EXERCISE-01 CHECK YOUR GRASP

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

1. Which of the following expressions is/are not true ?

(A) $[H^+] = [OH^-] = \sqrt{K_w}$ for a neutral solution at all temperatures.

(B) $[H^+] > \sqrt{K_w}$ & $[OH^-] < \sqrt{K_w}$ for an acidic solution

(C) $[H^+] < \sqrt{K_w}$ & $[OH^-] > \sqrt{K_w}$ for an alkaline solution

(D) $[H^+] = [OH^-] = 10^{-7}$ M for a neutral solution at all temperatures

2. Addition of HCl will not suppress the ionization of-

(A) acetic acid (B) Benzoic acid (C) H_2S (D) Sulphuric acid

3. An acid solution of pH 6 is diluted thousand times. The pH of solution becomes approx-

(A) 6.96 (B) 6 (C) 4 (D) 9

4. pOH of H_2O is 7.0 at 298 K. If water is heated at 350 K, which of the following should be true ?

(A) pOH will decrease

(B) pOH will increase

(C) pOH will remain 7.0

(D) concentration of H^+ ions will increase but that of OH^- will decrease

5. Which of the following solution will have a pH exactly equal to 8 ?

(A) 10^{-8} M HCl solution at 25°C (B) 10^{-8} M H^+ solution at 25°

(C) $2 Ч 10^{-6}$ M $Ba(OH)_2$ solution at 25° C (D) 10^{-6} M NaOH solution at 50° C

6. The number of hydrogen ions in 10 mL of a solution with pH = 13 is-

(A) 10^{13} (B) $6.023 Ч 10^8$ (C) $6.023 Ч 10^{13}$ (D) $6.023 Ч 10^{10}$

7. At 55° C autoprotolysis constant of water is $4 Ч 10^{-14}$. If a given sample of water has a pH of 6.9, then it is-

(A) acidic (B) basic (C) neutral (D) explosive

8. 0.1 mol HCl is dissolved in distilled water of volume V then $V \xrightarrow{\lim} \infty\ (pH)_{solution}$ is equal to-

(A) zero (B) 1 (C) 7 (D) 14

9. A 50 mL solution of pH = 1 is mixed with a 50 mL solution of pH = 2. then pH of the mixture will be nearly-

(A) 0.76 (B) 1.26 (C) 1.76 (D) 2.26

10. The pH of a solution obtained by mixing 50 mL of 0.4 N HCl and 50 mL of 0.2 N NaOH is-

(A) – log 2 (B) – log 0.2 (C) 1.0 (D) 2.0

11. The pH of a solution is 7.00. To this solution sufficient base is added to increase the pH to 12.0. The increase OH^- ion concentration is-

(A) 5 times (B) 1000 times (C) 10^5 times (D) 4 times

12. Which of the following solution will have pH close to 1.0 ?

(A) 100 mL of M/10HCl + 100 mL of M/10 NaOH

(B) 55 mL of M/10 HCl + 45 mL of M/10 NaOH

(C) 10 mL of M/10 HCl + 90 mL of M/10 NaOH

(D) 75 mL of M/5 HCl + 25 mL of M/5 NaOH.

13. The dissociation constants of two acids HA_1 and HA_2 are $3.0 Ч 10^{-4}$ and $1.8 Ч 10^{-5}$ respectively. The relative strengths of the acids will be approximately-

(A) 1 : 4 (B) 4 : 1 (C) 1 : 16 (D) 16 : 1

14. Which of the following is true-

(A) pk_b for OH^- is – 1.74 at 25°C

(B) the equilibrium constant for the reaction between HA ($pK_a = 4$) and NaOH at 25°C will be equal to 10^{10}

(C) the pH of a solution containing 0.1 M HCOOH (k_a = 1.8 Ч 10^{-4}) and 0.1 M HOCN. (k_a = 3.2 Ч 10^{-4}) will be nearly (3 – log7).

(D) all the above are correct.

15. Which statement/relationship is correct ?

(A) upon hydrolysis of salt of a strong base and weak acid gives a solution with pH < 7

(B) $pH = -\log \frac{1}{[H^+]}$

(C) only at 25 °C the pH of water is 7

(D) the value of pK_w at 25 °C is 7

16. If 50 mL of 0.2 (M) KOH is added to 40 mL of 0.5(M) HCOOH. The pH of the resulting solution is (K = 1.8 Ч 10^{-4}) :

(A) 3.75 (B) 5.6 (C) 7.5 (D) 3.4

17. 50% neutralization of a solution of formic acid (K_a = 2 Ч 10^{-4}) with NaOH would result in a solution having a hydrogen ion concentration of-

(A) 2 Ч 10^{-4} (B) 3.7 (C) 2.7 (D) 1.85

18. The correct order of increasing $[H_3O^+]$ in the following aqueous solution is-

(A) 0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_2$

(B) 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2S < 0.01 M H_2SO_4

(C) 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2S < 0.01 M H_2SO_4

(D) 0.01 M H_2S < 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2SO_4

19. The sodium salt of a certain weak monobasic organic acid is hydrolysed to an extent of 3% in its 0.1 M solution at 25 °C. Given that the ionic product of water is 10^{-14} at this temperature, what is the dissociation constant of the acid ?

(A) ≈ 1 Ч 10^{-10} (B) ≈ 1 Ч 10^{-9} (C) 3.33 Ч 10^{-9} (D) 3.33 Ч 10^{-10}

20. The correct order for the increasing extent of hydrolysis is-

(A) $PO_4^{3-} < HPO_4^{2-} < H_2PO_4^-$ (B) $H_2PO_4^- < HPO_4^{2-} < PO_4^{3-}$

(C) $HPO_4^{2-} < PO_4^{3-} < H_2PO_4^-$ (D) $PO_4^{3-} < H_3PO_4^- < HPO_4^{2-}$

21. The correct order of increasing pH of decimolar solution of each of the following in-

(A) $NH_4NO_3 < NaNO_3 < NaHCO_3 < Na_2CO_3$

(B) $NaNO_3 < NH_4NO_3 < NaHCO_3 < Na_2CO_3$

(C) $NaNO_3 < NH_4NO_3 < Na_2CO_3 < NaHCO_3$

(D) $Na_2CO_3 < NaHCO_3 < NaNO_3 < NH_4NO_3$

22. When 100 mL of 0.4 M CH_3COOH are mixed with 100 mL of 0.2 M NaOH, the $[H_3O^+]$ in the solution is approximately : [$K_a(CH_3COOH)$ = 1.8 Ч 10^{-5}]

(A) 1.8 Ч 10^{-6} (B) 1.8 Ч 10^{-5} (C) 9 Ч 10^{-6} (D) 9 Ч 10^{-5}

23. A solution is 0.1 M CH_3COOH and 0.1 M CH_3COONa. Which of the following will change the pH significantly, of the solution ?

(A) addition of water

(B) addition of CH_3COONa without change in volume

(C) addition of CH_3COOH without change in volume

(D) none will change the pH significantly

24. What will be the pH at the equivalence point during the titration of a 100 mL 0.2 M solution of CH_3COONa with 0.2 M solution of HCl ? K_a = 2 Ч 10^{-5}

(A) $3 - \log\sqrt{2}$ (B) $3 + \log\sqrt{2}$ (C) $3 - \log 2$ (D) $3 + \log 2$

25. K_a for HCN is 5 Ч 10^{-10} at 25 °C. For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 mL of 2M HCN solution is-

(A) 4 mL (B) 7.95 mL (C) 2 mL (D) 9.3 mL

26. The pH of a solution obtained by mixing 100 mL of 0.2 M CH_3COOH with 100 mL of 0.2 M NaOH would be (pK_a for CH_3COOH = 4.74 and log2 = 0.301)

(A) 4.74 (B) 8.87 (C) 9.10 (D) 8.57

27. Which of the following when added to 1.0 L of 0.5 M HCl would result in maximum increase in pH?

(A) 0.5 mol CH_3COOH (B) 1.0 mol NaCl

(C) 0.4 mol NaOH (D) 0 .6 mole CH_3COONa

28. What % of the carbon in the H_2CO_3, HCO_3^-. Buffer should be in the form of HCO_3^- so as to have a neutral solution ? (K_a = 4 Ч 10^{-7})

(A) 20 % (B) 40 % (C) 60 % (D) 80 %

29. Which of the following solution would have same pH ?

(A) 100 mL of 0.2 M HCl + 100 mL of 0.4 M NH_3

(B) 50 mL of 0.1 M HCl + 50 mL of 0.2 M NH_3

(C) 100 mL of 0.3 M HCl + 100 mL of 0.6 M NH_3

(D) All will have same pH

30. 50 mL of 0.1 M NaOH is added to 60 mL of 0.15 M H_3PO_4 solution (K_1, K_2 and K_3 may be taken as 10^{-3}, 10^{-8} and 10^{-13} respectively). The pH of the mixture would be about-

(A) 3.1 (B) 5.5 (C) 4.1 (D) 6.5

31. The solubility of a certain sparingly soluble substance MX_n is nearly 1.4 Ч 10^{-4} M. If the solubility product is 1.1 Ч 10^{-11}, what is the value of n ?

(A) 1 (B) 2 (C) 3 (D) 1.5

32. The concentration of Mg^{2+} in the solution made by mixing 10 mL of 0.25 M $Mg(NO_3)_2$ and 25 mL of 0.2 M NaF will be (K_{sp}(MgF_2 = 8 Ч 10^{-8})

(A) 0.0027 M (B) 0.0714 M (C) 0.0030 M (D) 0.0060 M

33. The pH of a saturated solution of $Mg(OH)_2$ in water will be (K_{sp} = 4 Ч 10^{-12})

(A) $4 - \log 2$ (B) $10 - \log 2$ (C) $4 + \log 2$ (D) $10 + \log 2$

34. When NaCl is added to the reaction mixture of an oil and caustic soda, the soap is thrown out because-

(A) NaCl is an ionic compound

(B) soap is insoluble in the presence of choride ions

(C) the solubility product of NaCl decreases in the presence of soap

(D) the solubility product of the soap is exceeded due to the increased concentration of Na^+ ions.

35. 16.6 mg of solid silver chromate (molar mass = 332) when put into 500 mL water, silver ion and chromate ion are obtained. On adding more solid, the concentration of ions does not increase. If 100 mg of solid is put into 2 litre of water, then the amount of solid remained undissociated would be-

(A) 33.6 mg (B) 3.36 mg (C) 66.4 mg (D) 6.64 mg

36. In which of the following solvents will AgBr has highest solubility-

(A) 10^{-3} M NaBr (B) 10^{-3} M NH_4OH (C) pure water (D) 10^{-3} M HBr

37. In the system $CaF_2(s)$ □□□ $Ca^{+2}(aq) + 2F^-$ increasing the concentration of Ca^{2+} ions 4 times will cause the equilibrium concentration of F^- ions to change to .... times the initial value.

(A) 4 (B) 1/2 (C) 2 (D) 1/4

38. The solubility of $Fe(OH)_3$ would be maximum in-

(A) 0.1 M NaOH (B) 0.1 M HCl (C) 0.1 M KOH (D) 0.1 M H_2SO_4

39. Arrange in increasing order of solubility of AgBr in solutions given :

(i) 0.1 M NH_3 (ii) 0.1 M $AgNO_3$ (iii) 0.2 M NaBr (iv) pure water

(A) (iii) < (ii) < (iv) < (i) (B) (iii) < (ii) < (i) < (iv)

(C) (iii) < (ii) = (i) < (iv) (D) (ii) < (iii) < (iv) < (i)

40. The solubility product of $BaCrO_4$ is 2.4 Ч 10^{-10} M^2. The maximum concentration of $Ba(NO_3)_2$ possible without precipitation in a 6 Ч 10^{-4} M K_2CrO_4 solution is-

(A) 4 Ч 10^{-7} M (B) 1.2 Ч 10^{10} M (C) 6 Ч 10^{-4} M (D) 3 Ч 10^{-4}M

41. At 25 °C, the solubility product values of AgCl and AgCNS are 1.7 Ч 10^{-10} and 1.0 Ч 10^{-12} respectively. When water is saturated with both solids, calculate the ratio $[Cl^-]/[CNS^-]$ and also $[Ag^+]$ in the solution.

(A) 1.3 Ч 10^2, 1.7 Ч 10^{-5} M (B) 1.7 Ч 10^2, 1.308 Ч 10^{-5} M

(C) 1.3 Ч 10^4, 1.308 Ч 10^{-4} M (D) 1.7 Ч 10^3, 1.67 Ч 10^{-6} M

42. When pure water is saturated with $CaCO_3$ and CaC_2O_4, the concentration of calcium ion in the solution under equilibrium is 8.426 Ч 10^{-5} M. If the ratio of the solubility product of $CaCO_3$ to that of CaC_2O_4 is 2.087, what is the solubility product of $CaCO_3$ in pure water ?

(A) 4.80 Ч 10^{-8} (B) 9.60 Ч 10^{-9} (C) 9.60 Ч 10^{-8} (D) 4.80 Ч 10^{-9}

43. The solubility of Ag_2CO_3 in water at 25 °C is 1 Ч 10^{-4} mole/litre. What is its solubility in 0.1 M Na_2CO_3 solution ? Assume no hydrolysis of CO_3^{2-} ion.

(A) 6.323 Ч 10^{-6} mole/litre (B) 4.74 Ч 10^{-5} mole/litre

(C) 3.16 Ч 10^{-6} mole/litre (D) 5.51 Ч 10^{-5} mole/litre

44. The solubility of calcium phosphate in water is x mol L^{-1} at 25 °C. Its solubility product is equal to-

(A) 108 x^2 (B) 36 x^3 (C) 36 x^5 (D) 108 x^5

45. The solubility product of AgCl is 1.8 Ч 10^{-10}. Precipitation of AgCl will occur only when equal volumes of solutions of-

(A) 10^{-4} M Ag^+ and 10^{-4} M Cl^- are mixed (B) 10^{-7} M Ag^+ and 10^{-7} M Cl^- are mixed

(C) 10^{-5} M Ag^+ and 10^{-5} M Cl^- are mixed (D) 10^{-10} M Ag^+ and 10^{-10} M Cl^- are mixed

46. The solubility of CaF_2 (K_{sp} = 3.4 Ч 10^{-11}) in 0.1 M solution of NaF would be-

(A) 3.4 Ч 10^{-12} M (B) 3.4 Ч 10^{-10} M (C) 3.4 Ч 10^{-9} M (D) 3.4 Ч 10^{-13} M

47. The precipitate of CaF_2(K_{sp} = 1.7 Ч 10^{-10}) is obtained when equal volumes of the following are mixed.

(A) 10^{-4} M Ca^{2+} + 10^{-4} M F^- (B) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(C) 10^{-5} M Ca^{2+} + 10^{-3} M F^- (D) 10^{-3} M ca^{2+} + 10^{-5} M F^-

48. Let the solubilities of AgCl in H_2O, 0.01 M $CaCl_2$, 0.01 M NaCl & 0.05 M $AgNO_3$ be S_1, S_2, S_3 & S_4 respectively what is the correct relationship between these quantities. Neglect any complexation.

(A) $S_1 > S_2 > S_3 > S_4$ (B) $S_1 > S_2 = S_3 > S_4$

(C) $S_1 > S_3 > S_2 > S_4$ (D) $S_4 > S_2 > S_3 > S_1$

49. The solubility product $Mg(OH)_2$ in water at 25 °C is 8.9 Ч 10^{-13} (mole $dm^{-3})^3$ while that of $Al(OH)_3$ is 5 Ч 10^{-33} (mol $dm^{-3})^4$. If S_1 and S_2 are the solubilities of $Mg(OH)_2$ and $Al(OH)_3$ in water in mol dm^{-3} at 25 °C, what is the order of magnitude of the ratio, S_1/S_2 ?

(A) 10^5 (B) 10^4 (C) 10^6 (D) 10^3

50. When HCl gas is passed through a saturated solution of common salt, pure NaCl is precipitated because-

(A) HCl is highly ionised in solution

(B) HCl is highly soluble in water

(C) the solubility product of NaCl is lowered by HCl

(D) the ionic product of $[Na^+]$ $[Cl^-]$ exceeds the solubility product of NaCl

51. A certain indicator (an organic dye) has $pK_a = 5$. For which of the following titrations may it be suitable.
(A) acetic acid against NaOH
(B) aniline hydrochloride against NaOH
(C) sodium carbonate against HCl
(D) barium hydroxide against oxalic acid

52. The pH indicators are-
(A) salts of strong acids & strong bases
(B) salts of weak acids & weak bases
(C) either weak acids or weak bases
(D) either strong acids or strong bases

53. What fraction of an indicator HIn is in the basic form at a pH of 6 if pK_a of the indicator is 5 ?
(A) $\frac{1}{2}$ (B) $\frac{1}{11}$ (C) $\frac{10}{11}$ (D) $\frac{1}{10}$

54. An acid-base indicator which is a weak acid has a pK_a value = 5.5. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms ? pK_a of acetic acid = 4.75
(A) 4.93 : 1 (B) 6.3 : 1 (C) 5.62 : 1 (D) 2.37 : 1

CHECK YOUR GRASP

ANSWER KEY

EXERCISE -1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	D	D	A	A	B	B	B	C	B	C	C	D	B	D	C
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	A	A	C	A	B	A	B	D	A	C	B	D	D	D	A
Que.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
Ans.	B	A	D	D	A	B	B	D	A	A	B	D	C	D	A
Que.	46	47	48	49	50	51	52	53	54						
Ans.	C	B	C	B	D	C	C	C	C						

EXERCISE–02 BRAIN TEASERS

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

1. The conjugate acid of NH_2^- is-

(A) NH_3 (B) NH_2OH (C) NH_4^+ (D) N_2H_4

2. Out of the following, amphiprotic species are

(I) HPO_3^{2-} (II) OH^- (iii) $H_2PO_4^-$ (IV) HCO_3^-

(A) I, III, IV (B) I and III (C) III and IV (D) All

3. pH of an aqueous solution of NaCl at 85 °C should be-

(A) 7 (B) > 7 (C) < 7 (D) 0

4. 1 CC of 0.1 N HCl is added to 99 CC solution of NaCl. The pH of the resulting solution will be-

(A) 7 (B) 3 (C) 4 (D) 1

5. 10 mL of $\frac{M}{200}$ H_2SO_4 is mixed with 40 mL of $\frac{M}{200}$ H_2SO_4. The pH of the resulting solution is-

(A) 1 (B) 2 (C) 2.3 (D) none of these

6. If pK_b for fluoride ion at 25 °C is 10.83, the ionization constant of hydrofluoric acid in water at this temperature is-

(A) 1.74 Ч 10^{-5} (B) 3.52 Ч 10^{-3} (C) 6.75 Ч 10^{-4} (D) 5.38 Ч 10^{-2}

7. If K_1 & K_2 be first and second ionisation constant of H_3PO_4 and $K_1 >> K_2$ which is incorrect-

(A) $[H^+] = [H_2PO_4^-]$ (B) $[H^+] = \sqrt{K_1[H_3PO_4]}$

(C) $K_2 = [HPO_4^{-2}]$ (D) $[H^+] = 3[PO_4^{3-}]$

8. The degree of hydrolysis of a salt of weak acid and weak base in it's 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be-

(A) 100 % (B) 50 % (C) 25 % (D) none of these

9. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3 Ч 10^{-9} and K_w = 1.0 Ч 10^{-14}

(A) 2.48 (B) 5.26 (C) 8.2 (D) 9.6

10. pH of 0.01 M $(NH_4)_2SO_4$ and 0.02 M NH_4OH buffer solution (pK_a of NH_4^+ = 9.26) is-

(A) 9.26 (B) 4.74 (C) 4.74 + log 2 (D) none

11. The range of most suitable indicator which should be used for titration of X^-Na^+ (0.1 M, 10 mL) with 0.1 M HCl should be (Given : $k_{b(X^-)} = 10^{-6}$)

(A) 2 – 3 (B) 3 – 5 (C) 6 – 8 (D) 8-10

12. When NO_2 is bubbled into water, If disproportionates completely into HNO_2 and HNO_3.

$$2NO_2 + H_2O(\ell) \longrightarrow HNO_2(aq.) + HNO_3(aq.)$$

The concentration of NO_2^- in a solution prepared by dissolving 0.05 mole of NO_2 gas in 1 litre H_2O is {$K_a(HNO_2)$ = 5 Ч 10^{-4}}

(A) ~ 5 Ч 10^{-4} (B) ~ 4.8 Ч 10^{-5}

(C) ~ 4.8 Ч 10^{-3} (D) ~ 2.55 Ч 10^{-2}

13. If K_{sp} for $HgSO_4$ is 6.4 Ч 10^{-5}, then solubility of this substance in mole per m^3 is-

(A) 8 Ч 10^{-3} (B) 6.4 Ч 10^{-5} (C) 8 Ч 10^{-6} (D) none of these

14. Which of the following is most soluble in water ?

(A) $MnS(K_{sp}$ = 8 Ч $10^{-37})$ (B) $ZnS(K_{sp}$ = 7 Ч $10^{-16})$

(C) $Bi_2S_3(K_{sp}$ = 1 Ч $10^{-72})$ (D) $Ag_3(PO_4)$ $(K_{sp}$ = 1.8 Ч $10^{-8})$

15. How many moles NH_3 must be added to 2.0 litre of 0.80 M $AgNO_3$ in order to reduce the Ag^+ concentration to 5 Ч 10^{-8} M. K_f of $[Ag(NH_3)_2^+]$ = 10^8

(A) 0.4 (B) 2 (C) 3.52 (D) 4

16. The solubility product of BaF_2 has the value, 1.7 Ч 10^{-4}. If V_1 mL of $BaCl_2$ Solution (10^{-1} M) and V_2 mL of NaF solution (10^{-2} M) are mixed, what is the ratio $V_1 : V_2$ so that a precipitate may be obtained?

(A) 1 : 1

(B) 2 : 1

(C) 1 : 2

(D) precipitate cannot obtained for any possible ratio

17. At 18 °C, the solubility of CdS in water is 6.33 Ч 10^{-15} M. What is the concentration of Cd^+ ion in a solution of pH = 1 saturated with H_2S gas, in which concentration of H_2S = 0.1 M ? The product of the first and second ionization constants of H_2S is 1.1 Ч 10^{-22} at this temperature.

(A) 6.343 Ч 10^{-8} M (B) 4. 368 Ч 10^{-8} M

(C) 4.368 Ч 10^{-9} M (D) 3.643 Ч 10^{-8} M

18. 100 mL of 0.02 M benzoic acid (pK_a = 4.2) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are-

(A) 3.50,7 (B) 4.2, 7 (C) 4.2, 8.1 (D) 4.2, 8.25

19. What is the pH of solution made by adding 3.9 g $NaNH_2$ into water to make a 500 mL solution $K_b(NH_3)$ = 2 Ч 10^{-5} [Na = 23, N = 14, H = 1]

(A) 13.3 (B) 0.7 (C) 5.3 (D) 13.7

20. 10.2 g of acetic anhydride was added to 989.8 g of water to make a solution with a density of 1g/mL. If the k_a of acetic acid is 2 Ч 10^{-5}, the pH of the solution would be [C = 12, H = 1, O = 16]

(A) 2.7 (B) 3.7 (C) 4.7 (D) 5.7

21. A well is dug in a bed of rock containing fluorspar (CaF_2). If the well contains 20000 L of water, what is the amount of F^- in it ? K_{sp} = 4 Ч 10^{-11}

(A) 4.3 mol (B) 6.8 mol (C) 8.6 mol (D) 13.6 mol

22. If HA + NaOH $\longrightarrow$ NaA + H_2O ΔH = – 12 kcal

and HB + NaOH $\longrightarrow$ NaB + H_2O ΔH = –11 kcal

then equimolar solution of which acid has higher pH-

(A) HA (B) HB

(C) both have same pH (D) information insufficient

23. Aniline behaves as a weak base. When 0.1 M, 50 mL solution of aniline was mixed with 0.1 M, 25 mL solution of HCl the pH of resulting solution was 8. Then the pH of 0.01 M solution of aniliniumchloride will be (K_w = 10^{-14})

(A) 6 (B) 6.5 (C) 5 (D) 5.5

24. pH of a mixture of 1 M benzoic acid (pK_a = 4.20) and 1M C_6H_5COONa is 4.5, what is the volume of benzoic acid required to prepare a 300 mL buffer [log 2 = 0.3] ?

(A) 200 mL (B) 150 mL (C) 100 mL (D) 50 mL

25. What is the difference in pH for 1/3 and 2/3 stages of neutralisation of 0.1 M CH_3COOH with 0.1 M NaOH.

(A) – 2 log 3 (B) 2log(1/4) (C) 2log(2/3) (D) – 2 log 2

26. An acid HA(k_a = 10^{-5}) reacts with NaOH at 298 K. What would be the value of the rate constant of the reverse reaction at the same temperature if the rate constant of the forward reaction is 10^{-11} mol^{-1} L sec^{-1} ?

(A) 10^{-9} (B) 10^{9} (C) 10^{-5} (D) 10^{-20}

27. The pH of 1.0 M $NaHSO_4$ solution will be (given that K_1 and K_2 for H_2SO_4 equal to ∞ and 10^{-2} respectively)-

(A) nearly 1.0
(B) between 2 and 3
(C) between 1.2 and 1.8
(D) between 3 and 4

28. 0.1 millimole of $CdSO_4$ are present in 10 mL acid solution of 0.08 N HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. The pH of the solution after filtering off precipitate, boiling off H_2S and making the solution 100 mL by adding H_2O is-

(A) 2
(B) 4
(C) 6
(D) 8

29. Zn salt is mixed with $(NH_4)_2$ S of molarity 0.021 M. The amount of Zn^{2+} remains unprecipitated in 12 mL of this solution would be (Given : K_{SP} ZnS = 4.51 Ч 10^{-24})

(A) 1.677 Ч 10^{-22} g
(B) 1.767 Ч 10^{-22} g
(C) 2.01 Ч 10^{-23} g
(D) none of these

30. The self ionisation constant for pure formic acid, K = $[HCOOH_2^+]$ $[HCOO^-]$ has been estimated as 10^{-6} at room temperature. The density of formic acid is 1.22 g/cm^3. The percentage of formic acid molecules in pure formic acid that are concerted to formate ion would be-

(A) 0.002 %
(B) 0.004 %
(C) 0.006 %
(D) 0.008 %

BRAIN TEASERS

ANSWER KEY

EXERCISE -2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A	C	C	B	B	C	D	B	A	A	B	A	D	D	D
Que.	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Ans.	D	D	C	A	A	C	B	C	C	D	D	A	A	A	B

ERCISE–03 MISCELLANEOUS TYPE QUESTIONS

TRUE / FALSE

1. When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point, $pH = \frac{1}{2} pK_a$
2. A solution of sodium acetate and ammonium acetate can act as a buffer.
3. If the solubility of the salt $Li_3Na_3(AlF_6)_2$ is x, then its solubility product would be $2916\ x^8$.
4. A buffer has maximum buffer capacity when the ratio of salt to acid is 10.
5. In the presence of a common ion (incapable of froming complex ion), the solubility of salt decreases.
6. The ionic product of water changes if a few drops of acid or base are added to it.
7. When equilibrium is attained, the concentration of each of the reactants & products become equal.
8. The reaction, $HCN + OH^- \Leftrightarrow CN^- + H_2O$ is displaced to the right indicating that the acid strength of HCN is greater than water & the base strength of CN^- is greater than that of OH^-.
9. The hydroxyl ion is hydrated to give several ionic species like $H_2O_2^{-2}$, $H_3O_3^{-3}$ and $H_4O_4^{-4}$.
10. Ostwald's dilution formula is applicable to weak as well as strong electrolytes.
11. CO_2 is a Lewis base
12. Solution whether neutral, acidic or basic contain both H^+ & OH^- ions.
13. The ionic product of a saturated solution is equal to solubility product constant of its solute.
14. A Lewis base is a substance which can donate a pair of electrons ?
15. If ionic product is less than k_{sp}, no precipitation will occur.
16. A buffer has definite pH value which changes on keeping it or on diluting it.
17. A salt of strong acid with a strong base does not undergo hydrolysis
18. HCl does not act as an acid in benzene
19. Water acts as a base when ammonia is dissolved in it.
20. In the reaction, $SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$, $SnCl_4$ is a Lewis acid.
21. The strength of an oxy acid increases with increase in the EN value of central atom.
22. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$

FILL IN THE BLANKS

1. In a mixture of weak acid and its salt, the ratio of concentration of salt to acid is increased ten fold. The pH of the solution would .... by .... unit.
2. The solubility of CH_3COOAg in water considering hydrolysis of CH_3COO^- ions would be .... than that ignoring the hydrolysis.
3. From an equimolar solution of Cl^- and Br^- ions, the addition of Ag^+ will selectively precipitates .... (K_{sp} of AgCl & AgBr are 1 Ч 10^{-10} & 1 Ч 10^{-13} respectively).
4. The solubility of AgCl in NH_3 is ...... than the solubility in pure water because of complex ion, $[Ag(NH_3)_2]^+$ formation.
5. The hydrolytic constant K_h for the hydrolytic equilibrium

   $H_2PO_4^- + H_2O \longrightarrow H_3PO_4 + OH^-$ is 1.4 Ч 10^{-12}

   The value of ionization constant for the $H_3PO_4 + H_2O \longrightarrow H_2PO_4^- + H_3O^+$ is ....
6. Given the equilibrium constants

   $Cl^- + HgCl^+ \rightleftharpoons HgCl_2$; K_1 = 3 Ч 10^6

   $HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-$; $K_2 = 8.9$

   The equilibrium constants for the dispropotionation equilibrium.

   $2HgCl_2 \rightleftharpoons HgCl^+ + HgCl_3^-$ is-

7. If the salts M_2X, QY_2 and PZ_3 have same solubilities (<<< 1), their K_{sp} values are related as ....

8. K_a for an acid HA is $1 Ч 10^{-6}$. K_b for A^- would be ....

9. An aqueous solution of K_2SO_4 has pH nearly equal to ....

10. The pH of a solution which is 0.1 M sodium acetate and 0.01 M acetic acid (pK_a = 4.74) would be ....

11. The conjugative acid of sulphate (SO_4^{2-}) is ....

12. The value of K_w .... with increase in temperature.

13. AgCl is .... soluble in aqueous sodium chloride solution than in pure water.

14. The buffer HCOOH/HCOONa will have pH .... than 7.

15. In the reaction $I_2 + I^- \longrightarrow I_3^-$, I_2 acts as ....

16. An equimolar solution of $NaNO_2$ and HNO_2 can act as a .... solution.

17. Larger the value of pK_a, ... is the acid

18. Between Na^+ & Ag^+ ion, ... is a stronger Lewis acid.

19. Salt of strong acids and weak base undergo .... hydrolysis

20. For salts of weak acid with weak bases, degree of hydrolysis is .... of concentration of the salt in solution.

21. The solubility of $KAl(SO_4)_2$ in terms of its solubility product is ....

22. The dissociation constant of NH_4OH is $1.8 Ч 10^{-5}$. The hydrolysis constant of NH_4^+ ions at 25 °C would be ....

23. solution of $CuSO_4$ is .... due to the hydrolysis of .... ions

24. The colour of unionized form of phenolphthalein is .... whereas that of ionized form is ....

25. In general, in aqueous solution pH + pOH = ... at all temperatures.

26. The ionization constant of water is related to ionic product by the expression ....

27. The smaller the value of K_a of a weak acid, ... is the hydrolysis constant of its conjugate base.

MATCH THE COLUMN

1. Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II) :

	Column-I		Column-II
(A)	25 mL of NaOH	(p)	pK_a
(B)	50 mL of NaOH	(q)	$pK_a + \log 3$
(C)	75 mL of NaOH	(r)	$pK_a - \log 3$
(D)	100 mL of NaOH	(s)	$\frac{1}{2}[pK_w + pK_a - \log 2]$

2. When we titrate sodium carbonate solution (in beaker) with hydrochloric acid.

	Column-I		Column-II
(A)	At the start of titration	(p)	Buffer solution of HCO_3^- and CO_3^{2-}
(B)	Before the first equivalent point	(q)	Buffer solution of H_2CO_3 and HCO_3^-
(C)	At the first equivalent point	(r)	Amphiprotic anion, $pH = 1/2(pK_{a_1} + pK_{a_2})$
(D)	Between the first and second equivalent points	(s)	Hydrolysis of CO_3^{2-}

ASSERTION & REASON

These questions contains, Statement I (assertion) and Statement II (reason).

(A) Statement-I is true, Statement-II is true ; Statement-II is correct explanation for Statement-I.

(B) Statement-I is true, Statement-II is true ; Statement-II is NOT a correct explanation for statement-I

(C) Statement-I is true, Statement-II is false

(D) Statement-I is false, Statement-II is true

1. **Statement-I** : On dilution of a concentrated solution of CH_3COOH, the concentration of $[H^+]$ decreases
Because
Statement-II : Because increase in the volume is more than the increase in degree of ionisation

2. **Statement-I** : pH of boiling water is less than the water at 4 °C
Because
Statement-II : Because density of water is maximum at 4 °C

3. **Statement-I** : Solubility of $BaSO_4$ in 0.1 M Na_2SO_4 is 10^{-9} M hence its K_{sp} is 10^{-18}
Because
Statement-II : Because for $BaSO_4$ $K_{sp} = (s)^2$

4. **Statement-I** : Aqueous solution of CH_3COONH_4 is found to be neutral
Because
Statement-II : because this salt does not undergo hydrolysis

5. **Statement-I** : An aqueous solution of HCl is a much better conductor of electricity than an aqueous solution of CH_3COOH of the same concentration.
Because
Statement-II : The freezing point depression and the boiling point elevation of weak electrolytes are significantly less than for strong electrolytes of the same concentration.

6. **Statement-I** : $CH_3NH_3^+$ CH_3NH_2 is acid base conjugate pair.
Because
Statement-II : H_3O^+, OH^- is acid base conjugate pair.

7. **Statement-I** : The equilibrium constant for the reaction,
$HONO(aq.) + CN^-(aq) \rightleftharpoons HCN\ (aq.) + ONO^-(aq.)$ is 1.1×10^6
Because
Statement-II : This shows that CN^- is stronger base than ONO^-

COMPREHENSION BASED QUESTIONS

Comprehension # 1

The importance of pH maintenance in Blood

Maintenance of the pH in blood and in intracellular fluids is absolutely crucial to the processes that occur in living organisms. This primarily because the functioning of enzymes-catalysts for these processes - is sharply pH dependent. The normal pH value of blood plasma is 7.4. Severe illness or death can result from sustained variations of a few tenths of pH unit.

Among the factors that lead to a condition of acidosis, in which there is decreases in the pH of blood are heart failure, kidney failure diabetes mellitus, persistent diarrhoea or a long term high protein diet. A temporary condition acidosis may result from prolonged, intensive exercise. Alkalosis, which causes increase in pH of blood, may occur as a result of severe vomiting overbreathing or exposure to high altitudes.

Several factors are involved in the control of the pH of blood. A particularly important one is the ratio of dissolved HCO_3^- to H_2CO_3. $CO_2(g)$ is moderately soluble in water and in aqueous solution reacts only to a limited extent to produce H_2CO_3.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3\ (aq)$$

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+, \qquad pK_{a_1} = 6.11$$

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+\ ; \qquad pK_{a_2} = 10.25$$

In the H_2CO_3, HCO_3^- buffer system we deal only with the first ionisation step (K_{a_1}) : H_2CO_3 is weak acid and HCO_3^- is the conjugate base (salt). CO_2 enters the blood from tissues as the by - product of metabolic reaction. In lungs, CO_2 (g) is exchanged for O_2 (g), which is transported throughout the body by the blood.

1. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentration. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3 in order to maintain its pH? :

(A) 40 mL (B) 38 mL (C) 50 mL (D) 78 mL

2. Important diagnostic analysis in the blood is :

(A) $[H_2PO_4^-]/[HPO_4^-]$ (B) $[HCO_3^-]/[CO_2]$

(C) $[CO_3^{2-}]/[HCO_3^{2-}]$ (D) $[PO_4^{3-}]/[HPO_4^{2-}]$

3. Following reaction occurs in the body :

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

If CO_2 escapes from the system :

(A) pH will decreases

(B) pH will increases

(C) $[H_2CO_3]$ remains unchanged

(D) forward reaction is promoted

Comprehension # 2

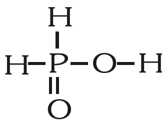
Phosphoric acid is of great importance in fertilizer production. Besides, phosphoric acid and its various salts have a number of application in metal treatment, food, detergent and toothpaste industries.

$$pK_{a_1} = 2.12, pK_{a_2} = 7.21, pK_{a_3} = 12.32$$

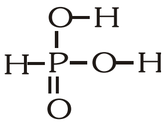
Small quantities of phosphoric acid are extensively used to impart the sour or tart taste to many soft drinks such as colas and roots beers, in which a density of 1.00 g mL^{-1} contains 0.05% by weight of phosphoric acid.

Phosphoric acid is used as a fertiliser for agriculture and an aqueous soil digesting. 1.00 Ч 10^{-3} M phosphoric acid is found to have pH = 7. Zinc is an essential micronutrient for plant growth. Plants can absorb zinc in water soluble from only. In the given soil, zinc phosphate is only the source of zinc and phosphate ions, K_{sp} (zinc phosphate) = 9.1 Ч 10^{-33}.

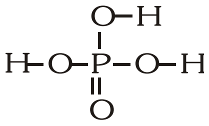
1. Phosphoric acid is a tribasic acid with three-step ionisation constants. Thus, its structure is :

(A) 

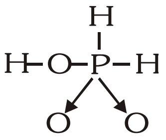
$H-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{P}}-O-H$

(B) 

$H-\underset{\underset{O}{\|}}{\overset{\overset{O-H}{|}}{P}}-O-H$

(C) 

$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O-H}{|}}{P}}-O-H$

(D) 

2. What is the pH of the cola assuming that the acidity of the cola arises only from phosphoric acid and second and third ionisation constants are of no importance ?

(A) 2.2 (B) 3.3 (C) 4.4 (D) 1.8

3. Molar concentration of phosphate ion in the soil with pH 7 is :

(A) 1.2 Ч 10^{-4} M (B) 2.2 Ч 10^{-4} M

(C) 1 Ч 10^{-3} M (D) 1.1 Ч 10^{-10} M

4. Concentration of $[Zn^{2+}]$ in the soil is :

(A) 9.1 Ч 10^{-5} M (B) 5.7 Ч 10^{-9} M

(C) 4.0 Ч 10^{-10} M (D) 3.0 Ч 10^{-6} M

MISCELLANEOUS TYPE QUESTION

ANSWER KEY

EXERCISE -3

- *True / False*

1.	F	2.	F	3.	T	4.	F
5.	T	6.	F	7.	F	8.	F
9.	F	10.	F	11.	F	12.	T
13.	T	14.	T	15.	T	16.	F
17.	T	18.	T	19.	F	20.	T
21.	T	22.	T				

- *Fill in the Blanks*

1.	Increase, one	2.	Greater	3.	Br^- ion	4.	Greater
5.	7.14 Ч 10^{-3}	6.	3 Ч 10^{-6}	7.	$M_2X = QY_2 > PZ_3$	8.	10^{-8}
9.	7	10.	5.74	11.	HSO_4^-	12.	Increases
13.	Less	14.	Less	15.	Lewis acid	16.	Buffer
17.	Weaker	18.	Ag^+	19.	Cationic	20.	Independent
21.	$(K_{sp}/4)^{1/4}$	22.	5.556 Ч 10^{-10}	23.	Acidic, Cu^{++}	24.	Colourless, Pink
25.	pK_w (not 14 !!)	26.	$k_W = k[H_2O]$	27.	Greater		

- *Match the Column*

1. A - (r), B - (p), C - (q), D - (s) **2.** A - (s), B - (p), C - (r), D - (q)

- *Assertion - Reason Questions*

1.	A	2.	B	3.	D	4.	C
5.	B	6.	C	7.	A		

- *Comprehension Based Questions*

Comprehension #1 : 1. D 2. B 3. B

Comprehension #2 : 1. C 2. A 3. B 4. B

EXERCISE–04 [A] CONCEPTUAL SUBJECTIVE EXERCISE

1. Calculate

(i) K_a for H_2O ($K_w = 10^{-14}$) (ii) K_b for $B(OH)_4^-$, $K_a(B(OH)_3)$ = 6 Ч 10^{-10}

(iii) K_a for HCN, $K_b(CN^-)$ = 2.5 Ч 10^{-5}

2. Calculate the ratio of degree of dissociation (α_2/α_1) when 1 M acetic acid solution is diluted to $\frac{1}{100}$ times. (Given K_a = 1.8 Ч 10^{-5})

3. Calculate the ratio of degree of dissociation of acetic acid and hydrocyanic acid (HCN) in 1 M their respective solution of acids (Given $K_{a(CH_3COOH)}$ = 1.8 Ч 10^{-5} ; $K_{a(HCN)}$ = 6.2 Ч 10^{-10}]

4. Calculate :

(a) K_a for a monobasic acid whose 0.10 M solution has pH of 4.50

(b) K_b for a monoacidic base whose 0.1 M solution has a pH of 10.50

5. Calculate pH of following solution :

(a) 0.1 M HCl (b) 0.1 M H_2SO_4 (50 mL) + 0.4 M HCl 50 (mL)

(c) 0.1 M CH_3COOH (K_a = 1.8 Ч 10^{-5}) (d) 0.1 M NH_4OH (K_b = 1.8 Ч 10^{-5})

(e) 10^{-8} M HCl (f) 10^{-10} M NaOH

(g) 10^{-6} M CH_3COOH (h) 10^{-8} M CH_3COOH

(i) 0.1 M HA + 0.1 M HB [K_a(HA) = 2 Ч 10^{-5} ; K_a(HB) = 4 Ч 10^{-5}]

(j) Decimolar solution of Baryta ($Ba(OH)_2$), diluted 100 times.

(k) 10^{-3} mole of KOH dissolved in 100 L of water.

(l) 0.5 M HCl (25 mL) + 0.5 M NaOH (10 mL) + 40 mL H_2O

(m) equal volume of HCl solution (PH = 4) + 0.0019 N HCl solution

6. The value of K_w at the physiological temperature (37° C) is 2.56 Ч 10^{-14}. What is the pH at the neutral point of water at this temperature, where there are equal number of H^+ and OH^- ?

7. Calculate the number of H^+ present in one mL of solution whose pH is 13

8. Calculate change in concentration of H^+ ion in one litre of water, when temperature changes from 298 K to 310 K. Given K_w(298) = 10^{-14}, K_w(310) = 2.56 Ч 10^{-14}.

9. (i) K_w for H_2O is 9.62 Ч 10^{-14} at 60 °C. What is pH of water at 60 °C.

(ii) What is the nature of solution at 60°C whose.

(a) pH = 6.7 (b) pH = 6.35

10. The pH of aqueous solution of ammonia is 11.5. Find molarity of solution. $K_b(NH_4OH)$ = 1.8 Ч 10^{-5}.

11. The solution of weak monoprotic acid which is 0.01 M has pH = 3. Calculate K_a of weak acid.

12. Boric acid is a weak monoprotic acid. It ionizes in water as

$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$: K_a = 5.9 Ч 10^{-10}

Calculate pH of 0.3 M boric acid.

13. Calculate [H^+] and [$CHCl_2COO^-$] in a solution that is 0.01 M in HCl and 0.01 M in $CHCl_2COOH$. Take (K_a = 2.55 Ч 10^{-2}).

14. Calculate [H^+], [CH_3COO^-] and [$C_7H_5O_2^-$] in a solution that is 0.02 M in acetic acid and 0.01 M in benzoic acid. K_a(acetic) = 1.8 Ч 10^{-5}, K_a (benzoic) = 6.4 Ч 10^{-5}.

15. At 25 °C, the dissociation constant of HCN and HF are 4 Ч 10^{-10} and 6.7 Ч 10^{-4}. Calculate the pH of a mixture of 0.1 M HF and 0.1 M HCN.

POLYPROTIC ACIDS & BASES

16. Determine the $[S^{2-}]$ in a saturated (0.1 M) H_2S solution to which enough HCl has been added to produce a $[H^+]$ of 2 Ч 10^{-4}. $K_1 = 10^{-7}$, $K_2 = 10^{-14}$

17. Calculate $[H^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$ and $[PO_4^{3-}]$ in a 0.01 M solution of H_3PO_4.
Take K_1 = 7.225 Ч 10^{-3}, K_2 = 6.8 Ч 10^{-8}, K_3 = 4.5 Ч 10^{-13}.

18. Calculate the pH of a 0.1 M solution of $H_2NCH_2CH_2NH_2$; ethylenediamine (en). Determine the en H_2^{2+} concentration in the solution. K_{b_1} and K_{b_2} values of ethylenediamine are 8.5 Ч 10^{-5} and 7.1 Ч 10^{-8} respectively.

19. What are the concentration of H^+, HSO_4^-, SO_4^{-2} & H_2SO_4 in a 0.20 M solution of sulphuric acid ?
Given : $H_2SO_4 \longrightarrow H^+ + HSO_4^-$; strong
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$; K_2 = 1.3 Ч 10^{-2} M

BUFFER SOLUTION

20. Determine $[OH^-]$ of a 0.050 M solution of ammonia to which has been added sufficient NH_4Cl to make the total $[NH_4^+]$ equal to 0.100. [$K_{b(NH_3)}$ = 1.8 Ч 10^{-5}]

21. Calculate the pH of a solution prepared by mixing 50.0 mL of 0.200 M $HC_2H_3O_2$ and 50.0 mL of 0.100 M NaOH. [$K_{a(CH_3COOH)}$ = 1.8 Ч 10^{-5}]

22. A buffer of pH 9.26 is made by dissolving x moles of ammonium sulphate and 0.1 mole of ammonia into 100 mL solution. If pK_b of ammonia is 4.74, calculate value of x.

23. 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, salculate pH.

24. (a) Determine the pH of a 0.2 M solution of pyridine C_5H_5N. K_b = 1.5 Ч 10^{-9}
(b) Predict the effect of addition of pyridinium ion $C_5H_5NH^+$ on the position of the equilibrium. Will the pH be raised or lowered ?
(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $C_5H_5NH^+Cl$, has been added, assuming no change in volume.

25. A buffer solution was prepared by dissolving 0.02 mol propionic acid & 0.015 mol sodium propionate in enough water to make 1.00 L of solution. (K_a for propionic acid is 1.34 Ч 10^{-5})
(a) What is the pH of the buffer ?
(b) What would be the pH if 1.0 Ч 10^{-5} mol HCl were added to 10 mL of the buffer ?
(c) What would be the pH if 1.0 Ч 10^{-5} mol NaOH were added to 10 mL of the buffer.
(d) Also report the percent change in pH of original buffer in case (b) and (c)

26. A solution was made up of 0.01 M in chloroacetic acid $ClCH_2COOH$ and also 0.002 M in sodium chloracetate $ClCH_2COONa$. What is $[H^+]$ in the solution? K_a = 1.5 Ч 10^{-3}.

INDICATORS

27. A certain solution has a hydrogen ion concentration 4 Ч 10^{-3} M. For the indicator thymol blue, pH is 2.0 when half the indicator is in unionised from. Find the % of indicator in unionised form in the solution with $[H^+]$ = 4 Ч 10^{-3} M.

28. Bromophenol blue is an indicator with a K_a value of 6 Ч 10^{-5}. What % of this indicator is in its basic form at a pH of 5 ?

29. An acid base indicator has a K_a of 3 Ч 10^{-5}. The acid form of the indicator is red & the basic form is blue. By how much must the pH change in order to change the indicator form 75% red to 75% blue ?

HYDROLYSIS

30. What is the OH^- concentration of a 0.08 M solution of CH_3COONa. [$K_a(CH_3COOH)$ = 1.8 Ч 10^{-5}]

31. Calculate the pH of a 2.0 M solution of NH_4Cl.[$K_b(NH_3)$ = 1.8 Ч 10^{-5}]

32. 0.25 M solution of pyridinium chloride $C_5H_6N^+Cl^-$ was found to have a pH of 2.699. What is K_b for pyridine, C_5H_5N ?

33. Calculate the extent of hydrolysis & the pH of 0.02 M CH_3COONH_4
[$K_b(NH_3)$ = 1.8 Ч 10^{-5}, $K_a(CH_3COOH)$ = 1.8 Ч 10^{-5}]

34. Calculate the percent hydrolysis in a 0.06 M solution of KCN.[K_a(HCN) = 6 Ч 10^{-10}]

35. Calculate the extent of hydrolysis of 0.005 M K_2CrO_4. [K_2 = 3.1 Ч 10^{-7} for H_2CrO_4]
(It is essentially strong for first ionization).

36. A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 4.0. What is the hydrolysis constant k_h for PuO_2^{2+} , and what is K_b for PUO_2OH^+ ?

37. Calculate the pH of 1.0 Ч 10^{-3} M sodium phenolate, $NaOC_6H_5$ K_a for HOC_6H_5 is 1.05 Ч 10^{-10} .

38. What is the pH of 0.1 M $NaHCO_3$? K_1 = 4.5 Ч 10^{-7}, K_2 = 4.5 Ч 10^{-11} for carbonic acids.

39. Calculate pH of 0.05 M potassium hydrogen phthalate, $KHC_8H_4O_4$.

$$H_2C_8H_4O_4 + H_2O \rightleftharpoons H_3O^+ + HC_8H_4O_4^- \qquad pK_1 = 2.94$$

$$HC_8H_4O_4^- + H_2O \rightleftharpoons H_3O^+ + C_8H_4O_4^{2-} \qquad pK_2 = 5.44$$

40. Calculate OH^- concentration at the equivalent point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for the acid = 1.9 Ч 10^{-5}.

41. The acid ionization hydrolysis constant of Zn^{2+} is 1.0 Ч 10^{-9}
   (a) Calculate the pH of a 0.001 M solution of $ZnCl_2$
   (b) What is the basic dissociation constant of $Zn(OH)^+$?

ACID BASE REACTIONS & TITRATIONS

42. Calculate the hydronium ion concentration and pH at the equivalence point in the reaction of 22.0 mL of 0.10 M acetic acid, CH_3COOH, with 22.0 mL of 0.10 M NaOH.

43. Calculate the hydronium ion concentration and the pH at the equivalence point in a titration of 50.0 mL of 0.40 M NH_3 with 0.40 M HCl.

44. In the titration of a solution of a weak acid HX with NaOH, the pH is 5.8 after 10.0 mL of NaOH solution has been added and 6.402 after 20.0 mL of NaOH has been added. What is the ionization constant of HX ?

45. The equivalent point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.75 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid ?

46. A weak base (50.0 mL) was titrated with 0.1 M HCl. The pH of the solution after the addition of acid 10.0 mL and 25.0 mL were found to be 9.84 and 9.24, respectively. Calculate K_b of the base and pH at the equivalence point.

47. A weak acid (50.0 mL) was titrated with 0.1 M NaOH. The pH values when 10.0 mL and 25.0 mL of base have been added are found to be 4.16 and 4.76, respectively. Calculate K_a of the acid and pH at the equivalence point.

48. CH_3COOH (50 mL, 0.1 M) is titrated against 0.1 M NaOH solution. Calculate the pH at the addition of 0 mL, 10 mL, 20 mL, 25 mL, 40 mL, 50 mL of NaOH. K_a of CH_3COOH is 2 Ч 10^{-5}.

SOLUBILITY & SOLUBILITY PRODUCT'S

49. The values of K_{sp} for the slightly soluble salts MX and OX_2 are each equal to 4.0 Ч 10^{-18}. Which salt is more soluble ? Explain your answer fully.

50. The solubility of $PbSO_4$ water is 0.038 g/L. Calculate the solubility product constant of $PbSO_4$.

51. Calculate the solubility of $Mg(OH)_2$ in water. K_{sp} = 1.2 Ч 10^{-11}.

52. How many mol CuI($K_{sp} = 5 \times 10^{-12}$) will dissolve in 1.0 L of 0.10 M NaI solution ?

53. What is the solubility (in mol/L) of $Fe(OH)_3$ in a solution of pH = 8.0? [K_{sp} for $Fe(OH)_3 = 1.0 \times 10^{-36}$]

54. Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. For A_2X_3, [$K_{sp} = 1.1 \times 10^{-23}$]

55. What mass of Pb^{2+} ion is left in solution when 50.0 mL of 0.20 M $Pb(NO_3)_2$ is added to 50.0 mL of 1.5 M NaCl ? [Given K_{sp} for $PbCl_2$ 1.7×10^{-4}]

56. A solution has a Mg^{2+} concentration of 0.0010 mol/L. will $Mg(OH)_2$ precipitate if the OH^- concentration of the solution is [$K_{sp} = 1.2 \times 10^{-11}$]

    (a) 10^{-5} mol/L (b) 10^{-3} mol/L ?

57. Calculate solubility of PbI_2($K_{sp} = 1.4 \times 10^{-8}$) in water at 25°, which is 90% dissociated.

58. Calculate the Simultaneous solubility of AgSCN and AgBr. $K_{sp}(AgSCN) = 1.1 \times 10^{-12}$, $K_{sp}(AgBr) = 5 \times 10^{-13}$.

59. Calculate F^- in a solution saturated with respect of both MgF_2 and SrF_2. $K_{sp}(MgF_2) = 9.5 \times 10^{-9}$, $K_{sp}(SrF_2) = 4 \times 10^{-9}$.

COMPLEXATION EQUILIBRIA

60. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.010 mol AgCl in 100 L solution. [$K_f(AgCl_2^-) = 3 \times 10^5$, $K_{sp} = (AgCl) = 1 \times 10^{-10}$]

61. How much AgBr could dissolve in 1.0 L of 0.40 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed. [$K_f(Ag(NH_3)_2^+) = 1 \times 10^8$, $K_{sp}(AgBr) = 5 \times 10^{-13}$]

62. A solution of 0.1 M Cl^-, 0.1 M Br^- and 0.1 M I^- solid $AgNO_3$ is gradually added to this solution. Assuming that the addition of $AgNO_3$ does not change the volume. Answer the following :

    (a) What conc. of Ag^+ ions will be required to start precipitation of each of the three ions.

    (b) Which ion will precipitate first

    (c) What will be the conc. of this ion when the second ion start precipitating.

    (d) What will be the conc. of both ions when the third ion start precipitating.

    Given : $K_{sp}(AgCl) = 1.7 \times 10^{-10}$, $K_{sp}(AgBr) = 5 \times 10^{-13}$
    $K_{sp}(AgI) = 8.5 \times 10^{-17}$.

63. The solubility of $CaCO_3$ is 7 mg/litre. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{+2} and Ba^{+2}, no precipitate is formed until 90% of Ba^{+2} has been precipitated as $BaCO_3$.

64. A solution containing 0.10 M Zn^{2+} and 0.10 M Fe^{2+} is saturated with H_2S. What must be the H^+ concentration to separate these ions by selective precipitating ZnS. What is the smallest Zn^{2+} concentration that can be achieved without precipitating any of Fe^{2+} as FeS.

    $K_{sp}ZnS = 1.2 \times 10^{-23}$, $K_{sp}FeS = 3.7 \times 10^{-19}$.
    [Take : $[H_2S] = 0.1$ M and $K_1 = 1.1 \times 10^{-7}$, $K_2 = 1 \times 10^{-14}$]

65. (a) Will $Mg(OH)_2$ precipitate from a solution that is 0.01 M in $MgCl_2$ and also 0.10 M in NH_3.

    (b) What NH_4^+ must maintained to prevent the precipitation of $Mg(OH)_2$ from a solution that is 0.010 $MgCl_2$ in 0.1 MNH_3 K_{sp} $Mg(OH)_2 = 2.5 \times 10^{-11}$, K_b $NH_3 = 1.8 \times 10^{-5}$

66. Calculate the solubility of AgCN in a buffer solution of pH 3. Neglect any complexation. Take $K_{sp}(AgCN) = 3.2 \times 10^{-16}$, $K_a(HCN) = 6.4 \times 10^{-10}$.

67. Silver ion forms $Ag(CN)_2^-$ in the presence of excess CN^-. How much KCN should be added to 1 litre of a 0.0005 M Ag^+ solution in order to reduce $[Ag^+]$ to 1×10^{-19} K_b $Ag(CN)_2^- = 1 \times 10^{-21}$.

68. How many moles of solid NaOH must be added to 1.0 litre of H_2O in order to dissolve 0.10 mole of $Zn(OH)_2$ according to the equation

$$Zn(OH)_2 + 2OH^- \rightleftharpoons Zn(OH)_4^{2-}$$

$K_{sp}Zn(OH)_2 = 4.5$ Ч 10^{-17}, $K_{inst}Zn(OH)_4^{2-} = 3.6$ Ч 10^{-16}.

CONCEPTUAL SUBJECTIVE EXERCISE

ANSWER KEY

EXERCISE-4(A)

1. (i) 1.8 Ч 10^{-16}, (ii) 1.66 Ч 10^{-5}, (iii) 4 Ч 10^{-10} **2.** 10 **3.** 170.4
4. (a) $K_a = 10^{-8}$, (b) $K_b = 10^{-6}$
5. (a) +1, (b) 0.522, (c) 2.87, (d) 11.13 (e) 6.97,
(f) 6.996, (g) 6.01, (h) 6.97, (i) 2.61, (j) 11.30
(k) 9 (l) 1, (m) 3
6. 6.795 **7.** 6.022 Ч 10^{7} **8.** 0.6 Ч 10^{-7}
9. (i) 6.51 ; (ii) (a) Basic, (b) Acidic
10. 0.556 M **11.** 1.11 Ч 10^{-4} **12.** 4.87
13. $[H^+] = 1.612$ Ч 10^{-2}M, $[CHCl_2COO^-] = 6.126$ Ч 10^{-3} M
14. $[H^+] = 10^{-3}$M, $[CH_3COO^-] = 3.6$ Ч 10^{-4} M, $[C_7H_5O_2^-] = 6.4$ Ч 10^{-4} M
15. 2.08 **16.** $[S^{2-}] = 2.5$ Ч 10^{-15}
17. $[H^+] = [H_2PO_4^-] = 5.623$ Ч 10^{-3}, $[HPO_4^{-2}] = 6.8$ Ч 10^{-8}, $[PO_4^{3-}] = 5.441$ Ч 10^{-18}
18. pH = 11.46,$[enH_2^{2+}] = 7.1$ Ч 10^{-8} **19.** 0.2216 M, 0.1884 M, 0.0116 M, 0
20. $[OH^-] = 9.0$ Ч 10^{-6} **21.** 4.74 **22.** 0.05 mol
23. 9.56 **24.** (a) pH = 9.239(b) lowered (c) pH = 4.699
25. (a) 4.7525 (b) 4.697(c) 4.798 (d) 1.134% on acid addition 0.96 % on base addition.
26. $[H^+] = 2.5$ Ч 10^{-3} **27.** $[HI_n] = 28.57$ % **28.** 85.71% **29.** ΔpH=0.954
30. $[OH^-] = 6.664$Ч10^{-6} **31.** pH = 4.477**32.** $K_b = 6.25$ Ч 10^{-10}
33. 0.56%, pH=7 **34.** 1.667 % **35.** 0.26% **36.** 10^{-6} ; 10^{-8}
37. pH = 10.43 **38.** 8.34 **39.** 4.19 **40.** 5.12Ч10^{-6} M
41. (a) 6 (b) 1 Ч 10^{-5} **42.** 8.71 **43.** 4.98
44. 7.94 Ч 10^{-7} **45.** $K_a = 2.37$ Ч 10^{-6} **46.** 1.73 Ч 10^{-5}, 5.27
47. $K_a = 1.73$ Ч 10^{-5}, pH = 8.73
48. (i) 2.85, (ii) 4.0969, (iii) 4.5229,(iv) 4.699 (v) 5.301 (vi) 8.699
49. OX_2 is more soluble **50.** 1.6 Ч 10^{-8} **51.** 1.4 Ч 10^{-4} **52.** $[Cu^+] = 5$ Ч 10^{-11} M
53. 10^{-18} M **54.** 1.0 Ч 10^{-5} mol/lit **55.** 12 mg
56. (a) no precipitation will occur, (b) a precipitate will form **57.** 1.6 Ч 10^{-3}
58. 4 Ч 10^{-7} mol/L AgBr, 9 Ч 10^{-7} mol/L AgSCN **59.** $[F^-] = 3$ Ч 10^{-3} M
60. 19.5 kg **61.** 2.8 Ч 10^{-3} M
62. (a) 8.5 Ч 10^{-16}, 5 Ч 10^{-12}, 1.7 Ч 10^{-9} (b) I^- (c) 1.7 Ч 10^{-5} (d) $Br^- = 2.9$ Ч 10^{-4}, $I^- = 5$ Ч 10^{-8}
63. 4.9 Ч 10^{-10} **64.** 5.5 Ч $10^{-3} \leq [H^+] < 0.96$, 3.24 Ч 10^{-6}
65. (a) yes (b) 0.036 M **66.** s = 2.236 Ч 10^{-5} M **67.** 3.236 Ч 10^{-3} mol **68.** 1.09 mol

EXERCISE–04 [B] BRAIN STORMING SUBJECTIVE EXERCISE

1. A solution of volume V contains n_1 moles of QCl and n_2 moles of RCl where QOH and ROH are two weak bases of dissociation constants k_1 and k_2 respectively. Show that the pH of the solution is given by

$$pH = \frac{1}{2}\log\left[\left(\frac{k_1k_2}{k_W}\right)\frac{V}{(n_1k_2 + k_1n_2)}\right]$$

State assumptions, if any.

2. EDTA, often abbreviated as H_4Y, forms very stable complexes with almost all metal ions. Calculate the fraction of EDTA in the fully protonated form, H_4Y in a solution obtained by dissolving 0.1 mol Na_4Y in 1 lit. The acid dissociation constants of H_4Y :

$k_1 = 1.02 \times 10^{-2}$, $k_2 = 2.13 \times 10^{-3}$, $k_3 = 6.92 \times 10^{-7}$, $k_4 = 5.50 \times 10^{-11}$:

3. Calculate the solubility of solid zinc hydroxide at a pH of 5,9 and 13. Given :

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)$ $k_1 = 10^{-6}\,M$ (1)

$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+ + OH^-$ $k_2 = 10^{-7}\,M$ (2)

$Zn(OH)^+ \rightleftharpoons Zn^{2+} + OH^-$ $k_3 = 10^{-4}\,M$ (3)

$Zn(OH)_2(aq) + OH^- \rightleftharpoons Zn(OH)_3^-$ $k_4 = 10^{3}\,M^{-1}$ (4)

$Zn(OH)_3^- + OH^- \rightleftharpoons Zn(OH)_4^{2-}$ $k_5 = 10\,M^{-1}$ (5)

4. The standard free energy of formation for AgCl at 298 K is –109.7 kJ $mole^{-1}$.

$\Delta G°\,(Ag^+) = 77.2$ kJ/mole, $\Delta G°\,(Cl^-) = -131.2$ kJ/mole. Find the solubility of AgCl in 0.05 M KCl. Neglect any complication due to complexation :-

5. Salt mixture containing $Cu_3(AsO_4)_2$ ($K_{sp} = 8 \times 10^{-36}$) and $Pb_3(AsO_4)_2$ ($K_{sp} = 4.096 \times 10^{-36}$) is shaken with water. Find the concentration of metal cations in the solution at equilibrium. Neglect any hydrolysis of the dissolved ions.

6. (a) At what minimum pH will 1.0×10^{-3} mol of $Al(OH)_3$ go into 1 L solution as $[Al(OH)_4^-]$.

(b) At what minimum pH will 1.0×10^{-3} mol of $Al(OH)_3$ go into 1 L solution as Al^{3+} ?

Given : $K_{sp}[Al(OH)_3] = 5.0 \times 10^{-33}$ and for $[Al(OH)_4^-] \Leftrightarrow Al^{3+} + 4OH^-$. $K = 1.3 \times 10^{-34}$.

7. A solution contains HCl, $Cl_2HCCOOH$ & CH_3COOH at concentrations 0.09 M in HCl, 0.09 M in $Cl_2HCCOOH$ & 0.1 M in CH_3COOH, pH for the solution is 1. Ionization constant of $CH_3COOH = 10^{-5}$. What is the magnitude of K for dichloroacetic acid ?

8. A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of 0.935 $g.mL^{-1}$. What is the pH of the solution. Take K_b for protonation of ammonia $= 5.5 \times 10^{-6}$.

9. The k_w of water at two different temperature is :-

T	25°C	50°C
k_w	1.08×10^{-14}	5.474×10^{-14}

Assuming that ΔH of any reaction is independent of temperature, calculate the enthalpy of neutralization of a strong acid and strong base.

10. What is the pH of a 1.0 M solution of acetic acid ? To what volume must 1 litre of the solution be diluted so that the pH of the resulting solution will be twice the original value. Given $K_a = 1.8 \times 10^{-5}$:-

11. A handbook states that the solubility of methylamine CH_3NH_2 (g) in water at 1 atm pressure at 25°C is 959 volumes of CH_3NH_2 (g) per volume of water ($pk_b = 3.39$) :-

(a) Estimate the max. pH that can be attained by dissolving methylamine in water.

(b) What molarity NaOH (aq.) would be required to yield the same pH?

12. Mixture of solutions. Calculate the pH of the following solutions.

For H_3PO_4 ; $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, $K_{a_3} = 10^{-12}$

(a) 50 mL of 0.12 M H_3PO_4 + 20 mL of 0.15 M NaOH ;

(b) 50 mL of 0.12 M H_3PO_4 + 40 mL of 0.15 M NaOH ;

(c) 40 mL of 0.12 M H_3PO_4 + 40 mL of 0.18 M NaOH ;

(d) 40 mL of 0.10 M H_3PO_4 + 40 mL of 0.25 M NaOH.

13. Mixtured of solutions. Calculate the pH of the following solution.

Use data of above question & For H_2CO_3 ; $K_1 = 4.2 \times 10^{-7}$, $K_2 = 4.8 \times 10^{-11}$

(a) 40 mL of 0.050 M Na_2CO_3 + 50 mL of 0.040 M HCl ;

(b) 40 mL of 0.020 M Na_3PO_4 + 40 mL of 0.040 M HCl ;

(c) 50 mL of 0.10 M Na_3PO_4 + 50 mL of 0.10 M NaH_2PO_4 ;

(d) 40 mL of 0.10 M H_3PO_4 + 40 mL of 0.10 M Na_3PO_4.

14. When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl, the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution :-

15. A buffer solution was prepared by dissolving 0.05 mol formic acid & 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_a for formic acid is 1.80 Ч 10^{-4}.

(a) Calculate the pH of the solution.

(b) If this solution were diluted to 10 times its volume, what would be the pH ?

(c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?

16. How many moles of sodium hydroxide can be added to 1.00 L of a solution 0.1 M in NH_3 & 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit ? Assume no change in volume. $K_b(NH_3)$ = 1.8 Ч 10^{-5}.

17. Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 L of solution K_1 = 7.1 Ч 10^{-3}, K_2 = 6.3 Ч 10^{-8}, K_3 = 4.5 Ч 10^{-13}.

18. If 0.00050 mol $NaHCO_3$ is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3, HCO_3^- and CO_3^{2-} ? For H_2CO_3, K_1 = 5 Ч 10^{-7}, K_2 = 5 Ч 10^{-13}.

19. Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{+2}$ and H^+ is 6.5 Ч 10^{-3}. What is the max. pH, which could be used so that at least 95% of the total Fe^{3+} in a dilute solution. exists as Fe^{3+}.

20. How much Na_2HPO_4 must be added to one litre of 0.005 M solution of NaH_2PO_4 in order to make a 1 L of the solution of pH = 6.7 ? K_1 = 7.1 Ч 10^{-3}, K_2 = 6.3 Ч 10^{-8} , K_3 = 4.5 Ч 10^{-13} for H_3PO_4.

21. The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50% of the new indicator is in ionic form :-

22. A buffer solution, 0.080 M in Na_2PO_4 and 0.020 M in Na_3PO_4, is prepared. The electrolytic oxidation of 1.0 m mol of the organic compound RNHOH is carried out in 100 mL of the buffer. The reaction is

$$RNHOH + H_2O \longrightarrow RNO_2 + 4H^+ + 4e$$

Calculate the approximate pH of the solution after the oxidation is complete ?

23. A solution of weak acid HA was titrated with base NaOH. The equivalence point was reached when 36.12 mL of 0.1 M NaOH has been added. Now 18.06 mL of 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 mL of 0.2 M NaOH and 10 mL of 0.2 M HA :-

24. A weak base BOH was titrated against a strong acid. The pH at 1/4th equivalence point was 9.24. Enough strong base was now added (6m. eq.) to completely convert the salt. The total volume was 50 mL. Find the pH at this point :-

25. An organic monoprotic acid [0.1 M] is titrated against 0.1 M NaOH. By how much does the pH change between one fourth and three fourth stages of neutralization ? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid ? Between what stages of neutralization may the pH change by 2 units ?

26. The salt $Zn(OH)_2$ is involved in the following two equilibria,

$Zn(OH)_2\,(s) \rightleftharpoons Zn^{2+}\,(aq) + 2OH^-\,(aq)$; $K_{sp} = 1.2 \times 10^{-17}$

$Zn(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons [Zn(OH)_4]^{2-}\,(aq)$; $K_c = 0.13$

Calculate the pH of solution at which solubility is minimum.

27. What is the solubility of AgCl in 0.20 M NH_3 ?

Given : $K_{sp}(AgCl) = 1.7 \times 10^{-10}\ M^2$, $K_1 = [Ag(NH_3)^+] / [Ag^+][NH_3] = 2.33 \times 10^3\ M^{-1}$ and $K_2 = [Ag(NH_3)_2^+] / [Ag(NH_3)^+]\,[NH_3] = 7.14 \times 10^3\ M^{-1}$.

28. Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $KAg(CN)_2$. Given $K_{inst}\,(Ag(CN)_2^-) = 4.0 \times 10^{-19}\ M^2$ and $K_{sp}\,(AgCl) = 2.8 \times 10^{-10}\ M^2$.

29. Equal volumes of 0.02 M $AgNO_3$ and 0.02 M HCN were mixed. Calculate $[Ag^+]$ at equilibrium. Take $K_a(HCN) = 9 \times 10^{-10}$, $K_{sp}(AgCN) = 4 \times 10^{-16}$:-

30. Show that solubility of a sparingly soluble salt $M^{2+}A^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by :

$$S = \sqrt{K_{sp}\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right)}$$

where K_1 and K_2 are the dissociation constant of acid $H_2A.K_{sp}$ is solubility product of MA.

BRAIN STORMING SUBJECTIVE EXERCISE **ANSWER KEY** EXERCISE-4(B)

2. 3.82×10^{-26}

3. $10\,M,\ 1.12 \times 10^{-6}\,M,\ 2 \times 10^{-4}\,M$

4. $K_{sp} = 1.723 \times 10^{-10}$, $s = 3.446 \times 10^{-9}\ M$

5. $[Cu^{+2}] = 8.825 \times 10^{-8}$, $[Pb^{+2}] = 7.119 \times 10^{-8}$

6. (a) pH = 9.415 (b) pH = 4.23

7. $k_{a_2} = 1.25 \times 10^{-2}$

8. pH = 11.74

9. $\Delta H_{neut} = -51952.6\ J = -51.95$ kJ/mole

10. $V = 2.77 \times 10^4\ L$

11. (a) 13.097 (b) 0.1252

12. (a) 2.12 (b) 4.66 (c) 7.2 (d) 12

13. (a) 8.347 (b) 4.66 (c) 9.6 (d) 7.2

14. 9.1628

15. (a) pH = 3.823 (b) pH = 3.846 (c) pH = 3.9899

16. 0.0818 moles

17. $[OH^-] = 3.73 \times 10^{-2}\,M$, $[H_3PO_4] = 5.93 \times 10^{-18}\ M$

18. $[H_2CO_3] = 9.85 \times 10^{-6}\ M$, $[HCO_3^-] = 4.9 \times 10^{-4}\,M$, $[CO_3^{-2}] = 2.45 \times 10^{-8}\ M$

19. pH = 0.908

20. 1.6 m mole

21. pH = 7.9, 7.3

22. 7.81

23. pH = 9

24. pH = 11.22

25. 0.9542, $pk_a = 4.751$, $\frac{1}{11}^{th}$ & $\frac{10}{11}^{th}$ stages of neutralization

26. pH = 9.99, $s = 10^{-9}\ M$

27. $9.6 \times 10^{-3}\ M$

28. precipitate will occur

29. $[Ag^+] = 6.66 \times 10^{-5}\ M$

EXERCISE - 05 [A] JEE-[MAIN] : PREVIOUS YEAR QUESTIONS

1. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? [AIEEE–2013]

(A) 0.1 L (B) 0.9 L (C) 2.0 L (D) 9.0 L

2. The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, Ka of this acid is :- [AIEEE–2012]

(A) 1 Ч 10^{-7} (B) 3 Ч 10^{-7} (C) 1 Ч 10^{-3} (D) 1 Ч 10^{-5}

3. The K_{sp} for $Cr(OH)_3$ is 1.6 Ч 10^{-30}. The molar solubility of this compound in water is :- [AIEEE–2011]

(A) $\sqrt[2]{1.6\times10^{-30}}$ (B) $\sqrt[4]{1.6\times10^{-30}}$ (C) $\sqrt[4]{1.6\times10^{-30}/27}$ (D) 1.6 Ч $10^{-30}/27$

4. An acid HA ionises as

HA ⇌ $H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be :- [AIEEE–2011]

(A) 1 Ч 10^{-10} (B) 5 (C) 5 Ч 10^{-8} (D) 1 Ч 10^{-5}

5. Solubility product of silver bromide is 5.0 Ч 10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is :- [AIEEE–2010]

(A) 5.0 Ч 10^{-8} g (B) 1.2 Ч 10^{-10} g (C) 1.2 Ч 10^{-9} g (D) 6.2 Ч 10^{-5} g

6. In aqueous solution the ionization constants for carbonic acid are

K_1 = 4.2 Ч 10^{-7} and K_2 = 4.8 Ч 10^{-11}

Select the correct statement for a saturated 0.034 M solution of the carbonic acid :- [AIEEE–2010]

(A) The concentration of H^+ is double that of CO_3^{2-}

(B) The concentration of CO_3^{2-} is 0.034 M

(C) The concentration of CO_3^{2-} is greater than that of HCO_3^-

(D) The concentrations of H^+ and HCO_3^- are approximately equal

7. At 25° C, the solubility producct of $Mg(OH)_2$ is 1.0 Ч 10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? [AIEEE–2010]

(A) 8 (B) 9 (C) 10 (D) 11

8. Solid $Ba(NO_3)_2$ is gradully dissolved in a 1.0 Ч 10^{-4} M Na_2CO_3 solution.At what concentration of Ba^{2+} will a precipitate begin to form?

(K_{SP} for Ba CO_3 = 5.1 Ч 10^{-9}) [AIEEE-2009]

(A) 8.1 Ч 10^{-8} M (B) 8.1 Ч 10^{-7} M (C) 4.1 Ч 10^{-5} M (D) 5.1 Ч 10^{-5} M

9. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt. BA, will be - [AIEEE-2008]

(A) 9.58 (B) 4.79 (C) 7.01 (D) 9.22

10. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is - [AIEEE-2007]

$$AgIO_3 \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0 Ч 10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution ?

(A) 28.3 Ч 10^{-2} g (B) 2.83 Ч 10^{-3} g (C) 1.0 Ч 10^{-7} g (D) 1.0 Ч 10^{-4} g

11. The solubility product of a salt having general formula MX_2, in water is : 4 Ч 10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is - **[AIEEE-2005]**

(A) 1.0 Ч 10^{-4} M (B) 2.0 Ч 10^{-6} M (C) 4.0 Ч 10^{-10} M (D) 1.6 Ч 10^{-4} M

12. Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be - **[AIEEE-2005]**

(A) 3.88 Ч 10^{6} (B) 3.98 Ч 10^{8} (C) 3.98 Ч 10^{-6} (D) 3.68 Ч 10^{-6}

13. The molar solubility in mol L^{-1} of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP}. 's' is given in terms of K_{SP} by relation : **[AIEEE-2004]**

(A) $s = (K_{SP} / 128)^{1/4}$ (B) $s = (128K_{SP})^{1/4}$

(C) $s = (256K_{SP})^{1/5}$ (D) $s = (K_{SP}/256)^{1/5}$

14. The solubility of $Mg(OH)_2$ is x mole/lit. then its solubility product is- **[AIEEE-2002]**

(A) x^3 (B) $5x^3$ (C) $4x^3$ (D) $2x^2$

15. The solubility in water of a sparingly soluble salt AB_2 is 1.0 Ч 10^{-5} mol L^{-1}. Its solubility product will be **[AIEEE-2003]**

(A) 1 Ч 10^{-15} (B) 1 Ч 10^{-10} (C) 4 Ч 10^{-15} (D) 4 Ч 10^{-10}

JEE-[MAIN] : PREVIOUS YEAR QUESTIONS		ANSWER KEY				EXERCISE -5[A]	
1.	(D)	2.	(D)	3.	(C)	4.	(A)
5.	(C)	6.	(D)	7.	(C)	8.	(D)
9.	(C)	10.	(B)	11.	(A)	12.	(C)
13.	(D)	14.	(C)	15.	(C)		

EXERCISE - 05 [B] JEE-[ADVANCED] : PREVIOUS YEAR QUESTIONS

1. Which of the following statement(s) is/are correct ? **[JEE 1998]**

(A) the pH of 1.0 Ч 10^{-8} M solution of HCl is 8

(B) the conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

(C) autoprotolysis constant of water increases with temperature

(D) when a solution of a weak monoprotic acid is titrated against a strong base, at half - neutralization point pH = (1/2) pK_a.

2. A buffer solution can be prepared from a mixture of- **[JEE 1999]**

(A) sodium acetate and acetic acid in water

(B) sodium acetate and hydrochloric acid in water

(C) ammonia and ammonium chloride in water

(D) ammonia and sodium hydroxide in water.

3. The pH of 0.1 M solution of the following salts increases in the order- **[JEE 1999]**

(A) NaCl < NH_4Cl < NaCN < HCl

(B) HCl < NH_4Cl < NaCl < NaCN

(C) NaCN < NH_4Cl < NaCl < HCl

(D) HCl < NaCl < NaCN < NH_4Cl

4. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is- **[JEE 2001]**

(A) 40 mL (B) 20 mL (C) 10 mL (D) 4 mL

5. For sparingly soluble salt ApBq, the relationship of its solubility product (Ls) with its solubility (S) is- **[JEE 2001]**

(A) Ls = S^{p+q}, $p^p.q^q$ (B) Ls = S^{p+q}, $p^p.q^p$ (C) Ls = S^{pq} $p^p.q^q$ (D) Ls = S^{pq}, $(p\cdot q)^{p+q}$

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

(A) FeS (B) MnS (C) HgS (D) ZnS

7. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is- **[JEE 2004]**

(A) 0.01 % (B) 0.0001 % (C) 0.1 % (D) 0.5 %

8. CH_3NH_2(0.1 mole, K_b = 5 Ч 10^{-4}) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is- **[JEE 2005]**

(A) 1.6 Ч 10^{-11} (B) 8 Ч 10^{-11} (C) 5 Ч 10^{-5} (D) 2 Ч 10^{-2}

SUBJECTIVES :

9. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2\,NH_3$, $K_c = 6.2 \times 10^{-8}$ & K_{sp} of AgCl $= 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia. **[JEE 1998]**

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

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

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

13. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25 °C.

(a) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(b) If 6g of NaOH is added to the above solution, determine final pH. Assume there is no change in volume on mixing. K_a of acetic acid is 1.75×10^{-5} M. **[JEE 2002]**

14. Will the pH of water be same at 4 °C and 25 °C ? Explain. **[JEE 2003]**

15. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point.

Given $K_a(HA) = 5 \times 10^{-6}$ and $\alpha << 1$. **[JEE 2004]**

16. CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is

(A) 1.6×10^{-11} (B) 8×10^{-11} (C) 5×10^{-5} (D) 2×10^{-2} **[JEE 2005]**

17. The species present in solution when CO_2 is dissolved in water :

(A) $CO_2, H_2CO_3, HCO_3^-, CO_2^-$ (B) H_2CO_3, CO_3^{2-} **[JEE 2006]**

(C) CO_3^{2-}, HCO_3^- (D) CO_2, H_2CO_3

18. Solubility product constants (K_{SP}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order :

(A) $MX > MX_2 > M_3X$ (B) $M_3X > MX_2 > MX$ **[JEE 2008]**

(C) $MX_2 > M_3X > MX$ (D) $MX > M_3X > MX_2$

19. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C.

The concentration of H^+ at equivalence point is **[JEE 2008]**

($K_w = 1 \times 10^{-14}$ at 25°C)

(A) 3.7×10^{-13} M (B) 3.2×10^{-7} M (C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

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

21. In 1 L saturated solution of AgCl [K_{sp}(AgCl) = 1.6 Ч 10^{-10}], 0.1 mol of CuCl

[K_{sp}(CuCl) = 1.0 Ч 10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6 Ч 10^{-x}. The value of 'x' is. **[JEE 2011]**

22. The K_{sp} of Ag_2CrO_4 is 1.1 Ч 10^{-12} at 298 K. The solubility (in mol/L) of Ag_2 CrO_4 in a 0.1 M $AgNO_3$ solution is **[JEE 2013]**

(A) 1.1 Ч 10^{-11} *(B) 1.1 Ч 10^{-10} (C) 1.1 Ч 10^{-12} (D) 1.1 Ч 10^{-9}

23. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25□C. The K_a of HA is **[JEE 2013]**

*(A) 1 Ч 10^{-4} (B) 1 Ч 10^{-5} (C) 1 Ч 10^{-6} (D) 1 Ч 10^{-3}

JEE-[ADVANCED] : PREVIOUS YEAR QUESTIONS EXERCISE -5[B]

1.	B,C	2.	A,B,C
3.	B	4.	A
5.	A	6.	C
7.	A	8.	B
9.	$[Ag(NH_3)_2{}^+] = 0.0539$	10.	pH = 11.3010
11.	s = 1.203 Ч 10^{-3} M	12.	0.4948
13.	(a) 0.0175 %, pH = 1, (b) 4.75	14.	NO
15.	pH = 9	16.	B
17.	A	18.	D
19.	D	20.	8
21.	7	22.	A
23.	A		