CHAPTER

7

Ionic Equilibrium

EXERCISE I (JEE MAIN)

Basics

1. When rain is accompanied by a thunderstorm, the collected rain water will have a pH value
   (a) depending on the amount of dust in air.
   (b) slightly lower than that of rain water without thunderstorm.
   (c) slightly higher than that when the thunderstorm is not there.
   (d) uninfluenced by occurrence of thunderstorm.

2. The pH of water is 7.0 at 25ºC. If water is heated to 70ºC, then
   (a) pH will decrease and the sample becomes acidic.
   (b) pH will increase but the sample will remain neutral.
   (c) pH will remain constant as 7.
   (d) pH will decrease but the sample will remain neutral.

3. The degree of dissociation of water at 25°C is 1.8×10^{-7}% and the density is 1.0 g cm^{-3}. The ionic product for water is
   (a) 1.0×10^{-14}
   (b) 1.8×10^{-16}
   (c) 1.0×10^{-16}
   (d) 1.0×10^{-8}

4. The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9}. The dissociation constant, K_d of water, at 25°C is
   (a) 10^{-14}
   (b) 1.8×10^{-16}
   (c) 5.56×10^{-13}
   (d) 1.8×10^{-14}

5. What is the pH of a neutral solution at 37°C, where K_w equals 2.5×10^{-14}? ($\log 2 = 0.3$)
   (a) 7.0
   (b) 13.6
   (c) 6.8
   (d) 6.6

6. At 40ºC, the density of heavy water is 1.02 g/ml and its ionic product is 5.1×10^{-15}. Which of the following if the only incorrect information regarding heavy water at 40ºC?
   (a) The molar concentration of heavy water is 51 M.
   (b) The dissociation constant of heavy water is 10^{-16}.
   (c) Its degree of dissociation is 10^{-8}.
   (d) The molal concentration of heavy water is 50 m.

7. The ionic product of water is 1.0×10^{-14} at 25ºC. Assuming the density of water independent from change in temperature, the ionic product of water at 50ºC will be
   (a) 2.0×10^{-14}
   (b) 5.0×10^{-15}
   (c) 5.9×10^{-14}
   (d) 1.0×10^{-14}

8. The hydronium ion concentration in an aqueous solution of H_2SO_4 is 2.0×10^{-4} M at 25ºC. The hydroxide ion concentration in the solution is
   (a) 0
   (b) 2.0×10^{-4} M
   (c) 5×10^{3} M
   (d) 5×10^{-11} M

9. The pH of an aqueous solution of sodium chloride at 60°C is

(a) 7.0 (b) > 7.0
(c) < 7.0 (d) 0

10. The number of hydronium ions in 1 ml of an aqueous solution of pH 12.0 at 25°C is

(a) 0.01 (b) 10^{-12}
(c) 6.02×10^{8} (d) 6.02×10^{11}

Strong Acids and Bases

11. The pH of 4.0×10^{-4} M-HNO_3 solution is ($\log 2 = 0.3$)

(a) 4.6 (b) 3.4
(c) 3.6 (d) 4.0

12. The pH of 0.005 M-NaOH solution is ($\log 2 = 0.3$)

(a) 2.3 (b) 2.7
(c) 11.3 (d) 11.7

13. How many grams of HCl should be dissolved in sufficient water to get 500 ml of an aqueous solution of pH, 2.0?

(a) 0.01 (b) 0.005
(c) 0.1825 (d) 0.365

14. What is the pH of 10^{-7} M-HCl solution at 25°C?

(a) 7.0 (b) 6.70
(c) 6.62 (d) 6.79

15. What mass of NaOH should be dissolved in sufficient water to get 20 m^3 of an aqueous solution of pH 7.3 at 25°C?

(a) 0.16 g (b) 1.6×10^{-4} g
(c) 0.04 g (d) 0.12 g

16. What is the pH of solution made by mixing equal volumes of 0.1 N-H_2SO_4, 0.1 N-HNO_3, 0.1 N-HCl?

(a) 1 (b) 2
(c) 3 (d) 4

17. The following five solutions of KOH were prepared as first, 0.1 mole in 1 L; second, 0.2 mole in 2 L; third, 0.3 mole in 3 L; fourth, 0.4 mole in 4 L; fifth, 0.5 mole in 5 L. The pH of resultant solution, when all these solutions are mixed is

(a) 2 (b) 1
(c) 13 (d) 7

18. At 90°C, the hydronium ion concentration in pure water is 10^{-6} M. If 100 ml of 0.5 M-NaOH solution is mixed with 250 ml of 0.2 M-HNO_3 solution at 90°C, then pH of the resulting solution will be

(a) 7.0 (b) 6.0
(c) 8.0 (d) 0.85

19. Three solutions of strong electrolytes, 25 ml of 0.1 M-HX, 25 ml of 0.1 M-H_2Y and 50 ml of 0.1 N-$Z(OH)_2$ are mixed, the pOH of the resulting solution is

(a) 1.6 (b) 7.0
(c) 12.4 (d) 11.6

20. What will be the percentage error in measuring hydrogen ion concentration in a 10^{-6} M-HCl solution on neglecting the contribution of water at 25°C?

(a) 5% (b) 9.8%
(c) 1.98% (d) 0.98%

Weak Acids and Bases

21. When 0.05 moles of the following acids are dissolved in 1000 ml of H_2O, the $[H^+]$ will be greatest in

(a) HNO_2: $pK_a = 3.0$
(b) HCOOH: $pK_a = 3.75$
(c) HCN: $pK_a = 9.4$
(d) CH_3COOH: $pK_a = 4.75$

22. The concentration of acetate ions in 1 M acetic acid ($K_a = 2 \times 10^{-5}$) solution containing 0.1 M-HCl is

(a) 2×10^{-1} M
(b) 2×10^{-3} M
(c) 2×10^{-4} M
(d) 4.4×10^{-3} M

23. The dissociation constants of formic and acetic acids are 1.77×10^{-4} and 1.75×10^{-5}, respectively. Which of the following statement is correct?

(a) Formic acid is 3.18 times stronger than acetic acid at equal concentration.

(b) Acetic acid is 3.18 times stronger than formic acid at equal concentrations.

(c) Formic acid is 10.11 times stronger than acetic acid at equal concentrations.

(d) Formic acid is 10.11 times stronger than acetic acid at different concentrations.

24. The dissociation constant of acetic acid is 0.000018 and that for cyanoacetic acid is 0.0036 at 298 K. What would be the ratio of volumes of the two acid solutions, each containing equal moles of the acids, so that the solutions becomes isohydric?

(a) 1 : 1
(b) 1 : $\sqrt{200}$
(c) 1 : 200
(d) 200 : 1

25. The p*K*a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2 to 3 and the pH in the small intestine is about 8. Aspirin will be

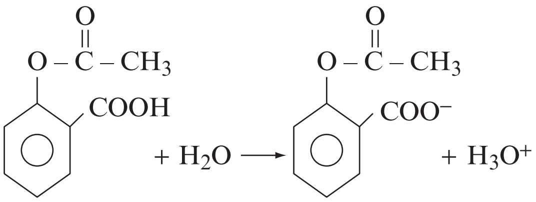
(a) unionized in the small intestine as well as in the stomach.

(b) completely ionized in the small intestine as well as in the stomach.

(c) ionized in the stomach and almost unionized in the small intestine.

(d) ionized in the small intestine and almost unionized in the stomach.

26. The active ingredient in aspirin is acetyl salicylic acid



with $K_a = 4.0 \times 10^{-9}$. The pH of the solution obtained by dissolving two aspirin tablets (containing 0.36 g of acetyl salicylic acid in each tablet) in 250 ml of water is ($\log 2 = 0.3$)

(a) 5.1
(b) 8.9
(c) 10.2
(d) 5.25

27. For weak electrolyte, AB, the degree of ionization would be (*V* = volume of solution having 1 mole of electrolyte and *K* is the ionization constant of the electrolyte)

(a) $\frac{K}{V^2}$
(b) $K.V$
(c) $\frac{K}{V}$
(d) $\sqrt{K \cdot V}$

28. What would be the pH of an ammonia solution if the pH of acetic acid solution of same strength is 3.2? The dissociation constants of ammonia and acetic acid are same.

(a) 3.2
(b) 3.8
(c) 10.2
(d) 10.8

29. Isohydric solutions are the solutions having the same concentration of hydronium ion. If 0.2 M-HA solution is isohydric with 4×10^{-4} M-HCl solution, then K_b of A^- is

(a) 8×10^{-7}
(b) 1.25×10^{-8}
(c) 1.25×10^{-6}
(d) 8×10^{7}

30. If pK_b for fluoride ion at 25°C is 10.3, the ionization constant of hydrofluoric acid in water at this temperature is ($\log 2 = 0.3$)

(a) 2×10^{-4}
(b) 2×10^{-3}
(c) 2×10^{-5}
(d) 5×10^{-11}

31. *n*-coproic acid $C_5H_{11}COOH$ found in coconut and palm oil is used in making artificial flavours and it has solubility in water equal to 11.6 g/L. The saturated solution has pH = 3.0. The K_a of acid is

(a) 10^{-6}
(b) 10^{-5}
(c) 2×10^{-5}
(d) 2×10^{-6}

32. The dissociation constant of formic acid is 0.00024. The hydrogen ion concentration in 0.002 M-HCOOH solution is nearly

(a) 6.93×10^{-4} M
(b) 4.8×10^{-7} M
(c) 5.8×10^{-4} M
(d) 1.4×10^{-4} M

33. Calculate the pH of 0.02 M – HA solution. The value of K_a for HA = 2×10^{-12} ($\log 2 = 0.3$, $\log 3 = 0.48$).

(a) 6.65
(b) 6.70
(c) 6.85
(d) 6.52

34. How much water must be added to 300 ml of 0.2 M solution of CH_3COOH for the degree of dissociation of the acid to double? The value of K_a for acetic acid = 1.8×10^{-5}.

(a) 1200 ml
(b) 300 ml
(c) 600 ml
(d) 900 ml

35. A solution has initially 0.1 M-HCOOH and 0.2 M-HCN. The value of K_a for HCOOH = 2.56×10^{-5}, K_a of HCN = 9.6×10^{-10}. The only incorrect statement for the solution is (log 2 = 0.3)

(a) $[H^+] = 1.6 \times 10^{-3}$ M
(b) $[HCOO^-] = 1.6 \times 10^{-3}$ M
(c) $[CN^-] = 1.2 \times 10^{-7}$ M
(d) pOH = 2.8

Polyprotic Acids and Bases

36. What is the pH of 4×10^{-3} M–$Y(OH)_2$ solution assuming the first dissociation to be 100% and second dissociation to be 50%, where Y represents a metal cation? (log 2 = 0.3, log 3 = 0.48)

(a) 11.78 (b) 11.22
(c) 2.22 (d) 2.78

37. The species present in solution when CO_2 is dissolved in water is

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

38. An aqueous solution is prepared by dissolving 0.1 mole H_2CO_3 in sufficient water to get 100 ml solution at 25°C. For H_2CO_3, $K_{a1} = 4.0 \times 10^{-6}$ and $K_{a2} = 5.0 \times 10^{-11}$. The only incorrect equilibrium concentration is

(a) $[H^+] = 6.32 \times 10^{-4}$ M
(b) $[HCO_3^-] = 2 \times 10^{-3}$ M
(c) $[CO_3^{2-}] = 5 \times 10^{-11}$ M
(d) $[OH^-] = 5 \times 10^{-12}$ M

39. Ascorbic acid (vitamin C) is a diprotic acid, $H_2C_6H_6O_6$. What is the pH of a 0.10 M solution? The acid ionization constants are $K_{a1} = 9.0 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$. (log 2 = 0.3, log 3 = 0.48).

(a) 3.52 (b) 2.52
(c) 1.52 (d) 2.48

40. The pH of 0.1 M – N_2H_4 solution is (For N_2H_4, $K_{b1} = 3.6 \times 10^{-6}$, $K_{b2} = 6.4 \times 10^{-12}$, log 2 = 0.3, log 3 = 0.48)

(a) 3.22 (b) 2.72
(c) 10.78 (d) 11.22

Buffer Solutions

41. The dissociation constant of a weak acid HX is 10^{-5}. The buffer HX + NaX can be best used to maintain the pH in the range

(a) 9–11 (b) 2–4
(c) 11–13 (d) 4–6

42. A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resists a change in pH yet contains only small concentrations of the buffering agents. Which one of the following weak acid together with its sodium salt would be best to use?

(a) *m*-chloro benzoic acid ($pK_a = 3.98$)
(b) *p*-chlorocinnamic acid ($pK_a = 4.41$)
(c) 2,5-dihydroxy benzoic acid ($pK_a = 2.97$)
(d) acetoacetic acid ($pK_a = 3.58$)

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

(a) 9.26 + log 2 (b) 9.26 – log 2
(c) 4.74 + log 2 (d) 9.26

44. The addition of sodium acetate to acetic acid solution will cause

(a) increase in its pH value.
(b) decrease in its pH value.
(c) no change in pH value.
(d) change in pH which cannot be predicted.

45. A 0.1 M acetic acid solution is titrated against 0.1 M-NaOH solution. What would be the difference in pH between 1/4 and 3/4 stages of neutralization of the acid?

(a) 2 log(0.75) (b) 2 log(0.25)
(c) log 3 (d) 2 log 3

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

(a) 1.25×10^{-4} M (b) 8×10^{-11} M
(c) 1.6×10^{-11} M (d) 2×10^{-3} M

47. A volume of 10 ml of a strong acid solution of pH = 2.0 are mixed with 990 ml of a buffer solution of pH = 4.0. The pH of the resulting solution will be

(a) 4.2 (b) 6.0
(c) 4.002 (d) 4.0

48. An amount of 0.15 mole of pyridinium chloride has been added into 500 ml of 0.2 M pyridine solution. Calculate pH of the resulting solution assuming no change in volume. The value of K_b for pyridine = 1.5×10^{-9} (log 2 = 0.3, log 0.3 = 0.48).

(a) 9.0 (b) 5.0
(c) 8.64 (d) 5.36

49. A volume of 20 ml of 0.8 M-HCN solution is mixed with 80 ml of 0.4 M-NaCN solution. Calculate the pH of the resulting solution. The value of K_a of HCN = 2.5×10^{-10} (log 2 = 0.3).

(a) 9.9 (b) 9.3
(c) 4.1 (d) 4.7

50. The base imidazole has a K_b of 1.0×10^{-7} at 25°C. In what volumes should 0.02 M-HCl and 0.02 M imidazole be mixed to make 120 ml of a buffer at pH = 7?

(a) 60 ml, 60 ml (b) 40 ml, 80 ml
(c) 30 ml, 90 ml (d) 20 ml, 100 ml

Hydrolysis of Salts

51. Separate solutions of NaW, NaX, NaY and NaZ, each of concentrations 0.1 M has pH 7.0, 9.0, 10.0 and 11.0, respectively, at 25°C. The strongest acid among these is

(a) HW (b) HX
(c) HY (d) HZ

52. If the pH of 0.001 M potassium propionate solution be 8.0, then the dissociation constant of propionic acid will be

(a) 10–3 (b) 10–2
(c) 10–2.5 (d) 10–5

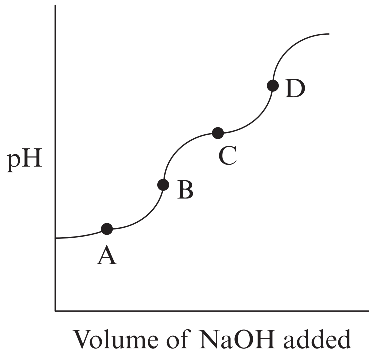
53. The correct order of increasing $[OH^-]$ in the following aqueous solution is

(a) 0.01 M-$NaHCO_3$ < 0.01 M-NaCN < 0.01 M-KCl
(b) 0.01 M-KCl < 0.01 M-NaCN < 0.01 M-$NaHCO_3$
(c) 0.01 M-KCl < 0.01 M-$NaHCO_3$ < 0.01 M-NaCN
(d) 0.01 M-NaCN < 0.01 M-KCl < 0.01 M-$NaHCO_3$

54. The pH of solutions of both ammonium acetate and sodium chloride is 7 due to

(a) hydrolysis in both case.
(b) the former hydrolyses and not the latter.
(c) no hydrolysis in both.
(d) hydrolysis of the latter but not the former.

55. For the titration of a dibasic weak acid H_2A $\left(p^{K_{a(2)}} - p^{K_{a(1)}} \geq 2\right)$ with a strong base, pH versus volume of the base graph is as shown in the figure. The value of $p^{K_{a(1)}}$ and $p^{K_{a(2)}}$ may be equal to the pH values corresponding to the points.

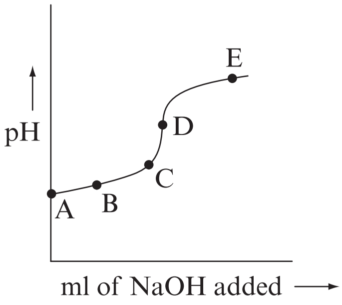


(a) B and D, respectively
(b) A and B, respectively
(c) C and D, respectively
(d) A and C, respectively

56. A salt of strong acid and a weak base is dissolved in water. Its hydrolysis in solution is

(a) not affected by heating.
(b) increased by adding the strong acid.
(c) suppressed by adding strong acid.
(d) suppressed by dilution.

57. 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 may be equal to that of its conjugate base?



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

58. The pH of 0.1 M solution of the following compounds increases in the order

(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$

59. The pH value of 0.1 M solutions of CH_3COONa (I), CH_3COOH (II), CH_3COONH_4 (III), NaOH (IV) and HCl (V) is in the order

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

60. A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX is

(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

61. The pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation is (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

(a) 7.0 (b) 7.5
(c) 6.5 (d) 4.3

62. What is the pH of a 0.50 M aqueous NaCN solution? The value of pK_b of CN^- is 4.70 (log 2 = 0.3).

(a) 3.5 (b) 11.5
(c) 4.7 (d) 9.3

63. The pH at the equivalence point when a solution of 0.01 M-CH_3COOH is titrated with a solution of 0.01 M-NaOH, is (pK_a of CH_3COOH = 4.7, log 5 = 0.7)

(a) 8.2 (b) 9.4
(c) 8.35 (d) 10.5

64. The acid ionization constant of Zn^{2+} is 2.0×10^{-10}. What is the pH of 0.001 M solution of $ZnCl_2$? (log 2 = 0.3)

(a) 9.7 (b) 4.85
(c) 6.35 (d) 3.35

65. The addition of ammonium chloride to acetic acid solution will cause

(a) increase in its pH value.
(b) decrease in its pH value.
(c) no change in pH value.
(d) change in pH which cannot be predicted.

Indicators

66. The indicator constant for an acidic indicator, HIn is 5×10^{-6} M. This indicator appears only in the colour of acidic form when $\frac{[In^-]}{[HIn]} \le \frac{1}{20}$ and it appears only in the colour of basic form when $\frac{[HIn]}{[In^-]} \le \frac{1}{40}$. The pH range of indicator is (log 2 = 0.3)

(a) 4.3 – 6.3 (b) 4.0 – 6.6
(c) 4.0 – 6.9 (d) 3.7 – 6.6

67. For the indicator thymol blue, the value of pH is 2.0 when half of the indicator is present in the unionized form. The percentage of the indicator in the unionized form in a solution of 4.0×10^{-3} M hydrogen ion concentration is

(a) 40% (b) 28.6%
(c) 71.4% (d) 60%

68. A certain sample of rainwater gives a yellow colour with methyl red [pH range 4.2 (red) – 6.2 (yellow)] and a yellow colour with phenol red [pH range 6.4 (yellow) – 8.0 (red)]. What is the approximate pH of the water? Is the rainwater acidic, neutral or basic?

(a) 6.3, acidic (b) 6.1, acidic
(c) 6.5, acidic (d) 6.3, basic

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

(a) 0.0 (b) 1.0
(c) 2.0 (d) 5.0

70. The range of most suitable indicator which should be used for titration of NaX (0.1 M, 10 ml) with 0.1 M HCl should be (K_b of $X^- = 10^{-6}$)

(a) 2–3 (b) 3–5
(c) 6–8 (d) 8–10

Solubility

71. If ionization of X_aY_b takes place then, the number of Y^{-a} ions will be equal to

(a) b/a times of X^{+b}
(b) a/b times of X^{+b}
(c) b/a times of X^{a+}
(d) equal to X^{+b}

72. The solubility of sparingly soluble salt A_3B_2 (molar mass = 'M' g/mol) in water is 'x' g/L. The ratio of molar concentration of B^{3-} to the solubility product of the salt is

(a) $\dfrac{108\,x^5}{M^5}$ (b) $\dfrac{x^4}{108\,M^4}$

(c) $\dfrac{x^4}{54\,M^4}$ (d) $\dfrac{M^4}{54\,x^4}$

73. The solubility product of $Zn(OH)_2$ is 10^{-14} at 25°C. What would be the concentration Zn^{+2} ion in 0.1 M-NH_4OH solution which is 50% ionized?

(a) 2×10^{-13} (b) 4×10^{-12}
(c) 4×10^{-8} (d) 2×10^{-11}

74. In which of the following, the solubility of AgCl will be maximum?

(a) 0.1 M-$AgNO_3$ (b) Water
(c) 0.1 M-NH_3(aq) (d) 0.1 M-NaCl

75. What is the equilibrium constant of the following reaction? $Fe(OH)_3(s) + 3H_3O^+ \rightleftharpoons Fe^{3+} + 6H_2O$? K_{sp} of $Fe(OH)_3 = 4 \times 10^{-38}$

(a) 2.5×10^{-5} (b) 4.0×10^{4}
(c) 4.0×10^{-4} (d) 4×10^{-80}

76. The solubility product of AgCl is 1.0×10^{-10}. The equilibrium constant of the reaction

$AgCl(s) + Br^- \rightleftharpoons AgBr(s) + Cl^-$

is 200 and that of the reaction

$2AgBr(s) + S^{2-} \rightleftharpoons Ag_2S(s) + 2Br^-$

is 1.6×10^{24}. What is the K_{sp} of Ag_2S?

(a) 3.2×10^{16} (b) 1.56×10^{-49}
(c) 3.95×10^{-25} (d) 3.13×10^{-17}

77. What is the solubility product of $Al(OH)_3$ in water? Given:

$Al(OH)_4^-(aq) \rightleftharpoons Al^{3+}(aq) + 4OH^-(aq)$ $K = 1.3 \times 10^{-34}$

$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq);\ K = 38.5$

(a) 3.1×10^{-35} (b) 5×10^{-33}
(c) 6.1×10^{-33} (d) 5×10^{-34}

78. A recent investigation of the complexation of SCN^- with Fe^{3+} led to values of 125, 20 and 1.0 for K_1, K_2 and K_3, respectively. What is the dissociation constant of $Fe(SCN)_3$ into its simplest ions on the basis of these data?

(a) 2.5×10^{3} (b) 4.0×10^{-4}
(c) 1.0 (d) 8.0×10^{-3}

79. Solubility of BaF_2 in a solution of $Ba(NO_3)_2$ will be represented by the concentration term

(a) $[Ba^{2+}]$ (b) $[F^-]$
(c) $0.5\,[F^-]$ (d) $2\,[NO_3^-]$

80. How many times the solubility of CaF_2 is decreased in 4×10^{-3} M-KF(aq) solution as compared to pure water at 25°C. Given: K_{sp} (CaF_2) = 3.2×10^{-11}

(a) 50 (b) 100
(c) 500 (d) 1000

81. The solubility of A_2X_3 is y mol dm^{-3}. It solubility product is

(a) $6y^4$ (b) $64y^4$
(c) $36y^4$ (d) $108y^5$

82. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_S) with its solubility (S) is

(a) $L_S = S^{p+q} \cdot p^p \cdot q^q$ (b) $L_S = S^{p+q} \cdot p^q \cdot q^p$
(c) $L_S = S^{pq} \cdot p^p \cdot q^q$ (d) $L_S = S^{pq} \cdot (pq)^{p+q}$

83. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]$; $K_1 = 1.6 \times 10^3$

$[Ag(NH_3)^+] + NH_3 \rightleftharpoons [Ag(NH_3)_2^+]$; $K_2 = 6.8 \times 10^3$

The formation constant of $[Ag(NH_3)_2^+]$ is

(a) 1.08×10^7 (b) 6.08×10^6
(c) 1.08×10^3 (d) 1.08×10^5

84. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature, T are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (in M) of the salts at temperature, T, are in the order

(a) $MX > MX_2 > M_3X$
(b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$
(d) $MX > M_3X > MX_2$

85. The solubility of AgCl in water is 0.001435 g per litre at 15°C. The solubility product of AgCl is (Ag = 108, Cl = 35.3)

(a) 10^{-5} (b) 10^{-10}
(c) 2×10^{-10} (d) 10^{-9}

86. The solubility of $Li_3Na_3(AlF_6)_2$ is 0.0744 g per 100 ml at 298 K. Calculate the solubility product of the salt (Atomic masses: Li = 7, Na = 23, Al = 27, F = 19).

(a) 2.56×10^{-22} (b) 2×10^{-3}
(c) 7.46×10^{-19} (d) 3.46×10^{-12}

87. The solubility product of CaF_2 is 1.08×10^{-10}. What mass of CaF_2 will dissolve in 500 ml water in order to make a saturated solution? (Ca = 40, F = 19)

(a) 3×10^{-4} g (b) 1.17×10^{-2} g
(c) 1.17 mg (d) 3×10^{-3} g

88. The solubility product of $Mg(OH)_2$ is 9.0×10^{-12}. The pH of an aqueous saturated solution of $Mg(OH)_2$ is (log 1.8 = 0.26, log 3 = 0.48)

(a) 3.58 (b) 10.42
(c) 3.88 (d) 6.76

89. The molar solubility of $Zn(OH)_2$ in 1 M ammonia solution at room temperature is (K_{sp} of $Zn(OH)_2$ = 1.6×10^{-17}; K_{stab} of $Zn(NH_3)_4^{2+}$ = 1.6×10^{10})

(a) 4×10^{-3} M (b) 1.58×10^{-6} M
(c) 4×10^{-9} M (d) 2.56×10^{-7} M

90. Assuming no change in volume, calculate the minimum mass of NaCl necessary to dissolve 0.01 mole of AgCl in 100 L solution. The value of K_{sp} of AgCl = 2.0×10^{-10} and K_f of $AgCl_2^-$ = 2.5×10^5.

(a) 117 g (b) 11.7 kg
(c) 58.5 kg (d) 585 g

91. The solubility product of AgC_2O_4 at 25°C is 2.3×10^{-11} M^3. A solution of $K_2C_2O_4$ containing 0.15 moles in 500 ml water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached.

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

At equilibrium, the solution contains 0.035 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

(a) 2.3×10^{-11} M^3 (b) 7.0×10^{-10} M^3
(c) 3.0×10^{-13} M^3 (d) 7.0×10^{-12} M^3

92. For the reaction $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant, at 25°C, is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$.

(a) 0 (b) 0.03 M
(c) 3×10^{-19} M (d) 7.5×10^{-18} M

93. A sample of AgCl was treated with 5.00 ml of 2.0 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.00355 g of Cl^- ions per litre. The solubility product of AgCl is (K_{sp} of Ag_2CO_3 is 8.0×10^{-12}).

(a) 2×10^{-10} (b) 1×10^{-10}
(c) 4×10^{-10} (d) 8×10^{-10}

94. Given $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$, $K_c = 7.2 \times 10^{-8}$ and K_{sp} of $AgCl = 1.8 \times 10^{-10}$ at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, then calculate the concentration of the complex in 1.0 M aqueous ammonia.

(a) 1.0 M (b) 0.091 M
(c) 0.0455 M (d) 0.023 M

95. The solubility of $Pb(OH)_2$ in water is 6.0×10^{-6} M. The solubility of $Pb(OH)_2$ in a buffer solution of pH = 8 is

(a) 8.64 M (b) 2.16 × 10−16 M
(c) 8.64 × 10−16 M (d) 8.64×10^{-4} M

96. The silver ion concentration in a 0.2 M solution of $Ag(NH_3)_2NO_3$ is ($K_{diss} = 6.8 \times 10^{-8}$, $1.5^3 = 3.4$)

(a) 0.2 M (b) 1.5 × 10−3 M
(c) 1.16 × 10−4 M (d) 6.8×10^{-8} M

97. The formation constant of $Cu(NH_3)_4^{2+}$ is 1.25×10^{12}. What will be the equilibrium concentration of Cu^{2+} if 0.0125 moles of Cu is oxidized and put into 1.0 L of 0.25 M–NH_3 solution?

(a) 2.5×10^{-11} M (b) 2.5×10^{-13} M
(c) 4×10^{-12} M (d) 6.25×10^{-12} M

98. The simultaneous solubilities of AgSCN and AgBr are, respectively (K_{sp} of AgSCN = 1×10^{-12}, K_{sp} of AgBr = 2.1×10^{-13}),

(a) 9.09×10^{-7} M, 1.909×10^{-7} M
(b) 1.909×10^{-7} M, 9.09×10^{-7} M
(c) 9.09×10^{-6} M, 1.909×10^{-7} M
(d) 1.1×10^{-6} M, 2.1×10^{-7} M

99. The solubility of AgCN in a buffer solution of pH = 3.0 is (K_{sp} of AgCN = 1.2×10^{-16}; K_a of HCN = 4.8×10^{-10})

(a) 1.58 × 10−5 M (b) 2.0 × 10−5 M
(c) 1.58×10^{-4} M (d) 2.5×10^{-9} M

100. The solubility of $PbCl_2$ when it is 80% ionized is

(a) 25% less than the solubility of $PbCl_2$ when it is 100% ionized.
(b) 50% less than the solubility of $PbCl_2$ when it is 100% ionized.
(c) More than the solubility of $PbCl_2$ when it is 100% ionized.
(d) is equal to the solubility of $PbCl_2$ when it is 100% ionized.

Precipitation

101. The solubility products of $Mg(OH)_2$, $Cd(OH)_2$, $Al(OH)_3$ and $Zn(OH)_2$ are 4×10^{-11}, 8×10^{-6}, 8.5×10^{-23} and 1.8×10^{-14}, respectively. The cation that will precipitate first as hydroxide, on adding limited quantity of NH_4OH in a solution containing equimolar amount of metal cations, is

(a) Al^{3+} (b) Zn^{2+}
(c) Mg^{2+} (d) Cd^{2+}

102. Silver ions are slowly added in a solution with $[Br^-] = [Cl^-] = [CO_3^{2-}] = [AsO_4^{3-}] = 0.1$ M. Which of the following compound will precipitate first?

(a) AgBr ($K_{sp} = 5 \times 10^{-13}$)
(b) AgCl ($K_{sp} = 1.8 \times 10^{-10}$)
(c) Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$)
(d) Ag_3PO_4 ($K_{sp} = 1 \times 10^{-22}$)

103. The K_{sp} of $Ag_2CrO_4 = 1.2 \times 10^{-11}$. What concentration of Ag^+ ion in aqueous solution will just fail to give a precipitate of Ag_2CrO_4 with a solution in which $[CrO_4^{-2}] = 3 \times 10^{-4}$ M?

(a) 10^{-3} M (b) 10^{-1} M
(c) 10^{-4} M (d) 2×10^{-4} M

104. A 0.1 mole of $AgNO_3$ is dissolved in 1 L of 1 M-NH_3. If 0.01 mole of NaCl is added to this solution, will AgCl(s) precipitate? The value of K_{sp} for AgCl = 1.8×10^{-10} and K_{stab} for $Ag(NH_3)_2^+$ = 1.6×10^7.

(a) Yes
(b) No
(c) Addition of NaCl in any amount can never result in precipitation.
(d) Addition of even smaller amount of NaCl may result in precipitation.

105. In 500 ml of 2.5×10^{-5} M – $AgNO_3$ solution, 2000 ml of 5.0×10^{-2} M – NaCl solution is added. The mass of precipitate of AgCl formed is (K_{sp} of AgCl = 2×10^{-10}, Ag = 108)

(a) 1.794 g
(b) 1.794 mg
(c) 5×10^{-6} g
(d) 1.25×10^{-2} g

106. The solubility product of PbI_2 is 7.2×10^{-9}. The maximum mass of NaI which may be added in 500 ml of 0.005 M-$Pb(NO_3)_2$ solution without any precipitation of PbI_2 is (I = 127)

(a) 0.09 g
(b) 1.2×10^{-3} g
(c) 6×10^{-4} g
(d) 1.08×10^{-5} g

107. What is the minimum mass of NaBr which should be added in 200 ml of 0.0004 M-$AgNO_3$ solution just to start the precipitation of AgBr? The value of K_{sp} of AgBr = 4×10^{-13} (Br = 80).

(a) 1.0×10^{-9} g
(b) 2×10^{-10} g
(c) 2.06×10^{-8} g
(d) 1.03×10^{-7} g

108. A sample of hard water contains 0.005 mole of $CaCl_2$ per litre. What is the minimum concentration of $Al_2(SO_4)_3$ which must be exceeded for removing Ca^{2+} ions from this water sample? The solubility product of $CaSO_4$ is 2.4×10^{-5}.

(a) 4.8×10^{-3} M
(b) 1.6×10^{-3} M
(c) 0.0144 M
(d) 2.4×10^{-3} M

109. To 100 ml of a solution, which contains 8.32×10^{-3} g lead ions, 10^{-4} moles of H_2SO_4 is added. How much lead remains in the solution unprecipitated? K_{sp} of $PbSO_4 = 1.6 \times 10^{-7}$. (Pb = 208)

(a) 4×10^{-4} g
(b) 2.67×10^{-4} g
(c) 2×10^{-4} g
(d) 4.16×10^{-3} g

110. An aqueous solution of a metal bromide MBr_2 (0.04 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate? The value of K_{sp} for MS = 6.0×10^{-21}; concentration of saturated H_2S = 0.1M, $K_1 = 10^{-7}$ and $K_2 = 1.5 \times 10^{-13}$ for H_2S.

(a) 1.0
(b) 1.3
(c) 13.0
(d) 0.7

111. An amount of 0.1 millimole of $CdSO_4$ is present in 10 ml acid solution of 0.08 M-HCl. Now H_2S is passed to precipitate all the Cd^{2+} ions. What would be the pH of solution after filtering off precipitate, boiling off H_2S and making the solution 100 ml by adding water?

(a) 3.0
(b) 2.0
(c) 4.0
(d) 2.22

112. A solution contains a mixture of Ag^+ (0.10 M) and Hg_2^{2+} (0.10 M), which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What per cent of that metal ion is precipitated before the start of precipitation of second metal ion? $K_{sp}(AgI) = 8.5 \times 10^{-17}$ and $K_{sp}(Hg_2I_2) = 2.5 \times 10^{-26}$.

(a) 5×10^{-13} M, 99.83%
(b) 8.5×10^{-16} M, 99.83%
(c) 2.5×10^{-25} M, 100%
(d) 5×10^{-13} M, 98.3%

113. 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 of $CaCO_3$ is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.

(a) 4.9×10^{-8}
(b) 4.9×10^{-9}
(c) 4.9×10^{-10}
(d) 7×10^{-4}

114. Small amount of freshly precipitated magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 M of NH_4Cl and 0.05 M of NH_4OH. $[Mg^{2+}]$ in the resulting solution is (K_b for $NH_4OH = 2.0 \times 10^{-5}$ and K_{sp} of $Mg(OH)_2 = 8.0 \times 10^{-12}$)

(a) 4×10^{-6} M
(b) 2×10^{-6} M
(c) 0.5 M
(d) 2.0 M

115. The solubility of metal sulphide in saturated solution of H_2S (concentration = 0.1 M) can be represented as follows.

$$MS(s) + 2H^+(aq) \rightleftharpoons M^{2+}(aq) + H_2S(aq);$$

$$K_{eq} = \frac{[M^{2+}][H_2S]}{[H^+]^2}$$

The values of K_{eq} for the metal sulphides, MnS, ZnS, CoS and PbS are 3×10^{10}, 3×10^{-2}, 3 and 3×10^{-7}, respectively. If the concentration of each metal ion in a saturated solution of H_2S is 0.01 M, then which metal sulphide(s) will precipitate at $[H^+]$ = 1.0 M?

(a) MnS, ZnS, CoS
(b) PbS
(c) PbS, ZnS, CoS
(d) PbS, ZnS

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. Liquid ammonia ionizes to slight extent. At −50°C, its self-ionization constant, $K = [NH_4^+][NH_2^-] = 10^{-30}\ M^2$. How many amide ions are present per ml of pure liquid ammonia? ($N_A = 6 \times 10^{23}$)

(a) 10^{-15} (b) 10^{-18}
(c) 6×10^5 (d) 6×10^8

2. For a sample of pure water,

(a) pH increases and pOH decreases with increase in temperature.
(b) pH decreases and pOH increases with increase in temperature.
(c) both pH and pOH increases with increase in temperature.
(d) both pH and pOH decrease with increase in temperature.

3. The pH at which water is maximum dissociated at 25°C, is

(a) 2 (b) 7
(c) 10 (d) 14

4. 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)?

(a) 2.7 (b) 11.3
(c) 3.7 (d) 10.3

5. When 20 ml of 0.2 M-DCl solution is mixed with 80 ml of 0.1 M-NaOD solution, pH of the resulting solution becomes 13.6. The ionic product of heavy water D_2O is

(a) 10^{-15} (b) 10^{-16}
(c) 4×10^{-15} (d) 4×10^{-16}

6. The equilibrium constant of T_2O (Tritium is an isotope of H) differ from those of H_2O at 298 K. Let at 298 K, pure T_2O has pT (like pH) 7.60. What is the pT of a solution prepared by adding 100 ml of 0.4 M-TCl to 400 ml of 0.2 M-NaOT? ($\log 2 = 0.3$)

(a) 1.1 (b) 0.08
(c) 6.5 (d) 14.1

7. The acid ionization constant of Zn^{2+} is 2.0×10^{-10}. What is the basic dissociation constant of $Zn(OH)^+$?

(a) 5×10^{-5} (b) 2.0×10^4
(c) 2×10^{-10} (d) 5×10^9

8. The dissociation constant of NH_3 at 27°C from the following data:

$NH_3 + H^+ \rightleftharpoons NH_4^+$; $\Delta H° = -52.21$ kJ/mol; $\Delta S° = +1.6\ JK^{-1}\ mol^{-1}$

$H_2O \rightleftharpoons H^+ + OH^-$; $\Delta H° = 54.70$ kJ/mol; $\Delta S° = -76.3\ JK^{-1}\ mol^{-1}$

Given: R = 8.3 J/K-mol

(a) e^{10} (b) e^{-10}
(c) e^{-8} (d) e^{-9}

9. How many moles of acetic acid should be added to 100 ml of 0.6 M formic acid solution such that the percentage dissociation of formic acid remains unchanged? The value of K_a for acetic acid $= 1.8 \times 10^{-5}$ and K_a for formic acid $= 2.4 \times 10^{-4}$.

(a) 0.8 (b) 0.08
(c) 8.0 (d) 0.6

10. The dissociation constant of a weak monoprotic acid is numerically equal to the dissociation constant of its conjugate base. What is the pH of 0.1M solution of this acid?

(a) 7.0 (b) 6.0
(c) 8.0 (d) 4.0

11. The ionization constant of NH_4^+ in water is 5.6×10^{-10} mol L^{-1} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol^{-1} s^{-1}. The rate constant for proton transfer from water to NH_3 at 25°C is

(a) $6.07 \times 10^5\ s^{-1}$ (b) $6.07 \times 10^{-18}\ s^{-1}$
(c) $1.65 \times 10^{-6}\ s^{-1}$ (d) $1.65 \times 10^{-19}\ s^{-1}$

12. A solution is prepared in which 0.1 mole each of HCl, CH_3COOH and $CHCl_2COOH$ is present in a litre. If the ionization constant of CH_3COOH is 10^{-5} and that of $Cl_2CHCOOH$ is 0.15, then the pH of solution is ($\log 2 = 0.3$, $\log 3 = 0.48$)

(a) 1.18 (b) 0.82
(c) 1.0 (d) 0.95

13. A solution contains 4.25 g ammonia per 250.0 ml of solution. Electrical conductivity measurement at 25°C shows that 0.40% of the ammonia has reacted with water. The pH of the solution is (log 2 = 0.3)

(a) 11.6 (b) 2.4
(c) 12.6 (d) 10.6

14. Morphine ($C_{17}H_{19}NO_3$) is administered medically to relieve pain. It is a naturally occurring base or alkaloid. What is the pH of a 0.0025 M solution of morphine at 25°C? The base-ionization constant K_b is 1.6×10^{-6} at 25°C. (log 2 = 0.3)

(a) 4.2 (b) 9.8
(c) 3.7 (d) 10.3

15. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by the formula HSac. A 4×10^{-4} mole amount of saccharin is dissolved in 200 ml water of pH 3.0. Assuming no change in volume, the concentration of Sac^- ions in the resulting solution at equilibrium is

(a) 4×10^{-12} M (b) 2×10^{-12} M
(c) 8×10^{-13} M (d) 6.32×10^{-8} M

16. Dissociation constants of acids HA and HB are 2.0×10^{-4} and 5×10^{-5}, respectively. The $[H^+]$ in the resulting solution obtained by mixing 20 ml of 0.5 M-HA solution and 30 ml of 0.2 M-HB solution is

(a) 1.05×10^{-2} M (b) 6.78×10^{-3} M
(c) 1.05×10^{-3} M (d) 6.78×10^{-2} M

17. At 25°C, the dissociation constants of acid HA and base BOH in aqueous solution is same. The pH of 0.01 M solution of HA is 5.0. The pH of 0.1 M solution of BOH is

(a) 5.0 (b) 9.0
(c) 9.5 (d) 8.5

18. An aqueous solution initially contains 0.01 M-RNH_2 ($K_b = 2.0 \times 10^{-6}$) and 10^{-4} M-NaOH. The final concentration of OH^- in the solution is about

(a) 10^{-4} M (b) 2.0×10^{-4} M
(c) 3.0×10^{-4} M (d) 1.414×10^{-4} M

19. What will be the effect of adding 100 ml of 0.001 M-HCl solution to 100 ml of a solution having 0.1 M-HA? The acid dissociation constant of HA is 10^{-5}.

(a) The degree of dissociation of HA will decrease but the pH of solution remains unchanged.
(b) The degree of dissociation of HA remains unchanged but the pH of solution decreases.
(c) Neither degree of dissociation nor pH of solution will change.
(d) The degree of dissociation as well as pH of solution will decrease.

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

(a) pH will increase (b) pH will decrease
(c) No change (d) pH becomes 7.0

21. An amount of 0.16 g of N_2H_4 is dissolved in water and the total volume is made up to 500 ml. What is the percentage of N_2H_4 that has reacted with water in this solution? The value of K_b for $N_2H_4 = 4.0 \times 10^{-6}$.

(a) 0.02% (b) 0.014%
(c) 2% (d) 2.82%

22. Water in equilibrium with air contains 4.4×10^{-5}% CO_2. The resulting carbonic acid (H_2CO_3) gives the solution a hydronium ion concentration of 2.0×10^{-6} M about 20 times greater than that of pure water. What is the pH of the solution at 298 K? (log 4.4 = 0.64, log 2 = 0.3)

(a) 5.36 (b) 5.70
(c) 8.30 (d) 5.64

23. What is the pH of 6.67×10^{-3} M aqueous solution of $Al(OH)_3$ if its first dissociation is 100%, second dissociation is 50% and the third dissociation is negligible.

(a) 2 (b) 12
(c) 11 (d) 3

24. The only incorrect information related with 0.09 M solution of ($NH_2CH_2CH_2NH_2$) ethylenediamine (en) is ($K_{b1} = 8.1 \times 10^{-5}$, $K_{b2} = 7.0 \times 10^{-8}$, log 3 = 0.48, log 7 = 0.85)

(a) pH = 11.44
(b) $[enH^+] = 2.7 \times 10^{-3}$ M
(c) $[enH_2^{2+}] = 7.0 \times 10^{-8}$ M
(d) $[H^+] = 2.7 \times 10^{-3}$ M

25. Calculate $[S^{2-}]$ in a solution originally having 0.1 M – HCl and 0.2 M – H_2S. For H_2S, $K_{a1} = 1.4 \times 10^{-7}$ and $K_{a2} = 1.0 \times 10^{-14}$.

(a) 0.1 M (b) 2.8×10^{-20} M
(c) 2.8×10^{-22} M (d) 1.4×10^{-20} M

26. For a tribasic acid, H_3A, $K_{a1} = 2 \times 10^{-5}$, $K_{a2} = 5 \times 10^{-9}$ and $K_{a3} = 4 \times 10^{-12}$. The value of $\frac{[A^{3-}]}{[H_3A]}$ at equilibrium in an aqueous solution originally having 0.2 M – H_3A is

(a) 5×10^{-17} (b) 5×10^{-9}
(c) 1×10^{-17} (d) 2×10^{-22}

27. H_3A is a weak tribasic acid with $K_{a1} = 10^{-5}$, $K_{a2} = 10^{-9}$ and $K_{a3} = 10^{-13}$. The value of pX of 0.1 M – H_3A solution, where $pX = -\log_{10}X$ and $X = \frac{[A^{3-}]}{[HA^{2-}]}$, is

(a) 5.0 (b) 4.0
(c) 9.0 (d) 10.0

28. To 20 ml of 0.1 M – NaOH solution, 3 ml of 1 M acetic acid solution is added. Is the solution now neutral, acidic or alkaline? How much more of the acetic acid solution we add to produce a change of pH = 0.3 unit? (pK_a for CH_3COOH = 4.74, log 2 = 0.3)

(a) acidic, 2 ml (b) alkaline, 1 ml
(c) acidic, 1 ml (d) neutral, 2 ml

29. A volume of 18 ml of acetic acid mixture and sodium acetate required 6 ml of 0.1 M-NaOH for neutralization of the acid and 12 ml of 0.1 M-HCl reaction with salt separately. If pK_a of acetic acid is 4.75, then what is the pH of the mixture? (log 2 = 0.3)

(a) 5.05 (b) 4.45
(c) 4.15 (d) 5.35

30. What is the ratio of pH of a solution containing 1 mole of CH_3COONa and 1 mole of HCl per litre and the other solution containing 1 mole of CH_3COONa and 1 mole of CH_3COOH per litre?

(a) 1 : 2 (b) 2 : 1
(c) pK_a : 2 (d) Zero

31. To a solution of acetic acid, solid sodium acetate is gradually added. When '*x* g' of the salt has been added, the pH has a certain value. When total '*y* g' of the salt has been added, the pH has been further raised by 0.6 units. What is the ratio of *x* : *y*? (log 3.98 = 0.6)

(a) 3.98 : 1 (b) 1 : 3.98
(c) 2 : 3.98 (d) 3.98 : 2

32. Two buffers, X and Y of pH 4.0 and 6.0, respectively, are prepared from acid HA and the salt NaA. Both the buffers are 0.50 M in HA. What would be the pH of the solution obtained by mixing equal volumes of the two buffers? The value of K_a for HA = 1.0×10^{-5} (log 5.05 = 0.7).

(a) 5.0 (b) 4.3
(c) 4.7 (d) 5.7

33. The buffer capacity (β) for a weak acid (A) – conjugate base (B) buffer is defined as the number of moles of strong acid or base needed to change the pH of 1 L of solution by 1 pH unit, where $\beta = \frac{2.303(C_A + C_B)K_a[H^+]}{([H^+]+K_a)^2}$. Under what condition will a buffer best resist a change in pH?

(a) pH = 3 pK_a (b) 2 pH = pK_a
(c) pH = pK_a (d) pH = 2 pK_a

34. A 40.0 ml solution of weak base, BOH is titrated with 0.1 N – HCl solution. The pH of the solution is found to be 10.0 and 9.0 after adding 5.0 ml and 20.0 ml of the acid, respectively. The dissociation constant of the base is (log 2 = 0.3)

(a) 2×10^{-5} (b) 1×10^{-5}
(c) 4×10^{-5} (d) 5×10^{-5}

35. How many grams of NaOH should be added in 500 ml of 2 M acetic acid solution to get a buffer solution of maximum buffer capacity?

(a) 20.0 (b) 10.0
(c) 40.0 (d) 30.0

36. A 0.28 g sample of an unknown monoprotic organic acid is dissolved in water and titrated with a 0.1 M sodium hydroxide solution. After the addition of 17.5 ml of base, a pH of 5.0 is recorded. The equivalence point is reached when a total of 35.0 ml of NaOH is added. The molar mass of the organic acid is

(a) 160 (b) 80
(c) 40 (d) 120

37. Equilibrium constant for the acid ionization of Fe^{3+} to $Fe(OH)^{2+}$ and H^+ is 9.0×10^{-3}. What is the maximum pH, which could be used so that at least 90% of the total Fe^{3+} in a dilute solution exists as Fe^{3+}? (log 3 = 0.48)

(a) 3.0 (b) 1.08
(c) 1.92 (d) 2.04

38. A student was given 0.01 mole of a weak organic acid and told to determine the K_a of the acid. He prepared 100 ml of an aqueous solution containing the sample. The volume of 50 ml of this solution was then titrated with NaOH to the equivalence point. The titrated solution was then mixed with the other 50 ml of the solution and the pH was determined. A value of 4.80 was obtained for the mixed solution. What is the approximate value of pK_a for the acid?

(a) 5.10 (b) 4.50
(c) 4.80 (d) 4.20

39. What is the aqueous ammonia concentration of a solution prepared by dissolving 0.15 mole of $NH_4^+CH_3COO^-$ in 1 L of water? Given: K_a $(CH_3COOH) = 1.8 \times 10^{-5}$; K_b $(NH_4OH) = 1.8 \times 10^{-5}$.

(a) 8.3×10^{-4} M (b) 0.15 M
(c) 5.52×10^{-3} M (d) 3.8×10^{-4} M

40. A volume of 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 ($K_w = 1 \times 10^{-14}$ 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

41. A volume of 10 ml of 0.1 M tribasic acid, H_3A is titrated with 0.1 M-NaOH solution. What is the ratio (approximate value) of $\frac{[H_3A]}{[A^{3-}]}$ at the second equivalent point? Given: $K_1 = 7.5 \times 10^{-4}$; $K_2 = 10^{-8}$; $K_3 = 10^{-12}$

(a) 10^{-4} (b) 10^{-3}
(c) 10^{-7} (d) 10^{-6}

42. The equilibrium carbonate ion concentration after equal volumes of 0.7 M-Na_2CO_3 and 0.7 M-HCl solutions are mixed, is (K_{a1} and K_{a2} for H_2CO_3 are 4.9×10^{-6} and 4.0×10^{-11}, respectively)

(a) 0.7 M (b) 0.35 M
(c) 0.002 M (d) 0.001 M

43. Calcium lactate is a salt of weak acid and represented as $Ca(Lac)_2$. A saturated solution of $Ca(Lac)_2$ contains 0.125 mole of salt in 0.50 L solution. The pOH of this is 5.60. Assuming complete dissociation of the salt, calculate K_a of lactate acid (log 2.5 = 0.4).

(a) 1.25×10^{-11} (b) 8.0×10^{-4}
(c) 3.2×10^{-17} (d) 4×10^{-5}

44. A volume of 50 ml of a solution which is 0.05 M in the acid HA ($pK_a = 3.80$) and 0.08 M in HB ($pK_a = 8.20$) is titrated with 0.2 M-NaOH solution. The pH of solution at the first equivalent point is (log 2 = 0.3, log 1.6 = 0.2)

(a) 6.0 (b) 9.2
(c) 4.8 (d) 5.9

45. Calculate the degree of hydrolysis of 0.005 M-K_2CrO_4. For H_2CrO_4, K_{a_1} = infinite, $K_{a_2} = 5 \times 10^{-7}$.

(a) 0.002 (b) 0.02
(c) 0.2 (d) 0.005

46. When glycinium hydrochloride ($NH_2CH_2COOH.HCl$) is titrated against NaOH, pH at the first half equivalence point is 2.40 and the pH at second half equivalence point is 9.60. The pH at first equivalence point is

(a) 2.40 (b) 9.60
(c) 6.00 (d) 7.20

47. An acid–base indicator has $K_a = 3.0 \times 10^{-5}$. The acid form of the indicator is red and the basic form is blue. The $[H^+]$ required to change the indicator from 75% blue to 75% red is

(a) 8×10^{-5} M (b) 9×10^{-5} M
(c) 1×10^{-5} M (d) 3.33×10^{-5} M

48. 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? The pK_a value of acetic acid = 4.75 [Antilog (0.75) = 5.62, Antilog (0.79) = 6.3, Antilog (0.69) = 4.93].

(a) 4.93 : 1 (b) 6.3 : 1
(c) 5.62 : 1 (d) 2.37 : 1

49. A volume of 224 ml of $CO_2(g)$ at 1 atm and 0°C was passed in 1 L of NaOH solution of unknown molarity. The resulting solution when titrated with 1.0 M-HCl solution requires 30 ml for the phenolphthalein end point. The molarity of NaOH solution used is

(a) 0.04 M (b) 0.02 M
(c) 0.03 M (d) 0.08 M

50. The correct increasing order of solubility of the following substances in g/100 ml is $PbSO_4$ ($K_{sp} = 2 \times 10^{-9}$), ZnS ($K_{sp} = 1 \times 10^{-22}$), AgBr ($K_{sp} = 4 \times 10^{-13}$), $CuCO_3$ ($K_{sp} = 1 \times 10^{-8}$). (Atomic masses: Pb = 208, Zn = 65, Ag = 108, Br = 80, Cu = 63)

(a) $PbSO_4 < ZnS < AgBr < CuCO_3$
(b) $PbSO_4 < CuCO_3 < AgBr < ZnS$
(c) $ZnS < AgBr < CuCO_3 < PbSO_4$
(d) $ZnS < AgBr < PbSO_4 < CuCO_3$

51. Calculate K_{form} for $HgCl_4^{2-}$ if the concentration of Hg^{2+} is 1.6×10^{-17} M in a solution prepared by dissolving 0.10 mole of $Hg(NO_3)_2$ in 1 L of solution containing 0.9 mole of NaCl.

(a) 10^{17} (b) 10^{16}
(c) 10^{18} (d) 6.25×10^{16}

52. Unexposed silver halides are removed from photographic film when they react with sodium thiosulphate to form the complex ion $Ag(S_2O_3)_2^{3-}$. What amount of $Na_2S_2O_3$ is needed to prepare 1 L of a solution that dissolves 0.1 moles of AgBr by the formation of $Ag(S_2O_3)_2^{3-}$? K_{sp} of AgBr = 4.0×10^{-13} and K_f of $Ag(S_2O_3)_2^{3-}$ = 1.6×10^{12}.

(a) 3.25 g (b) 3.25 moles
(c) 0.325 moles (d) 6.5 moles

53. A saturated solution of silver benzoate ($AgOCOC_6H_5$) has pH of 8.6. K_a for benzoic acid is 5.0×10^{-5}. The value of K_{sp} for silver benzoate is (log 2 = 0.3)

(a) 8.0×10^{-2} (b) 6.4×10^{-3}
(c) 6.4×10^{-4} (d) 0.282

54. The solubility product of $Co(OH)_3$ is 2.7×10^{-43}. The pH of saturated solution of $Co(OH)_3$ is about

(a) 7.0 (b) 11.0
(c) 3.0 (d) 3.48

55. In an attempted determination of the solubility product constant of Tl_2S, the solubility of this compound in pure CO_2 free water was determined as 2.0×10^{-6} M. Assume that the dissolved sulphide hydrolyses almost completely to HS^- and that the further hydrolysis to H_2S can be neglected, what is the computed K_{sp}? For H_2S, $K_{a1} = 1.4 \times 10^{-7}$, $K_{a2} = 1.0 \times 10^{-14}$

(a) 6.4×10^{-23} (b) 1.6×10^{-23}
(c) 3.2×10^{-17} (d) 3.2×10^{-24}

56. Calculate the formation constant for the reaction of a tripositive metal ion with thiocyanate ions to form the monocomplex if the total metal concentration in the solution is 2×10^{-3} M, the total SCN^- concentration is 1.51×10^{-3} M and the free SCN^- concentration is 1.0×10^{-5} M.

(a) 7.55×10^4 (b) 3×10^5
(c) 3.33×10^{-6} (d) 1.5×10^5

57. After solid $SrCO_3$ was equilibrated with a buffer at pH 8.6, the solution was found to have $[Sr^{2+}]$ = 2.0×10^{-4} M, what is the K_{sp} of $SrCO_3$? (K_{a2} for $H_2CO_3 = 5.0 \times 10^{-11}$, log 2 = 0.3)

(a) 4.0×10^{-8} (b) 8.0×10^{-8}
(c) $\frac{4}{51} \times 10^{-8}$ (d) $\frac{2}{51} \times 10^{-8}$

58. What is the solubility of MnS in pure water, assuming hydrolysis of S^{2-} ions? K_{sp} of MnS = 2.5×10^{-10}, $K_{a1} = 1 \times 10^{-7}$ and $K_{a2} = 1 \times 10^{-14}$ for H_2S. ($0.63^3 = 0.25$)

(a) 6.3×10^{-4} M (b) 2.5×10^{-4} M
(c) 6.3×10^{-3} M (d) 1.58×10^{-5} M

59. An amount of 0.10 moles of AgCl(s) is added to one litre of water. Next, the crystals of NaBr are added until 75% of the AgCl is converted to AgBr(s), the less soluble silver halide. What is Br^- at this point? K_{sp} of AgCl = 2×10^{-10} and K_{sp} of AgBr = 4×10^{-13}.

(a) 0.075 M (b) 0.025 M
(c) 1.5×10^{-4} M (d) 0.027 M

60. An amount of 0.01 moles of solid AgCN is rendered soluble in 1 L by adding just sufficient excess cyanide ion to form $Ag(CN)_2^-$ and the concentration of free cyanide ion is 2.5×10^{-7} M. Determine $[Ag^+]$ in the solution neglecting hydrolysis of cyanide ion. The value of K_{diss} for $Ag(CN)_2^-$ = 1.0×10^{-20}.

(a) 6.25×10^{-9} M (b) 1.6×10^{-9} M
(c) 1.6×10^{-7} M (d) 6.25×10^{-7} M

61. An amount of 2.0 M solution of Na_2CO_3 is boiled in a closed container with excess of CaF_2. Very little amount of $CaCO_3$ and NaF are formed. If the solubility product of $CaCO_3$ is 'x' and the molar solubility of CaF_2 is 'y', the molar concentration of F^- in the resulting solution after equilibrium is attained is

(a) $\sqrt{\frac{2y}{x}}$ (b) $\frac{8y^3}{x}$

(c) $\sqrt{\frac{8y^3}{x}}$ (d) $\sqrt{\frac{4y^3}{x}}$

62. Solid BaF_2 is added to a solution containing 0.1 mole of $Na_2C_2O_4$ solution (1 L) until equilibrium is reached. If the K_{sp} of BaF_2 and BaC_2O_4 is 10^{-6} mol^3 L^{-3} and 10^{-10} mol^2 L^{-2}, respectively, then find the equilibrium concentration of Ba^{2+} in the solution. Assume that addition of BaF_2 does not cause any change in volume.

(a) 0.2 M (b) 4×10^{-6} M

(c) 2.5×10^{-5} M (d) 2.5×10^{-6} M

63. What is the solubility of solid zinc hydroxide at a pH of 13? Given that

$Zn(OH)_2(s) \rightleftharpoons Zn(OH)_2(aq)$: $K_1 = 10^{-6}$ M

$Zn(OH)_2(aq) \rightleftharpoons Zn(OH)^+(aq) + OH^-(aq)$: $K_2 = 10^{-7}$ M

$Zn(OH)^+(aq) \rightleftharpoons Zn^{2+}(aq) + OH^-(aq)$: $K_3 = 10^{-4}$ M

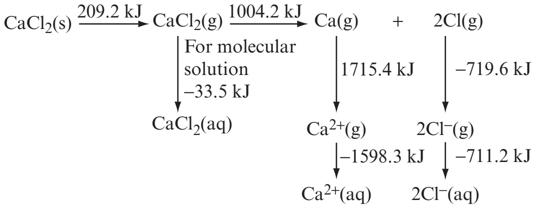
$Zn(OH)_2(aq) + OH^-(aq) \rightleftharpoons Zn(OH)_3^-(aq)$: $K_4 = 10^3$ M^{-1}

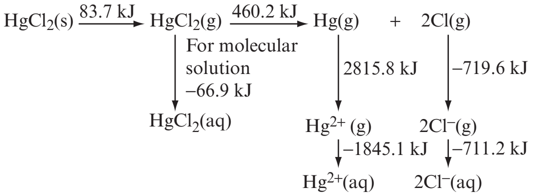
$Zn(OH)_3^-(aq) + OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$: $K_5 = 10$ M^{-1}

(a) 10^{-17} M (b) 10^{-6} M

(c) 10^{-4} M (d) 2×10^{-4} M

64. On dissolving a substance in water, it can produce either an ionic or molecular solution. From the following data, predict what type of solution is likely to be formed by $CaCl_2$ and $HgCl_2$ at 25°C?





The maximum contribution of $T\Delta S$ in dissolution process is 30 kJ at 25°C

(a) both ionic.

(b) both molecular.

(c) $CaCl_2$ is ionic but $HgCl_2$ is molecular.

(d) $CaCl_2$ is molecular but $HgCl_2$ is ionic.

65. A volume of 250 ml of saturated clear solution of $CaC_2O_4(aq)$ requires 6.0 ml of 0.001 M-$KMnO_4$ in acidic medium for complete oxidation of $C_2O_4^{2-}$ ions. What is the value of K_{sp} for CaC_2O_4?

(a) 3.6×10^{-9} (b) 6×10^{-5}

(c) 5.76×10^{-10} (d) 1.44×10^{-8}

66. Sr^{2+} forms a very unstable complex with NO_3^-. A solution that was 0.001 M-$Sr(ClO_4)_2$ and 0.05 M-KNO_3 was found to have only 75% of its strontium in the uncomplexed Sr^{2+} form, the balance being $Sr(NO_3)^+$. What is the value of K_f for complexation?

(a) 6.67 (b) 0.15

(c) 60 (d) 26.67

67. The concentration of CH_3COO^- ion in a solution prepared by adding 0.1 mole of $CH_3COOAg(s)$ in 1 L of 0.1 M-HCl solution is [Given: $K_a(CH_3COOH) = 10^{-5}$; $K_{sp}(AgCl) = 10^{-10}$; $K_{sp}(CH_3COOAg) = 10^{-8}$]

(a) 10^{-3} M (b) 10^{-2} M

(c) 10^{-1} M (d) 1 M

68. Among the different types of salts that have nearly the same solubility product constant K_{sp} but much smaller than one, the most soluble salt is that which

(a) produces maximum number of ions.

(b) produces minimum number of ions.

(c) produces high charge on ions.

(d) produces low charges on ions.

69. When excess oxalic acid is added to $CaCl_2$ solution, CaC_2O_4 is precipitated and the solution still contains some unprecipitated Ca^{2+}. The reason is

(a) CaC_2O_4 is a soluble salt.

(b) oxalic acid does not ionize at all.

(c) the solution becomes acidic and hence, ionization of $H_2C_2O_4$ is suppressed.

(d) the solution becomes basic and hence, ionization of $H_2C_2O_4$ increases.

70. At what pH, is the solubility of $Zn(OH)_2$ minimum? What is the minimum solubility?

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

$Zn(OH)_2(s) + 2OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$; $K_f = 0.12$

(a) 10.0, 2.4×10^{-9} M (b) 4.0, 2.4×10^{-9} M
(c) 10.0, 1.2×10^{-9} M (d) 10.0, 1.32×10^{-9} M

71. At what minimum pH will 10^{-3} M – $Al(OH)_3$ go into solution ($V = 1$ L) as $Al(OH)_4^-$ and at what maximum pH, it will be dissolved as Al^{3+}? Given: log 2 = 0.3

$Al(OH)_4^- \rightleftharpoons Al^{3+} + 4OH^-$; $K_{eq} = 1.6 \times 10^{-34}$
$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$; $K_{eq} = 8.0 \times 10^{-33}$

(a) 9.3, 4.7 (b) 4.7, 9.3
(c) 9.3, 9.3 (d) 4.3, 9.3

72. A 0.1 M solution of $[Cu(NH_3)_4]^+$ is stirred with an excess of potassium cyanide sufficient to convert all the ammonium complex to the corresponding cuprocyanide complex $[Cu(CN)_4]^{-3}$ and in addition to provide the solution with an excess of CN^- equal to 0.2 M. Calculate the maximum pH of the solution when the final solution is treated with hydrogen sulphide to maintain $[H_2S] = 0.1$ M and the precipitation of cuprous sulphide is prevented. The instability constant for $[Cu(CN)_4]^{-3}$ is 6.4×10^{-15}, $K_{a,overall}$ of $H_2S = 1.6 \times 10^{-21}$, K_{sp} of $Cu_2S = 2.56 \times 10^{-27}$.

(a) 4.0 (b) 10.0
(c) 10.8 (d) 3.2

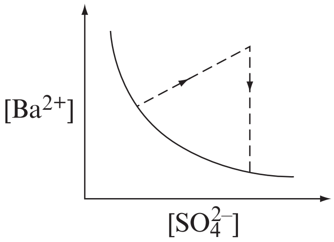
73. A particular water sample has 136 ppm $CaSO_4$. What percentage of water by mass must be evaporated in a container before solid $CaSO_4$ begins to deposit. Assume that the solubility of $CaSO_4$ does not change with temperature in the range 0°C to 100°C. The value of K_{sp} for $CaSO_4 = 1.6 \times 10^{-5}$.

(a) 80% (b) 50%
(c) 75% (d) 60%

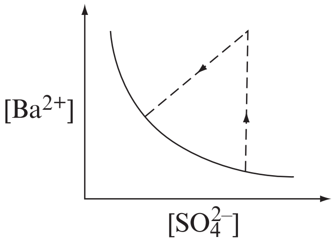
74. There exist an equilibrium between solid $BaSO_4$, Ba^{2+} and SO_4^{2-} ions in aqueous medium. Now, if equilibrium is disturbed by the addition of (a) $BaNO_3$ and (b) K_2SO_4 in different experiments and the equilibrium is re-achieved, then match the columns given below. (Thick line represents the initial equilibrium and the dotted line represents the approach of system towards equilibrium).

(a) Addition of $BaNO_3$.
(b) Addition of K_2SO_4.

(c)



(d)



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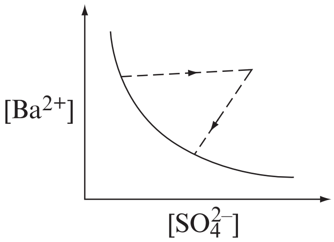
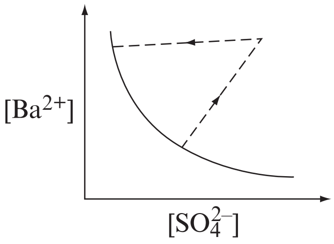


(f)



(a) ac, bd (b) ad, be
(c) ac, be (d) ae, bd

75. A volume of 1.0 L of solution which was in equilibrium with solid mixture of AgCl and Ag_2CrO_4 was found to contain 1×10^{-4} moles of Ag^+ ions, 1.0×10^{-6} moles of Cl^- ions and 8.0×10^{-4} moles of CrO_4^{2-} ions. The Ag^+ ions are added slowly to the above mixture (keeping the volume constant) till 8.0×10^{-7} moles of AgCl got precipitated. How many moles of Ag_2CrO_4 were precipitated simultaneously?

(a) 7.68×10^{-4} (b) 4.8×10^{-4}
(c) 8.0×10^{-4} (d) 7.68×10^{-5}

76. What concentration of free CN^- must be maintained in a solution that is 1.8 M-$AgNO_3$ and 0.16 M-NaCl to prevent AgCl from precipitating? The value of K_f for $Ag(CN)_2^-$ = 6.4×10^{17} and K_{sp} for AgCl = 1.8×10^{-10}.

(a) 2.5×10^{-9} M (b) 5×10^{-5} M
(c) 2.5×10^{-5} M (d) 1×10^{-4} M

77. A solution contains 0.1 M – Mg^{2+} and 0.1 M – Sr^{2+}. The concentration of H_2CO_3 in solution is adjusted to 0.05 M. Determine the pH range which would permit the precipitation of $SrCO_3$ without any precipitation of $MgCO_3$. The H^+ ion concentration is controlled by external factors. Given: $K_{sp}(MgCO_3) = 4 \times 10^{-8}\ M^2$; $K_{sp}(SrCO_3) = 9 \times 10^{-10}\ M^2$; $K_{a,overall}(H_2CO_3) = 5 \times 10^{-17}$; log 2 = 0.3; log 3 = 0.48.

(a) 4.78 to 5.6 (b) 4.6 to 5.78
(c) 5.78 to 6.4 (d) 5.22 to 5.4

78. A buffer solution is 0.25 M – CH_3COOH + 0.15 M – CH_3COONa, saturated in H_2S (0.1 M) and has $[Mn^{2+}] = 0.04$ M, $K_a(CH_3COOH) = 2.0 \times 10^{-5}$, $K_a(H_2S) = 1.0 \times 10^{-21}$ and $K_{sp}(MnS) = 2.5 \times 10^{-13}$. Which buffer component should be increased in concentration and to which minimum value to just start precipitation of MnS?

(a) CH_3COOH, 1.25 M
(b) CH_3COONa, 0.25 M
(b) CH_3COONa, 1.25 M
(d) CH_3COONa, 0.50 M

79. To 0.35 L of 0.1 M – NH_3 0.15 L of 0.1 M-$MgCl_2$ is added. What minimum mass of $(NH_4)_2SO_4$ should be added to cause the $Mg(OH)_2$ to re-dissolve? The value of K_{sp} for $Mg(OH)_2 = 1.2 \times 10^{-11}$, K_b for $NH_3 = 2.0 \times 10^{-5}$.

(a) 4.62 g (b) 2.31 g
(c) 9.24 g (d) 1.155 g

80. A volume of 500 ml of 0.01 M – $AgNO_3$ solution, 250 ml of 0.02 M – NaCl solution and 250 ml of 0.02 M – NaBr solution are mixed. The final concentration of bromide ion in the solution is (K_{sp} of AgCl and AgBr are 10^{-10} and 5×10^{-13}, respectively.)

(a) 0.01 M (b) 0.02 M
(c) 0.005 M (d) 2.5×10^{-5} M

Section B (One or More than one Correct)

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

(a) 100 ml of (M/10) HCl + 100 ml of (M/10) NaOH.
(b) 55 ml of (M/10) HCl + 45 ml of (M/10) NaOH.
(c) 10 ml of (M/10) HCl + 90 ml of (M/10) NaOH.
(d) 75 ml of (M/5) HCl + 25 ml of (M/5) NaOH.

2. Which of the following relation(s) is/are true for alkaline solution?

(a) $pH > \frac{pK_w}{2}$ (b) pH > pOH
(c) $pOH < \frac{pK_w}{2}$ (d) pH < pOH

3. Which of the following expression(s) for the degree of dissociation of weak monobasic acid in aqueous solution is/ are incorrect?

(a) $\sqrt{\frac{K_a}{C}}$ (b) $\frac{K_a}{K_a + [H^+]}$
(c) $\frac{[H^+]}{K_a + [H^+]}$ (d) $\frac{1}{1+10^{(pK_a - pH)}}$

4. Which of the following will occur if a 0.1 M solution of a weak acid is diluted to 0.01 M at constant temperature?

(a) $[H^+]$ will decrease.
(b) pH will increase.
(c) Percentage ionization will increase.
(d) K_a will increase.

5. The relation $pK_a = 14 - pK_b$ is true for which of the following pair(s)?

(a) $MeNH_3^+$, CH_3NH_2
(b) CH_3COOH, CH_3COO^-
(c) H_3O^+, OH^-
(d) Na^+, NaOH

6. Which would decrease the pH of 25 ml of a 0.01 M solution of hydrochloric acid? The addition of

(a) magnesium metal
(b) 25 ml 0.02 M of HCl
(c) 25 ml 0.005 M of HCl
(d) 50 ml water

7. Which of the following result(s) is/are correct for the equilibrium state in a solution originally having 0.1 M-CH_3COOH and 0.1 M-HCl? The value of K_a for $CH_3COOH = 1.8 \times 10^{-5}$.

(a) $[H^+] = 0.1$ M
(b) $[CH_3COO^-] = 1.8 \times 10^{-5}$ M
(c) Degree of dissociation of acetic acid $= 1.8 \times 10^{-4}$
(d) $[H^+]$ from water $= 10^{-13}$ M

8. The equilibrium constant for the ionization of $RNH_2(g)$ in water as

$$RNH_2(g) + H_2O(l) \rightleftharpoons RNH_3^+(aq) + OH^-(aq)$$

is 10^{-6} at 25°C. Which of the following is/are correct?

(a) pH of the solution is 11.0 at partial pressure of $RNH_2(g) = 1$ bar.
(b) Forward reaction is favoured by the addition of HCl(aq).
(c) Forward reaction is favoured by the addition of $H_2O(l)$.
(d) Forward reaction is favoured by the addition of $RNH_2(g)$.

9. Which of the following processes will increase $[OH^-]$ in NH_4OH solution?

(a) Addition of HCl solution.
(b) Addition of water.
(c) Addition of NH_4Cl solution.
(d) Addition of solid NH_4OH.

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

(a) The pH of 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 with the increase in temperature.
(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half neutralization point, $pH = pK_a/2$.

11. If K_1 and K_2 are the first and second ionization constants of H_2CO_3 and $K_1 >> K_2$, then the incorrect relation(s) is/are

(a) $[H^+] = [HCO_3^-]$
(b) $[H^+] = \sqrt{K_1.[H_2CO_3]}$
(c) $K_2 = [CO_3^{2-}]$
(d) $[H^+] = 2.\,[CO_3^{2-}]$

12. Which of the following may act as buffer in aqueous solution?

(a) $NH_4Cl + NH_4OH$
(b) $CH_3COOH + CH_3COONa$
(c) $CH_3COONa + NaCl$
(d) Borax + Boric acid

13. A buffer solution can be prepared from a mixture of

(a) NH_4Cl and NaOH in 2 : 1 mole ratio.
(b) CH_3COONa and HCl in 1 : 1 mole ratio.
(c) CH_3COONa and HCl in 2 : 1 mole ratio.
(d) CH_3COONa and HCl in 1 : 2 mole ratio.

14. Which of the following statements is/are correct?

(a) A buffer solution may contain a weak acid and its conjugate base.
(b) A buffer solution shows little change in pH on the addition of a small amount of acid or base.
(c) A buffer solution can be prepared by mixing a solution of ammonium acetate and acetic acid.
(d) The addition of solid potassium cyanide to water increases the pH of water.

15. A 2.5 g impure sample containing weak monoacidic base (Molecular weight = 45) is dissolved in 100 ml water and titrated with 0.5-M HCl at 25°C. When 1/5th of the base was neutralized, the pH was found to be 9 and at equivalent point, the pH of solution is 4.5 (log 2 = 0.3).

(a) K_b of base is less than 10^{-6}.
(b) Concentration of salt at equivalent point is 0.25 M.
(c) Volume of HCl used at equivalent point is 100 ml.
(d) Mass percentage of base in given sample is 80%.

16. H_2CO_3 ionizes as follows.

$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.0 \times 10^{-6}$

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 5.0 \times 10^{-11}$

Which of the following information is correctly related to 0.5 M – Na_2CO_3 solution?

(a) The degree of hydrolysis of Na_2CO_3 is 0.02.

(b) The pH of solution is 2.0.

(c) The pOH of solution is 2.0.

(d) $[H_2CO_3] = 2.5 \times 10^{-9}$ M

17. The amino acid glycine (NH_2CH_2COOH) is basic because of its $-NH_2$ group and acidic because of its –COOH group. By a process equivalent to base dissociation, glycine can acquire an additional proton to form $\overset{\oplus}{N}H_3\,CH_2COOH$. The resulting cation may be considered to be a diprotic acid, since one proton from the –COOH group and one from the $-\overset{\oplus}{N}H_3$ group may be lost. The pK_a values for these processes are 2.22 and 9.78, respectively. For a 0.01 M solution of neutral glycine (log 1.7 = 0.22, log 6 = 0.78),

(a) the pH is 6.0.

(b) percentage of the glycine in the cationic form is 0.017%.

(c) the pOH is 6.0.

(d) percentage of the glycine in the anionic form is 0.017%.

18. 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 acetate against HCl.

(d) Barium hydroxide against oxalic acid.

19. Which of the following statement(s) is/are incorrect?

(a) When water is added to KCN, a reaction occurs because the CN^- ion is a strong proton acceptor.

(b) No reaction occurs when KCl is dissolved in water because neither K^+ nor Cl^- can remove or accept proton from water.

(c) When water is added to sodium acetate, an acidic solution is produced because of the formation of free acetic acid from the action of water on CH_3COO^-.

(d) $(NH_4)_2CO_3$ smells strongly of NH_3 because the strong base CO_3^{2-} is able to remove protons from NH_4^+ ion.

20. An aqueous solution contains 0.02 M-$FeCl_2$ and 0.05 M-$FeCl_3$. The solubility products are 8×10^{-16} for $Fe(OH)_2$ and 4×10^{-28} for $Fe(OH)_3$. Identify the correct option(s) among the following regarding the precipitation of metal hydroxides.

(a) At pH = 9.0, neither $Fe(OH)_2$ nor $Fe(OH)_3$ will precipitate.

(b) At pH = 6.0, neither $Fe(OH)_2$ nor $Fe(OH)_3$ will precipitate.

(c) If pH of the solution is in between 5.3 and 7.3, only $Fe(OH)_3$ will precipitate but not $Fe(OH)_2$.

(d) If pOH of the solution is in between 6.7 and 8.7, only $Fe(OH)_2$ will precipitate but not $Fe(OH)_3$.

Section C (Comprehensions)

Comprehension I

Acetic acid tends to form dimer due to the formation of intermolecular hydrogen bonding.

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

The equilibrium constant for this reaction is 1.5×10^{2} M^{-1} in benzene solution and 3.6×10^{-2} M^{-1} in water. In benzene, monomer does not dissociate and however, in water, monomer dissociates simultaneously with acid dissociation constant 2.0×10^{-5} M. Dimer does not dissociate in benzene as well as water.

1. The molar ratio of dimer to monomer for 0.1 M acetic acid in benzene is equal to

(a) 150 : 1 (b) 1 : 150
(c) 5 : 2 (d) 2 : 5

2. The molar ratio of dimer to monomer for 0.1 M acetic acid in water (neglecting the dissociation of acetic acid in water) is equal to

(a) 250 : 1 (b) 1 : 250
(c) 9 : 2500 (d) 2500 : 9

3. The pH of 0.1 M acetic acid solution in water, considering the simultaneous dimerization of acid is

(a) 1 (b) 2.85
(c) 5.7 (d) 3.42

Comprehension II

The dissociation constant of acetic acid is 2.0×10^{-5}. An aqueous solution of acetic acid is prepared by dissolving 0.7 millimole acetic acid in sufficient water to get 10 m^3 of solution at 25°C.

4. What is the pH of the solution? (log 2 = 0.3, log 7 = 0.85, log 17 = 1.23, $\sqrt{4.49} = 2.1$)

(a) 7.15 (b) 6.77
(c) 6.85 (d) 7.0

5. What is the concentration of unionized acetic acid in the solution?

(a) 0 (b) 4.9×10^{-10} M
(c) 7×10^{-8} M (d) 2.45×10^{-10} M

Comprehension III

The concentration of hydrogen ion in a 0.2 M solution of formic acid is 8.0×10^{-3} M. To this solution, formate is added so as to adjust the concentration of sodium formate to 1.0 M. The degree of dissociation of sodium formate is 0.8 (log 2 = 0.3).

6. What will be the pH of the final solution?

(a) 4.1 (b) 2.1
(c) 2.9 (d) 4.9

7. The dissociation constant of formic acid is

(a) 2.4×10^{-4} (b) 3.2×10^{-4}
(c) 3.2×10^{-5} (d) 1.6×10^{-4}

Comprehension IV

A buffer solution contains 0.8 M-NH_4OH and 0.2 M-NH_4Cl. The value of K_a fo $NH_4^+ = 5.0 \times 10^{-10}$ (log 2 = 0.3, log 3 = 0.48).

8. The pH of the solution is

(a) 9.9 (b) 8.7
(c) 9.6 (d) 4.1

9. The pH of the resulting solution on adding 0.15 mole HCl in 500 ml of the buffer solution is

(a) 9.3 (b) 0.48
(c) 0.52 (d) 9.9

10. The pH of the resulting solution on adding 0.5 mole HCl in 500 ml of the buffer solution is

(a) 9.3 (b) 0.30
(c) 0.70 (d) 9.9

Comprehension V

Potash alum is $KAl(SO_4)_2 \cdot 12H_2O$. As a strong electrolyte, it is considered to be 100% dissociated into K^+, Al^{3+} and SO_4^{2-}. The solution is acidic due to the hydrolysis of Al^{3+}, but not so acidic as might be expected because the SO_4^{2-} can sponge up some of the H_3O^+ by forming HSO_4^-. Given a solution made by dissolving 11.85 g of $KAl(SO_4)_2 \cdot 12H_2O$ in enough water to make 100 cm^3 of solution. What is $[H_3O^+]$ of the solution if (K = 39, Al = 27)

11. None of the ion is hydrolysing.

(a) 10^{-7} M

(b) less than 10^{-7} M

(c) more than 10^{-7} M

(d) 0.0

12. Only Al^{3+} is hydrolysing and its first hydrolysis constant is 1.4×10^{-5} M.

(a) 1.87×10^{-3} M

(b) 6.24×10^{-4} M

(c) 0.09 M

(d) 6.32×10^{-7} M

13. Only SO_4^{2-} is hydrolysing and acid dissociation constant of HSO_4^- in water is 1.25×10^{-2}.

(a) 1.26×10^{-13} M

(b) 6.32×10^{-7} M

(c) 4.47×10^{-7} M

(d) 1.58×10^{-8} M

14. Both, Al^{3+} and SO_4^{2-} are hydrolysing.

(a) 2.97×10^{-4} M

(b) 0.0118 M

(c) 5.43×10^{-6} M

(d) 9.35×10^{-4} M

Comprehension VI

A 0.010 M solution of $PuO_2(NO_3)_2$ was found to have a pH of 3.80 [Antilog (–3.8) = 1.6×10^{-4}].

15. What is the hydrolysis constant, K_b, for PuO_2^{2+}?

(a) 2.56×10^{-6}

(b) 3.2×10^{-8}

(c) 5.12×10^{-4}

(d) 2.56×10^{-8}

16. What is the value of K_b for $PuO_2 \cdot OH^+$?

(a) 1.0×10^{-6}

(b) 3.9×10^{-8}

(c) 3.9×10^{-9}

(d) 3.9×10^{-10}

Comprehension VII

A volume of 100 ml of 0.1 M-H_3PO_4 solution is titrated with 0.5 M-NaOH solution till the second equivalence point. Then 10 ml of 0.5 M-HCl solution is mixed in the resulting solution. The dissociation constants of H_3PO_4 are 10^{-3}, 10^{-8} and 10^{-13}.

17. pH at the second equivalence point is

(a) 13.0 (b) 8.0

(c) 5.5 (d) 10.5

18. pH of the solution after adding HCl is

(a) 8.0 (b) 1.0

(c) 6.0 (d) 10.5

19. The solubility product of base $A(OH)_2$ is 4.0×10^{-30}. Its solubility in the final solution is

(a) 10^{-10} M

(b) 4.0×10^{-16} M

(c) 4.0×10^{-18} M

(d) 4.0×10^{-22} M

Comprehension VIII

Human blood has a narrow pH range of 7.3–7.4, which must be maintained for metabolic processes to function properly. To keep the pH in this range, it requires a delicate balance between the concentrations of the conjugate acid–base pairs, making up to the buffer system. The main buffer is a carbonic acid-hydrogen carbonate system, which involves the following equilibria.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

At the body temperature, the pK_a for carbonic acid is 6.40. However, the normal concentration of CO_2(g) in the lungs maintains a ratio of HCO_3^-(aq) and H_2CO_3(aq) in blood plasma at about 8 : 1. The H_2CO_3 concentration in blood is largely controlled by breathing and respiration and HCO_3^- concentration is largely controlled by excretion in urine.

If blood pH rises above 7.4, thena potentially life-threatening condition called alkalosis can result. It normally occurs in climbers suffering from oxygen deficiency at high altitude or in patients who are hyperventilating from severe anxiety (log 2 = 0.3).

20. The pH of blood at body temperature is

(a) 6.4 (b) 7.4
(c) 7.3 (d) 7.2

21. The maximum permissible value of $\frac{[H_2CO_3]}{[HCO_3^-]}$ in human blood to just prevent alkalosis is

(a) 0.1 (b) 10
(c) 8.0 (d) 0.125

22. Which of the following statement is correct?

(a) One way to treat alkalosis can be to get the patient to breathe more quickly so that the amount of CO_2 exhaled increases and the blood becomes deficient in CO_2.
(b) One way to treat alkalosis is to get the patient breathe into a bag so that the exhaled CO_2 is re-inhaled.
(c) The pH of blood is independent of the concentration of CO_2.
(d) Alkalosis cannot be controlled by breathing and respiration.

Comprehension IX

The first and second dissociation constants of H_2CO_3 are 4.0×10^{-6} and 2.5×10^{-11}, respectively. In a particular titration, 50 ml of 1.0 M-Na_2CO_3 is taken in a flask and 1.0 M-HCl solution is added drop by drop. Determine the pH of the resulting solution on adding the following volume of HCl solution. Assume thatvolume is additive. (log 2 = 0.3, log 3 = 0.48).

23. 0 ml?

(a) 1.7 (b) 12.3
(c) 3.7 (d) 10.3

24. 25 ml?

(a) 10.6 (b) 10.3
(c) 10.9 (d) 3.4

25. 50 ml?

(a) 10.6 (b) 5.4
(c) 8.0 (d) 6.0

26. 75 ml?

(a) 10.6 (b) 8.6
(c) 8.0 (d) 5.4

27. 100 ml?

(a) 2.94 (b) 11.06
(c) 5.4 (d) 5.88

Comprehension X

Amino acid glycine (NH_2–CH_2–COOH) exists as a zwitterion in aqueous solution. The K_a and K_b values of glycine are 1.6×10^{-10} (p$K_a = 9.8$) and 2.5×10^{-12} (p$K_b = 11.6$), respectively. The K_a and K_b values are for zwitterion of amino acid with the following structure $[\overset{+}{N}H_3 - CH_2 - COO^-]$.

28. What is the value of K_b for $-NH_2$ group in glycine?

(a) 4×10^{-3}

(b) 1.6×10^{-10}

(c) 6.25×10^{-5}

(d) 2.5×10^{-12}

29. An aqueous solution of glycine has pH

(a) nearly 7

(b) nearly 7.9

(c) nearly 6.1

(d) nearly 11.5

Comprehension XI

To find the K_{sp} of $AgBrO_3$, a student prepared 1 L of a just saturated solution by adding $AgBrO_3$ in water at 27°C. He found that a copper wire left in the solution overnight became covered with silver and Cu^{2+} ions were also formed in the solution. The wire was cleaned, dried and found to weigh 6.35 mg less that its original weight.

$$Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s);\ \Delta G^o = -120\ kJ$$

$$(R = 8.0\ J/K\text{-mol};\ Cu = 63.5)$$

30. The number of moles of Cu reacted was

(a) 1.0×10^{-4}

(b) 1.0

(c) 0.10

(d) 1.0×10^{-3}

31. The concentration of Ag^+ in the original saturated solution was

(a) 1.0×10^{-2}

(b) 1.0×10^{-4}

(c) 2.0×10^{-4}

(d) 5.0×10^{-5}

32. The K_{sp} for $AgBrO_3$ is

(a) 1.0×10^{-8}

(b) 3.0×10^{-9}

(c) 1.6×10^{-4}

(d) 4.0×10^{-8}

Comprehension XII

The solubility product of AgCN is 1.0×10^{-16} and the formation constant of $Ag(CN)_2^-$ is 1.5×10^{17}.

33. The solubility of AgCN in 0.02 M-KCN solution, assuming no complex formation, is

(a) 1.0×10^{-8} M

(b) 5.0×10^{-15} M

(c) 0.02 M

(d) 5.0×10^{-14} M

34. The solubility of AgCN in 0.02 M-KCN solution, assuming complex formation, is

(a) 0.3 M

(b) 0.02 M

(c) 1.33×10^{-19} M

(d) 1.87×10^{-2} M

35. At what $[CN^-]$ in the solution, the solubility of AgCN will be minimum?

(a) 3.65×10^{-9} M

(b) 1.33×10^{-17} M

(c) 2.58×10^{-9} M

(d) 5.48×10^{-8} M

Section D (Assertion–Reason)

The following questions consist of two statements. Mark the answer as follows.

(a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.

(b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.

(c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.

(d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** An aqueous solution having pH 6.8 must be acidic.

   Statement II: An aqueous solution having $[H^+] > \sqrt{K_w}$ must be acidic.

2. **Statement I:** The pH of 10^{-7} M-NaOH solution is in between 7.0 to 7.3 at 25°C.

   Statement II: Due to common ion effect, ionization of water is reduced.

3. **Statement I:** 10^{-4} M-HCl solution is more acidic compared to 1 M-HCOOH solution ($K_a = 10^{-3}$ M).

   Statement II: HCl is stronger acid as compared to HCOOH.

4. **Statement I:** When an aqueous solution of weak base like BOH is diluted, $[OH^-]$ increases.

   Statement II: On dilution, the degree of dissociation of weak electrolytes increases.

5. **Statement I:** The pH of acidic buffer solution always increases on dilution.

   Statement II: The pH of any aqueous solution of acid always increases on dilution.

6. **Statement I:** An aqueous solution containing a weak acid (HA) and its conjugate base (A^-) may behave as buffer solution.

   Statement II: At 25°C, the pH of such buffer solution must be less than 7.0.

7. **Statement I:** Aqueous solutions of NaCl and CH_3COONH_4 are neutral (pH = 7.0 at 25°C).

   Statement II: Both the salts do not undergo hydrolysis.

8. **Statement I:** In general, phenolphthalein is used as an indicator for the titration of weak acid against strong base.

   Statement II: At equivalent point, solution is basic and the pH range of phenolphthalein is about 8.0 to 10.0.

9. **Statement I:** Phenolphthalein does not show any change in colour during the titration of $NaHCO_3$ with HCl.

   Statement II: In the presence of phenolphthalein, HCl does not react with $NaHCO_3$.

10. **Statement I:** Moles of Sr^{2+} furnished by sparingly soluble substance $Sr(OH)_2$ decreases due to dilution.

    Statement II: Solubility product of $Sr(OH)_2$ is not affected by dilution.

Section E (Column Match)

1. Match the columns.

Column I	Column II
(A) NaCl	(P) True electrolyte.
(B) HCl	(Q) Strong electrolyte in water.
(C) CH_3COOH	(R) Potential electrolyte.
(D) $CrCl_3 \cdot 3NH_3$	(S) Weak electrolyte in water.
	(T) Non-electrolyte in water.

2. Match the columns.

Column I (pH value)	Column II (Solution)
(A) 5.0	(P) pH at which $Mg(OH)_2$ just start precipitating from 2.0×10^{-3} M-Mg^{2+} solution (K_{sp} of $Mg(OH)_2 = 2 \times 10^{-6}$ M^3).
(B) 9.0	(Q) Maximum pH at which 0.1 mole of $Al(OH)_3$ dissolves completely as Al^{3+} in 1 L solution (K_{sp} of $Al(OH)_3 = 1 \times 10^{-28}$ M^4).
(C) 12.5	(R) pH at which 0.1 M-CH_3COOH dissociates 1000/11% (K_a of $CH_3COOH = 1.0 \times 10^{-5}$ M).
(D) 6.0	(S) pH of 0.001 M-HA (weak acid) solution (pK_a of HA = pK_b of A^-).
	(T) pH of 3×10^{-5} M-CaA_2 solution (CaA_2 dissociates completely in water; K_a of HA = 5×10^{-9}).

3. Match the columns.

Column I	Column II
(A) NaCl	(P) Cationic hydrolysis
(B) Na_2CO_3	(Q) Anionic hydrolysis
(C) NH_4Cl	(R) pH = 7.0 at 25°C
(D) CH_3COONH_4	(S) pH < 7.0 at 25°C
	(T) pH > 7.0 at 25°C

4. For a tribasic acid, H_3A, $K_{a1} = 10^{-4}$, $K_{a2} = 10^{-8}$ and $K_{a3} = 10^{-12}$. Match the pH (Column II) of the resulting solution (Column I) at 25°C.

Column I	Column II
(A) Equimolar mixture of H_3A and NaH_2A.	(P) 12.0
(B) Equimolar mixture of NaH_2A and Na_2HA.	(Q) 8.0
(C) Equimolar mixture of Na_2HA and Na_3A.	(R) 4.0
(D) Equimolar mixture of H_3A and NaOH.	(S) 6.0
(E) Equimolar mixture of NaH_2A and NaOH.	(T) 10.0

5. Match the columns.

Column I	Column II
(A) $\frac{pK_{a,H_2O} + pK_{b,H_2O}}{2}$ at 25°C ($d_{water} = 1.0$ g/ml)	(P) $\frac{pK_w}{2}$
(B) pH of CH_3COONH_4(aq) ($K_{a,CH_3COOH} = K_{b,NH_4OH}$)	(Q) 16 – log 1.8
(C) pH of pure water at 320 K.	(R) $-\log K_{a,H_2O}$
	(S) < 7.0

Section F (Subjective)

Single-digit Integer Type

1. The ionic product of heavy water (D_2O) is 1.0×10^{-16} at 7°C. The P^D value of pure heavy water at 7°C is

2. The self-ionization constant for pure formic acid, $K = [HCOOH_2^+][HCOO^-]$ has been estimated as 10^{-6} M^2 and the density of formic acid is 1.15 g/cm^3 at room temperature. If 'x %' of formic acid molecules in pure formic acid is converted to formate ions, then the value of '1000x' is

3. An aqueous solution contains 10% ammonia by mass and has a density of 0.85 g/ml. If $[H_3O^+]$ in this solution is 'xM', then the value of '$x \times 10^{12}$' is (K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M)

4. Boric acid $B(OH)_3$ is used as a mild antiseptic. What is the pH of a 0.0025 M aqueous solution of boric acid? The hydrogen ion arises principally from the following reaction.

$B(OH)_3(aq) + H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H^+(aq)$; $K = 4.0 \times 10^{-10}$

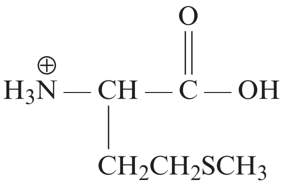
5. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.28 gm litre^{-1} and the pK_a of H_2SO_3 is 2.0, estimate the pH of rain on that day.

6. An artificial fruit beverage contains 30.0 g of tartaric acid ($H_2C_4H_4O_6$) and 18.8 g of its salt, potassium hydrogen tartrate per litre. What is the pH of the beverage? For tartaric acid, $K_{a1} = 5.0 \times 10^{-4}$, $K_{a2} = 4 \times 10^{-9}$ (log 2 = 0.3).

7. When 0.05 mole of HCl is added in 200 ml of a buffer solution, the pH of the solution decreases by 0.05 unit. What is the buffer capacity of the solution?

8. A solution of weak acid was titrated with base NaOH. The equivalence point was reached when 36.12 ml of 0.1 M-NaOH have been added. Now, 18.06 ml of 0.1 M-HCl was added to the titrated solution, the pH was found to be 5.0. The pK_a of acid is

9. A volume of 30 ml of 0.06 M solution of the protonated form of an amino acid, methionine (H_2A^+) is titrated with 0.09 M-NaOH. The pH of the resulting solution after addition of 20 ml of base, is ($pK_{a1} = 2.28$, $pK_{a2} = 9.72$)



$\overset{\oplus}{H_3N}-\underset{CH_2CH_2SCH_3}{CH}-\overset{O}{\overset{\|}{C}}-OH$

(Methionine cation)

10. The pH range of a basic indicator (InOH) is 3.4 – 4.6. Determine the ratio $[In^+]/[InOH]$ above which the solution appears only in the colour of In^+? (log 2 = 0.3)

Four-digit Integer Type

1. An aqueous solution of aniline of concentration 0.2 M is prepared. How many milligrams of NaOH should be added in 500 ml of this solution so that anilinium ion concentration in the solution becomes 10^{-8} M? K_b of $C_6H_5NH_2 = 4.0 \times 10^{-10}$.

2. How many milligram of sodium acetate should be added in 500 ml of 0.2 M acetic acid solution in order to make the $[H^+]$ in the solution 4×10^{-4} M. K_a of $CH_3COOH = 1.8 \times 10^{-5}$.

3. For H_2SO_4, K_{a1} = infinite and $K_{a2} = 1.2 \times 10^{-2}$. The molarity of H_2SO_4 solution of pH 2.0 is 'xM'. The value of $1.7 \times 10^5\,x$ is

4. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M-$NaHCO_3$ solution should be mixed with a 10 ml sample of blood which is 2 M in H_2CO_3 in order to maintain a pH of 7.4? The value of K_a for H_2CO_3 in blood is 8.0×10^{-7} (log 2 = 0.3).

5. The hydronium ion concentration (in millimole per litre) in a solution containing 1.8 g $NaHSO_4$ per 100 ml is (K_a for HSO_4^- is 4.0×10^{-2})

6. The acid ionization of hydrated aluminium ion is

$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons Al(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$; $K_a = 1.0 \times 10^{-5}$

How many milligrams of $AlCl_3$ should be dissolved in sufficient water to get 400 ml of solution of pH 3.0?

7. A weak acid-type indicator was found to be 60% dissociated at pH = 9.18. What will be the percentage dissociation at pH = 9.0? (log 2 = 0.3, log 3 = 0.48)

8. A saturated solution of iodine in water contains 0.254 g of I_2 in 1 L. More than this can dissolve in a KI solution because of the following equilibrium.

$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$

A 0.1 M-KI solution actually dissolved 12.7 g of iodine per litre, most of which is converted to I_3^-. Assuming that the concentration of I_2 in all saturated solutions is the same, calculate the equilibrium constant for the above reaction (Take: $0.96 \times 5.1 = 4.9$, atomic mass of iodine = 127).

9. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 3.2×10^{-5}. A 500 ml of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 1.6 M-NaOH. How much $Ca(OH)_2$ (in milligrams) is precipitated?

10. Most ordinary soaps are sodium salt of long chain fatty acids and are soluble in water. Soaps of divalent cations such as Ca^{2+} are only slightly soluble and are often seen in the common soap is calcium palmitate, $Ca[CH_3(CH_2)_{14}COO]_2$. A handbook of chemistry lists the solubility of this soap as 0.0055 g per 100 ml at 25°C. If sufficient sodium soap is used to produce a final concentration of palmitate ion equal to 0.10 M in a water sample having 40 ppm Ca^{2+} initially, then how many milligrams of calcium palmitate would precipitate in a bowl containing 10 L of this water sample?

Answer Keys **Exercise I**

Basics

1. (b) 2. (d) 3. (a) 4. (b) 5. (c) 6. (c) 7. (c) 8. (d) 9. (c) 10. (c)

Strong Acids and Bases

11. (b) 12. (d) 13. (c) 14. (d) 15. (d) 16. (a) 17. (c) 18. (b) 19. (c) 20. (d)

Weak Acids and Bases

21. (a) 22. (c) 23. (a) 24. (c) 25. (d) 26. (a) 27. (d) 28. (d) 29. (b) 30. (a)
31. (b) 32. (c) 33. (a) 34. (d) 35. (d)

Polyprotic Acids and Bases

36. (a) 37. (a) 38. (a) 39. (b) 40. (c)

Buffer Solutions

41. (d) 42. (d) 43. (d) 44. (a) 45. (d) 46. (b) 47. (d) 48. (b) 49. (a) 50. (b)

Hydrolysis of Salts

51. (a) 52. (d) 53. (c) 54. (b) 55. (d) 56. (c) 57. (d) 58. (b) 59. (c) 60. (b)
61. (c) 62. (b) 63. (a) 64. (c) 65. (b)

Indicators

66. (c) 67. (c) 68. (a) 69. (c) 70. (b)

Solubility

71. (a) 72. (d) 73. (b) 74. (c) 75. (b) 76. (b) 77. (b) 78. (b) 79. (c) 80. (b)
81. (d) 82. (a) 83. (a) 84. (d) 85. (b) 86. (c) 87. (b) 88. (b) 89. (a) 90. (b)
91. (d) 92. (d) 93. (b) 94. (c) 95. (d) 96. (d) 97. (d) 98. (a) 99. (a) 100. (c)

Precipitation

101. (a) 102. (a) 103. (d) 104. (b) 105. (b) 106. (a) 107. (c) 108. (b) 109. (d) 110. (a)
111. (b) 112. (a) 113. (c) 114. (c) 115. (b)

Answer Keys Exercise II

Section A (Only one Correct)

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

Section B (One or More than one Correct)

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

Section C

Comprehension I

1. (c) 2. (c) 3. (b)

Comprehension II

4. (c) 5. (b)

Comprehension III

6. (a) 7. (b)

Comprehension IV

8. (a) 9. (a) 10. (c)

Comprehension V

11. (a) 12. (a) 3. (d) 14. (a)

Comprehension VI

15. (a) 16. (c)

Comprehension VII

17. (d) 18. (a) 19. (c)

Comprehension VIII

20. (c) 21. (a) 22. (b)

Comprehension IX

23. (b) 24. (a) 25. (c)
26. (d) 27. (a)

Comprehension X

28. (c) 29. (c)

Comprehension XI

30. (a) 31. (c) 32. (d)

Comprehension XII

33. (b) 34. (d) 35. (c)

Section D (Assertion – Reason)

1. (d) 2. (a) 3. (d) 4. (d) 5. (d) 6. (c) 7. (c) 8. (a) 9. (c) 10. (d)

Section E (Column Match)

1. A → P, Q; B → Q, R; C → R, S; D → T
2. A → Q, S; B → T; C → P; D → R
3. A → R; B → Q, T; C → P, S; D → P, Q, R
4. A → R; B → Q; C → P; D → S; E → T
5. A → Q, R; B → P; C → P, S

Section F (Subjective)

Single-digit Integer Type

1. (8) 2. (4) 3. (1) 4. (6) 5. (2) 6. (3) 7. (5) 8. (5) 9. (6) 10. (4)

Four-digit Integer Type

1. (0160) 2. (0369) 3. (1100) 4. (0080) 5. (0060)
6. (5340) 7. (0050) 8. (0960) 9. (0740) 10. (5500)

HINTS AND EXPLANATIONS

EXERCISE I (JEE MAIN)

Basics

1. Dissociation of water into ions will increase

2. Dissociation of water into ions will increase and hence P^H will decrease. Water will remain neutral.

3.
$$\begin{array}{llll} & H_2O & \rightleftharpoons H^+ & + \quad OH^- \\ & CM = \dfrac{1000}{18}M & 0 & 0 \\ \text{Equilibrium} & C(1-\alpha)M & C\alpha M & C\alpha M \end{array}$$

$$K_w = [H^+][OH^-] = C\alpha \cdot C\alpha = \alpha^2 \cdot C^2$$

$$= (1.8 \times 10^{-9})^2 \times \left(\frac{1000}{18}\right)^2$$

$$= 1.0 \times 10^{-14}$$

4. $$K_d = \frac{[H^+][OH^-]}{[H_2O]}$$

$$= \frac{\alpha^2 \cdot C}{1-\alpha} \approx \alpha^2 \cdot C = (1.8 \times 10^{-9})^2 \times \frac{1000}{18}$$

$$= 1.8 \times 10^{-16}$$

5. $[H^+] = \sqrt{K_w} \Rightarrow P^H = -\log(2.5 \times 10^{-14})^{1/2} = 6.8$

6. (a) $[D_2O] = \dfrac{d}{M} = \dfrac{1.02 \times 10^3\,g/L}{20\,g/mol} = 51\,M$

(b) $K_d = K_w/[D_2O] = \dfrac{5.1 \times 10^{-15}}{51} = 10^{-15}$

(c) $[D^+] = [OD^-] = \sqrt{K_w}$

$$\therefore\ \alpha = \frac{\sqrt{K_w}}{C} = \frac{\sqrt{5.1 \times 10^{-15}}}{51} = \frac{10^{-8}}{\sqrt{51}}$$

(d) Molality $= \dfrac{1000}{20} = 50$ m

7. $$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or, $$\ln\frac{K_2}{10^{-14}} = \frac{13.7 \times 10^3}{2}\left(\frac{1}{298} - \frac{1}{323}\right)$$

$\Rightarrow K_2 = 5.9 \times 10^{-14}$

8. $$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{10^{-14}}{2 \times 10^{-4}} = 5 \times 10^{-11}\,M$$

9. NaCl solution is neutral and at 60°C, $P^H < 7$

10. No. of H_3O^+ ions $\dfrac{1 \times 10^{-12}}{1000} \times 6.02 \times 10^{23} = 6\ 02 \times 10^8$

Strong Acids and Bases

11. $P^H = -\log(4 \times 10^{-4}) = 3.4$

12. $P^{OH} = -\log(0.005) = 2.3$

$\therefore\ P^H = 14 - 2.3 = 11.7$

13. $$M = \frac{500 \times 10^{-2}}{1000} \times 36.5 = 0.1825\text{ gm}$$

14. As the acid is very dilute, the contribution of water should be taken. Let H_2O dissociates only upto xM in presence of HCl.

$$\begin{array}{llll} & H_2O \rightleftharpoons & H^+ & + \quad OH^- \\ \text{Equilibrium} & & (x + 10^{-7})\,M & xM \end{array}$$

Now, $[H^+][OH^-] = K_w \Rightarrow (x + 10^{-7}) \cdot x = 10^{-14}$

$\Rightarrow x = 6.18 \times 10^{-8}$

$\therefore\ [H^+] = (x + 10^{-7})\,M = 1.618 \times 10^{-7}\,M$

$\Rightarrow P^H = 6.79$

15. P^H is close to 7.0 and hence, contribution of water is considered. let water dissociates only upto 'x' M is presence of CM-NaOH.

$$\begin{array}{llll} & H_2O \rightleftharpoons H^+ & + & OH^- \\ \text{Equilibrium} & xM & & (x + C)\,M \end{array}$$

Now, $x = 10^{-7.3}$ and $x + C = \dfrac{10^{-14}}{x} = 10^{-6.7}$

$\therefore$ C = $10^{-6.7} - 10^{-7.3} = 2 \times 10^{-7} - 5 \times 10^{-8}$

$= 1.5 \times 10^{-7}$ M

$\therefore$ Mass of NaOH = $(20 \times 10^{3}) \times 1.5 \times 10^{-7} \times 40$

$= 0.12$ gm

16. $$[\mathrm{H}^+]_{\text{final}} = \frac{V \times 0.1 + V \times 0.1 \times V \times 0.1}{3V}$$

$= 0.1\ N = 0.1\ M$

$\therefore$ $\mathrm{P^H} = -\log(0.1) = 1.0$

17. As all have 0.1 M concentration, $[\mathrm{KOH}]_{\text{final}} = 0.1$ M

$\therefore$ $\mathrm{P^{OH}} = -\log(0.1) = 1.0$ and $\mathrm{P^H} = 13$

18. $$n_{\mathrm{OH^-}} \text{ taken} = \frac{100 \times 0.5}{1000} = 0.05$$

$$n_{\mathrm{H^+}} \text{ taken} = \frac{250 \times 0.2}{1000} = 0.05$$

Hence, resulting solution is neutral $\mathrm{P^H} = -\log(10^{-6})$

$= 6.0$

19. $$n_{\text{eq}} \text{ of } \mathrm{H^+} = \frac{25 \times 0.1}{1000} \times 1 + \frac{25 \times 0.1}{1000} \times 2 = 7.5 \times 10^{-3}$$

$$n_{\text{eq}} \text{ of } \mathrm{OH^-} = \frac{50 \times 0.1}{1000} = 5 \times 10^{-3}$$

$\therefore$ n_{eq} of $\mathrm{H^+}$ left $= 2.5 \times 10^{-3}$

$$\Rightarrow [\mathrm{H^+}] = \frac{2.5 \times 10^{-3}}{100} \times 1000 = 0.025 \text{ M}$$

$\therefore$ $\mathrm{P^H} = -\log(0.025) = 1.6 \Rightarrow \mathrm{P^{OH}} = 14 - 1.6 = 12.4$

20. On neglecting the contribution of water, $[\mathrm{H^+}] = 10^{-6}$ M

When contribution of water is considered,

$$\begin{array}{lccc} & \mathrm{H_2O} \rightleftharpoons & \mathrm{H^+} \quad + & \mathrm{OH^-} \\ \text{Equilibrium} & & (x + 10^{-6})\text{ M} & x\text{M} \end{array}$$

Now, $(x + 10^{-6}) \cdot x = 10^{-14} \Rightarrow x = 9.9 \times 10^{-9}$

$\therefore$ $[\mathrm{H^+}]_2 = (x + 10^{-6})$ M $= 1.0099 \times 10^{-6}$ M

$$\text{Now, \% error in}[\mathrm{H^+}] = \frac{[\mathrm{H^+}]_2 - [\mathrm{H^+}]}{[\mathrm{H^+}]_2}[\mathrm{H^+}] \times 100\%$$

$= 0.98\%$

Weak Acids and Bases

21. Smaller $\mathrm{P^{Ka}}$, stronger acid, greater $[\mathrm{H^+}]$

22. $$\begin{array}{lccc} & \mathrm{CH_3COOH} \rightleftharpoons & \mathrm{CH_3COO^-} \,+ & \mathrm{H^+} \\ & 1\text{M} & 0 & 0.1\text{ M} \\ \text{Equilibrium} & 1 - x & x & 0.1 + x \\ & \simeq 1\text{M} & & \simeq 0.1\text{M} \end{array}$$

$$\text{Now, } K_a = \frac{[\mathrm{CH_3COO^-}][\mathrm{H^+}]}{[\mathrm{CH_3COOH}]} \Rightarrow 2 \times 10^{-5} = \frac{x \times 0.1}{1}$$

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

23. $$\frac{[\mathrm{H^+}]_{\mathrm{HCOOH}}}{[\mathrm{H^+}]_{\mathrm{CH_3COOH}}} = \frac{(\sqrt{K_a \cdot C})_{\mathrm{HCOOH}}}{(\sqrt{K_a \cdot C})_{\mathrm{CH_3COOH}}}$$

$$= \sqrt{\frac{1.77 \times 10^{-4}}{1.75 \times 10^{-5}}} = 3.18$$

24. $$[\mathrm{H^+}]_{\mathrm{CH_3COOH}} = [\mathrm{H^+}]_{\mathrm{CH_2(CN)COOH}}$$

$$\text{or, } \sqrt{0.000018 \times \frac{n}{V_1}} = \sqrt{0.0036 \times \frac{n}{V_2}} \Rightarrow \frac{V_1}{V_2} = \frac{1}{200}$$

25. $\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$

low $\mathrm{P^H} \Rightarrow$ High $[\mathrm{H^+}]$

$\Rightarrow$ Equilibrium in backward direction

High $\mathrm{P^H} \Rightarrow$ low $[\mathrm{H^+}]$

$\Rightarrow$ Equilibrium in forward direction

26. $$\text{Conc. of aspirin} = \frac{2 \times 0.36/180}{0.250} = 0.016\ M$$

$$\text{Now, } [\mathrm{H^+}] = \sqrt{K_a \cdot C} = \sqrt{4 \times 10^{-9} \times 0.016}$$

$= 8 \times 10^{-6}$ M

$\therefore$ $\mathrm{P^H} = 5.1$

27. $$\alpha = \sqrt{\frac{K}{C}} = \sqrt{\frac{K}{1/V}} = \sqrt{K \cdot V}$$

28. $$\mathrm{P^H_{CH_3COOH}} = \mathrm{P^{OH}_{NH_3}} = 3.2 \Rightarrow \mathrm{P^H_{NH_3}} = 14 - 3.2 = 10.8$$

29. $$(\sqrt{K_a \cdot C})_{\mathrm{HA}} = [\mathrm{H^+}]_{\mathrm{HCl}}$$

$$\text{or, } \sqrt{K_a \times 0.2} = 4 \times 10^{-4} \Rightarrow K_a = 8 \times 10^{-7}$$

$$\therefore K_b \text{ of } A^- = \frac{10^{-14}}{8 \times 10^{-7}} = 1.25 \times 10^{-8}$$

30. $P^{K_b} = 10.3 = -\log K_b \Rightarrow K_b = 5 \times 10^{-11}$

$$\therefore\ K_{a(\mathrm{HF})} = \frac{K_w}{K_b(F^-)} = \frac{10^{-14}}{5\times10^{-11}} = 2\times10^{-4}$$

31. $[\mathrm{C_5H_{11}COOH}] = \dfrac{11.6}{116} = 0.1\,\mathrm{M}$

Now, $[\mathrm{H^+}] = \sqrt{K_a \cdot C} \Rightarrow 10^{-3} = \sqrt{K_a \times 0.1}$

$\Rightarrow K_a = 10^{-5}$

32. $\alpha = \sqrt{\dfrac{K_a}{C}} = \sqrt{\dfrac{0.00024}{0.002}} = 0.346 \text{ or } 34.6\%$

Hence, α can not be neglected.

$$K_a = \frac{\alpha^2 \cdot C}{1-ga} \Rightarrow 0.00024 = \frac{\alpha^2 \times 0.002}{1-\alpha} \Rightarrow \alpha = 0.29$$

Now, $[\mathrm{H^+}] = C\alpha = 0.002 \times 0.29 = 5.8 \times 10^{-4}$

33. $[\mathrm{H^+}] = \sqrt{K_a \cdot C} = \sqrt{2\times10^{-12} \times 0.02} = 2\times10^{-7}\ \mathrm{M}$

As $[\mathrm{H^+}]$ is very small, contribution of $\mathrm{H^+}$ from water must be considered.

$$\begin{array}{lccccc} & \mathrm{HA} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{A^-} \\ \text{Equilibrium} & (0.02-x)\mathrm{M} & & (x+y)\,\mathrm{M} & & x\mathrm{M} \end{array}$$

$$\begin{array}{lccccc} & \mathrm{H_2O} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{OH^-} \\ \text{Equilibrium} & & & (x+y)\,\mathrm{M} & & y\mathrm{M} \end{array}$$

Now, $K_a = \dfrac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$

$$\Rightarrow 2\times10^{-12} = \frac{(x+y)\cdot x}{(0.02-x)} \approx \frac{(x+y)\cdot x}{0.02}$$

or, $4\times10^{-14} = (x+y)\cdot x$ (1)

and $K_w = [\mathrm{H^+}][\mathrm{OH^-}] \Rightarrow 10^{-14} = (x+y)\cdot y$ (2)

From (1) + (2), $(x+y) = \sqrt{5\times10^{-14}}\ \mathrm{M} = [\mathrm{H^+}]$

$\therefore\ \mathrm{P^H} = -\log(5\times10^{-14})^{1/2} = 6.65$

34. $\alpha_2 = 2\times\alpha_1 \Rightarrow \sqrt{\dfrac{K_a}{n}\times V_2} = 2\times\sqrt{\dfrac{K_a}{n}\times V_1}$

$\Rightarrow V_2 = 4 \times V_1 = 4 \times 300 = 1200$ ml

$\therefore\ V_{\text{water added}} = 1200 - 300 = 900$ ml

35.

$$\begin{array}{lccccc} & \mathrm{HCN} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{CN^-} \\ \text{Equilibrium} & (0.2-x)\mathrm{M} & & (x+y)\mathrm{M} & & x\mathrm{M} \end{array}$$

$$9.6\times10^{-10} = \frac{(x+y)\cdot x}{(0.2-x)} \approx \frac{y\cdot x}{0.2}$$

$$\begin{array}{lccccc} & \mathrm{HCOOH} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{HCOO^-} \\ \text{Equilibrium} & (0.1-y)\mathrm{M} & & (x+y)\mathrm{M} & & y\mathrm{M} \end{array}$$

$$2.56\times10^{-5} = \frac{(x+y)\cdot y}{(0.1-y)} \approx \frac{y\cdot y}{0.1}$$

$\therefore\ y = 1.6 \times 10^{-3}$ and $x = 1.2 \times 10^{-7}$

Option (d) may be answered without solving because solution is acidic.

Polyprotic Acids and Bases

36.

$$\begin{array}{lccccc} & \mathrm{Y(OH)_2} & \rightleftharpoons & \mathrm{Y(OH)^+} & + & \mathrm{OH^-} \\ & 4\times10^{-3}\,\mathrm{M} & & 0 & & 0 \\ \text{Final} & 0 & & 4\times10^{-3}\,\mathrm{M} & & 4\times10^{-3}\,\mathrm{M} \end{array}$$

$$\begin{array}{ccccc} \mathrm{Y(OH)^+} & \rightleftharpoons & \mathrm{Y^{2+}} & + & \mathrm{OH^-} \\ 4\times10^{-3} - 2\times10^{-3} & & 2\times10^{-3}\,\mathrm{M} & & 4\times10^{-3} + 2\times10^{-3} \\ = 2\times10^{-3}\,\mathrm{M} & & & & = 6\times10^{-3}\,\mathrm{M} \end{array}$$

$\therefore\ \mathrm{P^{OH}} = -\log(6\times10^{-3}) = 2.22 \Rightarrow \mathrm{P^H} = 11.78$

37. All are correct answers, but if only one is to select, then (a), because it have more species.

38.

$$\begin{array}{lccccc} & \mathrm{H_2CO_3} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{HCO_3^-} \\ & \dfrac{0.1}{100}\times1000\,\mathrm{M} & & 0 & & 0 \\ \text{Equilibrium} & (1-x)\,\mathrm{M} & & (x+y)\,\mathrm{M} & & (x-y)\,\mathrm{M} \end{array}$$

$$\begin{array}{lccccc} & \mathrm{HCO_3^-} & \rightleftharpoons & \mathrm{H^+} & + & \mathrm{CO^2} \\ \text{Equilibrium} & (x-y)\,\mathrm{M} & & (x+y)\,\mathrm{M} & & y\mathrm{M} \end{array}$$

Now, $K_{a_1} = \dfrac{[\mathrm{H^+}][\mathrm{HCO_3^-}]}{[\mathrm{H_2CO_3}]}$

$$\Rightarrow 4\times10^{-6} = \frac{(x+y)\cdot(x-y)}{(1-x)} \approx \frac{x\cdot x}{1}$$

$\therefore\ x = 2 \times 10^{-3}$

and $K_{a_2} = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

$\Rightarrow\ 5\times10^{-11} = \dfrac{(x+y)\cdot y}{(x-y)} \approx \dfrac{x\cdot y}{x}$

$\therefore\ y = 5 \times 10^{-11}$

$\therefore\ [H^+] = (x + y) \approx x = 2 \times 10^{-3}$ M

$[HCO_3^-] = (x - y) \approx x = 2 \times 10^{-3}$ M

$[CO_3^-] = y = 5 \times 10^{-11}$ M

$[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{10^{-14}}{2\times10^{-3}} = 5\times10^{-12}$ M

39. For. P^H, 2nd dissociation may be neglected.

$[H^+] = \sqrt{K_{a_1}\cdot C} = \sqrt{9\times10^{-5}\times0.1} = 3\times10^{-3}$M

$\therefore\ P^H = -\log(3 \times 10^{-3}) = 2.52$

40. For P^{OH}, 2nd protonation may be neglected

$[OH^-] = \sqrt{K_{b_1}\cdot C} = \sqrt{3.6\times10^{-6}\times0.1} = 6\times10^{-4}$M

$\therefore\ P^{OH} = -\log(6 \times 10^{-4}) = 3.22 \Rightarrow P^H = 10.78$

Buffer Solutions

41. $P^{Ka} = 5 \Rightarrow P^H$ range = 4 to 6

42. For maximum buffer capacity, $P^H = P^{Ka}$

43. $P^H = P^{K_a(NH_4^+)} + \log\dfrac{[NH_3]_0}{[NH_4^+]_0}$

$= 9.26 + \log\dfrac{0.02}{0.01\times2} = 9.26$

44. Sodium acetate is basic in nature.

45.

$$\begin{array}{lcccc} & CH_3COOH & + \ OH^- & \rightleftharpoons & CH_3COO^- \ + \ H_2O \\ & a \text{ mole} & x \text{ mole} & & 0 \\ \text{Final} & (a-x)\text{mole} & 0 & & x \text{ mole} \end{array}$$

$P^H = P^{K_a} + \log\dfrac{x}{a-x}$

For $\dfrac{1}{4}th$ neutralization,

$P_1^H = P^{K_a} + \log\dfrac{a/4}{a-a/4} = P^{K_a} + \log\dfrac{1}{3}$

For $\dfrac{3}{4}th$ neutralization,

$P_2^H = P^{K_a} + \log\dfrac{3a/4}{a-3a/4} = P^{K_a} + \log 3$

$\therefore\ \Delta P^H = P_2^H - P_1^H = 2\log 3$

46.

$$\begin{array}{lcccc} & CH_3NH_2 & + \ H^+ & \rightleftharpoons & CH_3NH_3^+ \\ & 0.1 \text{ mole} & 0.08 \text{ mole} & & 0 \\ \text{Final} & 0.02 \text{ mole} & 0 & & 0.08 \text{ mole} \end{array}$$

$P^{OH} = P^{K_b} + \log\dfrac{[CH_3NH_3^+]_0}{[CH_3NH_2]_0}$

$= -\log(5\times10^{-4}) + \log\dfrac{0.08}{0.02}$

$\therefore\ [OH^-] = \dfrac{5\times10^{-4}}{4} \Rightarrow [H^+] = \dfrac{10^{-14}}{[OH^-]} = 8\times10^{-11}$M

47. On adding acid, P^H should decrease slightly. As none of the option is slightly less than 4.0, answer is 4.0

48. $[OH^-] = \dfrac{K_6\cdot[\text{Pyridine}]}{[\text{Pyridinium ion}]} = \dfrac{1.5\times10^{-9}\times0.2}{\left(\dfrac{0.15}{500}\times1000\right)}$

$= 1\times10^{-9}$M

$\therefore\ P^{OH} = -\log(10^{-9}) = 9.0 \Rightarrow P^H = 5.0$

49. $P^H = P^{K_a} + \log\dfrac{[CN^-]_0}{[HCN]_0}$

$= -\log(2.5\times10^{-10}) + \log\dfrac{80\times0.4/100}{20\times0.8/100}$

$= 9.9$

50.

$$\begin{array}{lcccc} & \underset{\text{(Imidazole)}}{B} & + \ H^+ & \rightleftharpoons & BH^+ \\ & \dfrac{V\times0.02}{120}\text{M} & \dfrac{(120-V)\times0.02}{120}\text{M} & & 0 \\ \text{Final} & \dfrac{(2V-120)\times0.02}{120}\text{M} & 0 & & \dfrac{(120-V)\times0.02}{120}\text{M} \end{array}$$

$P^{OH} = P^{K_b} + \log\dfrac{[BH^+]_0}{[B]_0} \Rightarrow 7 = 7 + \log\dfrac{120-V}{2V-120}$

$\Rightarrow V = 80$

Hydrolysis of Salts

51. Stronger the acid, smaller is P^H.

52. Potassium propionate is the salt of strong base and weak acid and hence.

$$P^H = 7 + \frac{1}{2}(P^{K_a} + \log C)$$

$$\text{or, } 8 = 7 + \frac{1}{2}(P^{k_a} + \log 0.001)$$

$$\Rightarrow P^{K_a} = 5 \Rightarrow K_a = 10^{-5}$$

53. The order of acidic strength is HCl > H_2CO_3 > HCN

54. NaCl does not hydrolysis but CH_3COONH_4 undergoes cationic as well as anionic hydrolyisis.

55. $\text{Point A: Buffer } H_2A + HA^-;\ P^H = P^{K_a} + \log\frac{[HA^-]_0}{[H_2A]_0}$

Point B: 1st equivalent point HA^-;

$$P^H = \frac{1}{2}(P^{K_{a1}} + P^{K_{a2}})$$

$\text{Point C: Buffer } HA^- + A^{2-};\ P^H = P^{K_{a2}} + \log\frac{[A^{2-}]_0}{[HA^-]_0}$

Point D: 2nd equivalent point, A^{2-};

$$P^H = 7 + \frac{1}{2}(P^{K_{a1}} + \log C)$$

56. $B^+ + H_2O \rightleftharpoons BOH + H^+$; ΔH = positive

57. Point B : Buffer HA + A^-

58. NaCl = Neutral, NH_4Cl = Acidic, NaCN = Basic, HCl = Acid

59. CH_3COONa = Basic, CH_3COOH = Weak acid, CH_3COONH_4 = Neutral, NaOH = strong base, HCl = strong acid

60. $$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4} \text{ or } 0.01\%$$

61. $$P^H = 7 + \frac{1}{2}(P^{K_a} - P^{K_b}) = 7 + \frac{1}{2}(3.8 - 4.8) = 6.5$$

62. P^{K_b} of $CN^- = 4.70 \Rightarrow P^{K_a}$ of HCN = 9.30

$$\text{Now, } P^H = 7 + \frac{1}{2}(P^{K_a} + \log C)$$

$$= 7 + \frac{1}{2}(9.30 + \log 0.5) = 11.5$$

63. Equal volumes of both will consume and hence,

$$[CH_3COONa] = \frac{0.01}{2} = 0.005$$

$$\text{Now, } P^H = 7 + \frac{1}{2}(P^{K_a} + \log C)$$

$$= 7 + \frac{1}{2}(4.7 + \log 0.005) = 8.2$$

64.
$$\begin{array}{lccc} & Zn^{2+} + H_2O & \rightleftharpoons\ Zn(OH)^+ & + H^+ ; \\ \text{Equilibrium} & (0.001 - x)M & xM & xM \end{array}$$

$$K_a = 2 \times 10^{-10}$$

$$\text{Now, } 2 \times 10^{-10} = \frac{x \cdot x}{(0.001 - x)} \approx \frac{x^2}{0.001}$$

$$\Rightarrow x = \sqrt{2 \times 10^{-13}}$$

$$\therefore P^H = -\log x = -\log(2 \times 10^{-13})^{1/2} = 6.35$$

65. Ammonium chloride is acidic in nature.

Indicators

66. $$P^{K_{1n}} = -\log K_{1n} = -\log(5 \times 10^{-6}) = 5.3$$

$$\text{Now, } P^H = P^{K_{1n}} + \log\frac{[1n^-]}{[HIn]}$$

$$\text{Only for acidic form, } P^H \le \left(5.3 + \log\frac{1}{20}\right) = 4.0$$

$$\text{Only for basic form, } P^H \ge (5.3 + \log 40) = 6.9$$

67. $$P^H = P^{K_{In}} + \log\frac{[In^-]}{[HIn]}$$

$$\Rightarrow 2 = P^{k_{In}} + \log\frac{C}{C} \Rightarrow P^{K_{In}} = 2$$

$$\text{Now, } P^H = P^{K_{In}} + \log\frac{[In^-]}{[HIn]}$$

$$\Rightarrow -\log(4 \times 10^{-3}) = 2 + \log\frac{100 - x}{x}$$

$$\therefore x = 71.4$$

68. Yellow colour with methyl red means $P^H > 6.2$

Yellow colour with phenol red means $P^H < 6.4$

69. For complete colour change, P^H should change from , $P^H \leq \left(P^{k_{\text{In}}} + \log\frac{1}{10}\right)$ to $P^H \geq \left(P^{k_{\text{In}}} + \log 10\right)$ and hence, minimum P^H change should be of 2.0 units.

70.

$$\begin{array}{lcccc} & X^- & + & H^+ & \rightleftharpoons & HX \\ & \frac{10\times0.1}{20}M & & \frac{10\times0.1}{20}M & & 0 \\ \text{Final} & 0 & & 0 & & 0.05\text{ M} \end{array}$$

(10 ml HCl solution is needed for equivalent point)

At equivalent point $[H^+] = \sqrt{K_a \times C}$

$= \sqrt{10^{-6} \times 0.05}$

$\therefore P^H = -\log(5 \times 10^{-8})^{1/2} = 3.65$

Solubility

71. $X_aY_b \rightleftharpoons aX^{b+} \quad + \quad bY^{a-}$

$\qquad a \text{ mole} \qquad b \text{ mole}$

$\therefore$ Moles of $Y^{a-} = \frac{b}{a} \times$ moles of X^{b+}

72. $A_3B_2(s) \rightleftharpoons 3A^{2+} + 2B^{3-}$ $\quad$ (Solubility $= \frac{x}{M}$ mol/l)

$\qquad \frac{3x}{M} \qquad \frac{3x}{M}$

$$K_{sp} = [A^{2+}]^3[B^{3-}]^2 = \left(\frac{3x}{M}\right)^3 \cdot \left(\frac{2x}{M}\right)^2 = \frac{108x^5}{M^5}$$

$$\therefore \frac{[B^{3-}]}{K_{sp}} = \frac{2x/M}{108x^5/M^5} = \frac{M^4}{54\,x^4}$$

73. $[OH^-] = 0.1 \times \frac{50}{100} = 0.05\text{ M}$

$$\therefore [Zn^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{10^{-14}}{(0.05)^2} = 4 \times 10^{-12}\text{ M}$$

74. Ag^+ form complex with NH_3

75. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$;

$K_{sp} = [Fe^{3+}][OH^-]^3$

Now, for given reaction,

$Fe(OH)_3(s) + 3H_3O^+ \rightleftharpoons Fe^{3+} + 6H_2O$

$$K_{eq} = \frac{[Fe^{3+}]}{[H_3O^+]^3} \times \frac{[OH^-]^3}{[OH^-]^3} = \frac{K_{sp}}{K_w^3}$$

$$= \frac{4 \times 10^{-38}}{(10^{-14})^3} = 4 \times 10^4$$

76. (a) $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$; $K_1 = 10^{-10}$

(b) $AgCl(s) + Br^- \rightleftharpoons AgBr(s) + Cl^-$; $K_2 = 200$

(c) $2\,AgBr(s) + S^{2-} \rightleftharpoons Ag_2S(s) + 2Br^-$; $K_3 = 1.6 \times 10^{24}$

From 2(a) – 2(b) – 2(c); $Ag_2S(s) \rightleftharpoons 2Ag^+ + S^{2-}$;

$$K = \frac{(10^{-10})^2}{(200)^2 \times 1.6 \times 10^{24}} = 1.5625 \times 10^{-49}$$

77. Adding both reactions, $K_{sp} = 1.3 \times 10^{-34} \times 38.5$

$\approx 5 \times 10^{-33}$

78. $K_{\text{formation}} = K_1 \cdot K_2 \cdot K_3 = 125 \times 20 \times 1 = 2500$

$$\therefore K_{\text{dissociation}} = \frac{1}{K_{\text{formation}}} = 4 \times 10^{-4}$$

79. $BaF_2(s) \rightleftharpoons Ba^{2+} \quad + \quad 2F^-$

$\qquad (S + C)\text{ M} \qquad 2S\text{ M}$

where S = solubility of BaF_2 in CM-$Be(NO_3)_2$ solution

Hence, Solubility, $S = \frac{[F^-]}{2}$

80. $CaF_2(s) \rightleftharpoons Ca^{2+} \quad + \quad 2F^-$

$\qquad S_1M \qquad 2S_1M$

Now, $K_{sp} = S_1 \cdot (2S_1)^2$

$$\Rightarrow S_1 = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2 \times 10^{-11}}{4}\right)^{1/3} = 2 \times 10^{-4}\text{ M}$$

Now, in KF solution,

$$S_2 = \frac{K_{sp}}{[F^-]^2} = \frac{3.2 \times 10^{-11}}{(4 \times 10^{-3})^2} = 2 \times 10^{-6}\text{ M}$$

Now, $\frac{S_2}{S_1} = \frac{2 \times 10^{-6}}{2 \times 10^{-4}} = \frac{1}{100}$

81. $A_2X_3(s) \rightleftharpoons 2A^{3+} + 3X^{2-}$

$\qquad\qquad 2y\text{M} \quad 3y\text{M}$

$K_{sp} = [A^{3+}]^2 [X^{2-}]^3 = (2y)^2 \cdot (3y)^3 = 108y^5$

82. $A_pB_q(s) \rightleftharpoons pA^{2+} + qB^{P-}$

$\qquad\qquad p \cdot s\ \text{M} \quad q \cdot s\ \text{M}$

Solubility product, $L_s = (p \cdot s)^p \cdot (q \cdot s)^q$

$= p^p \cdot q^q \cdot s^{(p+q)}$

83. $K_f = K_{f_1} \cdot K_{f_2} = 1.6\times10^3 \times 6.8\times10^3 = 1.08\times10^7$

84. For MX : Solubility $= \sqrt{K_{sp}} = \sqrt{4\times10^{-8}}$

$= 2\times10^{-4}\,\text{M}$

For MX_2 : Solubility $= \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2\times10^{-14}}{4}\right)^{1/3}$

$= 2\times10^{-5}\,\text{M}$

For M_3X : Solubility $= \left(\frac{K_{sp}}{27}\right)^{1/4} = \left(\frac{2.7\times10^{-15}}{27}\right)^{1/3}$

$= 1\times10^{-4}\,\text{M}$

$\therefore$ Order of solubility $= MX_2 < M_3X < MX$

85. $S = \frac{0.001435}{143.5} = 10^{-5}\,\text{M}$

$\therefore$ Solubility product, $K_{sp} = S^2 = 10^{-10}$

86. Solubility, $S = \frac{0.0744/372}{100/1000} = 2\times10^{-3}$ M

$Li_3Na_3(AlF_6)_2\ (s) \rightleftharpoons 3Li^+ + 3Na^+ + 2AlF_6^{3-}$

$\qquad\qquad 3S \quad 3S \quad 2S$

$K_{sp} = [Li+]^3\,[Na^+]^3\,[AlF_6^{3-}]^2 = (3S)^3 \cdot (3S)^3 \cdot (2S)^2$

$= 7.46496 \times 10^{-19}$

87. For CaF_2 : $K_{sp} = 4S^3$

$\Rightarrow S = \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{1.08\times10^{-10}}{4}\right)^{1/3}$

$= 3 \times 10^{-4}$ M

$\therefore$ Mass of CaF_2 needed $= \left(\frac{500\times3\times10^{-4}}{1000}\right)\times78$

$= 1.17 \times 10^{-2}$ gm

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

$\qquad\qquad SM \quad 2SM$

Now, $K_{sp} = 4S^3 \Rightarrow S = \left(\frac{9\times10^{-12}}{4}\right)^{1/3}$ M

Now, $[OH^-] = 2S = 2\times\left(\frac{9\times10^{-12}}{4}\right)^{1/3}$

$= (18\times10^{-12})^{1/3}\text{M}$

$\therefore P^{OH} = -\log(18 \times 10^{-12})^{1/3} = 3.58 \Rightarrow P^H = 10.42$

89. $Zn(OH)_2(s) + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+} + 2OH^-$

$\qquad\qquad 1\ \text{M} \qquad 0 \qquad 0$

Equilibrium $(1 - 4S)$M $\quad$ SM $\quad$ 2SM

$$K_{eq} = \frac{[Zn[NH_3]_4^{2+}[OH^-]^2}{[NH_3]^4} \times \frac{[Zn^{2+}]}{[Zn^{2+}]}$$

$= K_{sp} \cdot K_{stab} = 1.6 \times 10^{-17} \times 1.6 \times 10^{10} = 2.56 \times 10^{-7}$

Now, $2.56\times10^{-7} = \frac{S\times(2S)^2}{(1-4S)^4} \approx \frac{4S^3}{1}$

$\Rightarrow S = 4 \times 10^{-3}$M

90. $AgCl(s) + Cl^- \rightleftharpoons AgCl_2^-$

$\qquad\qquad a\text{M} \qquad 0$

Final $\left(a - \frac{0.01}{100}\right)$M $\qquad 10^{-4}$ M

Now, $K_{eq} = \frac{[AgCl_2^-]}{[Cl^-]} \times \frac{[Ag^+][Cl^-]}{[Ag^+][Cl^-]} = {}_{sp} \cdot K_f$

$= 2\times10^{-10} \times 2.5\times10^5 = 5\times10^{-5}$

$\therefore 5\times10^{-5} = \frac{10^{-4}}{(a-10^{-4})} \Rightarrow a \approx 2\text{M}$

Hence, the minimum mass of NaCl added = $(100 \times 2) \times 58.5 = 11700$ gm

91. $Ag_2CO_3(s) + C_2O_4^{2-} \rightleftharpoons Ag_2C_2O_4(s) \quad CO_3^2$

Initial $\quad \frac{0.15}{500}\times1000 \qquad\qquad 0$

$\qquad = 0.3$ M

Final $\quad 0.3 - x \qquad\qquad x = \frac{0.035}{500}\times1000$

$\qquad = 0.23$ M $\qquad\qquad = 0.07$ M

Now, $K_{eq} = \dfrac{[CO_3^{2-}]}{[C_2O_4^{2-}]} \times \dfrac{[Ag^+]^2}{[Ag^+]^2} = \dfrac{K_{sp}(Ag_2CO_3)}{K_{sp}(Ag_2C_2O_4)}$

or, $\dfrac{0.07}{0.23} = \dfrac{K_{sp}(Ag_2CO_3)}{2.3 \times 10^{-11}}$

$\Rightarrow K_{sp}(Ag_2CO_3) = 7 \times 10^{-12}$

92. $Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$;

$$K = \frac{1}{4 \times 10^{-19}} = 2.5 \times 10^{18}$$

$$\begin{array}{lcccc} & 0.03\text{ M} & 0.1\text{ M} & 0 \\ 100\% & 0 & (0.1 - 0.06)\text{M} & 0.03\text{ M} \\ & & = 0.04\text{ M} & \\ \text{Eqn.} & x\text{M} & (0.04 + 2x)\text{M} & (0.03 - x)\text{M} \\ & & \approx 0.04\text{ M} & \approx 0.03\text{ M} \end{array}$$

Now, $2.5 \times 10^{18} = \dfrac{0.03}{x \times (0.04)^2}$

$\Rightarrow [Ag^+] = x = 7.5 \times 10^{-18}$ M

93. $2AgCl(s) + CO_3^{2-} \rightleftharpoons Ag_2CO_3(s) + 2Cl^-$

$$\begin{array}{lcc} & 2.0\text{ M} & 0 \\ \text{Equ.} & (2 - x)\text{M} & 2x = \dfrac{0.00355}{35.5} \\ & \approx 2\text{M} & \therefore x = 5 \times 10^{-5} \end{array}$$

Now, $K_{eq} = \dfrac{[Cl^-]^2}{[CO_3^{2-}]} \times \dfrac{[Ag^+]^2}{[Ag^+]^2} = \dfrac{K_{sp}^2(AgCl)}{K_{sp}(Ag_2CO_3)}$

or, $\dfrac{(5 \times 10^{-5})^2}{2} = \dfrac{K_{sp}^2(AgCl)}{8 \times 10^{-12}}$

$\Rightarrow K_{sp}(AgCl) = 1 \times 10^{-10}$

94. $AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$

$$\begin{array}{lccc} & 1.0\text{ M} & 0 & 0 \\ \text{Eqn.} & (1 - 2x)\text{M} & x\text{M} & x\text{M} \end{array}$$

Now, $K_{eq} = \dfrac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} \times \dfrac{[Ag^+]}{[Ag^+]} = \dfrac{K_{sp}}{K_c}$

$= \dfrac{1.8 \times 10^{-10}}{7.2 \times 10^{-8}} = \dfrac{1}{400}$

Now, $\dfrac{x \cdot x}{(1 - 2x)^2} = \dfrac{1}{400} \Rightarrow x = \dfrac{1}{22} = 0.045$M

95. For saturated solution of $Pb(OH)_2$ in water,

$K_{sp} = 4.\ S^3$

$= 4 \times (6 \times 10^{-6})^3 = 8.64 \times 10^{-16}$

Now, for the given buffer, $[OH^-] = 10^{-6}$ M

$\therefore$ Solubility, $S = [Pb^{2+}] = \dfrac{K_{sp}}{[OH^-]^2} = \dfrac{8.64 \times 10^{-16}}{(10^{-6})^2}$

$= 8.64 \times 10^{-4}$ M

96. $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$; $K_{eq} = 6.8 \times 10^{-8}$

$$\begin{array}{lccc} & 0.2\text{ M} & 0 & 0 \\ \text{Eqn} & 0.2 - x & x\text{M} & 2x\text{M} \\ & = 0.2\text{ M} & & \end{array}$$

Now, $6.8 \times 10^{-8} = \dfrac{x \times (2x)^2}{0.2}$

$\Rightarrow x = 1.5 \times 10^{-3}$ M $= [Ag^+]$

97. $Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$;

$K_{eq} = 1.25 \times 10^{12}$

$$\begin{array}{lccc} & 0.0125\text{ M} & 0.25\text{ M} & 0 \\ 100\% & 0 & 0.25 - 0.05 & 0.0125\text{ M} \\ & & = 0.20\text{ M} & \\ \text{Equ.} & x\text{M} & 0.2 + 4x & 0.0125 - x \\ & & \approx 0.2\text{ M} & \approx 0.0125\text{ M} \end{array}$$

Now, $1.25 \times 10^{12} = \dfrac{0.0125}{x \times (0.2)^4} \Rightarrow x = 6.25 \times 10^{-12}$

98. $AgSCN(s) \rightleftharpoons Ag^+ + SCN^-$

$(x + y)$M $\quad x$M

$AgBr(s) \rightleftharpoons Ag^+ + Br^-$

$(x + y)$M $\quad y$M

Now, $(x + y) \cdot x = 1 \times 10^{-12}$ (1) $\quad x = 9.09 \times 10^{-7}$

$(x + y) \cdot y = 2.1 \times 10^{-13}$ (2) $\quad y = 1.909 \times 10^{-7}$

99. $AgCN(s) \rightleftharpoons Ag^+ + CN^-$; $K_{sp} = 1.2 \times 10^{-16}$

$CN^- + H^+ \rightleftharpoons HCN$; $k_{eq} = \dfrac{1}{K_a} = \dfrac{1}{4.8 \times 10^{-10}}$

Adding both reactions,

$AgCN(s) + H^+ \rightleftharpoons Ag^+ + HCN$;

$K_{eq} = \dfrac{K_{sp}}{K_a} = \dfrac{1}{4 \times 10^6}$

$10^{-3} \quad$ SM $\quad$ SM

Now, $\dfrac{1}{4 \times 10^6} = \dfrac{S \cdot S}{10^{-3}} \Rightarrow 1.58 \times 10^{-5}$ M

100. $PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^-$

$\qquad\qquad S_1M \quad 2S_1M$

When it is 80% ionized, then

$PbCl_2(s) \rightleftharpoons Pb^{2+} + 2Cl^-$

$\qquad\qquad 0.8\,S_2\,M \quad 1.6\,S_2$

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

or, $S_1 \times (2S_1)^2 = (0.8S_2) \times (1.6S_2)^2 \Rightarrow S_1 = 0.512S_2$

$\Rightarrow S_2 > S_1$

Precipitation

101. $[OH^-]_{min}$ to start ppt. of $Mg(OH)_2 = \sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}}$

$$= \sqrt{\frac{4\times10^{-11}}{x}}$$

For $Cd(OH)_2$, $[OH^-]_{min} = \sqrt{\dfrac{8\times10^{-6}}{x}}$

For $Al(OH)_3$, $[OH^-]_{min} = \left(\dfrac{8.5\times10^{-23}}{x}\right)^{1/3}$

For $Zn(OH)_2$, $[OH^-]_{min} = \sqrt{\left(\dfrac{1.8\times10^{-14}}{x}\right)}$

Considering significant concentration of metal ion (x is not extremely small), $[OH^-]$ needed is minimum for Al^{3+} and hence, it will precipitate first.

102. $[Ag^+]_{min}$ for the start of precipitation of

$AgBr = \dfrac{K_{sp}(AgBr)}{[Br^-]} = \dfrac{5\times10^{-13}}{0.1} = 5\times10^{-12}\ M$

For Cl^- : $[Ag^+]_{min} = \dfrac{1.8\times10^{-10}}{0.1} = 1.8\times10^{-9}M$

For CO_3^{2-} : $[Ag^+]_{min} = \sqrt{\dfrac{8.1\times10^{-12}}{0.1}} = 9\times10^{-6}M$

For AsO_4^{3-} : $[Ag^+]_{min} = \left(\dfrac{1\times10^{-22}}{0.1}\right)^{1/3} = 1\times10^{-7}M$

As [Ag+] needed is minimum for AgBr, it will precipitate first.

103. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$

To prevent ppt (backward reaction),

$Q \le K_{sp}$

or, $[Ag^+]^2 \times 3 \times 10^{-4} \le 1.2 \times 10^{-11}$

$\therefore [Ag^+]_{max} = 2 \times 10^{-4}$ M

104.

	Ag^+	$+$	$2NH_3$	$\rightleftharpoons$	$Ag(NH_3)_2^+$; $K_{stab} = 1.6 \times 10^7$
	0.1 M		1M		0
100%	0		(1 – 0.2) M = 0.8 M		0.1 M
Equ.	xM		$0.8 + 2x$ ≈ 0.8 M		$0.1 - x$ ≈ 0.1 M

Now, $1.6 \times 10^7 = \dfrac{0.1}{x\times(0.8)^2} \Rightarrow x = 9.76 \times 10^{-9}$ M

Now, on adding NaCl, $Q = [Ag^+][Cl^-]$

$= 9.76 \times 10^{-9} \times 0.01$

$= 9.76 \times 10^{-11} < K_{sp}$

Hence, no precipitation of AgCl.

105.

	Ag^+	$+$	Cl^-	$\rightleftharpoons$	$AgCl(s)$; $K_{eq} = \dfrac{1}{K_{sp}} = \dfrac{1}{2\times10^{-10}}$
	$\dfrac{500\times2.5\times10^{-5}}{2500}$ $= 5 \times 10^{-6}$ M		$\dfrac{2000\times5\times10^{-2}}{2500}$ $= 4 \times 10^{-2}$ M		
100%	0		$(4 \times 10^{-2} - 5 \times 10^{-6})$ $\approx 4 \times 10^{-2}$ M		
Equ.	xM		$(4 \times 10^{-2} + x) \approx 4 \times 10^{-2}$ M		

Now, $\dfrac{1}{2\times10^{-10}} = \dfrac{1}{x\times4\times10^{-10}} \Rightarrow x = 5 \times 10^{-9}$

Hence, Ag^+ ppt $= (5 \times 10^{-6} - 5 \times 10^{-9}) \approx 5 \times 10^{-6}$ M

$\therefore$ Mass of AgCl ppt

$$= \left(\frac{2500\times5\times10^{-6}}{1000}\right)\times143.5 = 1.79\times10^{-2}\ \text{gm}$$

106. $PbI_2\ (s) \rightleftharpoons Pb^{2+} + 2I^-$

To prevent ppt, $Q \le K_{sp}$

or, $0.005 \times [I^-]^2 \le 7.2 \times 10^{-9}$

$\therefore [I^-]_{max} = 1.2 \times 10^{-3}$ M

Hence, maximum mass of NaI

$$= \left(\frac{500\times1.2\times10^{-3}}{1000}\right)\times150 = 0.09 \text{ gm}$$

107. $AgBr\,(s) \rightleftharpoons Ag^{+} + Br^{-}$

For precipitation, $Q > K_{sp}$

or, $0.0004\times[Br^{-}] > 4\times10^{-13}$

$\therefore\ [Br^{-}] > 10^{-9}$ M

Hence, minimum mass of NaBr needed

$$= \left(\frac{200\times10^{-9}}{1000}\right)\times103 = 2.06\times10^{-8}\text{gm}$$

108. $CaSO_4\,(s) \rightleftharpoons Ca^{2+} + SO_4^{2-}$

To start ppt, $Q > K_{sp}$

or, $0.005\times[SO_4^{2-}] > 2.4\times10^{-5}$

$\therefore\ [SO_4^{2-}] > 4.8\times10^{-3}$ M

$$\therefore\ [Al_2(SO_4)_3]_{\min} = \frac{4.8\times10^{-3}}{3} = 1.6\times10^{-3}\text{M}$$

109. $Pb^{2+} \quad + \quad SO_4^{2-} \quad \rightleftharpoons PbSO_4\,(s)\,;$

$$K_{eq} = \frac{1}{K_{sp}} = \frac{1}{1.6\times10^{-7}}$$

$$\frac{8.32\times10^{-3}/200}{100/1000} \qquad \frac{10^{-4}}{100/1000}$$

$$= 4\times10^{-4} \qquad = 10^{-3}$$

100% $\quad 0 \quad (10^{-3} - 4\times10^{-4})$

$= 6\times10^{-4}$ M

Equ. $\quad x$M $\quad (6\times10^{-4} + x)$M

As $[Pb^{2+}][SO_4^{2-}] = K_{sp} \Rightarrow x\cdot(6\times10^{-4}+x) = 1.6\times10^{-7}$

$\Rightarrow x = 2\times10^{-4}$ M

$\therefore$ Mass of lead unprecipitated

$$= \left(\frac{100\times2\times10^{-4}}{1000}\right)\times208$$

$$= 4.16\times10^{-3} \text{ gm}$$

110. $M^{2+} + H_2S \rightleftharpoons MS(s) + 2H^{+}$

For ppt. of MS(s), $Q < k_{eq}$

$$\text{or, } \frac{[H^{+}]}{[M^{2+}][H_2S]} < \frac{K_{a_1}\cdot K_{a_2}}{K_{sp}}$$

$$\text{or, } \frac{[H^{+}]^2}{0.04\times0.1} < \frac{10^{-7}\times1.5\times10^{-13}}{6\times10^{-21}}$$

$\therefore\ [H^{+}]_{\max} = 0.1\text{ M} \Rightarrow P^{H}_{\min} = 1.0$

111. $Cd^{2+} \quad + \quad H_2S \quad \rightleftharpoons \quad CdS(s) + 2H^{+}$

0.1×10^{-3} mole $\qquad \dfrac{10\times0.08}{1000}$

$= 0.8\times10^{-3}$ mole

Final $\quad 0 \qquad 0.8\times10^{-3} + 0.2\times10^{-3}$

$= 10^{-3}$ mole

$$\therefore\ [H^{+}]_{\text{final}} = \frac{10^{-3}}{100}\times1000 = 0.01\text{ M} \Rightarrow P^{H} = 2.0$$

112. $[I^{-}]_{\min}$ for ppt of AgI

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

$[I^{-}]_{\min}$ for ppt of Hg_2I_2

$$= \sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}} = \sqrt{\frac{2.5\times10^{-26}}{0.1}} = 5\times10^{-13}\text{M}$$

Hence, AgI will precipitate first. The $[I^{-}]$ to start precipitation of other metal ion $= 5\times10^{-13}$ M

Now, $[Ag^{+}]_{\text{left}}$ when Hg_2I_2 start precipitating

$$= \frac{K_{sp}}{[I^{-}]} = \frac{8.5\times10^{-17}}{5\times10^{-13}} = 1.7\times10^{-4}\text{ M}$$

Hence, % of Ag^{+} precipitate

$$= \frac{0.1 - 1.7\times10^{-4}}{0.1}\times100 = 99.83\%$$

113. K_{sp} of $CaCO_3 = \left(\dfrac{7\times10^{-3}}{100}\right)^2 = 4.9\times10^{-9}$

Let initial $[Ca^{2+}] = [Ba^{2+}] = x$M. From question final $[Ba^{2+}] = x\times\dfrac{10}{100} = 0.1xM$. But $[CO_3^{2-}]$ is same for both. Hence,

$$\frac{K_{sp}(BaCO_3)}{K_{sp}(CaCO_3)} = \frac{[Ba^{2+}][CO_3^{2-}]}{[Ca^{2+}][CO_3^{2-}]}$$

$$\Rightarrow \frac{K_{sp}(BaCO_3)}{4.9\times10^{-9}} = \frac{0.1x}{x} \ \therefore\ K_{sp}(BaCO_3) = 4.9\times10^{-10}$$

114.

$$[OH^{-}] = K_b\cdot\frac{[NH_4OH]}{[NH_4^{+}]} = 2\times10^{-5}\times\frac{0.05}{0.25} = 4\times10^{-6}\text{ M}$$

$$\therefore\ [Mg^{2+}] = \frac{K_{sp}}{[OH^{-}]^2} = \frac{8\times10^{-12}}{(4\times10^{-6})^2} = 0.5\text{ M}$$

115. For ppt, $Q > K_{eq}$

For the metal sulphides,

$$Q = \frac{[M^{2+}][H_2S]}{[H^{+}]^2} = \frac{0.01\times0.1}{(1.0)^2} = 10^{-3} > K_{eq}\text{ for PbS only}$$

Hence, only Pbs will precipitate.

EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. $[NH_2^-] = \sqrt{10^{-30}} = 10^{-15}\,M$

$\therefore$ Number of NH_2^- ions per ml

$= \dfrac{10^{-15}\times 1}{1000}\times(6\times10^{23}) = 6\times10^{5}$

2. On increasing temperature, the dissociation of water will increase. It will result increase in $[H^+]$ and as well as in $[OH^-]$ and hence, decreases in P^H and as well as P^{OH}.

3. For maximum dissociation, $[H^+] = [OH^-]$.

4. $[H^+] = 10^{-2}\,M \Rightarrow n_{H^+} = \dfrac{200\times10^{-2}}{1000} = 2\times10^{-3}$

$[OH^-] = 10^{-2}\,M \Rightarrow n_{OH^-} = \dfrac{300\times10^{-2}}{1000} = 3\times10^{-3}$

$\therefore$ Moles of excess OH^- remained $= 1\times10^{-3}$

$[OH^-] = \dfrac{1\times10^{-3}}{500}\times1000 = 2\times10^{-3}\,M$

$\therefore P^{OH} = -\log(2\times10^{-3}) = 2.7 \Rightarrow P^H = 11.3$

5. $[OD^-]_{excess} = \dfrac{80\times0.1-20\times0.2}{100} = 0.04\,M$

$\therefore P^{OD} = -\log(0.04) = 1.4$

Now, P^{Kw} of $D_2O = P^D + P^{OD} = 13.6 + 1.4 = 15$

$\therefore Kw = 1\times10^{-15}$

6. $[OT^-]_{excess} = \dfrac{400\times0.2-100\times0.4}{500} = 0.08\,M$

$\therefore P^{OT} = -\log(0.08) = 1.1$

Now, $PT = P^{Kw} - P^{OT} = 2\times7.60 - 1.1 = 14.1$

7. $K_b = \dfrac{Kw}{Ka} = \dfrac{10^{-14}}{2\times10^{-10}} = 5\times10^{-5}$

8. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$\Delta H° = (-52.21) + (54.70) = 2.49$ kJ

$\Delta S° = 1.6 + (-76.3) = -74.7$ J/K

Now, $\Delta H° = -RT.\ln K_{eq}$

or, $2490 - 300\times(-74.7) = -8.3\times300\times\ln K_{eq}$

$\therefore K_{eq} = e^{-10}$

9. $[H^+]_{HCOOH} = [H^+]_{CH_3COOH}$

or, $\sqrt{2.4\times10^{-4}\times0.6} = \sqrt{1.8\times10^{-5}\times C} \Rightarrow C = 8\,M$

$\therefore$ Moles of CH_3COOH added $= \dfrac{100\times8}{1000} = 0.8$

10. $K_a(HA) = K_b(A^-) = \sqrt{Kw} = 10^{-7}$

Now, $[H^+] = \sqrt{10^{-7}\times0.1} = 10^{-4}\,M \Rightarrow P^H = 4.0$

11. $NH_4^+ + OH^- \xrightleftharpoons[K_b\,=\,?]{K_f\,=\,3.4\times10^{10}\,M^{-1}S^{-1}} NH_3 + H_2O$

Given : $NH_4^+ \rightleftharpoons NH_3 + H^+;\ K_1 = 5.6\times10^{-10}\,M$

and $H_2O \rightleftharpoons H^+ + OH^-;\ K_2 = 1.0\times10^{-14}\,M^2$

$\therefore\ NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O;\ K_{eq} = \dfrac{K_1}{K_2}$

Now, $\dfrac{3.4\times10^{10}}{K_b} = \dfrac{5.6\times10^{-10}}{10^{-14}}$

$\Rightarrow K_b = 6.07\times10^{5}\,S^{-1}$

12. $\underset{0.1-x}{CH_3COOH} \rightleftharpoons \underset{x}{CH_3COO^-} + \underset{0.1+x+y\approx0.1+y}{H^+}$

$\underset{0.1-y}{Cl_2CHCOOH} \rightleftharpoons \underset{y}{Cl_2CHCOO^-} + \underset{0.1+x+y\approx0.1+y}{H^+}$

$0.15 = \dfrac{y\times(0.1+y)}{(0.1-y)} \Rightarrow y = 0.05$

$\therefore [H^+] = 0.1 + x + y \approx 0.1 + y = 0.15\,M$

$\therefore P^H = -\log(0.15) = 0.82$

13. $[OH^-] = \dfrac{0.4}{100}\times\dfrac{4.25/17}{250/1000} = 0.004\,M$

$P^{OH} = -\log(0.004) = 2.4$

$\therefore P^H = 14 - 2.4 = 11.6$

14. $[OH^-] = \sqrt{K_b\times C} = \sqrt{1.6\times10^{\ \ 6}\times0.0025}$

$= \sqrt{4\times10^{-9}}\,M$

$P^{OH} = -\log\sqrt{4\times10^{-9}} = 4.2 \Rightarrow\ \ ^{H} = 9.8$

15. $[HSaC]_O = \dfrac{4\times10^{-4}}{200/1000} = 2\times10^{-3}M$

and $P^H = 3.0 \Rightarrow [H^+] = 10^{-3}$ M

Now, $2\times10^{-12} = \dfrac{[SaC^-]\times10^{-3}}{2\times10^{-3}}$

$\Rightarrow [SaC^-] = 4\times10^{-12}M$

16. $[HA]_O = \dfrac{20\times0.5}{50} = 0.2$ M

$[HB]_O = \dfrac{30\times0.2}{50} = 0.12$ M

$$\underset{0.2-x}{HA} \rightleftharpoons \underset{x+y}{H^+} + \underset{x}{A^-}$$

$$\underset{0.12-y}{HB} \rightleftharpoons \underset{x+y}{H^+} + \underset{y}{B^-}$$

Now, $2\times10^{-4} = \dfrac{(x+y)\cdot x}{0.2-x} \approx \dfrac{(x+y)\cdot x}{0.2}$

$\therefore (x + y) \cdot x = 4 \times 10^{-5}$ (1)

and, $5\times10^{-5} = \dfrac{(x+y)\cdot y}{(0.12-y)} \approx \dfrac{(x+y)\cdot y}{0.12}$

$\therefore (x + y) \cdot y = 6 \times 10^{-6}$ (2)

From (1) and (2), $[H^+] = x + y = 6.78 \times 10^{-3}$ M

17. $10^{-5} = \sqrt{K_a\times0.01} \Rightarrow K_a = 10^{-8}$

Now, $[OH^-] = \sqrt{10^{-8}\times0.1} = 10^{-4.5} \Rightarrow P^{OH} = 4.5$

$\therefore P^H = 9.5$

18. $$\underset{0.01-x}{RNH_2} + H_2O \rightleftharpoons \underset{x}{RNH_3^+} + \underset{x+10^{-4}}{OH^-}$$

$2\times10^{-6} = \dfrac{x(x+10^{-4})}{0.01-x} \Rightarrow x = 10^{-4}$

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

19. As on adding HCl, $[H^+]$ is not changing and will remain unchanged.

20. $$\underset{\substack{\downarrow\\ \text{Decrease}}}{Co_2} + H_2O \underset{\substack{\leftarrow\\ \text{Shiftleft}}}{\rightleftharpoons} HCo_3^- + H^+$$

As $[H^+]$ decreases, P^H increases.

21. $[W_2H_4]_O = \dfrac{0.16/32}{500/1000} = 0.01$ M

$\therefore \propto = \sqrt{\dfrac{4\times10^{-6}}{0.01}} = 0.02$ or 2%

22. $P^H = -\log(2\times10^{-6}) = 5.70$

23. $[OH–] = 6.67\times10^{-3} + \dfrac{6.67\times10^{-3}}{2} + 0 \approx 10^{-2}M$

$\therefore P^{OH} = -\log(10^{-2}) = 2.0 \Rightarrow P^H = 12.0$

24. $$\underset{(0.09-x)M}{en} + H_2O \rightleftharpoons \underset{(x-y)M}{enH^+} + \underset{(x+y)M}{OH^-}; K_{b_1} = 8.1\times10^{-5}$$

$$\underset{(x-y)M}{enH^+} + H_2O \rightleftharpoons \underset{yM}{enH_2^{2+}} + \underset{(x+y)M}{OH^-}; K_{b_2} = 7.0\times10^{-8}$$

Now, $8.1\times10^{-5} = \dfrac{(x-y)(x+y)}{(0.09-x)}K \approx \dfrac{x\cdot x}{0.09}$

$\Rightarrow x = 2.7\times10^{-3}$

and $7.0\times10^{-8} = \dfrac{y\cdot(x+y)}{(x-y)} \approx \dfrac{y\cdot x}{x} \Rightarrow y = 7.0\times10^{-8}$

$\therefore [en\,H^+] = (x - y) \approx x M = 2.7\times10^{-3}$ M

$[enH_2^{2+}] = y = 7.0\times10^{-8}M$

$\therefore [OH^-] = (x + y) = x = 2.7\times10^{-3}$ M

and $P^{OH} = -\log(2.7\times10^{-3}) = 2.56 \Rightarrow P^H = 11.44$

25. $K_{a_1}\cdot K_{a_2} = \dfrac{[H^+]^2[5^{2-}]}{[H_2S]}$

or, $(1.4\times10^{-7})\times(1.0\times10^{-14}) = \dfrac{(0.1)^2\times[5^{2-}]}{0.2}$

$\Rightarrow [5^{2-}] = 2.8\times10^{-20}M$

26. $[H^+] = \sqrt{0.2\times2\times10^{-5}} = 2\times10^{-3}M$

Now, $(2\times10^{-5})\times(5\times10^{-9})\times(4\times10^{-12})$

$= \dfrac{(2\times10^{-3})^3\times[A^{3+}]}{[H_3A]}$

$\therefore \dfrac{[A^{3-}]}{[H_3A]} = 5\times10^{-17}$

27. $[H^+] = \sqrt{0.1\times10^{-5}} = 10^{-3}M$

Now, $K_{a_3} = \dfrac{[H^+][A^{3-}]}{[HA^{2-}]} \Rightarrow \dfrac{[A^{3-}]}{[HA^{2-}]} = \dfrac{10^{-13}}{10^{-3}} = 10^{-10}$

$\therefore P^X = 10$

28. $$\begin{array}{lcccc} & OH^- & + ACOH & \rightleftharpoons & ACO^- + H_2O \\ & 2\text{ m mol} & 3\text{ m mol} & & 0 \\ \text{Final} & 0 & 1\text{ m mol} & & 2\text{ m mol} \end{array}$$

$p^H = 4.74 + \log\dfrac{2}{1} = 5.04$ (Acidic)

Addition of 1 ml ACOH will decrease P^H by 0.3 unit.

29. Millimoles of ACOH $= 6 \times 0.1 = 0.6$

Millimoles of $\text{ACO}^{-} = 12.\times 0.1 = 1.2$

$$\therefore \quad \text{p}^{\text{H}} = 4.75 + \log\frac{1.2}{0.6} = 5.05$$

30. 1st solution will finally have 1 mole of CH_3COOH.

$$\therefore \quad \text{P}_1^{\text{H}} = \frac{1}{2}\text{P}^{\text{Ka}}$$

and for 2nd solution, $\text{P}_2^{\text{H}} = \text{P}^{\text{Ka}}$

31. $\text{P}_2^{\text{H}} = \text{P}_1^{\text{H}} + 0.6$

$$\text{p}^{\text{K}_a} + \log\frac{y/\text{M}}{\text{C}} = \text{P}^{\text{K}_a} + \log\frac{x/\text{M}}{\text{C}} + \log 3.98$$

$$\therefore \frac{y}{x} = 3.98$$

32. $4.0 = 5.0 + \log\dfrac{\text{C}_1}{0.5} \Rightarrow \text{C}_1 = 0.05\text{ M}$

$$6.0 = 5.0 + \log\frac{\text{C}_2}{0.5} \Rightarrow \text{C}_2 = 5.0\text{ M}$$

Now, final $\text{P}^{\text{H}} = 5.0 + \log\dfrac{V\times 0.05 + V\times 5.0}{V\times 0.5 + V\times 0.5} = 5.7$

33. For maximum $\beta, \dfrac{\alpha\beta}{\alpha[\text{H}^+]} = 0 \Rightarrow \text{P}^{\text{H}} = \text{P}^{\text{K}_a}$

34.

$$\begin{array}{lccc}
 & \text{BOH} \;+ & \text{H}^+ \;\rightleftharpoons & \text{B}^+ + \text{H}_2\text{O} \\
 & \dfrac{40\times\text{C}}{40+V}M & \dfrac{\text{V}\times 0.1}{40+V}M & 0 \\
\text{Final} & \dfrac{40\text{C-}0.1V}{40+V} & 0 & \dfrac{0.1V}{40+V}
\end{array}$$

H^+ must be a limiting reagent because both P^{H} are above >.0.

Now, $\text{P}^{\text{OH}} = \text{P}^{\text{K}_b} + \log\dfrac{0.1\text{V}}{40\text{C} - 0.1\text{V}}$

$$14 - 10 = \text{P}^{\text{K}_b} + \log\frac{0.1\times 5}{40\text{C} - 0.1\times 5} \qquad (1)$$

$$14 - 9 = \text{P}^{\text{K}_b} + \log\frac{0.1\times 20}{40\text{C} - 0.1\times 20} \qquad (2)$$

$\therefore \text{K}_b = 2 \times 10^{-5}$

35. For maximum buffer capacity:

$$\frac{[\text{ACOH}]}{[\text{NaOH}]} = \frac{2}{1} \Rightarrow [\text{NaOH}] = \frac{2\text{ M}}{2} = 1\text{ M}$$

$\therefore$ Mass of NaOH added $= \dfrac{500\times 1}{1000}\times 40 = 20$ gm

36. $n_{\text{HA}} = n_{\text{OH}^-} \Rightarrow \dfrac{0.28}{\text{M}} = \dfrac{35\times 0.1}{1000} \Rightarrow \text{M} = 80$

37. $\underset{0.9x\text{M}}{\text{Fe}^{3+}} + \text{H}_2\text{O} \rightleftharpoons \underset{0.1x\text{M}}{\text{Fe(OH)}^{2+}} + \underset{?}{\text{H}^+}$

$$9\times 10^{-3} = \frac{0.1x\times[\text{H}^+]}{0.9x} \Rightarrow [\text{H}^+] = 0.081 \Rightarrow \text{P}^{\text{H}} = 1.08$$

38. In final solution: $[\text{HA}] = [\text{A}^-]$

39. $[\text{NH}_3] = \sqrt{\dfrac{\text{K}_w}{\text{K}_a\cdot\text{K}_b}}\times\text{C} = 8.33\times 10^{-4}\text{ M}$

40. For equivalence point, $2.5\times\dfrac{2}{5} = \text{V}_{\text{Hcl}}\times\dfrac{2}{15}$

$\therefore \text{V}_{\text{HCl}} = 7.5$ ml

$$\text{BOH} + \text{H}^+ \rightleftharpoons \text{B}^+ + \text{H}_2\text{O};\; \text{K}_{\text{aq}} = \frac{10^{-12}}{10^{-14}} = 10^2$$

$$\begin{array}{lccc}
 & \dfrac{2.5\times\frac{2}{5}}{10}\text{M} & \dfrac{7.5\times\frac{2}{15}}{10}\text{M} & 0 \\
 & 0 & 0 & 0.1\text{M} \\
\text{Eqn.} & x\text{M} & \text{XM} & (0.1-x)\text{M}
\end{array}$$

$$100 = \frac{0.1 - x}{x\cdot x} \Rightarrow x = 2.7\times 10^{-2}\text{M} = (\text{H}^+)$$

41. At 2nd equation point:

$$\text{P}^{\text{H}} = \frac{1}{2}(\text{P}^{\text{K}_{a_2}} + \text{P}^{\text{K}_{a_3}}) = \frac{8+12}{12} = 10$$

Now, $\text{K}_{a_1}\cdot\text{K}_{a_2}\cdot\text{K}_{a_3} = \dfrac{[\text{H}^+][\text{A}^{3-}]}{[\text{H}_3\text{A}]}$

or $7.5\times 10^{-4}\times 10^{-8}\times 10^{-12} = \dfrac{(10^{-10})^3\times[\text{A}^{3-}]}{[\text{H}_3\text{A}]}$

$$\therefore \frac{[\text{H}_3\text{A}]}{[\text{A}^{3-}]} = \frac{10^{-6}}{7.5} = 1.33\times 10^{-7}$$

42.

$$\begin{array}{lccc}
 & \text{CO}_3^{2-} \;+ & \text{H}^+ \;\rightleftharpoons & \text{HCO}_3^-;\ \text{K}\quad \dfrac{1}{4\times 10^{-11}} \\
 & 0.35\text{ M} & 0.35\text{ M} & 0 \\
100\%\text{ run} & 0 & 0 & 0.35\text{ M}
\end{array}$$

For HCO_3^- solution,

$$[\text{H}^+] = \sqrt{\text{K}_{a_1},\text{K}_{a_2}} = 1.4\times 10^{-8}\text{M}$$

Now, $\text{K}_{a_2} = \dfrac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

$$\therefore [\text{CO}_3^{2-}] = \frac{4\times 10^{-11}\times 0.35}{1.4\times 10^{-8}} = 10^{-3}\text{M}$$

43. $$[\mathrm{LaC^-}]_0 = \frac{0.125}{0.5} \times 2 = 0.5\ \mathrm{M}$$

Now, $$\mathrm{P^{OH}} = 7 - \frac{1}{2}(\mathrm{P^{K_a}} + \log \mathrm{C})$$

$$5.6 = 7 - \frac{1}{2}(\mathrm{P^{K_a}} + \log 0.5)$$

$$\therefore \mathrm{P^{K_a}} = 3.1 \Rightarrow \mathrm{K}_a = 8 \times 10^{-4}$$

44. As HA is stronger acid, it will react first. For first equivalent point, $\mathrm{V_{NaOH}} \times 0.2 = 50 \times 0.05 \Rightarrow \mathrm{V_{NaOH}} = 12.5\ \mathrm{ml}$

At first equivalent point,

$$[\mathrm{A^-}] = \frac{50 \times 0.05}{62.5} = 0.04\ \mathrm{M}$$

$$[\mathrm{HB}] = \frac{50 \times 0.08}{62.5} = 0.064\ \mathrm{M}$$

Now, $$\underset{\substack{0.04-x\\ \simeq 0.04}}{\mathrm{A^-}} + \underset{\substack{0.064-x\\ \simeq 0.064}}{\mathrm{HB}} \rightleftharpoons \underset{x}{\mathrm{B^-}} + \underset{x}{\mathrm{HA}};$$

$$\mathrm{K_{eq}} = \frac{\mathrm{K_a(HB)}}{\mathrm{K_a(HA)}} = \frac{10^{-8.2}}{10^{-3.8}} = 10^{-4.4} = 4 \times 10^{-5}$$

$$4 \times 10^{-5} = \frac{x \cdot x}{0.04 \times 0.064} \Rightarrow x = 3.2 \times 10^{-4}$$

Now, $$\mathrm{K_a(HA)} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\Rightarrow 1.6 \times 10^{-4} = \frac{[\mathrm{H^+}] \times 0.04}{3.2 \times 10^{-4}}$$

$$\therefore [\mathrm{H^+}] = 1.28 \times 10^{-6} \Rightarrow \mathrm{P^H} = 5.9$$

45. $$\underset{0.005-x}{\mathrm{CrO_4^{2-}}} + \mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{HCrO_4^-}} + \underset{x}{\mathrm{OH^-}};$$

$$\mathrm{K_h} = \frac{\mathrm{Kw}}{\mathrm{K}_{a_2}} = 2 \times 10^{-8}$$

$$2 \times 10^{-8} = \frac{x \cdot x}{0.005 - x} \approx \frac{x^2}{0.005} \Rightarrow x = 10^{-5}$$

$$\therefore\ h = \frac{10^{-5}}{0.005} = 0.002$$

46. $\mathrm{P}^{\mathrm{K}_{a_1}} = 2.40$ and $\mathrm{P}^{\mathrm{K}_{a_2}} = 9.60$

$$\therefore \text{ Required pH} = \frac{1}{2}(2.40 + 9.60) = 6.00$$

47. $$\underset{\text{Red}}{\mathrm{HA}} \rightleftharpoons \mathrm{H^+} + \underset{\text{Blue}}{\mathrm{A^-}}$$

$$[\mathrm{H^+}] = \frac{\mathrm{K}_a \cdot [\mathrm{HA}]}{[\mathrm{A^-}]}$$

$$\therefore [\mathrm{H^+}]_{\text{required}} = [H^+]_2 - [H^+]_1 = K_a\left(\frac{75}{25} - \frac{25}{75}\right)$$

$$= 8 \times 10^{-5}\ \mathrm{M}$$

48. $$5.5 = 4.75 + \log \frac{[\mathrm{ACo^-}]_\mathrm{O}}{[\mathrm{ACOH}]_\mathrm{O}}$$

$$\therefore \frac{[\mathrm{ACo^-}]_\mathrm{O}}{[\mathrm{ACOH}]_\mathrm{O}} = \frac{5.62}{1}$$

49. $$n_{\mathrm{CO_2}} = \frac{224}{22400} = 0.01 \text{ and } n_{\mathrm{H^+}} \text{ used} = \frac{30 \times 1}{1000} = 0.03$$

$$\underset{\text{0.01 mole (L.R.)}}{\mathrm{CO_2 + OH^-}} \longrightarrow \underset{\text{0.01 mole or less}}{\mathrm{HCO_3^-}}$$

Hence, moles of $\mathrm{H^+}$ used should be 0.01 or less and titration of $\mathrm{HCO_3^-}$ and H+ should not be detected by phenolphthalein. Hence, $\mathrm{OH^-}$ must be in excess.

$$\underset{\text{0.01 mole}}{\mathrm{CO_2}} + \underset{\text{0.02 mole}}{\mathrm{2OH^-}} \longrightarrow \underset{\text{0.01 mole}}{\mathrm{CO_3^{2-}}} + \mathrm{H_2O}$$

Thus, 0.01 mole of $\mathrm{CO_3^{2-}}$ will require only 0.01 mole of $\mathrm{H^+}$ in the presence of phenolphthalein. As the mole of $\mathrm{H^+}$ used is 0.03, 0.02 mole $\mathrm{OH^-}$ must be present in excess.

Hence, total moles of $\mathrm{OH^-}$ used = 0.02 + 0.02 = 0.04,

$$\therefore [\mathrm{NaOH}]_{\text{used}} = \frac{0.04}{1} = 0.04\ \mathrm{M}$$

50. $$\mathrm{PbSO_4} = \sqrt{2 \times 10^{-9}} \times \frac{304}{10} \simeq 1.36 \times 10^{-3}\ \mathrm{g/100ml}$$

$$\mathrm{ZaS} = \sqrt{10^{-22}} \times \frac{97}{10} = 9.7 \times 10^{-11}\ \mathrm{g/100ml}$$

$$\mathrm{AgBr} = \sqrt{4 \times 10^{-13}} \times \frac{188}{10} = 1.19 \times 10^{-5}\ \mathrm{g/100ml}$$

$$\mathrm{CuCo_3} = \sqrt{10^{-8}} \times \frac{123}{10} = 1.23 \times 10^{-3}\ \mathrm{g/100ml}$$

51. $$\begin{array}{lccc} & \mathrm{Hg^{2+}} & +\,4\mathrm{Cl^-} \rightleftharpoons & \mathrm{HgCl_4^{2-}} \\ & 0.1\ \mathrm{M} & 0.9\ \mathrm{M} & 0 \\ \text{100\% ram} & 0 & 0.5\mathrm{M} & 0.1\mathrm{M} \\ \text{Eqn.} & 1.6\times10^{-17}\ \mathrm{M} & 0.5\mathrm{M} & 0.1\mathrm{M} \end{array}$$

$$\therefore \mathrm{K_{form}} = \frac{0.1}{1.6 \times 10^{-17} \times (0.5)^4} = 10^{17}$$

52. $$\underset{\substack{0.1\\ \text{Eqn/final}\ \ 0}}{\mathrm{AgBr(s)}} + \underset{\substack{\mathrm{aM}\\ \mathrm{a}-0.2}}{2\mathrm{S_2O_3^{2-}}} \rightleftharpoons \underset{\substack{0\\ 0.1}}{\mathrm{Ag(S_2O_3)_2^{3-}}} + \underset{\substack{0\\ 0.1}}{\mathrm{Br^-}}$$

$$\mathrm{K_{eq}} = 4\times10^{-13}\times1.6\times10^{12} = \frac{0.1\times0.1}{(a-0.2)^2} \Rightarrow a = 0.325$$

53. $$\mathrm{Tl_2S(S)} \rightleftharpoons \underset{\mathrm{2SM}}{2\mathrm{Tl^+}} + \underset{x}{\mathrm{S^{2-}}}$$

$$\underset{x\mathrm{M}}{\mathrm{S^{2-}}} + \mathrm{H_2O} \rightleftharpoons \underset{\mathrm{SM}}{\mathrm{HS^-}} + \underset{\mathrm{SM}}{\mathrm{OH^-}};\ \mathrm{K_h} = \frac{\mathrm{Kw}}{\mathrm{K_{a_2}}}$$

$$\frac{10^{-14}}{10^{-14}} = \frac{2\times10^{-6}\times2\times10^{-6}}{x} \Rightarrow x = 4\times10^{-12}$$

$$\therefore K_{sp} = (2\times2\times10^{-6})^2\times4\times10^{-12} = 6.4\times10^{-23}$$

56. $$\underset{\substack{2\times10^{-3}\,\mathrm{M}\\ \text{Eqn.}\ \ 2\times10^{-3}-x\\ =5\times10^{-4}\,\mathrm{M}}}{\mathrm{M^{3+}}} + \underset{\substack{1.51\times10^{-3}\,\mathrm{M}\\ 1.51\times10^{-3}-x\\ =1.0\times10^{-5}\,\mathrm{M}}}{\mathrm{SCN^-}} \rightleftharpoons \underset{\substack{0\\ x\mathrm{M}\\ =1.5\times10^{-3}\,\mathrm{M}}}{\mathrm{M(SCN)^{2+}}}$$

$$\therefore\ K_f = \frac{1.5\times10^{-3}}{5\times10^{-4}\times1\times10^{-5}} = 3\times10^5$$

57. $$\mathrm{SrCO_3(s)} \rightleftharpoons \underset{2\times10^{-4}\,\mathrm{M}}{\mathrm{Sr^{2+}}} + \underset{2\times10^{-4}-x}{\mathrm{CO_3^{2-}}}$$

$$\underset{(2\times10^{-4}-x)\mathrm{M}}{\mathrm{CO_3^{2-}}} + \mathrm{H_2O} \rightleftharpoons \underset{x\mathrm{M}}{\mathrm{HCO_3^-}} + \underset{4\times10^{-6}\,\mathrm{M}}{\mathrm{OH^-}}$$

$$\text{Now, } \frac{10^{-14}}{5\times10^{-11}} = \frac{x\times4\times10^{-6}}{(2\times10^{-4}-x)} \Rightarrow x = \frac{0.01}{51}$$

$$\therefore \mathrm{K_{sp}} = (2\times10^{-4})\times(2\times10^{-4}-x) = \frac{4}{51}\times10^{-8}$$

58. $$\mathrm{MnS(S)} \rightleftharpoons \underset{\mathrm{SM}}{\mathrm{Mn^{2+}}} + \underset{(\mathrm{S}-x)\mathrm{M}}{\mathrm{S^{2-}}}$$

$$\underset{(\mathrm{S}-x)\mathrm{M}}{\mathrm{S^{2-}}} + \mathrm{H_2O} \rightleftharpoons \underset{x\mathrm{M}}{\mathrm{HS^-}} + \underset{x\mathrm{M}}{\mathrm{OH^-}}$$

$$\frac{10^{-14}}{10^{-14}} = \frac{x\cdot x}{(\mathrm{S}-x)} \text{ and } 2.5\times10^{-10} = \mathrm{S}\cdot(\mathrm{S}-x)$$

$$\therefore \mathrm{S} = 6.3\times10^{-4}\ \mathrm{M}$$

59. $$\underset{0.1-0.075}{\mathrm{AgCl(s)}} + \underset{x\mathrm{M}}{\mathrm{Br^-(aq)}} \rightleftharpoons \underset{0.075}{\mathrm{AgBr(s)}} + \underset{0.075\mathrm{M}}{\mathrm{Cl^-}}\mathrm{(aq)}$$

$$\mathrm{K_{eq}} = \frac{[\mathrm{Cl^-}]}{[\mathrm{Br^-}]} = \frac{\mathrm{K_{sp}(AgCl)}}{\mathrm{K_{sp}(AgBr)}} \Rightarrow \frac{0.075}{[\mathrm{Br^-}]} = \frac{2\times10^{-10}}{4\times10^{-13}}$$

$$\therefore [\mathrm{Br^-}] = 1.5\times10^{-4}\ \mathrm{M}$$

60. $[\mathrm{Ag(CN)_2^-}] = 0.01\mathrm{M}$

$$\mathrm{K_{diss}} = \frac{[\mathrm{Ag^+}][\mathrm{CN^-}]^2}{[\mathrm{Ag^+(CN)_2^-}]} \Rightarrow 1\times10^{-20} = \frac{[\mathrm{Ag^+}]\times(2.5\times10^{-7})^2}{0.01}$$

$$\therefore [\mathrm{Ag^+}] = 1.6\times10^{-9}\ \mathrm{M}$$

61. $[\mathrm{CO_3^{2-}}] = 2.0\ \mathrm{M}$

$$\text{Now, } \frac{\mathrm{K_{sp}(CaCO_3)}}{\mathrm{K_{sp}(CaF_2)}} = \frac{[\mathrm{CO_3^{2-}}]}{[\mathrm{F^-}]^2}$$

$$\Rightarrow \frac{x}{4y^3} = \frac{2}{[\mathrm{F^-}]} \Rightarrow (\mathrm{F^-}) = \sqrt{\frac{8y^3}{x}}$$

62. $$\mathrm{BaF_2(s)} + \underset{(0.1-x)\mathrm{M}}{\mathrm{C_2O_4^{2-}(aq)}} \Rightarrow \mathrm{BaC_2O_4(s)} + \underset{2x\mathrm{M}}{2\mathrm{F^-}}\mathrm{(aq)}$$

$$\mathrm{K_{eq}} = \frac{[\mathrm{F^-}]}{[\mathrm{C_2O_4^{2-}}]} = \frac{\mathrm{K}_{sp}(\mathrm{BrF_2})}{\mathrm{K_{sp}(BrC_2O_4)}} = \frac{10^{-6}}{10^{-10}} = 10^4$$

$$\therefore\ x \approx 0.1 \Rightarrow [\mathrm{F^-}] = 0.2\ \mathrm{M}$$

$$\therefore [\mathrm{Ba^{2+}}] = \frac{10^{-6}}{(0.2)^2} = 2.5\times10^{-5}\ \mathrm{M}$$

63. $$\mathrm{S} = [\mathrm{Zn(OH)_2(aq)}] + [\mathrm{Zn(OH)^+}] + [\mathrm{Zn^{2+}}] + [\mathrm{Zn(OH)_3^-}] + [\mathrm{Zn(OH)_4^{2-}}]$$

$$= \mathrm{K_1} + \frac{\mathrm{K_2\cdot K_1}}{[\mathrm{OH^-}]} + \frac{\mathrm{K_3\cdot K_2K_1}}{[\mathrm{OH^-}]^2} + \mathrm{K_4K_1}[\mathrm{OH^-}] + \mathrm{K_5K_4K_1}[\mathrm{OH^-}]^2$$

$$= 10^{-6} + \frac{10^{-7}\times10^{-6}}{0.1} + \frac{10^{-4}\times10^{-7}\times10^{-6}}{(0.1)^2} + 10^3\times10^{-6}\times0.1 + 10\times10^3\times10^{-6}\times(0.1)^2$$

$$= 10^{-6} + 10^{-12} + 10^{-15} + 10^{-4} + 10^{-4} \approx 2\times10^{-4}\ \mathrm{M}$$

64. For molecular solubility of $\mathrm{CaCl_2}$,

$\Delta H_{\text{solution}} = 209.2 + (-33.5) = 175.7$ KJ > 30 KJ

For ionic solubility of $\mathrm{CaCl_2}$,

$\Delta H_{\text{solution}} = 209.2 + 1004.2 + 1715.4 - 1598.3 - 719.6 - 711.2 = -100.3$ KJ

For molecular solubility of $\mathrm{HgCl_2}$,

$\Delta H_{\text{solution}} = 83.7 - 66.9 = 16.8$ KJ < 30 KJ

For ionic solubility of $\mathrm{HgCl_2}$,

$\Delta H_{\text{solution}} = 83.7 + 460.2 + 2815.8 - 1845.1 - 719.6 - 711.2$

$= 83.3$ KJ > 30 KJ

Hence, $\mathrm{CaCl_2}$ is ionic and $\mathrm{HgCl_2}$ is molecular solubility.

65. $$[\mathrm{C_2O_4^{2-}}] = \frac{6\times0.001\times5}{250\times2} = 6\times10\quad\mathrm{M}$$

$$\therefore \mathrm{K_{sp}} = (6\times10^{-5})^2 = 3.6\times10^{-9}$$

66.
$$\begin{array}{lccc} & \text{Sr}^{2+} & +\ \text{NO}_3^- \rightleftharpoons & \text{Sr(NO}_3)^+ \\ & 0.001\text{M} & 0.05\text{M} & 0 \\ \text{Eqn.} & 0.001-x & 0.05-x & x \\ & =0.001\times\frac{75}{100} & \simeq 0.05\text{M} & \end{array}$$

$\therefore\ x = 0.00025$

Now, $K_f = \dfrac{2.5\times10^{-4}}{7.5\times10^{-4}\times0.05} = \dfrac{20}{3}$

67. $\underset{0.1\,\text{Mole}}{\text{ACOAg(s)}} + \underset{0.1\,\text{M}}{\text{H}^+} + \underset{0.1\,\text{M}}{\text{Cl}^-} \rightleftharpoons \text{ACOH} + \text{AgCl(s)}$

$$K_{\text{eq}} = \frac{[\text{ACOH}]}{[\text{H}^+][\text{Cl}^-]}\times\frac{[\text{ACO}^-]}{[\text{ACO}^-]}\times\frac{[\text{Ag}^+]}{[\text{Ag}^+]}$$

$$= \frac{K_{\text{sp}}[\text{ACOAg}]}{K_{\text{sp}}(\text{AgCl})\times K_a}$$

$$= \frac{10^{-8}}{10^{-10}\times10^{-5}} = 10^7 \Rightarrow \text{Almost complete reaction}$$

$$\therefore [\text{ACOH}] \simeq 0.1\text{M}, [\text{H}^+] = \sqrt{\frac{0.1}{10^7}} = 10^{-4}\ \text{M}$$

and $[\text{ACO}^-] = \dfrac{\text{Ka}\times[\text{ACOH}]}{[\text{H}^+]} = 0.01\,\text{M}$

68. $\text{A}_x\text{B}_y(\text{s}) \rightleftharpoons x\text{A}^{y+} + y\text{B}^{x-}$

$$K_{\text{sp}} = x^x\cdot y^y\cdot s^{x+y} \Rightarrow s = \left(\frac{K_{\text{sp}}}{x^x\cdot y^y}\right)^{\frac{1}{x+y}}$$

As $K_{\text{sp}} << 1$, greater the value of $(x + y)$, greater is s.

69. Theory based

70. $s = [\text{Zn}^{2+}] + [\text{Zn(OH)}_4^-] = \dfrac{\text{K}_{\text{sp}}}{[\text{OH}^-]^2} + \text{K}_\text{f}[\text{OH}^-]^2$

For maximum or minimum S, $\dfrac{\text{dS}}{\text{d}[\text{OH}^-]} = 0$

or, $\dfrac{-2\text{K}_{\text{sp}}}{[\text{OH}^-]^3} + 2\,\text{K}_\text{f}[\text{OH}^-] = 0$

$$\Rightarrow [\text{OH}^-] = \left(\frac{K_{\text{sp}}}{K_f}\right)^{\frac{1}{4}} = 10^{-4}\ \text{M}$$

$\therefore$ $\text{P}^\text{H} = 10$ and $\text{S}_{\text{min}} = 2.4\times10^{-9}$ M

71.
$$\begin{array}{lccc} & \text{Al(OH)}_3(\text{s}) & +\ \text{OH}^- \rightleftharpoons & \text{Al(OH)}_4^-; \\ \text{From question} & & ? & 10^{-3}\ \text{M} \end{array}$$

$$K = \frac{8\times10^{-33}}{1.6\times10^{-34}} = 50$$

$$50 = \frac{10^{-3}}{[\text{OH}^-]} \Rightarrow [\text{OH}^-] = 2\times10^{-5}\text{M} \Rightarrow \text{P}^\text{H} = 9.30$$

As the calculated [OH⁻] is minimum OH⁻, P^H is minimum.

$\text{Al(OH)}_3(\text{s}) \rightleftharpoons \underset{10^{-3}\ \text{M}}{\text{Al}^{3+}} + 3\text{OH}^-;\ \text{K} = 8\times10^{-33}$

$$8\times10^{-33} = 10^{-3}\times[\text{OH}^-]^3 \Rightarrow [\text{OH}^-] = 2\times10^{-10}\text{M}$$

$\Rightarrow \text{P}^\text{H} = 4.30$

As the calculated [OH⁻] is maximum OH⁻, P^H is maximum.

72. From the question,

$[\text{Cu(CN)}_4^{3-}] = 0.1\,\text{M}$ and $[\text{CN}^-] = 0.2$ M

$$\therefore [\text{Cu}^+] = \frac{K_{\text{Instab}}\cdot[\text{Cu(CN)}_4^{3-}]}{[\text{CN}^-]^4} = \frac{6.4\times10^{-15}\times0.1}{(0.2)^4}$$

$$= 4\times10^{-13}\ \text{M}$$

Now, $[\text{S}^{2-}] = \dfrac{K_{\text{sp}}(\text{Cu}_2\text{S})}{[\text{Cu}^+]^2} = \dfrac{2.56\times10^{-27}}{(4\times10^{-13})^2}$

$$= 1.6\times10^{-2}\ \text{M}$$

$$\therefore [\text{H}^+] = \sqrt{\frac{K_a\times[\text{H}_2\text{S}]}{[\text{S}^{2-}]}} = \sqrt{\frac{1.6\times10^{-21}\times0.1}{1.6\times10^{-2}}} = 10^{-10}\ \text{M}$$

and $\text{P}^\text{H} = 10.0$

73. $\text{S} = \sqrt{1.6\times10^{-5}} = 4\times10^{-3}\text{M} = \dfrac{4\times10^{-3}\times136}{10^3}\times10^6$

$= 4\times136$ ppm

For increase in concentration 4 times, volume should be $\dfrac{1}{4}^{\text{th}}$. Hence, 75% water should be evaporated.

74. During precipitation, the concentration of both Ba^{2+} and SO_4^{2-} ions will decrease.

75. $K_{\text{sp}}(\text{AgCl}) = 10^{-4}\times10^{-6} = 10^{-10}$

$K_{\text{sp}}(\text{Ag}_2\text{CrO}_4) = (10^{-4})^2\times8\times10^{-4} = 8\times10^{-12}$

After precipitation of AgCl, find the concentration of Cl⁻. $[\text{Cl}^-]_{\text{final}} = 1.0\times10^{-6} - 8\times10^{-7}\times2\times10^{-7}$ M

Now, $\dfrac{[\text{CrO}_4^{2-}]_{\text{final}}}{[\text{Cl}^-]^2_{\text{final}}} = \dfrac{\text{K}_{\text{sp}}(\text{AgCrO}_4)}{\text{K}^2_{\text{sp}}(\text{AgCl})}$

$$\frac{[\text{CrO}_4^{2-}]_{\text{final}}}{(2\times10^{-7})^2} = \frac{8\times10^{-12}}{(10^{-10})^2} \Rightarrow [\text{CrO}_4^{2-}]_{\text{final}} = 3.2\times10^{-5}\ \text{M}$$

Hence, moles of Ag_2CrO_4 precipitated

$$= 8\times10^{-4} - 3.2\times10^{-5} = 7.68\times10^{-4}$$

76. To prevent precipitation of AgCl, the concentration of Ag^+ needed in solution $= \dfrac{K_{sp}(\text{AgCl})}{(\text{Cl}^-)}$

$$= \frac{1.8\times10^{-10}}{0.16} << 1.8\ \text{M}$$

Hence, almost all Ag^+ ion must form complete with CN^- ions.

$$\underset{\frac{1.8\times10^{-10}}{0.16}\text{M}}{Ag^+} + \underset{\text{CM}}{2\,CN^-} \rightleftharpoons \underset{1.8\,\text{M}}{Ag(CN)_2^-};\ K_f = 6.4\times10^{17}$$

77. $[CO_3^{2-}] = K_a(\text{overall})\cdot\dfrac{[H_2CO_3]}{[H^+]^2}$

To prevent precipitation of MCO_3,

or, $[M^{2+}][CO_3^{2-}] \le K_{sp}$

or, $[M^{2+}]\cdot\dfrac{K_a\cdot[H_2CO_3]}{[H^+]^2} \le K_{sp}$

$$\therefore [H^+] \ge \sqrt{\frac{[M^{2+}]\cdot K_a[H_2CO_3]}{K_{sp}}}$$

For $MgCO_3 : [H^+] \ge \sqrt{\dfrac{0.1\times5\times10^{-17}\times0.05}{9\times10^{-8}}}$

$$= 2.5\times10^{-6}\,\text{M}$$

$\therefore P^H \le 5.6$

For $SrCO_3 : [H^+] \ge \sqrt{\dfrac{0.1\times5\times10^{-17}\times0.05}{9\times10^{-10}}}$

$$= \frac{5\times10^{-5}}{3}\ \text{M}$$

$\therefore P^H \le 4.78$

For precipitation of $SrCO_3$ without any precipitation of $MgCO_3$, the P^H range should be 4.78 to 5.6

78. $Mn^{2+}(aq) + H_2S(aq) \rightleftharpoons MnS(s) + 2H^+(aq)$

To just start precipitation of MnS, $Q < K_{eq}$

or, $\dfrac{[H^+]^2}{[Mn^{2+}][H_2S]} < \dfrac{K_a(H_2S)}{K_{sp}(MnS)}$

or, $\dfrac{[H^+]^2}{0.04\times0.1} < \dfrac{1.0\times10^{-21}}{2.5\times10^{-13}} \Rightarrow [H^+] < 4\times10^{-6}\ \text{M}$

Now, in the given buffer, $[H^+] = \dfrac{K_a\cdot[CH_3COOH]_O}{[CH_3COO^-]_O}$

$$= \frac{2\times10^{-5}\times0.25}{0.15} = 3.33\times10^{-5} > 4\times10^{-6}\ \text{M}$$

Hence, no precipitation. To start precipitation $[H^+]$ should decrease and hence, CH_3COONa should be added.

Now, $4\times10^{-6} = \dfrac{2\times10^{-5}\times0.25}{[CH_3COONa]_O}$

$\therefore [CH_3COONa]_O = 1.25$ M

79. $Mg(OH)_2(S) + 2NH_4^+ \rightleftharpoons Mg^{2+} + 2NH_4OH$

To re-dissolve $Mg(OH)_2$, $Q \le K_{eq}$

or, $\dfrac{[Mg^{2+}][NH_4OH]^2}{[NH_4^+]^2} \le \dfrac{K_{sp}}{K_b^2}$

or, $\dfrac{\left(\dfrac{0.15\times0.1}{0.5}\right)\left(\dfrac{0.35\times0.1}{0.5}\right)^2}{\left(\dfrac{n}{0.5}\right)^2} \le \dfrac{1.2\times10^{-11}}{(2.0\times10^{-5})^2}$

$\therefore n \ge 0.035$

Hence, minimum mass of $(NH_4)_2SO_4$ needed

$$= \frac{0.035}{2}\times132 = 2.31\ \text{gm}$$

80.

$$\begin{array}{lccc} & Ag^+ & + \quad Cl^- & \rightleftharpoons AgCl(S) \\ & \frac{500\times0.01}{1000} & \frac{250\times0.02}{1000} & \\ & =5\times10^{-3}\ \text{M} & =5\times10^{-3}\ \text{M} & \\ \text{Eq} & 5\times10^{-3}-(x+y)\,\text{M} & (5\times10^{-3}-x)\,\text{M} & \end{array}$$

$$\begin{array}{ccc} Ag^+ & + \quad Br^- & \rightleftharpoons AgBr(S) \\ =5\times10^{-3}\ \text{M} & =5\times10^{-3}\ \text{M} & \\ 5\times10^{-3}-(x+y)\,\text{M} & (5\times10^{-3}-y)\,\text{M} & \end{array}$$

As both reactions will tend towards completion, $(x + y) = 5\times10^{-3}$

Now, $[Ag^+](5\times10^{-3} - x) = 10^{-10}$ (1)

$\Rightarrow [Ag^+]\cdot y = 10^{-10}$

and $[Ag^+](5\times10^{-3} - y) = 5\times10^{-13}$ (2)

From (1) ÷ (2), $\dfrac{y}{5\times10^{-3} - y} = 200 \Rightarrow y = \dfrac{1}{201}$

$\therefore [Br^-] = 5\times10^{-3} - y \approx 2.5\times10^{-5}$ M

Section B (One or More than one Correct)

1. (a) Complete neutralization $\Rightarrow P^H = 7.0$

(b) $[H^+]_{\text{final}} = \dfrac{55\times0.1-45\times0.1}{100} = 0.01\,\text{M}$

$\Rightarrow P^H = 2.0$

(c) OH^- is in excess.

(d) $[H^+]_{\text{final}} = \dfrac{75\times\frac{1}{5}-25\times\frac{1}{5}}{100} = 0.1\,\text{M} \Rightarrow P^H = 1.0$

2. For basic solution: $[H^+] < [OH^-]$ and $[H^+] < \sqrt{Kw}$

$\therefore P^H > P^{OH}$ or $P^H > \dfrac{P^{kw}}{2}$ or $P^{OH} < \dfrac{P^{kw}}{2}$

3.

$$\underset{C(1-\alpha)M}{HA} \rightleftharpoons \underset{C\alpha M}{H^+} + \underset{C\alpha M}{A^-}$$

$$K_a = \frac{C\alpha\cdot C\alpha}{C(1-\alpha)} = \frac{\alpha^2\cdot C}{1-\alpha} \approx \alpha^2\cdot C \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$$

$$\text{Now, } K_a = \frac{[H^+]\cdot C\alpha}{C(1-\alpha)} = \frac{[H^+]\cdot\alpha}{1-\alpha} \Rightarrow \alpha = \frac{K_a}{K_a+[H^+]}$$

$$= \frac{1}{1+\dfrac{[H^+]}{K_a}} = \frac{1}{1+10^{(P^{Ka}-P^H)}}$$

4. Dilution results in increased degree of dissociation but decrease in concentrations of all active components.

5. Relation is valid only for conjugate pairs.

6. P^H may decrease only on increasing $[H^+]$.

7.

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

$$\begin{array}{ccc} (0.1-x)\,\text{M} & x\text{M} & (0.1+x)\,\text{M} \\ \simeq 0.1\,\text{M} & & \simeq 0.1\,\text{M} \end{array}$$

$$\text{Now, } 1.8\times10^{-5} = \frac{x\times0.1}{0.1} \Rightarrow x = 1.8\times10^{-5}$$

$$\text{and } \alpha = \frac{x}{0.1} = 1.8\times10^{-4}$$

$$\text{Now, } [H^T]_{\text{from water}} = [OH^-] = \frac{Kw}{[H^+]_{\text{acid}}} = 10^{-13}\,\text{M}$$

8.

$$\underset{1\,\text{bar}}{RNH_2(g)} + H_2O(l) \rightleftharpoons \underset{x\text{M}}{RNH_3^+(aq)} + \underset{x\text{M}}{OH^-(aq)}$$

$$10^{-6} = \frac{x\cdot x}{1} \Rightarrow x = 10^{-3} \Rightarrow P^{OH} = 3.0 \Rightarrow P^H = 11.0$$

9. $NH_4OH(aq) \rightleftharpoons NH_4^+ + OH^-$

Addition of solid NH_4OH will increase $NH_4OH(aq)$ concentration and hence, $[OH^-]$ will increase.

10. (c) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$; $\Delta H^\circ = +\text{ve}$

(d)

$$\begin{array}{lcccc} & HA & + \; OH^- & \rightleftharpoons \; A^- & + \; H_2O \\ & a & \frac{a}{2} & 0 & \\ \text{Final} & \frac{a}{2} & & \frac{a}{2} & \end{array}$$

$$P^H = P^{K_a} + \log\frac{a/2}{a/2} = P^{K_a}$$

11. $[H^+] >> [CO_3^{2-}]$

12. Theory based

13.

$$\begin{array}{lccccc} & NH_4Cl & + \; NaOH & \rightleftharpoons \; NH_4OH & + \; NaCl & \\ & a & b & 0 & & \\ \text{For buffer:} & (a-b) & \approx 0 & b & & \Rightarrow a>b \end{array}$$

$$\begin{array}{lccccc} & CH_3COONa & + \; HCl & \rightleftharpoons \; CH_3COOH & + \; NaCl & \\ & a & b & 0 & & \\ \text{For buffer:} & (a-b) & \approx 0 & b & & \Rightarrow a>b \end{array}$$

14. KCN is a salt of weak acid (HCN) and strong base (KOH).

15.

$$\begin{array}{lcccc} & BOH & + \; H^+ & \rightleftharpoons \; B^+ & + \; H_2O \\ & a\,\text{mole} & b\,\text{mole} & 0 & \\ \frac{1}{5}\text{th run} & a-\frac{a}{5} & 0 & \frac{a}{5} & \\ \text{Equivalent point} & \approx 0 & \approx 0 & a\,\text{mole} & \end{array}$$

$$\text{Now, for 1/5th reaction, } P^{OH} = P^{K_b} + \log\frac{[B^-]}{[BOH]}$$

$$\text{or, } (14-9) = P^{K_b} + \log\frac{a/5}{4a/5}$$

$$\therefore P^{K_b} = 5.6 \Rightarrow K_b = 2.5\times10^{-6}$$

$$\text{At equivalent point: } P^H => -\frac{1}{2}(P^{K_b} + \log C)$$

$$\text{or, } 4.5 => -\frac{1}{2}(5.6 + \log C) \Rightarrow C = 0.25\,\text{M}$$

Now, $n_{\text{HCl used}} = n_{B^+\text{ formed}}$

$$\text{or, } \frac{V\times0.5}{1000} = \frac{(100+V)\times0.25}{1000} \Rightarrow V_{HCl} = 100\,\text{ml}$$

Finally, $n_{\text{BOH takes}} = n_{\text{Hcl used for equivalent point}}$

or, $\frac{w}{45} = \frac{100 \times 0.5}{1000} \Rightarrow w = 2.25$ gm

$\therefore$ Percentage purity of base $= \frac{2.25}{2.5} \times 100 = 90\%$

16. $$\underset{(0.5-x)\,M}{CO_3^{2-}} + H_2O \rightleftharpoons \underset{(x-y)M}{HCO_3^-} + \underset{(x+y)M}{OH^-}\ ;$$

$$K_{h_1} = \frac{Kw}{K_{a_2}} = 2 \times 10^{-4}$$

$$\underset{(x-y)M}{HCO_3^-} + H_2O \rightleftharpoons \underset{yM}{H_2CO_3} + \underset{(x+y)M}{OH^-}\ ;$$

$$K_{h_2} = \frac{Kw}{K_{a_1}} = 2.5 \times 10^{-9}$$

Now, $2 \times 10^{-4} = \frac{(x-y)\cdot(x+y)}{(0.5-x)} \approx \frac{x \cdot x}{0.5} \Rightarrow x = 10^{-2}$

and $2.5 \times 10^{-9} = \frac{y \cdot (x+y)}{(x-y)} \approx \frac{y \cdot x}{x} \Rightarrow y = 2.5 \times 10^{-9}$

Now, $h = \frac{x}{0.5} = 0.02$

$P^{OH} = -\log(x+y) \approx -\log(10^{-2}) = 2.0 \Rightarrow P^H = 12.0$

and $[H_2CO_3] = y = 2.5 \times 10^{-9}$ M

17. $\overset{+}{N}H_3CH_2COOH \xrightarrow{P^{K_{a1}}=2.22} \overset{+}{N}H_3CH_2COO^-$

$\xrightarrow{P^{K_{a2}}=9.78} NH_3CH_2COO^-$

$$P^H = \frac{1}{2}(P^{K_{a_1}} + P^{K_{a_2}}) = \frac{1}{2}(2.22 + 9.78) = 6.0$$

Now, $K_{a_1} = \frac{[\overset{\oplus}{N}H_3\,CH_2COO^-][H^+]}{[\overset{\oplus}{N}H_3\,CH_2COOH]}$

$$\Rightarrow 10^{-2.22} = \frac{0.01 \times 10^{-6}}{[\overset{\oplus}{N}H_3\,CH_2COOH]}$$

$\therefore [\overset{\oplus}{N}H_3\,CH_2COOH] = 10^{-5.78} = 1.7 \times 10^{-6}$ M

% of glycine in cationic form

$= \frac{1.7 \times 10^{-6}}{0.01} \times 100 = 0.017\%$

18. At equivalent point, the solution should be acidic.

19. Sodium acetate solution is basic.

20. For precipitation of $Fe(OH)_2$,

$$[OH^-]_{\min} = \sqrt{\frac{8 \times 10^{-16}}{0.02}} = 2 \times 10^{-7}$$

$\Rightarrow P^{OH}_{\max} = 6.7 \Rightarrow P^H_{\min} = 7.3$

For precipitation of $Fe(OH)_3$,

$$[OH^-]_{\min} = \left(\frac{4 \times 10^{-28}}{0.05}\right)^{1/3} = 2 \times 10^{-9}$$

$\Rightarrow P^{OH}_{\max} = 8.7 \Rightarrow P^H_{\min} = 5.3$

Section C (Comprehensions)

Comprehension I

1. $K = 1.5 \times 10^2 = \frac{[\text{Dimer}]}{[\text{Monomer}]^2} = \frac{x}{(0.1-2x)^2}$

$\Rightarrow x = \frac{5}{120}$

$\therefore \frac{[\text{Dimer}]}{[\text{Monomer}]} = \frac{x}{0.1-2x} = \frac{5}{2}$

2. $K = 3.6 \times 10^{-2} = \frac{(\text{Dimer})}{[\text{Monomer}]^2} = \frac{x}{(0.1-2x)}$

$\Rightarrow x = 3.6 \times 10^{-4}$

$\therefore \frac{(\text{Dimer})}{[\text{Monomer}]} = \frac{x}{0.1-2x} \Rightarrow \frac{x}{0.1} = \frac{9}{2500}$

3. $[H^+] \approx \sqrt{0.1 \times 2 \times 10^{-5}} = \sqrt{2} \times 10^{-3}$

(Dimerization is negative as Q. 2)

$\therefore P^H = 2.85$

Comprehension II

4. $[CH_3COOH]_O = \dfrac{0.7\times10^{-3}}{10\times10^{3}} = 7\times10^{-8}\,M$

The solution is so dilute that we may assume almost complete dissociation of acid.

$\therefore [H^+]_{acid} \approx 7\times10^{-8}$ M

Now, $H_2O \rightleftharpoons \underset{(7\times10^{-8}+x)M}{H^+} + \underset{xM}{OH^-}$

$10^{-14} = (7\times10^{-8}+x)\cdot x \Rightarrow x = 7\times10^{-8}$

$\therefore P^H = -\log(7\times10^{-8}+x) = 6.85$

5.

$$\begin{array}{lccc} & CH_3COOH \rightleftharpoons & CH_3COO^- + & H^+ \\ \text{Eqn.} & yM & 7\times10^{-8}M & 7\times10^{-8}+x \\ & & & =14\times10^{-8}\,M \end{array}$$

Now, $2.0\times10^{-5} = \dfrac{7\times10^{-8}\times14\times10^{-8}}{y}$

$\therefore\ y = 4.9\times10^{-10}$ M

Comprehension III

7. $K_a = \dfrac{(8\times10^{-3})^2}{0.2} = 3.2\times10^{-4}$

6. $K_a = 3.2\times10^{-4} = \dfrac{[H^+]\times(1.0\times0.8)}{0.2}$

$\therefore\ [H^+] = 8\times10^{-5} = \Rightarrow P^H = 4.1$

Comprehension IV

8. $p^H = p^{Ka}(NH_4^+) + \log\dfrac{[NH_3]_O}{[NH_4^+]}$

$= 9.3 + \log\dfrac{0.8}{0.2} = 9.9$

9.

$$\begin{array}{lccc} & NH_4OH + & H^+ \rightleftharpoons & NH_4^+ + H_2O \\ & 0.8M & 0.3M & 0.2M \\ \text{Final} & 0.5M & \approx 0 & 0.5M \end{array}$$

$p^H = p^{K_a(NH_4^+)} + \log\dfrac{[NH_3]_O}{[NH_4^+]_O} = 9.3 + \log\dfrac{0.5}{0.5} = 9.3$

10. H^+ added in excess. Final $[H^+] = 1.0 - 0.8 = 0.2$ M

$\therefore\ P^H = -\log(0.2) = 0.7$

Comprehension V

11. No hydrolysis $\Rightarrow p^H = 7.0$

12. Concentration of

$KAl(SO_4)_2.12H_2O = \dfrac{11.85/474}{100/1000}$

$= 0.25$ M

$$\underset{(0.25-x)M}{Al^{3+}} + H_2O \rightleftharpoons \underset{xM}{Al(OH)^{2+}} + \underset{xM}{H^+}$$

$1.4\times10^{-5} = \dfrac{x\cdot x}{(0.25-x)} \simeq \dfrac{x^2}{0.25}$

$\Rightarrow x = 1.87\times10^{-3}\,M = [H^+]$

13. $\underset{(0.5-x)M}{SO_4^{2-}} + H_2O \rightleftharpoons \underset{x}{HSO_4^-} + \underset{x}{OH^-}$

$\dfrac{10^{-19}}{1.25\times10^{-2}} = \dfrac{x\cdot x}{(0.5-x)} \simeq \dfrac{x^2}{0.5} \Rightarrow x = 6.32\times10^{-7}$ M

$\therefore [H^+] = \dfrac{10^{-14}}{6.32\times10^{-7}} = 1.58\times10^{-8}$ M

14.

$$\begin{array}{lccccc} & Al^{3+} + & SO_4^{2-} + H_2O \rightleftharpoons & Al(OH)^{2+} + & HSO_4^- \\ & 0.25M & 0.5M & 0 & 0 \\ \text{Eqn.} & (0.25-x)M & (0.5-x)M & x & x \end{array}$$

$\dfrac{1.4\times10^{-5}}{1.25\times10^{-2}} = \dfrac{x\cdot x}{(0.25-x)(0.5-x)} \simeq \dfrac{x^2}{0.25\times0.5}$

$\therefore\ x = 1.18\times10^{-2}$

Now, $1.4\times10^{-5} = \dfrac{1.18\times10^{-2}\times[H^+]}{0.25}$

$\therefore\ [H^+] = 2.97\times10^{-4}$ M

Comprehension VI

15. $$\begin{array}{lllll} \mathrm{PuO_2^{2+}} + \mathrm{H_2O} & \rightleftharpoons & \mathrm{PuO_2(OH)^+} + & \mathrm{H^+} \\ \begin{smallmatrix} 0.01-x \\ \approx 0.01 \end{smallmatrix} & & x & x=1.6\times10^{-4} \end{array}$$

$$\therefore K_h = \frac{x \cdot x}{0.01-x} \simeq \frac{x^2}{0.1} = 2.56\times10^{-6}$$

16. $K_a = \dfrac{Kw}{K_b} \Rightarrow K_b = 3.9\times10^{-9}$

Comprehension VII

17. $p^{\mathrm{H}} = \dfrac{1}{2}(\mathrm{P}^{\mathrm{K_{a_2}}} + \mathrm{P}^{\mathrm{K_{a_3}}}) = \dfrac{1}{2}(8+13) = 10.5$

18. For 2nd equivalent point,

$n_{\mathrm{NaoH}} = 2 \times n_{\mathrm{H_3PO_4}}$

$\dfrac{\mathrm{V}\times0.5}{1000} = 2\times\dfrac{100\times0.1}{1000} \Rightarrow \mathrm{V} = 40\ \mathrm{ml}$

After adding HCl,

$$\begin{array}{llll} & \mathrm{HPO_4^{2-}} + & \mathrm{H^+} & \rightleftharpoons \mathrm{H_2O_4^-} \\ & 10\text{ millimole} & 5\text{ millimole} & 0 \\ \text{Final} & 5 & \approx0 & 5 \end{array}$$

$$\therefore \mathrm{P^H} = 8 + \log\frac{5}{5} = 8.0$$

19. $\mathrm{S} = \dfrac{\mathrm{K_{sp}}}{[\mathrm{OH^-}]^2} = \dfrac{4.0\times10^{-30}}{(10^{-6})^2} = 4.0\times10^{-18}\ \mathrm{M}$

Comprehension VIII

20. $\mathrm{P^H} = \mathrm{P^{K_a}} + \log\dfrac{[\mathrm{HCO_3^-}]_\mathrm{O}}{[\mathrm{H_2CO_3}]_\mathrm{O}} = 6.4 + \log\dfrac{8}{1} = 7.3$

21. $7.4 = 6.4 + \log\dfrac{[\mathrm{HCO_3^-}]_\mathrm{O}}{[\mathrm{H_2CO_3}]_\mathrm{O}} \Rightarrow \dfrac{[\mathrm{H_2CO_3}]_\mathrm{O}}{[\mathrm{HCO_3^-}]_\mathrm{O}} = \dfrac{1}{10}$

22. More $\mathrm{CO_2}$ should dissolve in solution.

Comprehension IX

23. $\mathrm{pH} = 7 + \dfrac{1}{2}(\mathrm{P}^{K_{a_2}} + \log \mathrm{C}) = 7 + \dfrac{1}{2}(10.6 + \log 1) = 12.3$

24.
$$\begin{array}{llll} & \mathrm{CO_3^{2-}} + & \mathrm{H^+} & \rightleftharpoons \mathrm{HCO_3^-} \\ & \frac{50\times1}{75}\mathrm{M} & \frac{25\times1}{75}\mathrm{M} & 0 \\ \text{Final} & \frac{25}{75}\mathrm{M} & \approx0 & \frac{25}{75}\mathrm{M} \end{array}$$

$$\mathrm{pH} = P^{K_{a_2}} + \log\frac{[\mathrm{CO_3^{2-}}]_\mathrm{O}}{[\mathrm{HCO_3^-}]_\mathrm{O}} = 10.6 + \log\frac{1/3}{1/3} = 10.6$$

25.
$$\begin{array}{llll} & \mathrm{CO_3^{2-}} + & \mathrm{H^+} & \rightleftharpoons \mathrm{HCO_3^-} \\ & \frac{50\times1}{100}\mathrm{M} & \frac{50\times1}{100}\mathrm{M} & 0 \\ \text{Final} & \approx0 & \approx0 & \frac{50}{100}\mathrm{M} \end{array}$$

$$\therefore \mathrm{pH} = \frac{1}{2}(P^{K_{a_1}} + P^{K_{a_2}}) = \frac{1}{2}(5.4 + 10.6) = 8.0$$

26.
$$\begin{array}{llll} & \mathrm{CO_3^{2-}} + & \mathrm{H^+} & \rightleftharpoons \mathrm{HCO_3^-} \\ & \frac{50\times1}{125}\mathrm{M} & \frac{75\times1}{125}\mathrm{M} & 0 \\ \text{Final} & 0 & \frac{25}{125}\mathrm{M} & \frac{50}{125}\mathrm{M} \end{array}$$

$$\begin{array}{llll} & \mathrm{HCO_3^-} + & \mathrm{H^+} & \rightleftharpoons \mathrm{H_2CO_3} \\ & \frac{50}{125}\mathrm{M} & \frac{25}{125}\mathrm{M} & 0 \\ \text{Final} & \frac{25}{125}\mathrm{M} & =0 & \frac{25}{125}\mathrm{M} \end{array}$$

$$\therefore\ \mathrm{pH} = P^{K_a} + \log\frac{[\mathrm{HCO_3^-}]_\mathrm{O}}{[\mathrm{H_2CO_3}]_\mathrm{O}}$$

$$= 5.4 + \log\frac{25/125}{25/125} = 5.4$$

27. $[\mathrm{H_2CO_3}] = \dfrac{50\times10}{150} = \dfrac{1}{3}\ \mathrm{M}$

$$\therefore \mathrm{pH} = \frac{1}{2}(P^{K_{a_1}} + \log \mathrm{C}) = \frac{1}{2}(5.4 + \log\frac{1}{3}) = 2.94$$

Comprehension X

28. $\overset{+}{N}H_3-CH_3-COOH \underset{K_{a_1}=4\times10^{-3}}{\overset{K_{b_2}=2.5\times10^{-12}}{\rightleftharpoons}}$

$\overset{+}{N}H_3-CH_3-COO^- \underset{K_{b_1}=6.25\times10^{-5}}{\overset{K_{a_2}=1.6\times10^{-10}}{\rightleftharpoons}}$

$NH_2-CH_2-COO^-$

Required $K_b = K_{b_1} = 6.25\times10\times10^{-5}$

29. $\therefore \text{pH} = \frac{1}{2}(P^{K_{a1}} + P^{K_{a2}}) = \frac{1}{2}(2.4+9.8) = 6.1$

Comprehension XI

30. Moles of Cu reacted $= \dfrac{6.35\times10^{-3}}{63.5} = 10^{-4}$

$\therefore [Ag^+] = 2 \times$ Mole of Cu reacted $= 2\times10^{-4}$ M

31. $\ln K_{eq} = \dfrac{\Delta G^\circ}{-RT} = \dfrac{-120\times10^3}{-8.0\times300} = 50 \Rightarrow K_{eq} >>> 1$

32. $K_{sp} = [Ag^+][BRO_3^-] = (2\times10^{-4})^2 = 4\times10^{-8}\ M^2$

Comprehension XII

33. $S = \dfrac{K_{sp}[AgCN]}{[CN^-]} = \dfrac{1.0\times10^{-16}}{0.02} = 5.0\times10^{-15}$ M

34. $\underset{}{AgCN(s)} + \underset{(0.02-S)M}{CN^-} \rightleftharpoons \underset{SM}{Ag(CN)_2^-}$

$K_{eq} = K_{sp}\times K_f = 15$

$15 = \dfrac{s}{0.02-s} \Rightarrow s = \dfrac{0.3}{16} = 1.875\times10^{-2}\text{M}$

35. $s = [Ag^+] + \underset{5M}{[Ag(Cu)_2^-]}; \dfrac{K_{sp}}{[Cu^-]} + K_f\cdot K_{sp}\cdot[Cu^-]$

For minimum solubility: $\dfrac{ds}{d[Cu^-]} = 0$

or, $-\dfrac{K_{sp}}{[Cu^-]^2} + K_f\cdot K_{sp} = 0$

$\Rightarrow [Cu^-] = \sqrt{\dfrac{1}{K_f}} = 2.58\times10^{-9}\text{M}$

Section D (Assertion–Reason)

1. For acidic solution, pH < 7.0 at 25° C.
2. If there were no common ion effect, P^H should lie in between 7.0 and 7.3
3. $[H^+]_{HCl} = 10^{-4}\ M < [H^+]_{HCOOH} = 3.16\times10^{-2}$M
4. Dilution results decrease in concentration of BOH (aq), B^+ (aq) as well as OH^- (aq).
5. The pH of buffer remains constant on slight dilution but for acidic solution, the dilution results in the decrease in $[H^+]$ and hence, increase in pH.
6. pH of buffer containing H^A and A^- may be less than, greater than or equal to 7.0.
7. $K_a(CH_3COOH) = K_b(NH_4OH)$ and hence, CH_3COONH_4 solution is also neutral. But, it undergoes hydrolysis.
8. Theory based
9. Reaction occurs but at equivalent point, pH will be less than 7.
10. As dilution does not change the concentration of ions in saturated solution, the mole of ions will increase.

Section E (Column Match)

1. True electrolytes produce ions in pure liquid form as well as in solution. Potential electrolytes are molecular in pure liquid state but it produces ions in solution.

2. (P) [OH–] to just start precipitation $= \sqrt{\dfrac{K_{sp}}{[Mg^{2+}]}}$

$$= \sqrt{\frac{2\times10^{-6}}{2\times10^{-3}}} = 10^{-1.5}$$

$$\therefore\ p^{OH} = 1.5 \Rightarrow P^{H} = 12.5$$

(Q) $[OH^-]_{max} = \left(\dfrac{K_{sp}}{[Al^{3+}]}\right)^{1/3} = \left(\dfrac{10^{-28}}{0.1}\right)^{1/3}$

$$= 10^{-9}\ M$$

$$\therefore\ p^{OH}_{min} = 9 \Rightarrow p^{H}_{max} = 5.0$$

(R) $$\begin{array}{ccc} CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \\ \left(0.1-0.1\times\frac{10}{11}\right)M & 0.1\times\frac{10}{11}M & ? \\ =\frac{0.1}{11}M & =\frac{1}{11}M & \end{array}$$

$$\text{Now, } K_a = 10^{-5} = \frac{\frac{1}{11}\times[H^+]}{\frac{0.1}{11}} \Rightarrow [H^+] = 10^{-6}\,M$$

$$\therefore\ p^{H} = 6.0$$

(S) $[H^+] = \sqrt{K_a \cdot C} = \sqrt{10^{-7}\times0.001} = 10^{-5}\ M$

$\Rightarrow pH = 5.0$

(T) $$\begin{array}{cccc} A^- & + H_2O \rightleftharpoons & HA + & OH^-; \\ (6\times10^{-5}-x)\,M & & xM & xM \end{array}$$

$$\frac{Kw}{K_a} = 2\times10^{-6}$$

$$2\times10^{-6} = \frac{x\cdot x}{(6\times10^{-5}-x)} \Rightarrow x = 1\times10^{-5}$$

$$\therefore\ P^{OH} = 5 \Rightarrow pH = 9$$

3. Theory based

4. (A) $pH = P^{K_{a1}} + \log\dfrac{[H_2A^-]_O}{[H_3A]_O} = 4.0$

(B) $pH = P^{K_{a2}} + \log\dfrac{[HA^{2-}]_O}{[H_2A^-]_O} = 8.0$

(C) $pH = P^{K_{a3}} + \log\dfrac{[A^{3-}]_O}{[HA^{2-}]_O} = 12.0$

(D) $pH = \dfrac{1}{2}(P^{K_{a1}} + P^{K_{a2}}) = \dfrac{1}{2}(4+8) = 6.0$

(E) $pH = \dfrac{1}{2}(P^{K_{a2}} + P^{K_{a3}}) = \dfrac{1}{2}(8+12) = 10.0$

5. (A) $K_a(H_2O) = K_b(H_2O) = \dfrac{Kw}{[H_2O]} = \dfrac{10^{-14}}{\left(\frac{1000}{18}\right)}$

$$= 1.8\times10^{-16}$$

(C) On increasing temperature, Kw increases and hence, P^{Kw} decreases.

Section F (Subjective)

Single-digit Integer Type

1. $[D^+] = \sqrt{K_W} = \sqrt{10^{-16}} = 10^{-8}\ M$

$\Rightarrow P^{D} = -\log[D^+] = 8$

2. $[HCOOH]_O = \dfrac{1.15\times10^3}{46} = 25\ M = C$

$$\begin{array}{cccc} HCOOH + & HCOOH \rightleftharpoons & HCOOH_2^+ + & HCOO^- \\ C-x & C-x & x & x \end{array}$$

From given data: $x = \sqrt{K} = 10^{-3}\ M$

$\therefore$ Percentage of HCOOH molecules converted into $HCOO^-$

$$= \frac{x}{C}\times100 = \frac{10^{-3}}{25}\times100 = 4\times10^{-3}$$

3. $[NH_3]_O = \dfrac{10/17}{100/0.85}\times10^3 = 5\ M$

$$[OH^-] = \sqrt{K_b \cdot C} = \sqrt{\frac{Kw}{K_a(NH_4^+)} \cdot C}$$

$$= \sqrt{\frac{10^{-14}}{5\times10^{-10}} \times 5} = 10^{-2}\,M$$

$$\therefore [H_3O^+] = \frac{Kw}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}\ M$$

4. $[H^+] = \sqrt{K_a \cdot C} = \sqrt{4\times10^{-10}\times0.0025} = 10^{-6}\ M$

$\therefore P^H = -\log 10^{-6} = 6$

5. $[H_2SO_3]_O = \dfrac{1.28}{64} = 0.02\ M$

$$\begin{array}{lll} H_2SO_3 \rightleftharpoons & H^+ + & HSO_3^- \\ (0.02-x)\,M & xM & xM \end{array}$$

Now, $K_a = 10^{-2} = \dfrac{x \cdot x}{(0.02-x)}$

$\Rightarrow x = 0.01\,M \Rightarrow pH = -\log x = 2$

6. $pH = P^{K_{a_1}} + \log\dfrac{[HC_4H_4O_6^-]_O}{[H_2C_4H_4O_6]_O}$

$= 3.3 + \log\dfrac{18.8/18.8}{30/150} = 3$

7. Buffer capacity,

$$\beta = -\frac{[H^+]\,\text{added}}{\Delta\, P^H} = -\frac{0.05/0.2}{(-0.05)} = 5$$

8.

$$\begin{array}{lcccc} & HA & +\ OH^- & \rightleftharpoons\ A^- & + H_2O \\ & a\ \text{millimole} & 36.12\times0.1\ \text{millimole} & 0 & \\ \text{Equ.point} & \simeq0 & \simeq0 & 3.612\ \text{millimole} & \end{array}$$

$$\begin{array}{lccc} & A^- & +\ H^+ & \rightleftharpoons\ HA \\ & 3.612\ \text{mmole} & 18.06\times0.1\,\text{mmole} & 0 \\ \text{Final} & 1.806\ \text{mmole} & \simeq0 & 1.806\ \text{mmole} \end{array}$$

$$\therefore pH = P^{K_a} + \log\frac{[A^-]_O}{[HA]_O} = 5 + \log\frac{1.806}{1.806} = 5$$

9.

$$\begin{array}{lcccc} & H_2A^+ & +\ OH^- & \rightleftharpoons\ HA & + H_2O \\ & 30\times0.06\ \text{mmole} & 20\times0.09\ \text{mmole} & & \\ \text{Final} & \simeq0 & \simeq0 & 1.8\ \text{mmole} & \end{array}$$

$$\therefore pH = \frac{1}{2}(P^{K_{a_1}} + P^{K_{a_2}}) = \frac{1}{2}(2.28 + 9.72) = 6$$

10. For appearance of only $\ln^+$ colour,

$$\log\frac{[\ln^+]}{[\ln OH]} = \frac{4.6-3.4}{2} = 0.6 = \log 4$$

$$\therefore \frac{[\ln^+]}{[\ln OH]} = 4$$

Four-digit Integer Type

1.

$$\begin{array}{lcccc} & C_6H_5NH_2 + H_2O & \rightleftharpoons C_6H_5NH_3^+ & +\ OH^- \\ & 0.2\,M & 0 & CM \\ \text{Eqn.} & (0.2-x)\,M & xM & (C+x)\,M \\ & \simeq0.2\,M & =10^{-8}\,M & \simeq CM \end{array}$$

Now, $K_b = \dfrac{[C_6H_5NH_3^+][OH^-]}{C_6H_5NH_2}$

$\Rightarrow 4\times10^{-10} = \dfrac{10^{-8}\times C}{0.2}$

$\therefore C = 8\times10^{-3}\ M$

Now, mass of NaOH added

$= \dfrac{8\times10^{-3}}{1000}\times500\times40 = 0.16\,gm = 160\,mg$

2. $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

$\Rightarrow 1.8\times10^{-5} = \dfrac{4\times10^{-4}\times[CH_3COO^-]}{0.2}$

$\therefore [CH_3COO^-] = 9\times10^{-3}\ M$

$\therefore$ Mass of CH_3COONa added

$\dfrac{9\times10^{-3}\times500}{1000}\times82 = 0.369\ gm = 369\ mg$

3.

$$\begin{array}{lccc} & H_2SO_3 \rightleftharpoons & H^+ + & HSO_4^- \\ & CM & 0 & 0 \\ \text{Final} & \simeq0 & CM & CM \end{array}$$

$$\begin{array}{lccc} & HSO_4^- \rightleftharpoons & H^+ & +SO_4^{2-} \\ \text{Fianl }(C-x)M & & \begin{array}{c}(C+x)M \\ =0.01\text{ M}\end{array} & xM \end{array}$$

$$\text{Now, } 1.2\times10^{-2} = \frac{0.01\times x}{C-x} \Rightarrow x = \frac{6}{11}C$$

$$\text{and } C + x = 0.01 \Rightarrow C = \frac{0.01\times11}{17}\text{ M}$$

4. $$P^H = P^{K_a} + \log\frac{[NaHCo_3]_O}{[H_2Co_3]_O}$$

$$\text{or, } 7.4 = 6.1 + \log\frac{V\times5}{10\times2} \Rightarrow V = 80\text{ ml}$$

5. $$[HSO_4^-]_O = \frac{1.8/120}{100/1000} = 0.15\text{ M}$$

$$\begin{array}{ccc} HSO_4^- \rightleftharpoons & H^+ + & SO_4^{2-} \\ (0.15-x)M & xM & xM \end{array}$$

$$4\times10^{-2} = \frac{x\cdot x}{0.15-x}$$

$$\Rightarrow x = 6\times10^{-2}\text{ M} = 60\text{ millimole/L}$$

6. $$\begin{array}{lcccc} & Al(H_2O)_6^{3+} + H_2O \rightleftharpoons & Al(H_2O)_5^{OH^{2+}} & + H_3O^+ \\ & (C-x)M & xM & xM \\ \text{Now,} & 10^{-5} = & & \begin{array}{c}=10^{-3}M \\ C\approx0.1M\end{array} \end{array}$$

$\therefore$ Mass of $Al(OH)_3$ added = 400 × 0.1 × 133.5 = 5.34 gm = 5340 mg

7. $$9.18 = P^{K_a} + \log\frac{60}{40} \qquad (1)$$

$$9.00 = P^{K_a} + \log\frac{x}{100-x} \qquad (2)$$

$$\therefore\ x = 50$$

8. $$\begin{array}{lccc} & I_2 & + I^- \rightleftharpoons & I_3^- \\ & \begin{array}{c}\frac{12.7}{254} \\ =0.05M\end{array} & 0.1M & 0 \\ \text{Eqn.} & (0.05-x)M & 0.1-x & x \end{array}$$

$$= \frac{0.254}{254} = 0.001$$

$$\therefore\ x = 0.049$$

$$\text{Now, } K_c = \frac{x}{(0.05-x)(0.1-x)}$$

$$= \frac{0.049}{0.001\times0.051} = 960$$

9. Concentration of $Ca(OH)_2$ in its saturated solution

$$= \left(\frac{K_{sp}}{4}\right)^{1/3} = \left(\frac{3.2\times10^{-5}}{4}\right)^{1/3} = 0.02\,M$$

$$\begin{array}{lccc} \text{Now,} & Ca^{2+} + & 2OH^- \rightleftharpoons & Ca(OH)_2(s) \\ & 0.02M & 0.04M & \end{array}$$

On adding NaOH

$$\begin{array}{lcc} & 0.01\text{ M} & (0.02 + 0.8)\text{ M} \\ & & = 0.82\text{ M} \\ \text{Equ} & (0.01 - x)M = 0 & (0.82 - 2x) \\ & & M = 0.8M \end{array}$$

$$\therefore\ [Ca^{2+}]_{left} = \frac{3.2\times10^{-5}}{(0.8)^2} = 5\times10^{-5} << 0.01$$

$\therefore$ $Ca(OH)_2$ precipitated = 0.01 mole = 0.01 × 74 = 0.74 gm = 740 mg

10. $$S = \frac{0.0055/550}{100/1000} = 10^{-4}\text{ M}$$

$\therefore$ K_{sp} of $Ca(pam)_2 = 4S^3 = 4\times10^{-12}$ M

$$\begin{array}{lccc} \text{Now,} & Ca^{2+} & +2\,pam^- \rightleftharpoons & Ca(pam)_2(s) \\ & \frac{40/40}{10^6}\times10^2 & 0.1M & \\ & =10^{-3}\text{ M} & & \\ \text{Final} & =0 & 0.1M & \end{array}$$

$\therefore$ $Ca(pam)_2$ participated $= 10^{-3}\times10 = 0.01$ mole $= 0.01\times550 = 5.50$ gm $= 550$ mg