A and C respectively

54. The solubility of mercurous chloride in water is given by

(a) $S = K_{sp}$ (b) $S = K_{sp/4}$

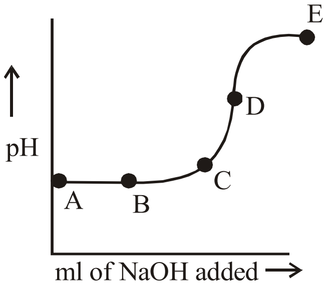
(c) $S = \left(\dfrac{K_{sp}}{4}\right)^{1/2}$ (d) $S = \left(\dfrac{K_{sp}}{4}\right)^{1/3}$

MARK YOUR RESPONSE	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ
	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ
	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ	54. ⓐⓑⓒⓓ		

55. Fear and excitement generally cause one to breathe rapidly and it results in the decrease of CO_2 concentration in the blood. In what way will it change the pH of the blood ?

(a) pH will decrease
(b) pH will increase
(c) pH will adjust to 7
(d) pH willl remain unchanged.

56. The curve in the figure shows the variation of pH during the course of titration of a weak acid, HA, with a strong base (NaOH). At which point in the titration curve is the concentration of the acid equal to that of its conjugate base ?



(a) Point *D* (b) Point *E*
(c) Point *C* (d) Point *B*

57. 25 ml of a weak acid, HA required 15 ml of 0.1 *M* NaOH for the end point. During titration, the pH of the acid solution is found to be 5.70 upon the addition of 10 ml of the above alkali. The pK_a of the weak acid is :

(a) 5.40 (b) 6.30
(c) 5.60 (d) 5.70

58. At 25°C the pH of 0.01 *M* KOH is 12. If the temperature of this solution is raised to 50°C without changing the volume, which of the following is correct ?

(a) Both pH and pOH will remain constant
(b) pH will decrease while pOH willl remain constant
(c) pH will increase while pOH will remain constant
(d) pH will increase while pOH will decrease.

59. Which of the following molar ratio of NH_3 and HCl in aqueous solution will constitute a buffer ?

(a) 1 : 2 (b) 1 : 3
(c) 1 : 1 (d) 2 : 1

60. What will be the volumes of 1 *M* NH_3 and 1 *M* HCl required to prepare 300 ml of a buffer of pH = 9.26 ($pK_a = 9.26$ for NH_4^+)

(a) 150.0 ml, 150 ml (b) 100 ml, 200 ml
(c) 200 ml, 100 ml (d) 225 ml, 75 ml

61. At 25°C, the ionization constants of CH_3COOH and NH_3 are almost equal. The pH of a solution of 0.01 *M* CH_3COOH is 4.0 at 25°C. The pOH of 0.01 *M* NH_4OH at the same temperature will be :

(a) 3.0 (b) 4.0
(c) 10.0 (d) 10.5

62. Which is the decreasing order of strength of the bases OH^-, NH_2^-, $H-C\equiv C^-$ and $CH_3CH_2^-$?

(a) $CH_3CH_2^- > NH_2^- > H-C\equiv C^- < OH^-$
(b) $H-C\equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3CH_2^-$
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3CH_2^-$

63. Which of the following processes represents hydrolysis ?

(a) $H_2PO_4^- + H_2O \longrightarrow HPO_4^{2-} + H_3O^+$
(b) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$
(c) $C_6H_5NH_3^+ + H_2O \longrightarrow C_6H_5NH_2 + H_3O^+$
(d) $HCO_3^- + H_2O \longrightarrow CO_3^{2-} + H_3O^+$

64. Calculate the pH of a solution obtained by mixing 2 ml of HCl of pH 2 and 3 ml of solution of KOH of pH = 12

(a) 10.30 (b) 3.70
(c) 11.30 (d) None of these

65. In the titration of 50 ml of 0.1*M* β-hydroxybutric acid $HC_4H_7O_3$ with 0.2 *M* NaOH, the pH after the addion of 20 ml of NaOH is ($pK_a = 4.39$)

(a) 3.99 (b) 4.99
(c) 4.57 (d) 4.80

MARK YOUR RESPONSE	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ
	60. ⓐⓑⓒⓓ	61. ⓐⓑⓒⓓ	62. ⓐⓑⓒⓓ	63. ⓐⓑⓒⓓ	64. ⓐⓑⓒⓓ
	65. ⓐⓑⓒⓓ				

66. The pH of blood is 7.4. If the buffer in blood is CO_2 and HCO_3^-, calculate the ratio of conjugate base to acid (H_2CO_3) to maintain the pH of the blood. Given K_1 of $H_2CO_3 = 4.5 \times 10^{-7}$

(a) 8.5 (b) 10.0
(c) 11.25 (d) none of these

67. pH of two solutions :

I. 50 ml of 0.2 M HCl + 50 ml of 0.2 M HA $(K_a = 1.0 \times 10^{-5})$ and

II. 50 ml of 0.2 M HCl + 50 ml of 0.2 M NaA will be respectively

(a) 0.70 and 2.85 (b) 1 and 2.85
(c) 1 and 3 (d) 3 and 1

68. Methylamine in water has a weak basic property. This is explained by the equilibrium

(a) $CH_3NH_3OH \rightleftharpoons CH_3NH_3^+ + OH^-$

(b) $CH_3NH_2 + 2H_2O \rightleftharpoons CH_3NH_2OH^- + H_3O^+$

(c) $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$

(d) none of these

69. In which of the following cases, $[H_2O]$ can not be omitted?

(a) $CH_3COOC_2H_5(0.1M) + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

(b) $CH_3COOH(0.2M) + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(c) $CH_3COOC_2H_5(0.2\text{mol}) + H_2O\ (0.3\text{ mol}) \rightleftharpoons CH_3COOH + C_2H_5OH$

(d) $NH_4^+(0.2M) + H_2O \longrightarrow NH_3^+ + H_3O^+$

70. Calculate the pH of a solution containing 0.1 mol of CH_3COOH, 0.2 mol of CH_3COONa and 0.05 mol of NaOH in 1L (pK_a for $CH_3COOH = 4.74$)

(a) 4.74 (b) 5.04
(c) 5.44 (d) 5.20

71. To 1L solution containing 0.1 mol each of NH_3 and NH_4Cl, 0.05 mol of NaOH is added. The change in pH will be (pK_b for $NH_3 = 4.74$)

(a) -0.48 (b) 0.48
(c) 0.30 (d) -0.30

72. The base imidazole has K_b of 1.0×10^{-7}. What volumes of 0.02 M HCl and 0.02 M imidazole should be mixed to make 150 mL of a buffer of pH 7 ?

(a) 100 mL and 50 mL (b) 50 mL and 100 mL
(c) 75 mL and 75 mL (d) 60 mL and 90 mL

73. Which of the following, when mixed, will give a solution with pH > 7 ?

(a) 100 ml 0.1 M HCl + 100 ml 0.1 M KCl

(b) 100 ml 0.1 M H_2SO_4 + 100 ml 0.1 M NaOH

(c) 100 ml 0.1 M CH_3COOH + 100 ml 0.1 M KOH

(d) 50 ml 0.1 M HCl + 50 ml 0.1 M CH_3COONa

74. What is OH^- ion concentration is 0.01 M solution of aniline hydrochloride (K_b for aniline = 4×10^{-10})?

(a) $2 \times 10^{-11} M$ (b) $2 \times 10^{-10} M$
(c) $5 \times 10^{-4} M$ (d) $5 \times 10^{-5} M$

75. In the titration of 100 ml of 0.01 M NH_3 with 0.1 M HCl, at the stages of addition of 5, 10 and 11 ml of acid solution, the pH values are 9.26, 5.62 and 3 respectively. The reaction $NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$ is expected to occur at

(a) half neutralization point
(b) equivalence point
(c) beyond the equivalence point
(d) isoelectric point

76. In the titrations of

I. $C_6H_5SO_3H$ with KOH solution

II. Pyridine with HCl solution

III. Propanoic acid with NaOH solution,

the equivalence points would be respectively

(a) acidic, neutral, basic (b) neutral, acidic, basic
(c) all acidic (d) all basic

MARK YOUR RESPONSE					
	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ	68. ⓐⓑⓒⓓ	69. ⓐⓑⓒⓓ	70. ⓐⓑⓒⓓ
	71. ⓐⓑⓒⓓ	72. ⓐⓑⓒⓓ	73. ⓐⓑⓒⓓ	74. ⓐⓑⓒⓓ	75. ⓐⓑⓒⓓ
	76. ⓐⓑⓒⓓ				

77. What concentration of NH_3 must be present which just prevents the precipitation of AgCl in 0.004 *M* Ag^+ and 0.001 *M* Cl^- ? Given K_{sp} of AgCl = 1.0×10^{-10}, K_d for $Ag(NH_3)_2^+ = 1.0\times10^{-8}$

(a) 0.01 *M* (b) 0.002 *M*
(c) 0.02 *M* (d) 0.1 *M*

78. The solubility of AgSCN in 0.002 *M* NH_3 is (K_{sp} for $AgSCN = 1.0\times10^{-12}$; K_d for $Ag(NH_3)_2^+ = 1.0\times10^{-8}$)

(a) 3×10^{-5} *M* (b) 4×10^{-4} *M*
(c) 4×10^{-5} *M* (d) 2×10^{-5} *M*

79. Which of the following is false ?

(a) $0.1\,M\,Fe^{2+} + 0.1\,M\,NH_3 \longrightarrow$ Precipitation of $Fe(OH)_2$

(b) $0.1\,M\,Mg^{2+} + 0.1\,M\,NH_3 + 0.1\,M\,NH_4^+ \longrightarrow$ No precipitation of $Mg(OH)_2$

(c) $0.01\,M\,Ag^+ + 0.1\,M\,NH_3 \longrightarrow$ Precipitation of AgOH

(d) $0.01\,M\,Ag^+ + 0.1\,M\,NH_3 \longrightarrow$ No precipitation of AgOH

80. Calculate the dissociation constant of the monocomplex of M^{3+} and SCN^-. Given that total metal concentration $= 2\times10^{-3}M$, total SCN^- concentration = $1.51\times10^{-3}M$ and free SCN^- concentration = $1.0\times10^{-5}M$.

(a) 2.0×10^{5} (b) 2.0×10^{-5}
(c) 3.0×10^{5} (d) 3.3×10^{-6}

81. Minimum moles of NH_3 required to be added to 1L solution so as to dissolve 0.1 mol of AgCl ($K_{sp} = 1.0\times10^{-10}$) by the reaction :

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_3^+] + Cl^- ;$$

K_f for $Ag(NH_3)_2^+ = 1.0\times10^{8}$

(a) 0.5 mol (b) 1.0 mol
(c) 1.1 mol (d) 1.2 mol

82. Calculate Ag^+ ion concentration in a solution containing 0.02 mol of $AgNO_3$ and 0.14 mol of NH_3 in 1 L (K_d for $Ag(NH_3)_2^+ = 1.0\times10^{-8}$

(a) 2×10^{-7} *M* (b) 1.0×10^{-8} *M*
(c) 2×10^{-8} *M* (d) 2×10^{-9} *M*

83. The increasing order of Ag^+ ion concentration in

I. Saturated solution of AgCl
II. Saturated solution of AgI
III. 1 *M* $Ag(NH_3)_2^+$ in 0.1 *M* NH_3
IV. 1 *M* $Ag(CN)_2^-$ in 0.1 *M* KCN

Given :

K_{sp} of AgCl = 1.0×10^{-10},
K_{sp} of AgI = 1.0×10^{-16},
K_d of $Ag(NH_3)_2^+ = 1.0\times10^{-8}$
K_d of $Ag(CN)_2^- = 1.0\times10^{-21}$

(a) I < II < III < IV (b) IV < III < II < I
(c) IV < II < III < I (d) IV < II < I < III

84. If 50 ml of 0.2 *M* NaCN is mixed with 50 ml of 0.2 *M* HCl, then (K_b for $CN^- = 2\times10^{-5}$)

(a) $[CN^-] = 0.1\,M$

(b) $[H_3O^+] = 0.1\,M$

(c) $HCN = 0.1\,M$

(d) $[H_3O^+] = [CN^-] = 7\times10^{-6}\,M$

85. An acid-base indicator HIn in a buffer of pH = $pK_{in} - 1$ is ionized to the extent of

(a) 90.9% (b) 9.1 %
(c) 10% (d) 90%

86. An acid-base indicator of $pK_a = 4$ will be suitable for the titration

(a) HCl with NH_3

(b) CH_3COOH with NH_3

(c) CH_3COOH with NaOH

(d) HCl with KOH

MARK YOUR RESPONSE	77. ⓐⓑⓒⓓ	78. ⓐⓑⓒⓓ	79. ⓐⓑⓒⓓ	80. ⓐⓑⓒⓓ	81. ⓐⓑⓒⓓ
	82. ⓐⓑⓒⓓ	83. ⓐⓑⓒⓓ	84. ⓐⓑⓒⓓ	85. ⓐⓑⓒⓓ	86. ⓐⓑⓒⓓ

87. 100 mL of 1.0 *M* solution of a monobasic aicd ($pK_a = 5$) is titrated against Ca $(OH)_2$ solution. At equivalence point the pH of solution is

(a) 7 (b) 6

(c) 4.5 (d) 9.5

88. If the pH value of 0.1 *M* HCN is 5.2, then its K_a value is

(a) 3.97×10^{-7} (b) 6.3×10^{-7}

(c) 3.97×10^{-10} (d) 6.3×10^{-10}

89. The number of H^+ ions in 1 cc of a solution, having pH = 13, is

(a) 6.023×10^{7} (b) 6.023×10^{13}

(c) 1×10^{16} (d) 1×10^{-13}

90. This reaction given below represents a titration reaction at equilibrium, when a strong monoacid base (BOH) is titrated against a monobasic asid.

$$B^+ + 2H_2O \rightleftharpoons BOH + H_3O^+$$

(a) at the start of titration

(b) before the equivalence point

(c) at the equivalence point

(d) after the equivalence point

91. The dissocation constant of a weak acid is 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is

(a) 1.0×10^{-4} (b) 1.0×10^{-10}

(c) 1.0×10^{10} (d) 1.0×10^{-14}

92. The degree of dissociation of acetic acid in an aqueous solution of the acid is practically unaffected

(a) by adding a pinch of NaCl

(b) by adding a drop of HCl

(c) by adding water

(d) by raising the temperature

93. According to Pearson, a hard base is one whose donor atom has

(a) low electronegativity, low polarizability and which is difficult to oxidise

(b) high electronegativity, high polarisability and easy to oxidise.

(c) high electronegativity, low polarisability and difficult to oxidise

(d) low electronegativity, high polarisability and difficult to oxidise.

94. Which of the following is a soft acid according to Pearson's concept of hard and soft acids?

(a) Ag^+ (b) I^{7+}

(c) Sr^{2+} (d) Al^{3+}

95. Which of the following is not a hard base according to Pearson's concept of hard and soft bases?

(a) F^- (b) I^-

(c) NO_3^- (d) O^{2-}

MARK YOUR RESPONSE					
	87. ⓐⓑⓒⓓ	88. ⓐⓑⓒⓓ	89. ⓐⓑⓒⓓ	90. ⓐⓑⓒⓓ	91. ⓐⓑⓒⓓ
	92. ⓐⓑⓒⓓ	93. ⓐⓑⓒⓓ	94. ⓐⓑⓒⓓ	95. ⓐⓑⓒⓓ	

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Acid-base indicator such as methyl-orange, phenolphthalein and bromothymol blue are substances which change colour according to the hydrogen ion concentration of solution to which they are added.

Most indicators are weak acids (or more rarely weak bases) in which the undissociated and dissociated forms have different and distinct colours. If methyl-orange is used as an example and the undissociated form is written as HMe, then dissociation occurs as shown below :

Reaction I : $\underset{\text{Red}}{HMe} \rightleftharpoons \underset{\text{Colourless}}{H^+} + \underset{\text{Yellow}}{Me^-}$

The indicator should have a sharp colour change at the equivalence point of the titration. Usually, the colour change of the indicator occurs over a range of about two pH units. It should be noted that the eye cannot detect the exact end point of the titration. The pK_a of the indicator should be near the pH of the solution at the equivalence point.

1. What factor must the hydrogen ion concentration change at the equivalence point for the indicator in solution to change colour?

   (a) 2 (b) 10
   (c) 100 (d) 200

2. Which of the following situation exists at the equivalence point of a titration?

   (a) $[H^+]=10^{-7}\,M$ (b) $[H^+]=[OH^-]$
   (c) $[OH^-]=10^{-7}\,M$ (d) $\frac{[H^+]}{[OH^-]}=10^{-14}$

3. Titration between equimolar concentration of hydrochloric acid and sodium hydroxide has an equivalence point with a pH of 7. Given the following information, which indicator is most suitable for detecting the end point of this titration?

Indicator	K_a
Bromothymol blue	3.16×10^{-7}
Cresol red	7.00×10^{-9}
Bromophenol blue	1.58×10^{-4}
$p-$Xylenol blue	1.10×10^{-2}

   (a) Bromothymol blue (b) Cresol red
   (c) Bromophenol blue (d) $p-$ Xylenol blue

4. Given that the K_a (methyl-orange) = 4.0×10^{-4}, a solution of pH = 2 containing the indicator would be :

   (a) orange (b) yellow
   (c) colourless (d) red

5. When indicators are used, what can be done to minimize their interfering with the titration?

   (a) Only add a few drops of the indicator
   (b) Add excess of the titrant to negate its effect
   (c) Add excess of the solution to be titrated to negate its effect
   (d) Only use indicators with large K_a values

PASSAGE-2

pH of mixture of acids and bases : In a mixture of strong acid and a strong base, concentration of H^+ ions or OH^- ions can be calculated as

$$[H^+]\text{ or }[OH^-]=\frac{\text{m eqvts of strong acid} \sim \text{m eqvts of strong base}}{\text{Total volume(ml) of mixture}}$$

At the equivalence point of titration of a strong acid with a strong base, pH = 7 at 25°C. The salt formed does not hydrolyse.

In case of weak acid with a strong base, before the equivalence point pH is calculated using the concept of acid buffer i.e., by using Henderson's equation. At the equivalence point, pH is calculated taking into consideration of salt hydrolysis.

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

Where K_a is the dissociation constant of the acid and C mol L^{-1} is the concentration of the salt formed, more correctly the concentration of the anion of the salt.

Beyond the equivalence point, there is an excess of base which mainly determines the pH.

In case of weak base with strong acid, before the equivalence point, buffer concept is used. At the equivalence point salt hydrolysis is taken into consideration.

$$\text{pH}=\frac{1}{2}(pK_w-pK_b-\log C)$$

Where K_b = dissociation constant of weak base and C mol L^{-1} is the concentration of the salt, more correctly that of the cation of the salt.

In case of titration of weak acid with a weak base, at the equivalence point pH is calculated considering the salt hydrolysis.

$$\text{pH}=\frac{1}{2}(pK_w+pK_a-pK_b)$$

6. 100ml of 0.1M HCl is titrated with 0.1 M NaOH. The pH of the reaction mixture after the addition of 50ml, 100ml and 150ml are respectively

   (a) 1.3, 7.0, 9.23 (b) 1.48, 7.0, 12.3
   (c) 1.48, 7.0, 1.7 (d) 7.0, 1.3, 12.3

7. 100 ml of 0.1 M monoacid weak base B ($K_b = 2\times10^{-5}$) is titrated with 0.1 M HCl. pH of the reaction mixture at the titre value of 50ml and 100ml are respectively

   (a) 9.3, 9.3 (b) 9.3, 6.6
   (c) 9.3, 5.3 (d) 4.7, 6.6

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ			

8. 50 ml of 0.1 M HCOOH ($K_a = 1.8 \times 10^{-4}$) is titrated with 0.1 M NH_3 $(K_b = 1.8 \times 10^{-5})$. pH at the equivalence point will be

(a) 7.0
(b) 6.5
(c) 7.5
(d) 5.5

9. Ionic product of water at 80°C is 4×10^{-14}. pH at the equivalence point of titration of 20 ml of 0.1 M HCl with 0.1 M NaOH at 80°C is

(a) 7.0
(b) 7.3
(c) 6.7
(d) None of these

10. When 50 ml of 0.2M HA $(K_a = 1.0 \times 10^{-5})$ is mixed with 50ml of 0.2 M KOH at 25°C, the pH of the resulting mixture would be

(a) 9.0
(b) 9.15
(c) 8.50
(d) 8.2

PASSAGE-3

The titration cure for a 0.100 M solution of the weak base piperazine with 0.200 M HCl is depicted in the Fig.-1. If the most basic form of piperazine is represented as B, then acid constants for the species $BH^+_{(aq)}$ and $BH_2{}^+_{(aq)}$ are given as follows :

$$BH_2{}^{2+}_{(aq)} \rightleftharpoons BH^+_{(aq)} + H^+_{(aq)}$$

$K_1 = 4.65 \times 10^{-6}$

$$BH^+_{(aq)} \rightleftharpoons B_{(aq)} + H^+_{(aq)}$$

$K_2 = 1.86 \times 10^{-10}$

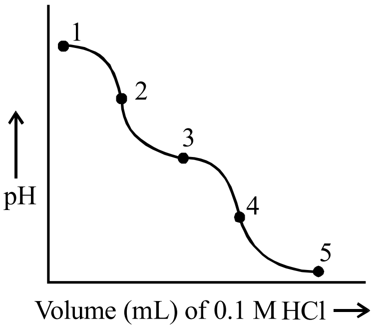


Figure - 1

11. At which the numbered points on the titration curve would the species $BH^+_{(aq)}$ and $BH_2{}^{2+}_{(aq)}$ be found in almost equal quantities?

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

12. If the original volume of 0.100 M B solution was 20mL, what is the approximate volume of acid that has been added at point 2?

(a) 5 mL
(b) 10 mL
(c) 15 mL
(d) 20 mL

13. What is the approximate pH at point 4 on the titration curve?

(a) 3
(b) 7
(c) 10
(d) 13

14. What is the predominant pH determining reaction in the titration flask before any HCl is added?

(a) $BH_2{}^+_{(aq)} \rightleftharpoons BH^+_{(aq)} + H^+_{(aq)}$

(b) $BH^+_{(aq)} \rightleftharpoons B_{(aq)} + H^+_{(aq)}$

(c) $B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$

(d) $BH^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons B_{(aq)} + H_2O_{(l)}$

PASSAGE-4

We know that sparingly soluble susbtance (e.g. AgCl, $BaSO_4$, $PbSO_4$ etc.) are only slightly soluble in water and thus in aqueous solution only this small amount of sparingly soluble susbtance remains completely ionised. Since no more of substance can be dissolved in solution at this temperature so it is a saturated solution.

The K_{sp} of sparingly soluble salt is equal to the product of ionic concentrations in a saturated solution at the specified temperature, each raised to appropriate powers.

For precipitation it is essential that the product of ionic concentrations is more than K_{sp}.

15. At 25°C the solubility of calcium phosphate (molecular weight = M) was found to be w g/100 ml. The K_{sp} for calcuim phosphate at 25°C is approximately.

(a) $10^2\left(\frac{w}{M}\right)^5$
(b) $10^4\left(\frac{w}{M}\right)^5$
(c) $10^7\left(\frac{w}{M}\right)^5$
(d) $10^9\left(\frac{w}{M}\right)^5$

MARK YOUR RESPONSE	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ
	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ		

16. The solubility product (K_{SP}) of a sparingly soluble salt MX at 25°C is 2.5×10^{-9}. The solubility of salt (in mol L^{-1}) at 25°C is

(a) 1×10^{-14} (b) 5.0×10^{-8}

(c) 1.25×10^{-9} (d) 5.0×10^{-5}

17. The K_{SP} of AgCl is 4.0×10^{-10} at 298K. The solubility of AgCl in 0.04 M $CaCl_2$ will be

(a) 2.0×10^{-5}m (b) 10×10^{-4}m

(c) 5.0×10^{-9}m (d) 2.2×10^{-4}m

PASSAGE-5

Henderson's equation can be used to calculate the pH values of buffer mixtures.

For an acidic buffer;

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

For a basic buffer

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

18. What will be the pH of a solution containing 0.05 M sodium acetate and 0.1 M acetic acid?

[pK_a for acetic acid = 4.73]

(a) 4.0 (b) 4.43

(c) 5.0 (d) 4.73

19. What will be the pH of a buffer solution containing 0.20 M NH_4OH and 0.25 M NH_4Cl per litre?

[Given : K_b for $NH_4OH = 1.80 \times 10^{-5}$]

(a) 7.0 (b) 8.0

(c) 9.16 (d) 10.32

20. The pK_a of a weak acid is 4. What should be the [salt] to [acid] ratio, if we have to prepare a buffer with pH equal to 5 using this acid and one of its salt ?

(a) 1 : 10 (b) 10 : 1

(c) 5 : 4 (d) 4 : 5

MARK YOUR RESPONSE	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : In the third group of qualitative analysis, NH_4Cl is added to NH_4OH medium.

Statement-2 : This is to convert the ions of group into their respective chlorides.

2. **Statement-1** : The pK_a of a weak acid becomes equal to pH of the solution at the midpoint of its titration.

Statement-2 : The molar concentrations of proton acceptor and proton donor become equal at the midpoint of titration of a weak acid.

3. **Statement-1** : The pH of the aq. solution of acetic acid remains unchanged on the addition of sodium acetate.

Statement-2 : The ionisation of acetic acid is suppressed by the addition of sodium acetate.

4. **Statement-1** : pH of a buffer solution changes with change in temperature.

Statement-2 : K_W of water changes with change in temperature.

5. **Statement-1** : A mixture of the solution of a weak acid and its sodium salt acts as a good buffer.

Statement-2 : The ratio of salt to acid in the mixture does not change substantially when small amounts of acids or alkalies are added to the buffer.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. Statement-1 : According to the principle of common ion affect, the solubility of HgI_2 is expected to be less in an aq. solution of KI than in water. But HgI_2 dissolves in an aq. solution of KI to form a clear solution.

Statement-2 : Iodide ion, I^-, is highly polarisable.

7. Statement-1 : The solubility of AgCl in water decreases if NaCl is added to it.

Statement-2 : NaCl is highly soluble in water whereas AgCl is sparingly soluble.

8. Statement-1 : H_2SO_4, HCl and HNO_3 are all equally strong in water but not equally strong in acetic acid.

Statement-2 : H_2O gives H^+ as well as OH^- ions, but CH_3COOH gives only H^+ and no OH^- ions.

9. Statement-1 : In a titration of weak acid and NaOH, the pH at half equivalence point is pK_a.

Statement-2 : At half equivalence point, it forms an acidic buffer and the buffer capacity is maximum where [acid] = [salt]

10. Statement-1 : Strong acids, like perchloric acid, hydrochloric acid, nitric acid and sulphuric acid have equal strengths in aqueous solutions but are not equally strong when acetic acid is used as a solvent. In acetic acid the order of strength is $HClO_4 > HBr > H_2SO_4 > HCl > HNO_3$.

Statement-2 : Water ionises to give H^+ as also OH^- ions where as the ionisation of acetic acid produces only H^+ ions.

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

11. Statement-1 : HF is weaker acid as compared to H_3BO_3.

Statement-2 : Higher the ionisation constant stronger is the acid.

MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ				

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Which of the solutions will be acidic?
   (a) $0.1\,M\,CH_3COONa$
   (b) $0.1\,M\,FeSO_4$
   (c) $0.1\,M\,K_2SO_4.Al_2(SO_4)_3.24H_2O$
   (d) $0.1\,M\,(NH_4)_2SO_4$

2. On addition of $(NH_4)_2SO_4$ to $0.1\,M\,NH_3$
   (a) OH^- ion concentration will decrease
   (b) H_3O^+ ion concentration will decrease
   (c) pH will increase
   (d) pH will decrease

3. To which of the following, addition of water would *not* affect the pH ?
   (a) 100 ml of $0.2\,M\,CH_3COOH$ + 100 ml of $0.2\,M$ NaOH
   (b) 200 ml of $0.2\,M\,CH_3COOH$ + 100 ml of $0.1\,M$ NaOH
   (c) 100 ml of $0.2\,M\,CH_3COOH$ + 200 ml of $0.2\,M$ NaOH
   (d) 100 ml of $0.2\,M\,CH_3COOH$ + 100 ml of $0.1\,M$ NaOH

4. Which of the following is not amphiprotic ?
   (a) $H_2PO_2^-$ (b) HPO_3^{2-}
   (c) H_3PO_4 (d) $H_2PO_4^-$

5. Which of the following represents hydrolysis ?
   (a) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$
   (b) $NH_4^+ + 2H_2O \rightleftharpoons NH_4OH + H_3O^+$
   (c) $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$
   (d) $HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$

6. A buffer solution can be prepared from a mixture of
   (a) CH_3COONa and HCl in 1 : 1 mole ratio
   (b) CH_3COONa and HCl in 2 : 1 mole ratio
   (c) CH_3COONa and HCl in 1 : 2 mole ratio
   (d) NH_4Cl and NaOH in 3 : 1 mole ratio

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ				

7. Pb^{2+} ion has been placed in both I and II groups of basic radicals because of :

(a) K_{sp} of $PbCl_2$ is not very small
(b) Pb^{2+} ion is not completely precipitated as $PbCl_2$ from cold water
(c) The remainder of Pb^{2+} ions get precipitated as PbS in II group
(d) $PbCl_2$ is sparingly soluble in water.

8. Molarity of NH_4^+ ion in 0.1 M NH_3 solution can be increased significantly by

(a) passing NH_3 into the solution
(b) passing HCl gas into the solution
(c) adding an ammonium salt
(d) adding 1 M NH_3 solution

9. Which of the following solutions will be neutral?

(a) 50 ml of 0.1 M CH_3COOH + 50 ml of 0.1 M NaOH
(b) 100 ml of 0.1M CH_3COOH + 50 ml of 0.2 M NH_3
(c) 100 ml of 0.1M HCl + 50 ml of 0.2 M KOH
(d) 50 ml of 0.1 M HCl + 50 ml of 0.1 M NH_3

10. Pick out the correct statement(s) of the following :

(a) Liquid NH_3, like water, is an amphiprotic solvent
(b) $C_6H_5NH_2$ is a weak organic base in aqueous solution
(c) $C_6H_5NH_2$ is a strong base in liquid acetic acid
(d) A solution containing NH_3 and NH_4Cl is less basic than NH_3.

11. Consider the following reaction :

$$\underset{\text{I}}{[Al(H_2O)_6]^{3+}} + \underset{\text{II}}{[Cu(H_2O)_3OH]^+} \longrightarrow \underset{\text{III}}{[Al(H_2O)_5OH]^{2+}} + \underset{\text{IV}}{[Cu(H_2O)_4]^{2+}}$$

Find the correct statements of the following :

(a) *I* is an acid and *II* the base
(b) *II* is an acid and *I* the base
(c) *III* is conjugate base of *I* and *IV* is conjugate acid of *II*
(d) *III* is conjugate acid of *I* and *IV* is conjugate base of *II*

12. Pick out the acid-base conjugate pairs of the following :

(a) H_3O^+ and OH^-
(b) $N_2H_6^{2+}$ and $N_2H_5^+$
(c) C_2H_5OH and $C_2H_5O^-$
(d) $C_5H_5NH^+$ and C_5H_5N

13. In which of the following solutions the use of equilibrium constant(s), mentioned in each case, permits the calculation of pH?

(a) 0.1 M each of NH_3 and NH_4Cl in the mixture : K_b of NH_3
(b) 0.1 M NH_3 : K_b of NH_3, K_w
(c) A solution 0.1 M in CH_3COOH and 0.2 M CH_3COONa : K_a of CH_3COOH
(d) 0.1 M CH_3COONa : K_a of CH_3COOH, K_w

14. An acid-base indicator has K_b of 1.0×10^{-5}. The acid form of the indicator is red and the basic form is blue. Then :

(a) pH is 8.4 when indicator is 80% red
(b) pH is 9.6 when indicator is 80% blue
(c) pH is 9.6 when indicator is 80% red
(d) pH is 8.4 when indicator is 80% blue

15. Which combinations of reactants will react less than 2% of the theoretically possible extent?

(a) $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$
(b) $CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$
(c) $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$
(d) $NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$

16. Which one of the following will react more than 98% of the limiting quantities?

(a) $CH_3COO^- + H_3O^+ \longrightarrow CH_3COOH + H_2O$
(b) $CH_3COOH + OH^- \longrightarrow CH_3COO^- + H_2O$
(c) $NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$
(d) $NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O$

17. Which of the following will not react with NaOH to form water?

(a) NaH_2PO_3
(b) Na_2HPO_3
(c) NaH_2PO_2
(d) Na_2HPO_4

MARK YOUR RESPONSE	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ
	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ
	17. ⓐⓑⓒⓓ				

18. The correct statements (s) is/are

(a) The pH of 1×10^{-8} M HCl solution is 8.

(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

(c) Autoprotolysis constant of water increases on increasing temperature.

(d) In the titration of a weak monoprotic acid and a strong base, the pH at half neutralisation point is equal to $\frac{1}{2}\,pK_a$

19. In an aqueous solution of Fe (III) and (SCN^-), the equilibrium can be represented as follows :

$$\underset{\text{Pale yellow}}{Fe^{3+}(aq)} + \underset{\text{Colourless}}{SCN^-(aq)} \rightleftharpoons \underset{\text{red}}{[Fe(NCS)]^{2+}(aq)}$$

For this choose correct statements

(a) When $FeCl_3$ is added to it there is no change is colour

(b) When KSCN is added to it there is no change in colour.

(c) When oxalic acid is added, there is a decrease in red colour

(d) When $HgCl_2$ (aq) is added the red colour disappears.

20. In which of the following solutions pH is less than 7?

(a) $Fe(ClO_4)_3$ (b) BaI_2

(c) $Cr(NO_3)_3$ (d) $[(CH_3)_3NH]Cl$.

21. Buffer solution can be prepared from a mixture of

(a) sodium acetate and acetic acid in water

(b) sodium acetate and HCl in water

(c) ammonia and ammomium chloride in water

(d) ammonia and sodium hydroxide in water

22. In a buffer solution consisting NaH_2PO_4 and Na_2HPO_4

(a) The NaH_2PO_4 is acid and Na_2HPO_4 is salt

(b) The pH of solution can be calculated using the relation $pH = pK_2 + \log\dfrac{[HPO_4^{2-}]}{[H_2PO_4]^-}$

(c) The Na_2HPO_4 is acid and NaH_2PO_4 is salt

(d) The pH cannot be calculated.

MARK YOUR RESPONSE	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ

E

MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:

If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	ⓠ	ⓡ	●	●
B	ⓟ	●	●	ⓢ	ⓣ
C	●	●	ⓡ	ⓢ	ⓣ
D	ⓟ	ⓠ	ⓡ	●	●

1. Match the following :

	Column I		**Column II**
(A)	Bronsted-lowry acid	p.	$CH_3^{\oplus}$
(B)	Bronsted-lowry base	q.	$CH_3^{\ominus}$
(C)	Lewis acid	r.	$H_2PO_4^-$
(D)	Lewis base	s.	NH_4^+

MARK YOUR RESPONSE

1.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

2. **Consider a buffer of CH_3COOH and CH_3COONa of maximum buffer-capacity and match the following :**

	Column I		**Column II**
(A)	For maximum buffer capacity	p.	No change in pH
(B)	Adding equal number of moles of CH_3COOH and CH_3COONa	q.	pH > pKa
(C)	Diluting buffer 10 times	r.	pH = pKa
(D)	Adding some NaOH to buffer	s.	$pOH = pK_b$

3. **K_w under conditions of high temperature and pressure is 1.0×10^{-10}. Match the following**

	Column I		**Column II**
(A)	Solution of pH 5.5	p.	Neutral
(B)	Solution of pH 5	q.	Acidic
(C)	Solution of pH 4	r.	$[OH^-] = 10^{-3} M$
(D)	Solution of pH 7	s.	Basic

4. **K_a and K_b are the dissociation constants of weak acid and weak base and K_w is the ionic product of water. Match the pH stated in column II with the solutions listed in column I at 25°C.**

	Column I - (Solution)		**Column II - (pH)**
(A)	0.1 *M* KCN	p.	7
(B)	0.1 *M* $C_6H_5NH_3Cl$	q.	$6.5 + \frac{1}{2}pK_a$
(C)	0.1 *M* KCl	r.	$7.5 - \frac{1}{2}pK_b$
(D)	0.1 *M* CH_3COONH_4	s.	$7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$

5. **Match the following**

	Column I		**Column II**
(A)	$NaHCO_{3(aq)}$	p.	Cationic hydrolysis
(B)	$CuSO_{4(aq)}$	q.	Anionic hydrolysis
(C)	$K_2SO_4.Al_2(SO_4)_3.24H_2O_{(aq)}$	r.	Acidic
(D)	$NaCN_{(aq)}$	s.	Basic

6.

	Column I - (Solution)		**Column II - (Nature of solution)**
(A)	Salt of a weak acid and weak base ($pK_a = pK_b$)	p.	Acidic
(B)	Salt of weak acid and strong base	q.	Basic
(C)	Salt of strong acid and strong base	r.	Neutral
(D)	Salt of strong acid and weak base	s.	pH can be predicted only in case K_a/K_b is given

7.

	Column I		**Column II**
(A)	HCl	p.	Bronsted base
(B)	NH_3	q.	Bronsted acid
(C)	H_2O	r.	Arrhenius acid
(D)	CN^-	s.	Lewis base in adduct displacement reaction

MARK YOUR RESPONSE

2.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

3.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

4.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

5.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

6.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

7.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

NUMERIC/INTEGER ANSWER TYPE

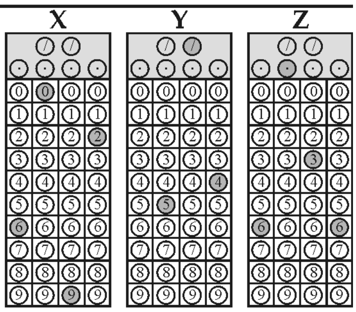
F

The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546).

The appropriate bubbles below the respective question numbers in the response grid have to be darkened.

For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following.

For single digit integer answer darken the extreme right bubble only.



1. To a solution that has $[\mathrm{CrO_4^{2-}}]^- = 0.010\,M$ and $[\mathrm{Br}] = 0.010\,M$ is gradually added 0.01 M $\mathrm{AgNO_3}$. What is $[\mathrm{Br^-}]$ remaining in solution (in terms of $10^{-8}\,M$) at the point where $\mathrm{Ag_2CrO_4}$ starts precipitating?

$K_{sp}(\mathrm{Ag_2CrO_4}) = 2.25 \times 10^{-12}$, K_{sp} (AgBr)$= 5.0 \times 10^{-13}$

2. What minimum concentration of ammonia would be required to prevent the precipitation of AgCl from 1.00 L of a solution containing 0.10 mole of $\mathrm{AgNO_3}$ and 0.010 mole of KCl.

$K_{sp}(\mathrm{AgCl}) = 1.8 \times 10^{-10}$; Formation constant of $[\mathrm{Ag(NH_3)_2}]^+ = 1.5 \times 10^7$

3. The solubility product for $\mathrm{Ag_2C_2O_4}$ at 25°C is 1.29×10^{-11}. A solution of $\mathrm{K_2C_2O_4}$ containing 0.154 ml in 500ml water is shaken at 25°C with excess of $\mathrm{Ag_2CO_3}$ till the following equilibrium is reached :

$$\mathrm{Ag_2CO_{3(s)} + K_2C_2O_{4(aq)} \rightleftharpoons Ag_2C_2O_{4(s)} + K_2CO_{3(aq)}}$$

At equilibrium, the solution contains 0.0358 mole of $\mathrm{K_2CO_3}$. Assuming the degree of dissociation of $\mathrm{K_2C_2O_4}$ and $\mathrm{K_2CO_3}$ to be equal, calculate the solubility product (in multiple of 10^{-12}) of $\mathrm{Ag_2CO_3}$.

4. Calculate equilibrium constant (in multiple of 10^4) of the following reaction

$$\mathrm{CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-}$$

$(K_b(\mathrm{CN^-}) = 2.04 \times 10^{-5}$, $K_b(\mathrm{CH_3COO^-}) = 5.55 \times 10^{-10}$

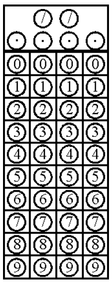
5. AgBr is sparingly soluble in water, $K_{sp}(\mathrm{AgBr}) = 12 \times 10^{-14}$. If 10^{-7} mol of $\mathrm{AgNO_3}$ are added to 1 L saturated solution of AgBr, calculate conductivity of the resulting solution in terms of 10^{-7} S m^{-1} units.

Given, $\lambda^\circ_{\mathrm{Ag^+}} = 6 \times 10^{-3}\,\mathrm{S\,m^2mol^{-1}}$,

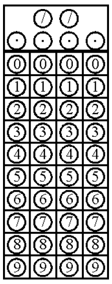
$\lambda^\circ_{\mathrm{Br^-}} = 8 \times 10^{-3}\,\mathrm{S\,m^2mol^{-1}}$, $\lambda^\circ_{\mathrm{NO_3^-}} = 7 \times 10^{-3}\,\mathrm{S\,m^2mol^{-1}}$

MARK YOUR RESPONSE

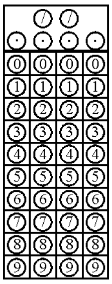
1.



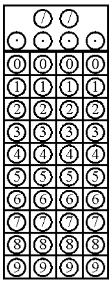
2.



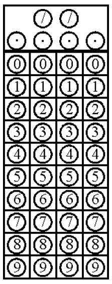
3.



4.



5.



Answerkey

A Single Correct Choice Type

1.	d	**2.**	a	**3.**	b	**4.**	b	**5.**	d	**6.**	a	**7.**	d	**8.**	a	**9.**	d	**10.**	c
11.	c	**12.**	c	**13.**	d	**14.**	b	**15.**	b	**16.**	c	**17.**	d	**18.**	c	**19.**	b	**20.**	a
21.	b	**22.**	b	**23.**	c	**24.**	b	**25.**	c	**26.**	c	**27.**	d	**28.**	c	**29.**	c	**30.**	d
31.	c	**32.**	d	**33.**	d	**34.**	b	**35.**	c	**36.**	d	**37.**	b	**38.**	b	**39.**	c	**40.**	b
41.	c	**42.**	b	**43.**	d	**44.**	d	**45.**	b	**46.**	c	**47.**	b	**48.**	d	**49.**	c	**50.**	b
51.	c	**52.**	b	**53.**	d	**54.**	d	**55.**	b	**56.**	d	**57.**	a	**58.**	b	**59.**	d	**60.**	c
61.	c	**62.**	a	**63**	c	**64**	c	**65**	b	**66**	c	**67**	c	**68**	c	**69**	c	**70**	c
71	b	**72**	b	**73**	c	**74**	a	**75**	b	**76**	b	**77**	c	**78**	d	**79**	c	**80**	d
81	d	**82**	c	**83**	c	**84**	d	**85**	b	**86**	a	**87**	d	**88**	c	**89**	a	**90**	c
91	c	**92**	a	**93**	c	**94**	a	**95**	b										

B Comprehension Type

1	c	**5**	a	**9**	c	**13**	a	**17**	c
2	b	**6**	b	**10**	a	**14**	c	**18**	b
3	a	**7**	c	**11**	b	**15**	c	**19**	c
4	d	**8**	b	**12**	d	**16**	d	**20**	b

C Reasoning Type

1	c	**3**	d	**5**	a	**7**	b	**9**	a	**11**	b
2	a	**4**	a	**6**	b	**8**	b	**10**	b		

D Multiple Correct Choice Type

1.	b,c,d	**2.**	a,d	**3.**	b,d	**4.**	a,b,c	**5.**	b,c	**6.**	b,d	**7.**	a,b,c	**8.**	b,c	**9.**	b,c	**10.**	a,b,c,d
11.	a,c	**12.**	b,c,d	**13.**	b,c,d	**14.**	a,d	**15.**	a,c	**16.**	a,b,c,d	**17.**	b,c	**18.**	b,c	**19.**	c,d	**20.**	a,c,d
21.	a,c	**22.**	a,b																

E Matrix-Match Type

1. A – r, s; B – q, R; C – p; D – q, r
2. A – r, s; B – p, r; C – p, r; D – q
3. A – s; B – p; C – q; D – r, s
4. A – q; B – r; C – p; D – p, s
5. A – q, s; B – p, r; C – p, r; D – q, s
6. A - r; B - q, s; C - r; D - p, s
7. A - q, r; B - p, s; C - p, q, s; D - p, s

F Numeric/Integer Answer Type

1	3.33	**2**	0.808	**3**	3.974	**4**	3.68	**5**	55

Solutions

A SINGLE CORRECT CHOICE TYPE

1. **(d)** $HA + BOH \longrightarrow BA + H_2O, K = \dfrac{K_a K_b}{K_w}$

$$= \frac{2 \times 10^{-5} \times 5 \times 10^{-6}}{1.0 \times 10^{-14}} = 1.0 \times 10^4$$

2. **(a)** $[H^+] = [OH^-] = \sqrt{40 \times 10^{-14}} = 2.0 \times 10^{-7}$

$$pH = pOH = -\log 2 \times 10^{-7} = 6.699$$

3. **(b)** K (for neutralization of weak base with strong acid)

$$= \frac{K_b}{K_w} = \frac{2.5 \times 10^{-6}}{1.0 \times 10^{-14}} = 2.5 \times 10^8$$

4. **(b)** $\alpha_1 = 0.005 = \sqrt{K_a/C}$ $(C_1 = 1 \text{ mol L}^{-1})$; Molarity of diluted solution, $C_2 = \dfrac{2}{32} = \dfrac{1}{16} \text{molL}^{-1}$

$$\alpha_2 = \sqrt{\frac{K_a}{C_2}} = 0.005\sqrt{16} = 0.02$$

$$[H_3O^+] = C_2 \alpha_2 = \frac{1 \times 0.02}{16} = 1.25 \times 10^{-3} M$$

5. **(d)** $K_H = \dfrac{K_w}{K_a K_b} = \dfrac{1.0 \times 10^{-14}}{(3 \times 10^{-7})^2} = \dfrac{1}{9}$

$$\frac{h}{1-h} = \sqrt{K_H} = \sqrt{\frac{1}{9}} \Rightarrow h = 0.25$$

6. **(a)** $NaCN_{(aq)} + HCl_{(aq)} \longrightarrow HCN_{(aq)} + NaCl_{(aq)}$

Excess milli mol of HCl = 50 × 0.2 − 50 × 0.1 = 5
$[HCl]_{excess} = 5/100 = 0.05\, M$
$[H_3O^+] = 0.05$, pH $= -\log 0.05 = 1.30$
(HCN remains practically unionised)

7. **(d)** All the salts undergo hydrolysis in aqueous solution. The acids formed have their strength in the order:

$$HCl > HCOOH > CH_3COOH$$

The strength of the bases formed follow the order : $NaOH > NH_4OH$.

8. **(a)** $pH = 14 - pOH = 14 - \left(pK_b + \log\dfrac{[salt]}{[base]}\right)$

$$= 14 + \log K_b - \log\frac{80}{20} \Rightarrow K_b = 1.0 \times 10^{-6}$$

9. **(d)** K_a of HA $= \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9}$;

(Given pH = 7.40)

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$$= -\log 10^{-9} + \log\frac{0.1}{0.3} = 9 - \log 3$$

10. **(c)** At the equivalence point, the volume of resulting solution is doubled.

Hence, $[NH_4Cl] = \dfrac{0.2}{2} = 0.1M[NH_4^+]$

The salt hydrolyses,

$$pH = \frac{1}{2}\left(pK_w - pK_b - \log[NH_4^+]\right)$$

$$= \frac{1}{2}(14 - 4.74 - \log 0.1) = 5.13$$

11. **(c)** $pH = 14 - pK_b - \log\dfrac{[B^+]}{[BOH]}$

V = volume of acid required for the equivalance point.

(i) $(pH)_1 = 9 = 14 - pK_b - \log\dfrac{10}{V-10}$

(ii) $(pH)_2 = 8 = 14 - pK_b - \log\dfrac{25}{V-25}$

(i) − (ii), $1 = \log\dfrac{25}{V-25} - \log\dfrac{10}{V-10} = \log\dfrac{25(V-10)}{10(V-25)}$

$\Rightarrow V = 30$ml

12. **(c)** $[CN^-] = 2 \times 0.5 = 1.0\, M$

$$pH = \frac{1}{2}(pK_w + pK_a + \log[CN^-])$$

$$= \frac{1}{2}[14 + (14 - pK_b) + \log 1] = \frac{1}{2}[28 - 9.30] = 9.35$$

13. **(d)** At the isoelectric pH, both the acidic and basic groups are equally ionized.

14. **(b)** $\mathrm{pH} = 14 - \mathrm{pK_b} - \log\dfrac{[\mathrm{B}^+]}{[\mathrm{BOH}]}$;

$[\mathrm{B}^+] = [\mathrm{BOH}]$ at half neutralization.

15. **(b)** On increasing T, K_w increases and so also $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$.

18. **(c)** (a) $[\mathrm{H_3O^+}] = \dfrac{0.1}{2} = 0.05$; $\mathrm{pH} = -\log 0.05 = 1.301$

(b) Complete neutralization of strong acid and strong base, pH = 7.

(c) Hydrolysis of the salt $\mathrm{CH_3COOK}$, pH > 7 (salt of weak acid with strong base)

(d) Hydrolysis of the salt $\mathrm{NH_4NO_3}$, pH < 7(salt of strong acid with weak base)

19. **(b)** $\mathrm{AB_{3(s)}} \rightleftharpoons \mathrm{A^{3+}_{(aq)}} + \mathrm{3B^-_{(aq)}}$

$K_{sp} = [\mathrm{A^{3+}}][\mathrm{B^-}]^3 = S \times (3S)^3 = 2.7 \times 10^{-19}$

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

20. **(a)** $[\mathrm{OH^-}] = [\mathrm{OH^-}]_{\mathrm{NaOH}} + [\mathrm{OH^-}]_{\mathrm{Mg(OH)_2}} = 0.1 + 2\mathrm{S} \approx 0.1M$

$(2\mathrm{S} << 0.1)$

$\mathrm{K_{sp}[Mg(OH)_2]} = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2 = [\mathrm{Mg^{2+}}] \times 0.1^2 = 4.0 \times 10^{-12} \Rightarrow [\mathrm{Mg^{2+}}] = 4.0 \times 10^{-12} M$

21. **(b)** $\mathrm{M[OH]_{2(s)}} \longrightarrow \mathrm{M^{2+}_{(aq)}} + \mathrm{2OH^-_{(aq)}}$,

$K_{sp} = S \times (2S)^2 = 4S^3 = 3.2 \times 10^{-11}$

$\Rightarrow S = 2 \times 10^{-4} M$

$[\mathrm{OH^-}] = 2S = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4} M$

$\mathrm{pH} = 14 - \mathrm{pOH} = 14 + \log 4 \times 10^{-4} = 10.60$

22. **(b)** $\mathrm{Al(OH)_{3(s)}} \rightleftharpoons \mathrm{Al^{3+}} + \mathrm{3OH^-}$;

$K_{sp} = 2.7 \times 10^{-23} = 27\,S^4 \Rightarrow S = 1.0 \times 10^{-6} M$

$[\mathrm{OH^-}]$ required for precipitation of $\mathrm{Al(OH)_3}$

$= 3S = 3.0 \times 10^{-6}\ \mathrm{mol\ L^{-1}}$

$\mathrm{Zn(OH)_{2(s)}} \rightleftharpoons \mathrm{Zn^{2+}_{(aq)}} + \mathrm{2OH^-_{(aq)}}$

$K_{sp} = 3.2 \times 10^{-14} = 4\,S^3 \Rightarrow S = 2 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$

$[\mathrm{OH}]^-$ required for precipitation of $\mathrm{Zn(OH)_2}$

$= 2S = 4 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$

23. **(c)** $[\mathrm{Ag^+}]$ required for commencement of precipitation

$$\text{of AgCl} = \frac{K_{sp}(\mathrm{AgCl})}{[\mathrm{Cl^-}]} = \frac{1.0 \times 10^{-10}}{0.1} = 1.0 \times 10^{-9} M$$

$[\mathrm{Br^-}]$ remaining at this stage

$$= \frac{K_{sp}(\mathrm{AgBr})}{[\mathrm{Ag^+}]} = \frac{1.0 \times 10^{-13}}{1.0 \times 10^{-9}} = 1.0 \times 10^{-4} M$$

% of $\mathrm{Br^-}$ remaining unprecipitated

$$= \frac{1.0 \times 10^{-4}}{0.1} \times 100 = 0.1$$

% of $\mathrm{Br^-}$ precipitated $= 100 - 0.1 = 99.9$

24. **(b)** $\mathrm{pOH} = 14 - \mathrm{pH} = 14 - 8.699 = 5.301$,

$[\mathrm{OH^-}] = 5 \times 10^{-6} M$; $[\mathrm{Mg^{2+}}] = 2.5 \times 10^{-6} M$

$K_{sp}[\mathrm{Mg(OH)_2}] = [\mathrm{Mg^{2+}}][\mathrm{OH^-}]^2$

$= 2.5 \times 10^{-6} \times (5 \times 10^{-6})^2 = 6.25 \times 10^{-17} M^3$

25. **(c)** $\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}$; $\mathrm{pH} = \mathrm{pK_{in}} + \log\dfrac{[\mathrm{In^-}]}{[\mathrm{HI_n}]}$

$$(\mathrm{pH})_1 = \mathrm{pK_{in}} + \log\frac{20}{80} = \mathrm{pK_{in}} - 2\log 2$$

$$(\mathrm{pH})_2 = \mathrm{pK_{in}} + \log\frac{80}{20} = \mathrm{pK_{in}} + 2\log 2$$

Hence $(\mathrm{pH})_2 - (\mathrm{pH})_1 = \mathrm{pK_{in}} + 2\log 2 - (\mathrm{pK_{in}} - 2\log 2)$

$= 4\log 2 = 1.20$

26. **(c)** $K_a K_b = 1.0 \times 10^{-14}$,

$$K_a = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-9}} = 1.0 \times 10^{-5}$$

$\mathrm{HIn} \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}$,

$$K_a = 1.0 \times 10^{-5} = \frac{[\mathrm{H^+}][\mathrm{In^-}]}{[\mathrm{HIn}]} \Rightarrow [\mathrm{H^+}] = 10^{-5}$$

$([\mathrm{In^-}] = [\mathrm{HIn}])$

28. **(c)** Solubility of

$\mathrm{AgCl} = \sqrt{K_{sp}} = \sqrt{1.0 \times 10^{-10}} = 1.0 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$

Mass dissolved in 10L = $10 \times 1.0 \times 10^{-5} \times 143.5 = 1.435 \times 10^{-2}$g

29. **(c)** $\mathrm{SrF_{2(s)}} \rightleftharpoons \mathrm{Sr^{2+}} + \mathrm{2F^-}$; $K_{sp} = 4S^3 = 3.2 \times 10^{-11}$

$\Rightarrow S = 2 \times 10^{-4} M$

$[\mathrm{F^-}] = 2S = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4}\ \mathrm{mol\ L^{-1}}$

30. **(d)** In the absence of dilute HCl, ionization of $\mathrm{H_2S}$ is not suppressed due to common ion effect. As a result, $[\mathrm{S^{2-}}]$ increases to such an extent that fourth group sulphides having higher K_{sp} values also get precipitated.

31. **(c)** The common ion effect is not observed as NaOH is a strong electrolyte.

32. **(d)** In presence of HCl, I.P. = $[\mathrm{Ba^{2+}}][\mathrm{Cl^{-2}}]$ exceeds K_{sp}. Hence $\mathrm{BaCl_2}$ gets precipitated.

33. **(d)** (c) : $[\mathrm{Cl^-}]_{\mathrm{common}} = 0.2M$,

(b) : $[\mathrm{Cl^-}]_{\mathrm{common}} = 0.1\ M$; (a) : $[\mathrm{Cl^-}]_{\mathrm{common}} = 0$

(d) : $\mathrm{Ag^+}$ ion forms complex ion with $\mathrm{NH_3}$ as :

$\mathrm{Ag^{2+}_{(aq)}} + \mathrm{2NH_{3(aq)}} \rightleftharpoons [\mathrm{Ag(NH_3)_2}]^+$

35. **(c)** Milli moles of HCl = $75 \times 0.2 = 15$;
Milli moles of NaOH = $25 \times 0.2 = 5$
Milli moles of HCl left un-neutralized = $15 - 5 = 10$;

$$[H_3O^+] = \frac{10}{75+25} = 0.1M \text{ ; pH} = 1$$

36. **(d)** pH = 8; pOH = 6; $[OH^-] = 10^{-6}\,M$;
I.P. of $Fe(OH)_2 = 0.2 \times (1.0 \times 10^{-6})^2 = 2 \times 10^{-13} > K_{sp}$ $(= 8.1 \times 10^{-16})$

37. **(b)**
$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = pK_a \text{ ;}$$

$\Rightarrow$ at 50ºC $pK_a < 4.74$

38. **(b)** pOH = 14 – 13 = 1; $[OH^-] = 1.0 \times 10^{-1}$;

$$S \text{ of } BaCl_2 = \frac{1.0 \times 10^{-1}}{2} = 0.05 \text{mol L}^{-1}$$

39. **(c)** (a) H_3O^+ can not take up proton, other species can give up and take up proton.

(b) H_2O and HPO_4^- give up and take up proton but $H_2PO_2^-$ can not give up proton (H_3PO_2 is monobasic acid)

(d) $C_2O_4^{2-}$ can not give up proton, $H_2PO_4^-$ and HSO_4^- can give up and take up proton.

40. **(b)** pH of buffer

$$= pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{500 \times 0.2}{500 \times 0.1} = 5.04$$

pH of a buffer does not change with dilution.

41. **(c)** pOH = 14 – pH = 14 – 8.26 = 5.74

$$= pK_b + \log\frac{[NH_4^+]}{[NH_3]} = 4.74 + \log\frac{[NH_4^+]}{0.1}$$

$$\Rightarrow \quad [NH_4^+] = 1\text{mol L}^{-1};\ [(NH_4)_2SO_4] = \frac{1}{2} = 0.5\text{mol L}^{-1}$$

43. **(d)** In case of (a), (b) and (c) pH < 7 due to cationic (NH_4^+) hydrolysis.
In case of $(NH_4)_3PO_4$, both the cation and anion undergo hydrolysis. pH ≈ 7

45. **(b)** $K_{sp}[Ca(OH)_2] = 4.0 \times 10^{-6} = [Ca^{2+}]\,[OH^-]^2$
$= 0.01 \times [OH^-]^2 \Rightarrow [OH^-] = 2 \times 10^{-2}$;
pOH = $-\log 2 \times 10^{-2} = 2 - \log 2$; pH = $14 - (2 - \log 2)$ $= 12 + 2\log 2$

46. **(c)** Cathodic reaction : $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$;
Anodic reaction : $2Cl^- \rightarrow Cl_2 + 2e^-$

$$\text{Mol. of OH}^- \text{ formed} = \frac{1 \times 9650}{96500} = 0.1$$

$[OH^-] = 0.1\ L^{-1}$; pOH = 1

47. **(b)** H_3PO_3 is a dibasic acid. It ionizes as :
$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^-$; $H_2PO_3^- \rightarrow H^+ + HPO_3^{2-}$

48. **(d)** $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$; milli mole of $CH_3COOH = 100 \times 0.1 = 10$;
milli mole of NaOH = $50 \times 0.3 = 15$; CH_3COOH is completely consumed and NaOH is left in excess.

49. **(c)** $NH_3 + HCl \rightarrow NH_4Cl$; milli mole of HCl added $= 10 \times 1 = 10$
(c) milli mole of $NH_3 = 100 \times 0.05 = 5$
There is excess of HCl.

50. **(b)**
$$K_a(H_2S) = 4 \times 10^{-21} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = \frac{0.1^2 \times [S^{2-}]}{0.1}$$

$$\Rightarrow [S^{2-}] = 4 \times 10^{-20}\,M$$

$K_{sp}(CoS) = 2 \times 10^{-21} = [Co^{2+}]\,[S^{2-}]$
$= [Co^{2+}] \times 4 \times 10^{-20} \Rightarrow [Co^{2+}] = 0.05\,M$

52. **(b)** At the half neutralization of weak base B, $[BH^+] = [B]$

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

$pH = 14 - pOH = 14 - pK_b$

53. **(d)** $pH = pK_{a(1)}$ when $[HA^-] = [H_2A]$
$pH = pK_{a(2)}$ when $[A^{2-}] = [HA^-]$
The points *A* and *C* represent half stages of the reactions :
(i) $H_2A + OH^- \rightarrow HA^- + H_2O$
(ii) $HA^- + OH^- \rightarrow A^{2-} + H_2O$

54. **(d)**
$$Hg_2Cl_{2(s)} \rightleftharpoons Hg_{2(aq)}^{2+} + 2Cl_{(aq)}^-$$

$$K_{sp} = [Hg_{2(aq)}^{2+}][Cl^-]^2 = S \times (2S)^2 = 4S^3$$

55. **(b)** $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
with the decrease in $[CO_2]$, the equilibrium shifts in reverse direction causing $[H^+]$ to decrease.

56. **(d)** The point of inflexion, D, represents the equivalence point of titration.

57. **(a)**
$$pH = (5.7) = pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log\frac{10}{15-10}$$

$$= pK_a + \log 2 \Rightarrow pK_a = 5.40$$

58. **(b)** KOH, being strong electrolyte, ionizes completely. Hence $[OH^-] = 0.01\,M$
which remains constant, even at 50ºC (volume of solution is supposed to be constant). Hence, pOH(= –log 0.01 = 2) remains constant. At 50ºC $pK_w < 14$. Hence pH at 50ºC = $(pK_w - 2) < 12$.

59. **(d)** In 2:1 molar ratio of NH_3 and HCl, the solution contains NH_3 and NH_4Cl in 1 : 1 molar ratio. In case of (a) and (b), the solution contains NH_4Cl and HCl (excess). In case of (c), the solution contains NH_4Cl only.

60. **(c)** Volume of HCl required = V ml

Volume of NH_3 required = $300 - V$ ml

For a buffer of a weak base and its salt with strong acid:

$$\mathrm{pH} = \mathrm{pK_a} - \log\frac{[\text{salt}]}{[\text{base}]};$$

$$9.26 = 9.26 - \log\frac{V}{(300-V)-V} \Rightarrow V = 100 \text{ ml}$$

61. **(c)** Since $K_a = K_b$, $[H_3O^+]$ in 0.01 M CH_3COOH = $[OH^-]$ in 0.01 M NH_4OH.

Hence, pOH of $NH_4OH_{(aq)}$ = pH of $CH_3COOH_{(aq)}$ = 4 ; pH of $NH_4OH = 14 - 4 = 10$

62. **(a)** The strength of the conjugate acids of the given bases follow the order : $CH_3\text{–}CH_3 < NH_3 < CH \equiv CH < H_2O$.

64. **(c)** $[H^+]$ in HCl solution (pH = 2) = $10^{-2} M$; $[OH^-]$ in KOH solution (pOH = 14 – 12 = 2) = 10^{-2} M

Excess m Mol of OH^- in 5 ml mixture $= 3\times10^{-2} - 2\times10^{-2} = 1.0\times10^{-2}$;

$$[OH^-] \text{ in mixture} = \frac{1.0\times10^{-2}}{5} = 2\times10^{-3}\ M;$$

$$\mathrm{pOH} = -\log 2\times10^{-3} = 3 - \log 2;$$

$$\mathrm{pH} = 14 - (3 - \log 2) = 11.30$$

65. **(b)** Volume of NaOH required for equivalence point

$$= \frac{50\times0.1}{0.2} = 25 \text{ ml}$$

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 4.39 + \log\frac{20}{25-20}$$

$$= 4.39 + \log 4 = 4.39 + 2\log 2 = 4.99$$

66. **(c)** $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$;

$$K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]} = 4.5\times10^{-7}$$

$$\text{or, } \frac{[HCO_3^-]}{[CO_2]} = \frac{4.5\times10^{-7}}{[H^+]} = \frac{4.5\times10^{-7}}{4\times10^{-8}} = 11.25$$

67. **(c)** (I) $[HCl]$ in the mixture $= \dfrac{50\times0.2}{100} = 0.1\,M$

In presence of strong acid HCl, the waek acid HA remains practically unionized. Hence

$$[H^+] = [H^+]_{HCl} = 0.1\,M, \ \mathrm{pH} = 1$$

(II) $NaA + HCl \longrightarrow NaCl + HA$;

$$[HA] = \frac{50\times0.2}{100} = 0.1\ M$$

No HCl is left. Hence $[H^+]$

$$= \sqrt{K_a C} = \sqrt{1.0\times10^{-5}\times0.1} = 1.0\times10^{-3};\ \mathrm{pH} = 3$$

69. **(c)** In case of (a), (b) and (d) water is present in large excess and $[H_2O]$ is constant practically.

In (c), concentration of ester and water are comparable.

70. **(c)** $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Moles of CH_3COOH neutralized = 0.05; Moles of CH_3COOH left = 0.1 – 0.05 = 0.05

Total moles of $CH_3COONa = 0.2 + 0.05 = 0.25$

Hence,

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{[\text{Salt}]}{[\text{Acid}]} = 4.74 + \log\frac{0.25}{0.05} = 4.74 + \log 5$$

$$= 5.44$$

71. **(b)** $NH_4Cl + NaOH \longrightarrow NaCl + NH_3 + H_2O$

Moles of NH_4^+ left = 0.1 – 0.05 = 0.05

Total moles of $NH_3 = 0.1 + 0.05 = 0.15$

$$(\mathrm{pOH})_1 = \mathrm{pK_b} + \log\frac{[\text{Salt}]}{[\text{Base}]} = \mathrm{pK_b} + \log\frac{0.1}{0.1} = \mathrm{pK_b}$$

$$(\mathrm{pOH})_2 = \mathrm{pK_b} + \log\frac{0.05}{0.15} = \mathrm{pK_b} - \log 3$$

Change in pOH = $(\mathrm{pOH})_2 - (\mathrm{pOH})_1 = -\log 3$

Change in pH = $\log 3 = 0.48$

72. **(b)** Let x ml of the acid be used. Volume of base mixed $= 150 - x$ ml

Volume of base left = $150 - x - x = 150 - 2x$

pOH = 14 – pH = 14 – 7 = 7

$$= pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} = -\log 1.0\times10^{-7} + \log\frac{x}{150-2x};$$

$$\log\frac{x}{150-2x} = 0 = \log 1$$

or, $$\frac{x}{150-2x} = 1 \Rightarrow x = 50\text{ml}$$

73. (c) (a) $[H^+] = \frac{100\times0.1}{200} = 0.05$, pH < 7

(b) Meq of $H_2SO_4 = 2\times0.1\times100 = 20$;

Meq of NaOH $= 0.1\times100 = 10$,

Meq of excess $H_2SO_4 = 20 - 10 = 10$; pH < 7

(c) $CH_3COOH + KOH \longrightarrow CH_3COOK + H_2O$;

$[\text{Salt}] = \frac{0.1\times100}{200} = 0.05\ M$; pH > 7 due to hydrolysis of salt of weak acid with a strong base. (anionic hydrolysis)

(d) $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$;

$$[CH_3COOH] = \frac{0.1\times50}{100} = 0.05\text{ M}, \text{pH} < 7$$

74. (a) $$C_6H_5NH_3^+ + H_2O \rightleftharpoons C_6H_5NH_2 + H_3O^+$$

$$K_H = \frac{K_w}{K_b} = \frac{10^{-14}}{4\times10^{-10}}$$

$$= \frac{[C_6H_5NH_2][H_3O^+]^2}{[C_6H_5NH_3^+]} = \frac{[H_3O^+]^2}{0.01}$$

$$\Rightarrow\ [H_3O^+] = 5.0\times10^{-4} M$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0\times10^{-14}}{5\times10^{-4}} = 2.0\times10^{-11} M$$

75. (b) On addition of 10 ml of HCl solution, neutralization is complete i.e., equivalence point reaches when only salt (of weak base with strong acid) is present. It hydrolyses to give the pH on the acid side (pH = 5.62). Before the equivalence point (excess of base) and after the equivalence point (excess of acid), no hydrolysis takes place.

76. (b) At the equivalence points only salt would be present.

(I) Salt of strong acid with strong base – No hydrolysis (pH = 7)

(II) Salt of weak base with strong acid – Acidic hydrolysis (pH < 7)

(III) Salt of weak acid with strong base – Basic hydrolysis (pH > 7)

77. (c) $[Ag^+]_{\text{maximum}}$ to prevent AgCl precipitation

$$= \frac{K_{sp}[AgCl]}{[Cl^-]} = \frac{1.0\times10^{-10}}{0.001} = 1.0\times10^{-7} M$$

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$$

$$K_f = \frac{1}{K_d} = \frac{1}{1.0\times10^{-8}}$$

$$= \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = \frac{0.004}{1.0\times10^{-7}[NH_3]^2}$$

$$\Rightarrow [NH_3] = 0.02 M$$

($K_f = 1.0\times10^8$, Ag^+ would largely form the complex ion. Hence $[Ag(NH_3)_2^+] = 0.004$)

78. (d) $$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3,$$

$$K_d = 1.0\times10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

If S mol L^{-1} = solubility of AgSCN, $[Ag(NH_3)_2^+] = S$; $[SCN^-] = S$

Hence, $$\frac{[Ag^+][0.002]^2}{S} = 1.0\times10^{-8}$$

$$\Rightarrow\ [Ag^+] = \frac{1.0\times10^{-8}S}{4\times10^{-6}} = 2.5\times10^{-3} S$$

Also, $K_{sp}[AgSCN] = 1.0\times10^{-12} = [Ag^+][SCN^-]$

$$= 2.5\times10^{-3} S\times S \Rightarrow S = 2.0\times10^{-5}\ \text{mol L}^{-1}$$

79. (c) (a) Sufficient $[OH^-]$ is present to precipitate $Fe(OH)_2$.

(b) Due to common ion effect, $[OH^-]$ is insufficient to precipitate $Mg(OH)_2$ which has large K_{sp}.

(c) Ag^+ ion forms the complex ion, $Ag(NH_3)_2^+$ and so its concentration decreases causing I.P. of AgOH < K_{sp} and hence no precipitation.

80. **(d)** $M^{3+} + SCN^- \rightleftharpoons M(SCN)^{2+}$;

$$K_d = \frac{[M^{3+}][SCN^-]}{[M(SCN)^{2+}]}$$

$[SCN]_{free} = 1.0\times10^{-5}$ M;

$[SCN^-]_{combined}$

$= 1.51\times10^{-3} - 1.0\times10^{-5} = 1.5\times10^{-3}\,M$

$[M(SCN)^{2+}] = 1.50\times10^{-3}$ M;

$[M^{3+}]_{free} = 2\times10^{-3} - 1.5\times10^{-3} = 5\times10^{-4}\,M$

Hence, $K_d = \dfrac{5\times10^{-4}\times1.0\times10^{-5}}{1.5\times10^{-3}} = 3.3\times10^{-6}$

81. **(d)** On dissolution of 0.1 mol of AgCl in 1 L, $[Cl^-] = 0.1\,M$

Then,

$$[Ag^+]_{free} = \frac{K_{sp}[AgCl]}{[Cl^-]} = \frac{1.0\times10^{-10}}{0.1} = 1.0\times10^{-9}\,M$$

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

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

$$= 1.0\times10^{8} = \frac{0.1}{1.0\times10^{-9}\times[NH_3]^2}$$

$[NH_3] = 1$ M;

Moles of NH_3 required = 1.0 (free) + 0.2 (combined) = 1.2

82. **(c)** $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$

$[Ag(NH_3)_2^+] = [Ag^+]_{added} = 0.02\,M$

$[NH_3]_{free} = 0.14 - 2\times0.02 = 0.10\,M$

$$K_d = 1.0\times10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{[Ag^+]\times0.10^2}{0.02} \Rightarrow$$

$[Ag^+] = 2.0\times10^{-8}\,M$

83. **(c)** I. $[Ag^+] = \sqrt{K_{sp}(AgCl)} = \sqrt{1.0\times10^{-10}} = 1.0\times10^{-5}\,M$

II. $[Ag^+] = \sqrt{K_{sp}(AgI)} = \sqrt{1.0\times10^{-16}} = 1.0\times10^{-8}\,M$

III. $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$;

$$K_d = 1.0\times10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{[Ag^+]\times0.1^2}{1.0}$$

$\Rightarrow [Ag^+] = 1.0\times10^{-6}\,M$

IV. $Ag(CN)_2^- \rightleftharpoons Ag^+ + 2CN^-$,

$KCN(0.1M) \longrightarrow K^+ + CN^-(0.1M)$

$$K_d = 1.0\times10^{-21} = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]}$$

$$= \frac{[Ag^+]\times0.1^2}{1.0}$$

$\Rightarrow [Ag^+] = 1.0\times10^{-19}\,M$

84. **(d)** $NaCN + HCl \longrightarrow HCN + NaCl$

$[HCN] = \dfrac{0.2\times50}{100} = 0.1\,M$

$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$

For the acid and its conjugate base, $K_aK_b = 10^{-14}$

Hence, K_a for HCN $= \dfrac{1.0\times10^{-14}}{2\times10^{-5}} = 5\times10^{-10}$

$[H_3O^+] = [CN^-] = \sqrt{K_aC}$

$= \sqrt{5\times10^{-10}\times0.1} = 7\times10^{-6}\,M$

85. **(b)** $pH = pK_{In} + \log\dfrac{[In^-]}{[HIn]} = pK_{In} - 1$ (given)

$\log\dfrac{[In^-]}{[HIn]} = -1 \Rightarrow \dfrac{[In^-]}{[HIn]} = 0.1$

% ionized $= \dfrac{0.1\times100}{0.1+1} = \dfrac{10}{1.1} = 9.1$

86. **(a)** In the titration of weak base with strong acid, the pH at the equivalence point lies on the acid side due to hydrolysis of the salt formed.

87. **(d)** The $[A^-]$ of the salt CaA_2 formed by the reaction between $Ca(OH)_2$ and HA (monobasic acid).

$[A^-] = 0.5 \times 2$ at equilvalence point $[CaA_2] = 0.5\,M$

$\therefore$ $\text{pH} = \frac{1}{2}[\text{pK}_w + \text{pK}_a + \log \text{C}]$

$= \frac{1}{2}[14 + 5 + 0] = 9.5$ $(\text{C} = [\text{A}^-] = 0.1\,M)$

88. **(c)** Given $\text{pH} = 5.2 \therefore [H^+] = 10^{-5.2}$

or $\log [H^+] = -5.2$ [Taking log]

or $[\text{H}^+] = 6.3 \times 10^{-6}$ [Taking antilog]

HCN is a weak said and in case of weak acids

$[\text{H}^+] = \text{C} \times \alpha$ [α = degree of dissociation of acid]

$\therefore$ $6.3 \times 10^{-6} = 0.1 \times \alpha$

or $\alpha = 6.3 \times 10^{-5}$

$\therefore$ $K_a = \text{C}\alpha^2 = 0.1 \times (6.3 \times 10^{-5})^2$

$= 3.97 \times 10^{-10}$

89. **(a)** Given the pH of solution = 13

$\therefore$ $[\text{H}^+] = 10^{-13}$ mol/litre

$= 10^{-13} \times 6.023 \times 10^{23}$ H^+ ions/litre

$= 6.023 \times 10^{10}$ H^+ ions/litre

$= 6.023 \times 10^{10} \times 10^{-3}$ H^+ ions/mL

$= 6.023 \times 10^{7}$ H^+/mL

90. **(c)** Since the equilibrium shows the hydrolysis of cations that occurs at equivalence point.

91. **(c)** For the weak acid HA, we have

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$= 1.0 \times 10^{-4}$ (given) ..(i)

The reaction of acid with base is

$$\text{HA} + \text{BOH} \rightleftharpoons \text{BA} + \text{H}_2\text{O}$$

(acid) (strong base)

or $\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$ [BOH is fully ionised]

$\therefore$ $$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} \quad ....(ii)$$

Also $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ ....(iii)

From equation (i), (ii) and (iii), we get

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

92. **(a)** (a) Na^+ ion is a weak acid and Cl^- ion is a weak base.

The reactions $\text{CH}_3\text{COO}^- + \text{Na}^+ \longrightarrow \text{CH}_3\text{COONa}$

and $\text{H}^+ + \text{Cl}^- \longrightarrow \text{HCl}$ do not occur.

(b) Ionization of CH_3COOH is suppressed due to common ion (H^+) effect by strong acid HCl.

(c) & (d) In these cases degree of dissociation increases.

B COMPREHENSION TYPE

1. **(c)** For the colour change of the indicator at the equivalence point, pH must change by 2 units.

$\text{pH} = -\log[\text{H}^+] = \pm 2 \quad \Rightarrow [\text{H}^+] = 10^{\pm 2}$ mol/L

2. **(b)** Answers (a) and (c) are characteristics of a neutral solution, which may not necessarily exist at the equivalence point of a titration.

3. **(a)** The pK_a of the indicator $(-\log K_a)$ should be near the equivalence point of the titration (pH = 7). Only bromothymol blue indicator has a K_a with a factor of 10^{-7}.

4. **(d)** Since the pH is less than pK_a of the indicator, the undissociated form predominates.

pH = 2;

$\text{pK}_a = -\log K_a = -\log 4 \times 10^{-4} = 4 - 2\log 2 > 2$

At $\text{pH} < \text{pK}_a$, the equilibrium of reaction -1 shifts to the left to give predominantly HMe, and hence the red colour.

5. **(a)** By only using a few drops of indicator, the number of H^+ ions that the indicator interacts with is kept to a minimum.

6. **(b)** On addition of 50ml NaOH,

$$[\text{H}^+] = \frac{100 \times 0.1 - 50 \times 0.1}{150} = \frac{1}{30}\ \text{mol L}^{-1}$$

$$\text{pH} = -\log\frac{1}{30} = \log 30 = 1.48$$

On addition of 100 ml NaOH, there is complete neutralization of the acid and base. pH = 7.0 (no salt hydrolysis)

On addition of 150ml NaOH,

$$[\text{OH}^-] = \frac{\text{meqvts of NaOH} - \text{meqvts of HCl}}{\text{Volume of mixture}}$$

$$= \frac{150 \times 0.1 - 100 \times 0.1}{150 + 100} = \frac{1}{50}\ \text{mol L}^{-1}$$

Hence, $[H^+] = \dfrac{1.0\times10^{-14}}{[OH^-]} = 1.0\times10^{-14}\times50$

$= 5\times10^{-13}$; $pH = 12.3$

7. **(c)** On addition of 50ml; $pH = 14 - pK_a - \log\dfrac{[\text{Salt}]}{[\text{Base}]}$

$$= 14 + \log 2\times10^{-5} - \log\frac{50\times0.1}{100\times0.1 - 50\times0.1} = 9.3$$

On addition of 100ml, the equivalence point is reached and the salt formed undergoes hydrolysis.

$$[\text{Salt}] = \frac{100\times0.1}{100+100} = 0.05\,\text{mol L}^{-1}$$

Hence, $pH = \dfrac{1}{2}[pK_w - pK_b - \log C]$

$$= \frac{1}{2}(14 + \log 2\times10^{-5} - \log 0.05) = 5.3$$

8. **(b)** At the equivalence point of titration of a weak acid with a weak base,

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

$$= \frac{1}{2}(14 - \log 1.8\times10^{-4} + \log 1.8\times10^{-5}) = 6.5$$

9. **(c)** At the equivalence point of titration of strong acid with a strong base, the solution will be neutral.

Hence, $[H^+] = [OH^-] = \sqrt{4\times10^{-14}} = 2\times10^{-7}$

$pH = -\log[H^+] = -\log 2\times10^{-7} = 6.7$

10. **(a)** Meq. of HA mixed $= 50\times0.2 = 10$

Meq. of KOH mixed $= 50\times0.2 = 10$

Hence, the complete neutralization of the acid and base.

But the salt formed (KA) will be hydrolysed to give basic solution (∵ stronger base than acid). Since at the equilibrium point, volume of solution is doubled,

salt concentration $= \dfrac{1}{2}\times0.2 = 0.1\,M$

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

$$= \frac{1}{2}(14 - \log 1.0\times10^{-5} + \log 0.1) = 9.0$$

11. **(b)** At point-2, first neutralization point of B reaches.

$$B + H^+ \longrightarrow BH^+$$

At point-4, second neutralization point of B reaches.

$$BH^+ + H^+ \longrightarrow BH^{2+}$$

At the half neutralization of BH^+ corresponding to point 3, $[BH^+] = [BH^{2+}]$

12. **(d)** Point-2 corresponds to the reaction,

$$B + H^+ \longrightarrow BH^+$$

Then, $M_1V_1 = M_2V_2$ or $0.1\times20 = 0.1\times V_2$

$\Rightarrow$ $V_2 = 20$ ml

13. **(a)** At point 4, the cation BH^{2+} of the salt formed will hydrolyse to give acidic solution. Hence pH < 7.

15. **(c)** Given solubility of calcium phosphate at 25°C

$= w$ g/100 mL

$= 10\,w$ g/1000 mL

$= 10\,w$ g/L

$= \dfrac{10w}{M}$ mol/L (molecular weight $= M$)

$Ca_3(PO_4)_2$ ionises in water as :

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2\,PO_4^{3-}$$

If solubility is 'S' then at equilibrium, we have the following concentration values.

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2\,PO_4^{3-}$$

(1 – S) 3S 2S

Thus $K_{sp} = (3S)^3\times(2S)^2$

$= 27S^3\times4S^2$

$= 108\,S^5$

Since the solubility of calcium phosphate at 25°C

$= \left(\dfrac{10w}{M}\right)$

We get $K_{sp} = 108\times\left(\dfrac{10w}{M}\right)^5$

$$= 1.08\times10^7\times\left(\frac{w}{M}\right)^5$$

$$\approx 1\times10^7\times\left(\frac{w}{M}\right)^5$$

16. **(d)** $MX \rightleftharpoons M^+ + X^-$

$(1 - S) \qquad S \qquad S$

$K_{sp} = S^2$

or $S = \sqrt{K_{sp}}$

$= \sqrt{2.5 \times 10^{-9}}$

$= \sqrt{25 \times 10^{-10}}$ or 5.0×10^{-5} mol L^{-1}

17. **(c)** $CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^-$

$CaCl_2$ is strong electrolyte and may be considered as completely ionised at 25°C

$\therefore$ $[Cl^-]$ in 0.04 M $CaCl_2 = 2 \times 004 = 0.08$ M

$K_{sp} = [Ag^+]\,[Cl^-] = 4.0 \times 10^{-10}$

$\therefore [Ag^+] = \dfrac{4.0 \times 10^{-10}}{0.08}$

$= 5.0 \times 10^{-9}$

18. **(b)** $pH = pK_a = \log \dfrac{[Salt]}{[acid]}$

$= 4.73 + \log \dfrac{0.05}{0.1} = 4.43$

19. **(c)** $pOH = pK_b + \log \dfrac{[Salt]}{[base]}$

$pK_b = -\log K_b = -\log 1.80 \times 10^{-5}$
$= 4.7447$

$\therefore \; pOH = 4.7447 + \log \dfrac{0.25}{0.20}$

$= 4.8417$

Also $pOH + pH = 14$

$\therefore \; pH = 14 - 4.8417 = 9.16$

20. **(b)** To find the ratio $\dfrac{[salt]}{[acid]}$ in an acidic buffer (containing an acid and its salt, we use the equation,

$pH = pK_a + \log \dfrac{[salt]}{[acid]}$.

Substituting the given values, we get

$5 = 4 + \log \dfrac{[salt]}{[acid]}$

$\log \dfrac{[salt]}{[acid]} = 5 - 4 = 1$

$= \log 10$

$\therefore \; \dfrac{[salt]}{[acid]} = 10$ (Taking antilog)

or [salt] : [acid] = 10 : 1 i.e. option (b).

C REASONING TYPE

1. **(c)** NH_4Cl suppresses the ionisation of NH_4OH due to common ion effect and concentration of OH^- ions is just sufficient to precipitate third group radicals as hydroxide. IV group hydroxides, having high K_{sp}, are not precipitated.

2. **(a)** According to Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{proton acceptor}]}{[\text{proton donor}]}$$

At midpoint of titration of weak acid

$[HA] = [A^-]$ and hence $pH = pK_a + \log 1.0 = pK_a$

3. **(d)** The pH of an aq. solution of acetic acid changes (increases) on addition of sodium acetate (due to suppression of dissociation of CH_3COOH and hence decrease in H^+ ion concentration).

4. **(a)** Reason is the correct explanation of Assertion.

5. **(a)** Reason is the correct explanation of Assertion.

6. **(b)** HgI_2 combines with KI to form the soluble complex K_2HgI_4. Also I^- ion, being large in size, is highly polarisable but reason is not the correct explanation of assertion.

7. **(b)** In presence of NaCl, $[Cl^-]$ increases very much. Hence $[Ag^+]$ decreases to keep $K_{sp} = [Ag^+][Cl^-]$ constant.

8. **(b)** H_2SO_4, HCl and HNO_3 dissociate to different extent in acetic acid because acetic acid is a poor proton acceptor and hence acts as a differentiating solvent.

9. **(a)** Both assertion and reason are correct and reason is the correct explanation of assertion.

10. **(b)** Both assertion and reason are correct, but reason is not the correct explanation of assertion.

In aqueous solution various given acids have equal strengths because the same acid hydronium ion, is common to all such solutions.

The tendency of all strong acids to ionize completely in water is known as levelling effect.

11. **(b)** Both assertion and reasons are correct but reason is not the correct explanation of assertion.

In HF there is inter-molecular hydrogen bonding which results in association.

D MULTIPLE CORRECT CHOICE TYPE

1. **(b, c, d)** In case of (b), (c) and (d), the salts are of weak bases with strong acids and undergo hydrolysis to give acidic solutions. CH_3COONa (salt of weak acid with a strong base) gives basic solution.

2. **(a, d)** Due to common ion effect of NH_4^+ ionisation of NH_3 is suppressed. As a result $[OH^-]$ decreases and so also pH.

3. **(b,d)** Solutions (a) and (c) are not buffers. (a) is CH_3COONa solution whereas (c) contains CH_3COONa and NaOH(excess).

4. **(a, b, c)** Amphiprotic species can accept and give up a proton.

$H_2SO_4^-$ & HSO_3^{2-} can accept H^+ only whereas H_3PO_4 can give up H^+ only.

5. **(b, c)** $H_2SO_4^-$ can accept and give up H^+.

(a) and (d) are ionisation reactions.

6. **(b,d)** (a) $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

(CH_3COONa and CH_3COOH in 1:1 mole ratio)

(c) $CH_3COONa + HCl \longrightarrow CH_3OOH + NaCl$

(HCl is in excess)

7. **(a, b, c)**

8. **(b, c)** In (a) and (d), $[NH_4^+]$ remains very small due to feeble ionization of the weak base, irrespective of its concentration.

In (b), ammonium salt $[NH_4Cl]$ is formed whereas in (c) the salt is added. Salt ionizes completely and causes ammonium ion concentration to increase drastically.

9. **(b,c)** (a) $50 \times 0.1 = 5$ m mol of CH_3COOH will neutralize completely $50 \times 0.1 = 5$ m mol of NaOH to form CH_3COONa and water. But acetate ion (being strong conjugate base of the weak acid CH_3COOH) of the salt hydrolyses to give basic solution.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad (pH > 7)$$

(b) $100 \times 0.1 = 10$ m mol of CH_3COOH and $50 \times 0.2 = 10$ m mol of NH_3 will neutralize each other completely to give CH_3COONH_4. Both anion and cation of the salt hydrolyse equally ($K_a = 1.8 \times 10^{-5}$; $K_b = 1.8 \times 10^{-5}$) to give neutral solution.

$$CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH \qquad (p^H = 7)$$

(c) $100 \times 0.1 = 10$ m mol of HCl and $5.0 \times 0.2 = 10$ m mol of KOH neutralize each other completely to give KCl. Neither K^+ ion (weak acid) nor Cl^- ion (weak base) hydrolyse (pH = 7)

(d) $50 \times 0.1 = 5$ m mol of HCl and $50 \times 0.1 = 5$ m mol of NH_3 neutralize one another completely. However, the cation (NH_4^+ ion) of the salt hydrolyses to give acidic solution.

$$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+ \quad (pH < 7)$$

10. **(a,b,c,d)** (a) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(Autoionization of NH_3)

(b) H_2O has weaker acid properties than acetic acid

(c) Liquid CH_3COOH has stronger acidic properties than water.

(d) In water NH_4^+ ion represses the ionization of NH_3 in the buffer. Hence buffer is less basic than NH_3.

11. **(a,c)** (a) $[Al(H_2O)_6]^{3+}$ gave up a proton while $[Cu(H_2O)_3OH]^+$ accepted it.

(c) I and III differ by a proton and so also II and IV.

12. **(b,c,d)** Acid-base conjugate pair, the acid and base differ by a proton.

13. **(b,c,d)** (a) K_b permitts the calculation of $[OH^-]$. For $[H^+]$ and hence pH calculation K_w is also required.

(b) From K_b value, $[OH^-]$ can be calculated. Using $K_w = 1.0 \times 10^{-14}$, $[H^+]$ can be calculated. Hence the pH.

(c) pH (acid buffer)

$$= pK_a + \log\frac{[A^-]}{[HA]} \quad (K_a \text{ suffices})$$

(d) The CH_3COO^- ion of the salt hydrolyses as

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log[\text{Anion}]$$

Both K_a and K_w are needed.

14. **(a,b)** For acid-base conjugate pair, $K_a K_b = 1.0 \times 10^{-14}$

$K_a = 1.0 \times 10^{-14} / K_b = 1.0 \times 10^{-14} / 1.0 \times 10^{-5} = 1.0 \times 10^{-9}$

For ionization of acid-base indicator HIn :

$$HIn \rightleftharpoons H^+ + In^-$$

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

(a) For 8% red form (HIn), $pH = 9 + \log\frac{20}{80} = 8.4$

(b) For 80% blue form (In^-), $pH = 9 + \log\frac{80}{20} = 9.6$

15. **(a,c)** (a), (c) CH_3COOH and NH_3 are weak acid and base respectively and ionise in aqueous solution to a small extent.

(b) Hydrolysis of CH_3COO^- ion (conjugate base of weak acid CH_3COOH) occurs to a small extent.

(d) The reaction is acid-base neutralization which goes almost to completion.

16. **(a,b,c,d)** (a) CH_3COO^- is a strong conjugate base of the weak acid CH_3COOH and takes up proton from a strong acid almost completely.

(b,d) Both reactions are acid-base neutralization and occur to nearly full extent.

(c) NH_4^+ ion (conjugate acid of weak base NH_3) and OH^- ion (strong conjugate base of weak acid H_2O) react almost completely.

17. **(b,c)** (a) $NaH_2PO_3 + NaOH \rightarrow Na_2HPO_3 + H_2O$ (H_3PO_3 is dibasic acid)

(b) Na_2HPO_3 is normal salt and does not react any more with NaOH

(c) NaH_2PO_2 is normal salt of the monobasic acid H_3PO_2 and does not react with NaOH.

(d) Na_2HPO_4 (acid salt) + NaOH $\rightarrow Na_3PO_4$ + H_2O (H_3PO_4 is tribasic acid)

18. **(b, c)** HPO_4^{2-} is conjugate base of $H_2PO_4^-$

There occurs an increase in the value of autoprotolysis constant of water when temperature is increased.

The pH of 1×10^{-8}M HCl is not 8. It is less than 7.

At half neutralization of weak acid with a strong base pH = pK_a $\because$ [Acid] = [Salt]

19. **(c, d)** On addition of oxalic acid ($C_2H_2O_4$) a stable complex of Fe^{3+} $[Fe(C_2O_4)_3]^{3-}$ is formed and it results in decrease of $[Fe^{3+}]$ in solution. Due to this the reaction shifts backwards and there is a decrease in red colour.

On addition of $HgCl_2$ (aq), Hg^{2+} combines with SCN^- and forms $[Hg(SCN)_4]^{2-}$ which shifts the equilibrium backwards.

20. **(a, c, d)** The pH of BaI_2 solution = 7.

In all other cases it will be less than 7 as it involves cationic hydrolysis.

21. **(a, c)** A buffer solution consists of a weak base or weak acid and its salt, so (b) and (d) are wrong.

22. **(a, b)** The more acidic is considered as acid. In this case NaH_2PO_4 is more acidic so it is acid. The other species is salt.

The equilibrium constant to be used in Hendersons equation for calculating pH should be one relating to the acid specices to its salt i.e.,

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} \quad H$$

So K_2 is the relevant equilibrium constant and the given equation can be used to calculate pH.

E Matrix-Match Type

1. **A – r, s; B – q, R; C – p; D – q, r**

(A) Bronsted-Lowry acid : Proton donor; $H_2PO_4^-$ and NH_4^+ can donate proton.

(B) Bronsted-Lowry base : Proton acceptor;

$CH_3^- + H^+ \longrightarrow CH_4$;

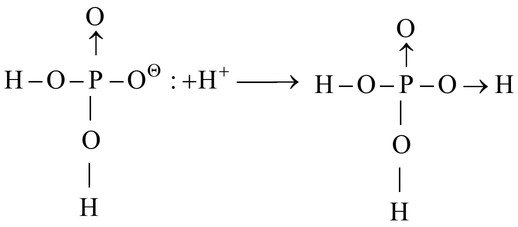
$H_2PO_4^- + H^+ \longrightarrow H_3PO_4$

(C) Lewis acid : An electron pair acceptor;

$CH_3^{\oplus} + :H^- \longrightarrow CH_4$

(D) Lewis base : An electron pair donor;

$CH_3^- : + H^+ \longrightarrow CH_4$



$$H-O-\underset{\underset{\underset{H}{|}}{O}}{\overset{\overset{O}{\uparrow}}{P}}-O^{\ominus} : + H^+ \longrightarrow H-O-\underset{\underset{\underset{H}{|}}{O}}{\overset{\overset{O}{\uparrow}}{P}}-O \rightarrow H$$

2. **A – r, s; B – p, r; C – p, r; D – q**

(A) For maximum buffer capacity, [acid] = [salt] or [base] = [salt]

For acid buffer with maximum capacity :

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

For basic buffer with maximum buffer capacity :

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

(B) On adding equal number of moles of CH_3COOH and CH_3COONa, the term $\log\frac{[CH_3COONa]}{[CH_3COOH]}$ remains constant, i.e. zero. Hence $pH = pK_a$, a constant

(C) On dilution of the buffer, the term $\frac{[CH_3COONa]}{[CH_3COOH]}$ remains constant. Hence $pH = pK_a$ = constant

(D) On adding of NaOH :

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Hence, $\frac{[CH_3COONa]}{[CH_3COOH]}$ increases and the log term becomes greater than zero, i.e $pH > pK_a$

3. **A – s; B – p; C – q; D – r, s**

At high temperature and pressure,

$K_w = [H_3O^+]\ \ [OH^-] = 1.0 \times 10^{-10}$

$[H_3O^+] = [OH^-]$ for pure water or neutral solution = 1.0×10^{-5} M

pH of neutral solution or pure water $= -\log 1.0 \times 10^{-5} = 5$

pH > 5 (basic); pH < 5 (acidic)

(D) $pH + pOH = 10$

$pOH = 10 - pH = 10 - 7 = 3$

$[OH^-] = 10^{-3}\,M$

4. **A – q; B – r; C – p; D – p; s**

(A) $KCN + H_2O \longrightarrow KOH + HCN$ (weak acid)

$$pH = \frac{1}{2}(pK_w + pK_a + \log[CN^-])$$

$$= \frac{1}{2}[14 + pK_a + \log 0.1] = 6.5 + \frac{1}{2}pK_a$$

(B) $C_6H_5NH_3Cl + H_2O \longrightarrow C_6H_5NH_3OH + HCl$ (Cataionic hydrolysis)

$$pH = \frac{1}{2}(pK_a - pK_b - \log[C_6H_5NH_3^+])$$

$$= \frac{1}{2}(14 - pK_b - \log 0.1] = 7.5 - \frac{1}{2}pK_b$$

(C) KCl – Salt of strong acid (HCl) and strong base (KOH), hence no salt hydrolysis; pH = 7

(D) $CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$

$$pH = \frac{1}{2}(pK_w + pK_b - pK_b) = \frac{1}{2}[14 + pK_a - pK_b] = 7$$

$(pK_a = pK_b \text{ in this case})$

5. **A – q, s; B – p, r; C – p, r; D – q, s**

(A) $HCO_3^- + H_2O \longrightarrow H_2CO_3 + OH^-$ (Anionic hydrolysis, basic)

(B) $Cu^{2+} + 2H_2O \longrightarrow Cu(OH)_2 + 2H^+$ (Cationic hydrolysis, acidic)

(C) $Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$ (cationic hydrolysis, acidic)

(D) $CN^- + H_2O \longrightarrow HCN + OH^-$ (Anionic hydrolysis, basic)

6. **A - r; B - q, s; C - r; D - p, s**

A → The salt of weak acid and weak base where $pK_a = pK_b$ will be neutral because all H^+ and OH^- ions will combine to form water. In solution there is neither excess of H^+ nor OH^- ions

B → In solution $[OH]^- > [H^+]$ so it is basic. Since K_a and K_b values are not given so pH of such a solution can not be predicted.

C → Such a solution is neutral

D → It will be acidic but its pH can't be predicted because K_a and K_b values are not given.

7. **A - q, r; B - p, s; C - p, q, s; D - p, s**

Bronsted bases are proton acceptors.

Bronsted acids are proton donors.

Arrhenius acids produce H^+ ions in aqueous solution.

Lewis bases are electron pair donors.

F NUMERIC/INTEGER ANSWER TYPE

1. Calculate $[Ag^+]$, needed separately to precipitate CrO_4^{2-} and Br^-. Smaller the value of $[Ag^+]$, earlier the precipitation of that species. Using $[Ag^+]$ required to precipitate the ion at later stage, concentration of the ion earlier precipitated can be calculated.

For precipitation of Ag_2CrO_4, $[Ag^+]^2[CrO_4^{2-}] > K_{sp}$

$$[Ag^+]_{\min} = \left(\frac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{2-}]}\right)^{\frac{1}{2}}$$

$$= \frac{2.25 \times 10^{-12}}{0.010} = 1.50 \times 10^{-5}\, M$$

For precipitation of AgBr, $[Ag^+][Br^-] > K_{sp}$ (AgBr)

$$[Ag^+]_{\min} = \frac{K_{sp}(\text{AgBr})}{[Br^-]} = \frac{5.0 \times 10^{-13}}{0.010} = 5.0 \times 10^{-11}\, M$$

$[Ag^+]$ required for precipitation of AgBr is less than that required for precipitation of Ag_2CrO_4. Hence, AgBr precipitates earlier than Ag_2CrO_4.

$[Ag^+]$ when Ag_2CrO_4 starts precipitating = $1.50 \times 10^{-5}\, M$

$[Br^-]$ remaining at this stage =

$$\frac{K_{sp}(\text{AgBr})}{[Ag^+]} = \frac{5.0 \times 10^{-13}}{1.5 \times 10^{-5}} = \mathbf{3.33} \times 10^{-8}\, M$$

2. For no precipitation to occur, $[Ag^+][Cl^-] \leq K_{sp}$

$$[Ag^+] \leq \frac{K_{sp}[AgCl]}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.010} = 1.8 \times 10^{-8} M$$

Since maximum concentration of uncomplexed (free) Ag^+ ion is $1.8 \times 10^{-8}\ M$, almost all $Ag^+ = (0.10\,M)$ must be complexed, i.e.

$$[(AgNH_3)_2^+] = 0.1M$$

$$Ag^+_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Ag(NH_3)_2]^+_{(aq)}$$

Formation constant $K_{(f)} = \dfrac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 1.5 \times 10^7$

$$\frac{0.1}{1.8 \times 10^{-8}[NH_3]^2} = 1.5 \times 10^7$$

$[NH_3]^2 = 0.370$ $\qquad$ $[NH_3]_{free} = 0.608M$

$[NH_3]$ needed by 0.1 M Ag^+ for the formation of complex, $Ag(NH_3)_2^+ = 2 \times 0.1 = 0.2\ M$

Hence, total concentration of

$NH_3 = 0.608 + 0.20 = \mathbf{0.808\ M}$

3. Mol of K_2CO_3 at equilibrium = mol of $K_2C_2O_4$ reacted $= 0.0358$

Mol of $K_2C_2O_4$ at equilibrium = initial mol – reacted mol $= 0.1520 - 0.0358 = 0.1162$

It x is the degree of dissociation of $K_2C_2O_4$ and K_2CO_3

then $[C_2O_4]^{2-} = \dfrac{\text{mol of } K_2C_2O_4 \times x}{\text{volume of solution (L)}} = \dfrac{0.1162 \times x}{0.5}$

$= 2 \times 0.1162 \times x \text{ mol L}^{-1}$

$$[CO_3^{2-}] = \frac{\text{mol of } K_2CO_3 \times x}{\text{volume of solution (L)}} = \frac{0.0358 \times x}{0.5}$$

$$= 2 \times 0.0358 \times x \text{ mol L}^{-1}$$

$$K_{sp}(Ag_2C_2O_4) = [Ag^+]^2[C_2O_4^{2-}]$$

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

Hence, $K_{sp}(Ag_2CO_3) = \dfrac{[CO_3^{2-}]}{[C_2O_4^{2-}]} \times K_{sp}(Ag_2C_2O_4)$

$$\frac{0.0358 \times 2 \times x}{0.1162 \times 2 \times x} \times 1.29 \times 10^{-11} = \mathbf{3.974} \times 10^{-12}$$

4. Ionisation of CN^-,

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

$$K_b = \frac{[HCN] \times [OH^-]}{[CN^-]} = 2.04 \times 10^{-5} \text{ ....(1)}$$

Ionisation of CH_3COO^-,

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$K_b' = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = 5.55 \times 10^{-10} \quad \text{....(2)}$$

Equilibrium constant of the reaction

$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ is given

by $K = \dfrac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]}$ $\quad$ ....(3)

From eq. (1), (2) and (3), $K = \dfrac{K_b}{K'_b} =$

$$\frac{2.04 \times 10^{-5}}{5.55 \times 10^{-10}} = \mathbf{3.68} \times 10^4$$

5. Let x mol L^{-1} be the solubility of AgBr in $1.0\times10^{-7}\,M$ AgNO$_3$. Then

$[\mathrm{Ag^+}] = x + 1.0\times10^{-7}\,\mathrm{mol L^{-1}}$; $[\mathrm{Br^-}] = x\,\mathrm{mol\ L^{-1}}$

$\mathrm{K_{sp}(AgBr)} = [\mathrm{Ag^+}][\mathrm{Br^-}] = (x + 1.0\times10^{-7})\times x =$

12×10^{-14} (given)

$x = 3\times10^{-7}\,M$

Hence, $[\mathrm{Ag^+}] = 3\times10^{-7} + 1.0\times10^{-7} = 4\times10^{-7}\,M$,

$[\mathrm{Br^-}] = 3\times10^{-7}\,M$

$[\mathrm{NO_3}^-] = 1.0\times10^{-7}\,M]$ $(\mathrm{S\ m^2 mol^{-1}})$

Conductivity (k) = molar conductance concentration

$(\mathrm{mol\,m^{-3}}\ )$

$$\mathrm{k(Ag^+)} = 6\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times4\times10^{-7}\,\frac{\mathrm{mol}}{\mathrm{dm^3}} =$$

$$6\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times\frac{4\times10^{-7}}{10^{-3}}\,\frac{\mathrm{mol}}{\mathrm{m^3}} = 24\times10^{-7}\mathrm{S\,m^{-1}}$$

$$\mathrm{k(Br^-)} = 8\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times3\times10^{-7}\,\frac{\mathrm{mol}}{\mathrm{dm^3}} =$$

$$8\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times\frac{3\times10^{-7}}{10^{-3}}\,\frac{\mathrm{mol}}{\mathrm{m^3}} = 24\mathrm{S\,m^{-1}}$$

$$\mathrm{k(NO_3^-)} = 7\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times1.0\times10^{-7}\,\frac{\mathrm{mol}}{\mathrm{dm^3}} =$$

$$7\times10^{-3}\mathrm{S\,m^2mol^{-1}}\times\frac{1.0\times10^{-7}}{10^{-3}}\,\frac{\mathrm{mol}}{\mathrm{m^3}} = 7\times10^{-7}\mathrm{S\,m^{-1}}$$

Conductivity of solution

$(\mathrm{k}) = \mathrm{k(Ag^+)} + \mathrm{k(Br^-)} + \mathrm{k(NO_3^-)}$

$(24\times10^{-7} + 24\times10^{-7} + 7\times10^{-7})\mathrm{S\,m^{-1}} = \mathbf{55}\times10^{-7}\mathrm{S\,m^{-1}}$

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