

EXERCISE

1

CBSE FLASH BACK

- Q.1** What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2 , CN^- , HClO_4 , F^- , OH^- , CO_3^{2-} , and S^{2-}
- Q.2** Which of the followings are Lewis acids? H_2O , BF_3 , H^+ , and NH_4^+
- Q.3** What will be the conjugate bases for the bronsted acids: HF , H_2SO_4 and HCO_3^- ?
- Q.4** Write the conjugate acids for the following bronsted bases: NH_2^- , NH_3 and HCOO^-
- Q.5** The species: H_2O , HCO_3^- , HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and base.
- Q.6** Classify the following species into Lewis acids and Lewis bases and show how these acts as Lewis acid/base:
(a) OH^- (b) F^- (c) H^+ (d) BCl_3
- Q.7** The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. What is its pH?
- Q.8** The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.
- Q.9** The ionization constant of HF , HCOOH and HCN at 298 K are 6.8×10^{-4} , 1.8×10^{-4} and 4.8×10^{-9} respectively. Calculate the ionization constants of the corresponding conjugate base.
- Q.10** The ionization constant of phenol is 1.0×10^{-10} . What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?
- Q.11** The first ionization constant of H_2S is 9.1×10^{-8} . Calculate the concentration of HS^- ion in its 0.1 M solution. How will this concentration be affected if the solution is 0.1 M in HCl also? If the second dissociation constant of H_2S is 1.2×10^{-13} . Calculate the concentration of S^{2-} under both conditions..
- Q.12** The ionization constant of acetic acid is 1.74×10^{-5} . Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH.
- Q.13** It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pK_a .
- Q.14** Assuming complete dissociation, calculate the pH of the following solutions:
(a) 0.003 M (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH
- Q.15** Calculate the pH of the following solutions:
(a) 2 g of TlOH dissolved in water to give 500 ml of solution.
(b) 0.3 g of Ca(OH)_2 dissolved in water to give 2 litre of solution
(c) 0.3 g of NaOH dissolved in water to give 200 mL of solution.
(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of solution
- Q.16** The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a of bromoacetic acid.
- Q.17** The pH of 0.005 M codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$) solution is 9.95. Calculate its ionization constant and pK_b .

- Q.18** What is the pH of 0.001 M aniline solution? The ionization constant of aniline is 4.27×10^{-10} . Calculate the degree of ionization of aniline in the solution. Also calculate the ionization constant of the conjugate acid of aniline
- Q.19** Calculate the degree of ionization of 0.05 M acetic acid if its pK_a value is 4.74. How is the degree of dissociation affected when its solution also contains
(a) 0.01M (b) 0.1 M in HCl
- Q.20** The ionization constant of dimethylamine is 5.4×10^{-4} . Calculate its degree of ionization in its 0.02 M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M NaOH?
- Q.21** Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below:
(A) Human muscle-fluid 6.83 (B) Human stomach fluid, 1.2
(C) Human blood, 7.38 (D) Human saliva, 6.4.
- Q.22** The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.
- Q.23** If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH?
- Q.24** The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution.
- Q.25** The ionization constant of propanoic acid is 1.32×10^{-5} . Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01 M in HCl also?
- Q.26** The pH of 0.1 M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution
- Q.27** The ionization constant of nitrous acid is 4.5×10^{-4} . Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis.
- Q.28** A 0.02 M solution of pyridinium hydrochloride has $pH = 3.44$. Calculate the ionization constant of pyridine.
- Q.29** Predict if the solutions of the following salts are neutral, acidic or basic.
NaCl, KBr, NaCN, NH_4NO_3 , $NaNO_2$ and KF
- Q.30** The ionization constant of chloroacetic acid is 1.35×10^{-3} . What will be the pH of 0.1M acid and its 0.1M sodium salt solution?
- Q.31** Ionic product of water at 310 K is 2.7×10^{-14} . What is the pH of neutral water at this temperature?
- Q.32** Calculate the pH of the resultant mixtures:
(A) 10 mL of 0.2M $Ca(OH)_2$ + 25 mL of 0.1 M HCl
(B) 10 mL of 0.1 M H_2SO_4 + 10 mL of 0.01 M $Ca(OH)_2$
(C) 10 mL of 0.1M H_2SO_4 + 10 mL of 0.1M KOH
- Q.33** Determine the solubilities of silver chromate ($K_{sp} = 1.1 \times 10^{-12}$), barium chromate ($K_{sp} = 1.2 \times 10^{-12}$), ferric hydroxide ($K_{sp} = 1.0 \times 10^{-38}$), lead chloride ($K_{sp} = 1.6 \times 10^{-5}$) and mercurous iodide ($K_{sp} = 4.5 \times 10^{-29}$) at 298 K from their solubility product constant. Determine also the molarities of individual ions.
- Q.34** The solubility product constant of Ag_2CrO_4 and AgBr are 1.1×10^{-12} and 5.0×10^{-13} respectively. Calculate the ratio of the molarities of their saturated solutions.
- Q.35** Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $K_{sp} = 7.4 \times 10^{-8}$)

- Q.36** The ionization constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water.
- Q.37** What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, $K_{sp} = 6.3 \times 10^{-18}$).
- Q.38** What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298K? (For calcium sulphate, K_{sp} is 9.1×10^{-6})
- Q.39** The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this is added to 5mL of 0.04 M solution of the following: FeSO_4 , MnCl_2 , ZnCl_2 and CdCl_2 , in which of these solutions precipitation will take place?
- Q.40** Calculate pH of a 1.0×10^{-8} M solution of HCl.
- Q.41** The ionisation constant of HF is 3.2×10^{-4} . Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present (H_3O^+ , F^- and HF) in the solution and its pH.
- Q.42** The pH of 0.1 M monobasic acid is 4.50. Calculate the concentration of species H^+ , A^- and HA at equilibrium. Also, determine the value of K_a and $\text{p}K_a$ of the monobasic acid.
- Q.43** Calculate the pH of 0.08 M solution of hypochlorous acid. HOCl. The ionization constant of the acid is 2.5×10^{-5} . Determine the percent dissociation of HOCl.
- Q.44** The pH of 0.004 M hydrazine solution is 9.7. Calculate its ionization constant K_b and $\text{p}K_b$.
- Q.45** Calculate the pH of solution formed on mixing 0.2 M NH_4Cl and 0.1 M NH_3 . The pOH of ammonia solution is 4.75.
- Q.46** Determine the degree of ionization and pH of a 0.05 M of ammonia solution. The ionization constant of ammonia is $= 1.77 \times 10^{-5}$. Also, calculate the ionic constant of the conjugate acid of ammonia.
- Q.47** Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10 M HCl. The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$.
- Q.48** The $\text{p}K_a$ of acetic acid and $\text{p}K_b$ of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.
- Q.49** Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A_2X_3 , $K_{sp} = 1.1 \times 10^{-23}$.
- Q.50** The values of K_{sp} of two sparingly soluble salt $\text{Ni}(\text{OH})_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble. Explain.
- Q.51** Calculate the molar solubility of $\text{Ni}(\text{OH})_2$ in 0.10 M NaOH. The ionic product of $\text{Ni}(\text{OH})_2$ is 2.0×10^{-15} .

EXERCISE

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CONCEPTUAL OBJECTIVE

[SINGLE CORRECT]

- Q.1** 100 mL of 1 M HCl is mixed with 50 mL of 2 M HCl. Hence, $[H_3O^+]$ is –
 (A) 1.00 M (B) 1.50 M (C) 1.33 M (D) 3.00 M
- Q.2** At a temperature under high pressure
 $K_w(H_2O) = 1 \times 10^{-10}$
 A solution of pH 5.4 under these conditions is said to be :
 (A) acidic (B) basic (C) neutral (D) amphoteric
- Q.3** Which has maximum pH ?
 (A) 0.01 M H_2SO_4 (B) 0.01 M HCl (C) 0.01 M $Ca(OH)_2$ (D) 0.01 M NaOH
- Q.4** We have acidic buffer of CH_3COONa and CH_3COOH . One or more of the following operations will not change pH :
 I : diluting the mixture ten times II : adding some HCl
 III : adding some NaOH IV : adding equal moles of CH_3COONa and CH_3COOH into the buffer
 Select correct alternate :
 (A) I, II, III, IV (B) II, III (C) I, IV (D) II, IV
- Q.5** Degree of ionisation of 1 M $HCOOH$ is decreased to a maximum extent in presence of :
 (A) 1 M $HCHO$ (B) 1 M NaOH (C) 1 M $HCOONa$ (D) equally in all
- Q.6** Buffer begins to lose its effectiveness when :
 (A) $\frac{[Salt]}{[weak\ electrolyte]} \leq 0.1$ (B) $\frac{[Salt]}{[weak\ electrolyte]} \geq 10$
 (C) both (A) and (B) (D) none of these
- Q.7** In what volume ratio should you mix 1.0 M solution of NH_4Cl and NH_3 to produce a buffer solution of pH 9.80 ? [$pK_b(NH_3) = 4.74$]
 (A) 1 : 3.5 (B) 3.5 : 1 (C) 2 : 1 (D) 1 : 2
- Q.8** Number of (OH^-) in 1 mL solution of pH = 13 is –
 (A) 1×10^{-13} (B) 6.00×10^7 (C) 6.00×10^{13} (D) 6.02×10^{19}
- Q.9** $pK_a(CH_3COOH)$ is 4.74. x mol of lead acetate and 0.1 mol of acetic acid in one L solution make a solution of pH = 5.04. Hence, x is –
 (A) 0.2 (B) 0.05 (C) 0.1 (D) 0.02
- Q.10** Some chemist at ISRO wished to prepare a saturated solution of a silver compound and they wanted it to have the highest concentration of silver ion possible. Which of the following compounds would they use ?
 $K_{sp}(AgCl) = 1.8 \times 10^{-10}$; $K_{sp}(AgBr) = 5.0 \times 10^{-13}$, $K_{sp}(Ag_2CrO_4) = 2.4 \times 10^{-12}$
 (A) AgCl (B) AgBr (C) Ag_2CrO_4 (D) any of them

- Q.11** Lemon juice normally has a pH of 2. If all the acid in the lemon juice is citric acid and there are no citrate salts present, then what will be the citric acid concentration [HCit] in the lemon juice ?
(Assume that only the first hydrogen of citric acid is important)
 $\text{HCit} \rightleftharpoons \text{H}^+ + \text{Cit}^-, K_a = 8.4 \times 10^{-4} \text{ mol L}^{-1}$
(A) $8.4 \times 10^{-4} \text{ M}$ (B) $4.2 \times 10^{-4} \text{ M}$ (C) $16.8 \times 10^{-4} \text{ M}$ (D) $12.0 \times 10^{-2} \text{ M}$
- Q.12** 10 mL of 10^{-6} M HCl solution is mixed with 90 mL H_2O . pH will change approximately –
(A) by 1 unit (B) by 0.3 unit (C) 0.7 unit (D) by 0.1 unit
- Q.13** The solubility product of BaSO_4 is 1.5×10^{-9} . The precipitation in a 0.01 M Ba^{2+} ions solution will start on adding H_2SO_4 of concentration –
(A) 10^{-9} M (B) 10^{-8} M (C) 10^{-7} M (D) 10^{-6} M
- Q.14** In a saturated solution of electrolytes, the ionic products of their concentration are constant at a particular temperature. This constant for an electrolyte is known as –
(A) ionic product (B) ionisation constant
(C) dissociation constant (D) solubility product
- Q.15** 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 neutralisation of acid ?
(A) $2 \log 3/4$ (B) $2 \log 1/4$ (C) $\log 1/3$ (D) $2 \log 3$
- Q.16** When 0.4 g of NaOH is dissolved in one litre of solution, the pH of the solution is –
(A) 12 (B) 2 (C) 6 (D) 10
- Q.17** The hydrogen ion concentration and pH of the solution made by mixing 100 mL of 1.0 M HNO_3 with 100 mL of 0.8 M KOH , are –
(A) $[\text{H}^+] = 0.1$, pH = 1 (B) $[\text{H}^+] = 0.01$, pH = 2
(C) $[\text{H}^+] = 1 \times 10^{-12}$, pH = 12 (D) $[\text{H}^+] = 1 \times 10^{-7}$, pH = 7
- Q.18** If the solubility of lithium sodium hexafluoro aluminate, $\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$ is 's' mol L^{-1} , its solubility product is equal to
(A) s^8 (B) $12s^3$ (C) $18s^3$ (D) $2916s^8$
- Q.19** 10 mL of 0.1 N HCl is added to 990 mL solution of NaCl. The pH of the resulting solution is –
(A) zero (B) 3 (C) 7 (D) 10

EXERCISE

3

CONCEPTUAL SUBJECTIVES

- Q.1** The degree of dissociation of acetic acid in a 0.1 N solution is 1.32×10^{-2} . At what concentration of nitrous acid, its degree of dissociation will be same as that of acetic acid? $K_a(\text{HNO}_2) = 4 \times 10^{-4}$
- Q.2** How many times is the H^+ concentration in the blood ($\text{pH} = 7.36$) greater than in the spinal fluid ($\text{pH} = 7.53$)?
- Q.3** Assuming first step of dissociation to be complete, find the concentration of all species in a 0.1 M H_2SO_4 solution. $K_2 = 1.2 \times 10^{-2}$.
- Q.4** Calculate the concentration of various species in a 0.1 M H_2S saturated solution. $K_1 = 1 \times 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$.
- Q.5** A 0.400 M formic acid solution freezes at -0.758°C . Calculate the K_a of the acid at that temperature. (Assume molarity equal to molality). $K_f(\text{H}_2\text{O})$ is $1.86^\circ\text{mol}^{-1}\text{kg}$.
- Q.6** The dissociation constants of HF and HNO_2 are 6.71×10^{-4} M and 4.5×10^{-4} M, respectively. Calculate the pH and the ratio of $[\text{F}^-]$ to $[\text{NO}_2^-]$ in a solution that is simultaneously 0.5 M in HF and 0.4 M in HNO_2 .
- Q.7** Solubility of AgCl is 10^{-5} mol litre $^{-1}$. A solution contains 1 mg AgCl in 900 mL water. What amount of AgCl should be more added to make it saturated?
- Q.8** 100 mL of solution S_1 contains 0.17 mg of AgNO_3 . Another 200 mL solution S_2 contains 0.117 mg of NaCl. On mixing these two solutions predict whether the precipitate of AgCl will appear or not $K_{sp} \text{AgCl} = 10^{-10} \text{ M}^2$
- Q.9** A sample of AgCl was treated with 5 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3 , the remaining solution contained 0.00266625 g/litre Cl^- ion. Calculate the solubility of AgCl in (a) 0.1 M AgNO_3 (b) 0.1 M BaCl_2 (c) 0.2 M NaNO_3 .
Given that solubility of Ag_2CO_3 in 500 mL $\text{H}_2\text{O} = 13.8$ mg.
- Q.10** By referring to the equilibrium constants listed below, find the equilibrium for each of the following :
(a) $\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}_3\text{O}^+ \rightleftharpoons \text{Fe}^{3+} + 6\text{H}_2\text{O}$
(b) $\text{PbSO}_4(\text{s}) + \text{CrO}_4^{2-} \rightleftharpoons \text{PbCrO}_4(\text{s}) + \text{SO}_4^{2-}$
Given $K_{sp} [\text{Fe}(\text{OH})_3] = 4 \times 10^{-38}$, $K_w = 10^{-14}$
 $K_{sp} [\text{PbSO}_4] = 2 \times 10^{-8}$; $K_{sp} [\text{PbCrO}_4] = 2 \times 10^{-14}$
- Q.11** The solubility of $\text{Mg}(\text{OH})_2$ is increased by addition of NH_4^+ ion. Calculate –
(a) K_c for the reaction, $\text{Mg}(\text{OH})_2 + 2\text{NH}_4^+ \rightleftharpoons 2\text{NH}_3 + 2\text{H}_2\text{O} + \text{Mg}^{2+}$
(b) Find solubility of $\text{Mg}(\text{OH})_2$ in a solution containing 0.5 M NH_4Cl before addition of $\text{Mg}(\text{OH})_2$ (K_{sp} of $\text{Mg}(\text{OH})_2 = 1 \times 10^{-11}$, K_b for $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$)
- Q.12** A chemist needs a buffer with pH 4.35. How many milliliters of pure acetic acid (density = 1.049 g/mL) must be added to 465 mL of 0.0941 M NaOH solution to obtain such buffer? ($K_a = 1.8 \times 10^{-5}$)
- Q.13** The value of ionic product of water at various temperature are given below
- | $\theta/^\circ\text{C}$ | 0 | 10 | 25 | 40 | 50 |
|---------------------------------|-------|-------|-------|-------|-------|
| $K_w \times 10^{14}/\text{M}^2$ | 0.114 | 0.292 | 1.008 | 2.919 | 5.474 |
- What are the pH value of the pure water at these temperatures ?
(i) 0°C (ii) 10°C (iii) 25°C (iv) 40°C (v) 50°C

- Q.14** At 25°C, the degree of ionization of water was found to be 1.8×10^{-9} . Calculate the ionization constant and the ionic product of water at this temperature.
- Q.15** The ionic product of water at 100°C is 55 times than that at 25°C. (i) Calculate the value of pH of water at 100°C. (ii) A given solution at 100°C has a pH value 5.0. Indicate whether the solution is acidic or alkaline or neutral.
- Q.16** At 25°C, the degree of ionization for water is 1.8×10^{-9} . How is this affected in the presence of 10^{-8} M HCl (assume complete ionization for the acid)? Calculate the total hydrogen ion concentration in the presence of the acid. What is the pH of the solution.
- Q.17** Given a solution that is 0.5 M CH_3COOH . To what volume at 25°C must one dm^3 of this solution be diluted in order to (a) double the pH; (b) double the hydroxide-ion concentration. Given that $K_a = 1.8 \times 10^{-5}$ M.
- Q.18** What are the concentrations of H^+ , $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- and $\text{C}_2\text{O}_4^{2-}$ in a 0.1 M solution of oxalic acid? ($K_1 = 5.9 \times 10^{-2}$ M and $K_2 = 6.4 \times 10^{-5}$ M.)
- Q.19** It is found that 0.1 M solution of three sodium salts NaX, NaY and NaZ have pHs 7.0, 9.0 and 11.0, respectively. Arrange the acids HX, HY and HZ in order of increasing strength. Where possible, calculate the ionisation constants of the acids.
- Q.20** Calculate the value of K_h , α_h and pH of the following solution at 25°C.
 (i) 0.1 M ammonium acetate $K_a = K_b = 1.8 \times 10^{-5}$ M
 (ii) 0.1 M anilinium acetate $K_a = 1.8 \times 10^{-5}$ M; $K_b = 4.6 \times 10^{-10}$ M
 (iii) 0.1 M ammonium carbonate $K_{a1} = 4.5 \times 10^{-7}$ M, $K_{a2} = 4.7 \times 10^{-11}$ M
- Q.21** Calculate the pH of the following aqueous solutions :
 (i) 5×10^{-8} M HCl (ii) 5×10^{-10} M HCl (iii) 10^{-8} M NaOH (iv) 10^{-10} M NaOH
- Q.22** Compute the pH of a solution at 25°C which is twice as alkaline as pure water.
- Q.23** Calculate the pH of each of the following solutions :
 (a) 100 ml 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH
 (b) 100 ml of 0.1 M CH_3COOH mixed with 50 ml of 0.1 M NaOH
 (c) 50 ml of 0.1 M CH_3COOH mixed with 100 ml of 0.1 M NaOH
 ($K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$, $K_w = 1 \times 10^{-14}$)
- Q.24** Calculate how many H^+ ions are present in one millionth part of 1 ml of pure water. The ionic product of water is 1×10^{-14} (mol/l)²
- Q.25** A weak base BOH of concentration 0.02 mole/litre has a pH value of 10.45. If 100 ml of this base is mixed with 10 ml of 0.1 M HCl, what will be the pH of the mixture ?
- Q.26** Calculate the pH of 0.1 M acetic acid solution if its dissociation constant is 1.8×10^{-5} . If 1 litre of this solution is mixed with 0.05 mole of HCl, what will be the pH of the mixture ?
- Q.27** 2.05 g of sodium acetate was added to 100 ml of 0.1 M HCl solution. Find the H^+ ion concentration of the resulting solution. If 6 ml of 1 M HCl is further added to it, what will be the new H^+ concentration?
- Q.28** Calculate the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 ml of an aqueous solution containing 150 ml of 1 M HCl. $K_a(\text{H}_2\text{CO}_3) = 4.2 \times 10^{-7}$; $K_a(\text{HCO}_3^-) = 4.8 \times 10^{-11}$
- Q.29** An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentrations corresponding to given pH range, calculate the ionization constant of the indicator.

- Q.30** Calculate the hydrolysis constant of NH_4Cl ; determine the degree of hydrolysis of this salt in 0.01 M solution and the pH of the solution. $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$
- Q.31** A 0.02 M solution of CH_3COONa in water at 25°C is found to have a H^+ concentration of 3×10^{-9} g ionic weight per litre. What is the hydrolytic constant of the salt? $K_w = 1.01 \times 10^{-14}$, $K_a(\text{CH}_3\text{COOH}) = 1.75 \times 10^{-5}$
- Q.32** What is the solubility product of Ag_2CrO_4 if 0.0166 g of the salt dissolves in 500 ml of water at 18°C ?
- Q.33** The solubility of lead sulphate in water is 1.03×10^{-4} . Calculate its solubility in a centinormal solution of H_2SO_4 . $K_{sp}(\text{PbSO}_4) = 1.6 \times 10^{-8}$.
- Q.34** Equal volumes of 0.02 N solution of CaCl_2 and Na_2SO_4 are mixed, Will there be a formation of CaSO_4 precipitate? $K_{sp}(\text{CaSO}_4) = 1.4 \times 10^{-4}$.
- Q.35** Find the solubility of CaF_2 in 0.05 M solution of CaCl_2 and water. How many times is the solubility in the second case greater than in the first? $K_{sp}(\text{CaF}_2) = 4 \times 10^{-11}$.
- Q.36** How will the concentration of Ag^+ in a saturated solution of AgCl diminish if such an amount of HCl is added to it that the concentration of the Cl^- in the solution becomes equal to 0.03 mole/litre.
[$K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$]
- Q.37** Calculate the simultaneous solubility of CaF_2 and SrF_2 .
(a) $K_{sp}(\text{CaF}_2) = 3.9 \times 10^{-11}$
(b) $K_{sp}(\text{SrF}_2) = 2.9 \times 10^{-9}$
- Q.38** (a) Determine the pH of a 0.2 M solution of pyridine $\text{C}_5\text{H}_5\text{N}$. $K_b = 1.5 \times 10^{-9}$
(b) Predict the effect of addition of pyridinium ion $\text{C}_5\text{H}_5\text{NH}^+$ on the position of the equilibrium. Will the pH be raised or lowered?
(c) Calculate the pH of 1.0 L of 0.10 M pyridine solution to which 0.3 mol of pyridinium chloride $\text{C}_5\text{H}_5\text{NH}^+\text{Cl}^-$, has been added, assuming no change in volume.
- Q.39** A solution was made up to be 0.01 M in chloroacetic acid, ClCH_2COOH and also 0.002 M in sodium chloroacetate $\text{ClCH}_2\text{COONa}$. What is $[\text{H}^+]$ in the solution? $K_a = 1.5 \times 10^{-3}$.

EXERCISE

4

BRAINSTORMING OBJECTIVES

[SINGLE CORRECT]

- Q.1** 100 mL solution of pH = 6 is diluted to 1000 mL. Resulting solution has pH :
 (A) 7.0 (B) 6.79 (C) 7.3 (D) 6.40
- Q.2** The K_a value for the acid HA is 1.0×10^{-6} . What is the value of K for the reaction ?
 $A^- + H_3O^+ \rightleftharpoons HA + H_2O$
 (A) 1.0×10^{-8} (B) 1.0×10^8 (C) 1.0×10^{-3} (D) 1.0×10^6
- Q.3** At 25°C, $[H_3O^+] = 1 \times 10^{-7}$ M in water, hence, K_a is –
 (A) 1×10^{-14} (B) 5.55×10^{-15} (C) 1.8×10^{-16} (D) 55.5×10^{-10}
- Q.4** What is the value of K_w in 0.01 M NaOH ?
 (A) 1×10^{-15} (B) 1×10^{-13} (C) 1×10^{-16} (D) 1×10^{-14}
- Q.5** $[H_3O^+]$ in 0.1 M H_2SO_4 at two stages $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$
 $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ are :
 (A) 0.1 M, 0.1 M (B) 0.1 M, > 0.01 M (C) > 0.1 M, > 0.1 M (D) 0.1 M, < 0.1 M
- Q.6** 20 mL of 0.2 M NaOH is added to 50 mL of 0.2 M CH_3COOH . Hence $(pH - pK_a)$ is –
 (A) $\log \frac{3}{2}$ (B) $\log \frac{2}{3}$ (C) $\log 2$ (D) $2 \log 2$
- Q.7** pH of a mixture which is 0.1 M in CH_3COOH and 0.05 M in $(CH_3COOH)_2Ba$ is
 $[pK_a \text{ of } CH_3COOH = 4.74]$
 (A) 4.74 (B) 5.04 (C) 4.44 (D) 7.00
- Q.8** In which case change in pH is maximum ?
 (A) 1 mL of pH = 2 is diluted to 100 mL
 (B) 0.01 mol of NaOH is added into 100 mL of 0.01 M NaOH solution
 (C) 100 mL of H_2O is added into 900 mL of 10^{-6} M HCl
 (D) 100 mL of pH = 2 solution is mixed with 100 mL of pH = 12
- Q.9** Which buffer solution has maximum pH ?
 (A) mixture which is 0.1 M in CH_3COOH and 0.1 M in CH_3COONa [$pK_a(CH_3COOH) = 4.74$]
 (B) mixture which is 0.2 M CH_3COOH and 0.2 M in CH_3COONa
 (C) mixture which is 0.1 M in NH_4Cl and 0.1 M in NH_4OH [$pK_a(NH_4^+) = 9.26$]
 (D) all the solution have equal pH which is 4.74
- Q.10** K_{sp} of CdS is 8.0×10^{-27} and that of H_2S is 1×10^{-22} , 1×10^{-14} M, $CdCl_2$ solution is precipitated on passing H_2S when pH is about –
 (A) 4 (B) 6 (C) 5 (D) 7
- Q.11** 100 mL of 0.02 M benzoic acid ($pK_a = 4.2$) is titrated using 0.02 M NaOH. pH after 50 mL and 100 mL of NaOH have been added are –
 (A) 3.50, 7 (B) 4.2, 7 (C) 4.2, 8.1 (D) 4.2, 8.25
- Q.12** The solubility products of $Al(OH)_3$ and $Zn(OH)_2$ are 8.5×10^{-23} and 1.8×10^{-14} at room temperature. If the solution contains Al^{3+} and Zn^{2+} ions, the ion first precipitated by adding NH_4OH is –
 (A) Al^{3+} (B) Zn^{2+} (C) both (D) none
- Q.13** To prepare a buffer of pH 8.26, amount of $(NH_4)_2SO_4$ to be added into 500 mL of 0.01 M NH_4OH solution [$pK_a(NH_4^+) = 9.26$] :
 (A) 0.05 mol (B) 0.025 mol (C) 0.10 mol (D) 0.005 mol

- Q.14** If the equilibrium constant of the reaction of weak acid HA with strong base is 10^9 , then pH of 0.1 M NaA is –
 (A) 5 (B) 9 (C) 7 (D) 8
- Q.15** pH of mixture of HA and A^- buffer is 5. K_b of $A^- = 10^{-10}$. Hence $[HA]/[A^-]$ will be :
 (A) 1 (B) 10 (C) 0.1 (D) 100
- Q.16** pH of 0.01 M aqueous solution of NaX, NaY and NaZ are 8, 9 and 10 respectively. Strongest acid among HX, HY and HZ is –
 (A) HX (B) HY (C) HZ (D) can't be predicted
- Q.17** How many grams of CaC_2O_4 dissolve in distilled water to make one litre of saturated solution ($K_{sp} = 2.5 \times 10^{-9}$ and its molecular mass is 128)
 (A) 0.0064 g (B) 0.0128 g (C) 0.0032 g (D) 0.0640 g
- Q.18** A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10} . The pH of the buffer is –
 (A) 4 (B) 7 (C) 10 (D) 14
- Q.19** When the pH changes from 4 to 2, the hydrogen ion concentration will increase by a factor –
 (A) 2 (B) 1/2 (C) 10^2 (D) $10^{0.5}$
- Q.20** pH of the buffer containing 0.6 g of acetic acid and 8.2 g of sodium acetate in 1 litre of water is (pK_a of acetic acid = 4.5)
 (A) 7.5 (B) 4.5 (C) 5.5 (D) 6.5
- Q.21** The correct order of increasing $[H_3O^+]$ in the following aqueous solution is –
 (A) $0.001\text{ M H}_2\text{S} < 0.01\text{ M H}_2\text{SO}_4 < 0.01\text{ M NaCl} < 0.01\text{ M NaNO}_2$
 (B) $0.01\text{ M NaCl} < 0.01\text{ M NaNO}_2 < 0.01\text{ M H}_2\text{S} < 0.01\text{ M H}_2\text{SO}_4$
 (C) $0.01\text{ M NaNO}_2 < 0.01\text{ M NaCl} < 0.01\text{ M H}_2\text{S} < 0.01\text{ M H}_2\text{SO}_4$
 (D) $0.01\text{ M H}_2\text{S} < 0.01\text{ M NaCl} < 0.01\text{ M NaNO}_2 < 0.01\text{ M H}_2\text{SO}_4$
- Q.22** Which of the following statement/relationship is not correct ?
 (A) Upon hydrolysis salt of strong base and weak acid gives solution with $pH > 7$
 (B) $pH = \log \frac{1}{[H^+]}$
 (C) only at 25°C , the pH of the pure water is 7
 (D) the value of pK_w at 25°C is seven
- Q.23** For a concentrated solution of a weak electrolyte $A_x B_y$ the degree of dissociation is given as –
 (A) $\alpha = \sqrt{K_{eq} / c(x+y)}$ (B) $\alpha = \sqrt{K_{eq} c / (x-y)}$
 (C) $\alpha = (K_{eq} / c^{x+y-1} x^x y^y)^{1/(x+y)}$ (D) $\alpha = \sqrt{K_{eq} / xy}$
- Q.24** The solubility of sparingly soluble electrolyte $M^m A^a$ in water given by the expression –
 (A) $s = \left[\frac{K_{sp}}{m^m a^a} \right]^{m+a}$ (B) $s = \left[\frac{K_{sp}}{m^m a^a} \right]^{1/(m+a)}$ (C) $s = \left[\frac{K_{sp}}{m^a a^m} \right]^{m+a}$ (D) $s = \left[\frac{K_{sp}}{m^a a^m} \right]^{1/(m+a)}$
- Q.25** If the salts M_2X , QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as –
 (A) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$ (B) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$
 (C) $K_{sp}(M_2X) = K_{sp}(QY_2) = K_{sp}(PZ_3)$ (D) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$
- Q.26** Four solutions of NH_4Cl are taken with concentrations 1 M, 0.1 M, 0.01 M and 0.001 M. Their degree of hydrolysis are h_1, h_2, h_3 and h_4 . What is the gradation of degree of hydrolysis ?
 (A) $h_1 > h_2 > h_3 > h_4$ (B) $h_1 = h_2 = h_3 = h_4$ (C) $h_4 > h_3 > h_2 > h_1$ (D) none of these

EXERCISE

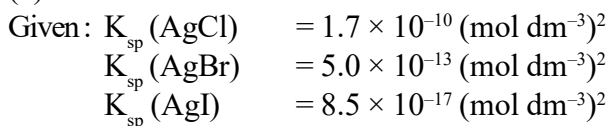
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BRAINSTORMING SUBJECTIVE

- Q.1** A weak base BOH was titrated against a strong acid. The pH at 1/4th equivalence point was 9.24. Enough strong base was now added (6 meq.) to completely convert the salt. The total volume was 50 ml. Find the pH at this point.
- Q.2** What is the pH of a 0.0050 M solution of Na_2S ? The ionization constants for H_2S are $K_1 = 1.0 \times 10^{-7}$ and $K_2 = 1.3 \times 10^{-14}$.
- Q.3** A buffer solution of pH 6.7 can be prepared by employing solution of NaH_2PO_4 and Na_2HPO_4 . If 0.005 mol of NaH_2PO_4 is weighed out, how much Na_2HPO_4 must be used to make 1 litre of the solution [K_2 for $\text{H}_3\text{PO}_4 = 6.3 \times 10^{-8}$]
- Q.4** An unknown volume and unknown concentration of weak acid HX is titrated with NaOH of unknown concentration. After addition of 10.0 cm³ of NaOH solution, pH of solution is 5.8 and after the addition of 20.0 cm³ of NaOH solution, the pH is 6.4. Calculate the pH of aqueous solution of 0.1 M NaX.
- Q.5** In an attempted determination of the solubility product constant of Ti_2S , the solubility of this compound in pure CO_2 free water was determined as 6.3×10^{-6} mol dm⁻³. Assume that the dissolved sulphide hydrolyzes almost completely to HS^- and that the further hydrolysis to H_2S can be neglected. What is the value of K_{sp} of the compound? [$K_2(\text{H}_2\text{S}) = 10^{-14}$]
- Q.6** Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in $\text{KAg}(\text{CN})_2$. Given $K_{inst}(\text{Ag}(\text{CN})_2^-) = 4.0 \times 10^{-19} \text{ M}^2$ and $K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10} \text{ M}^2$.
- Q.7** A solution containing zinc and manganese ions each at a concentration of 0.01 mol dm⁻³ is saturated with H_2S . Calculate (i) pH at which the MnS will form a precipitate (ii) conc. of Zn^{+2} ions remaining. Given : [H_2S] = 0.1 mol/lit, $K_{sp}(\text{ZnS}) = 1 \times 10^{-22} \text{ mol}^2 \text{ lit}^{-2}$, $K_{sp}(\text{MnS}) = 5.6 \times 10^{-16} \text{ mol}^2 \text{ lit}^{-2}$. K_1 and K_2 for H_2S are 1×10^{-7} and 1.1×10^{-14} .
- Q.8** (i) For the indicator thymol blue, the value of pH is 2.0, when half of the indicator is present in the unionised form. Calculate the percentage of the indicator in the unionized form in a solution of $4.0 \times 10^{-3} \text{ mol/dm}^3$ hydrogen ion concentration.
(ii) An indicator is a weak acid and the pH range of its colour is 3.1 to 4.5. If the neutral point of the indicator lies in the centre of the hydrogen ion concentration corresponding to given pH range Calculate the ionization constant of the indicator.
- Q.9** The solubility product of AgCl at 25°C is 10^{-10} . A solution of Ag^+ ion at a concentration of $4 \times 10^{-3} \text{ M}$ just fails to yields a precipitate of AgCl with a concentration of $1 \times 10^{-3} \text{ M}$ of Cl^- ion when the concentration of NH_3 in the solution is $2 \times 10^{-2} \text{ M}$. Calculate the magnitude of the equilibrium constant for :

$$[\text{Ag}(\text{NH}_3)_2]^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$$
- Q.10** The solubility of silver acetate in pure water at 25°C is 8.35 g lit⁻¹ and 61.8 lit⁻¹ in an acid buffer of pH = 3. Calculate the pH of 0.05 M CH_3COONa .
- Q.11** A solution of 0.1 mol dm⁻³ in Cl^- , 0.1 mol dm⁻³ in Br^- and 0.1 mol dm⁻³ in I^- . Solid AgNO_3 is gradually added to this solution. Assuming that the addition of AgNO_3 does not change the volume. Answer the following :
(a) What concentration of Ag^+ ions will be required to start precipitation of each of the three ions ?
(b) Which ion will precipitate first ?

- (c) What will be the concentration of this ion when the second ion starts precipitating ?
 (d) What will be the concentration of both the ions when the third ion starts precipitating ?



- Q.12** 10 g of NH_4Cl (mol. wt. = 53.5) when dissolved in 1000 g of water lowered the freezing point by 0.637°C . Calculate the degree of hydrolysis of the salt if its degree of dissociation is 0.75. The molal depression constant of water is $1.86 \text{ K kg mol}^{-1}$.
- Q.13** Tritium, T (an isotope of H) combines with fluorine to form weak acid TF, which ionises to give T^+ . Tritium is radioactive and is a β -emitter. A freshly prepared aqueous solution of TF has pT (equivalent of pH) of 1.5 and freezes at -0.372°C . If 600 ml of freshly prepared solution were allowed to stand for 24.8 years. Calculate.
 (i) Ionization constant of TF (ii) No. of β - particle emitted.
 [Given : K_f for water = $1.86 \text{ K Kg mol}^{-1}$, $t_{1/2}$ for tritium = 12.4 years]
- Q.14** The salt $\text{Zn}(\text{OH})_2$ is involved in the following two equilibria,
 $\text{Zn}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}), K_{sp} \text{Zn}(\text{OH})_2 = 1.2 \times 10^{-17}$
 $\text{Zn}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq}) \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}(\text{aq}), K_c = 0.13$
 Calculate the pH at which the solubility of $\text{Zn}(\text{OH})_2$ be minimum. Also find the solubility at this concentration.
- Q.15** Calculate the solubility of CaC_2O_4 in a solution with a fixed H^+ concentration of 10^{-4} M . The oxalate containing species ($\text{C}_2\text{O}_4^{2-}$, HC_2O_4^- , $\text{H}_2\text{C}_2\text{O}_4$) exist in solution and the relevant equilibria are
 $\text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}), K_{sp} = 2.3 \times 10^{-9}$
 $\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HC}_2\text{O}_4^-, K_1 = 5.36 \times 10^{-2}$
 $\text{HC}_2\text{O}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{O}_4^{2-}, K_2 = 5.42 \times 10^{-5}$
- Q.16** Given that 2×10^{-4} mole each of Mn^{2+} and Cu^{2+} was contained in one litre of a 0.003 M HClO_4 solution, and this solution was saturated with H_2S . Determine whether or not each of these ions, Mn^{2+} and Cu^{2+} will precipitate as sulphide. The solubility of H_2S , 0.1 mole per litre is assumed to be independent of the presence of other materials in the solution.
 $K_{sp}(\text{MnS}) = 3 \times 10^{-14}$, $K_{sp}(\text{CuS}) = 8 \times 10^{-37}$
 K_1 and K_2 for H_2S are 1×10^{-7} and 1.1×10^{-14} respectively. Also calculate % of Cu remaining unprecipitated. Will MnS precipitate if the above solution is made neutral by lowering the $[\text{H}^+]$ to 10^{-7} M ?
- Q.17** A buffer solution is $0.25 \text{ M CH}_3\text{COOH} - 0.15 \text{ M CH}_3\text{COONa}$, saturated in H_2S (0.1 M) and has $[\text{Mn}^{2+}] = 0.015 \text{ M}$. $K_a(\text{CH}_3\text{COOH}) = 1.74 \times 10^{-5}$, $K_a(\text{H}_2\text{S}) = 1.1 \times 10^{-21}$ and $K_{sp}(\text{MnS}) = 2.5 \times 10^{-13}$
 (a) will MnS precipitate ?
 (b) Which buffer component should be increased in concentration and to which minimum value to just start precipitation of MnS ?
- Q.18** Calculate the solubility of AgCN in a buffer solution pH 3.00 assuming no complex formation. $K_a(\text{HCN}) = 6.2 \times 10^{-10}$ and $K_{sp}(\text{AgCN}) = 2.2 \times 10^{-16}$.
- Q.19** What is the nature of 0.01 M NaHCO_3 solution ? Calculate its pH. K_1 and K_2 for H_2CO_3 are 4.5×10^{-7} and 4.7×10^{-11} respectively.
- Q.20** What is the concentration of Ag^+ ions in 0.01 M AgNO_3 that is also 1.0 M NH_3 ? Will AgCl precipitate from a solution that is 0.01 M AgNO_3 , 0.01 M NaCl and 1 M NH_3 ? $K_d(\text{Ag}[\text{NH}_3]_2^+) = 5.88 \times 10^{-8}$, $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$.

Q.21 Equal volumes of 0.02 M AgNO_3 and 0.02 M HCN were mixed. Calculate $[\text{Ag}^+]$ at equilibrium assuming no cyano complex formation. $K_{\text{sp}}(\text{AgCN}) = 2.2 \times 10^{-16}$, $K_{\text{a}}(\text{HCN}) = 6.2 \times 10^{-10}$.

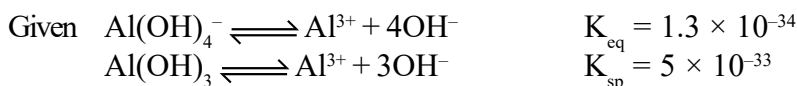
Q.22 9.4 g of phenol is added to 1200 mL of water. The ratio of number of phenoxide ions to those of unionised molecules of phenol is found to be 10^{-4} . Find the pH of this solution. Now a 2 litre solution of phenol of 10^{-5} M concentration is prepared. Calculate the pH of this solution.

Q.23 When 40 g of NaOH reacts with a mixture of 1 mole each of acids HX and HY , it is found that 75% HX is neutralised. If the value of K_{a} of HX is 9×10^{-6} then calculate pH of 1 M solution of HY in water and its degree of ionisation.

Q.24 An aqueous solution (2 litre volume) is "C" molar with respect to H_2A (dissociation constant K_{a}) and 2C molar with respect to H_2SO_4 (dissociation constant $K_{\text{a}} = \infty$); then prove that :

$$[\text{A}^{2-}] = \frac{K_{\text{a}}}{16C}; \frac{[\text{H}^+] - [\text{OH}^-]}{2} = 2C + [\text{A}^{2-}]$$

Q.25 At what minimum pH will 10^{-3} M $\text{Al}(\text{OH})_3$ go into solution ($V = 1$ litre) as $\text{Al}(\text{OH})_4^-$ and at what pH it will dissolved as Al^{3+} ?



Q.26 A 50.00 mL sample of 0.1 M $\text{La}(\text{NO}_3)_3$ is mixed with 50.00 mL of a $\text{NH}_4^+/\text{NH}_3$ buffer that is 0.20 M in NH_4^+ and 0.40 M in NH_3 . What percentage of the original La^{3+} has been precipitated as $\text{La}(\text{OH})_3$ when the mixture comes to equilibrium?

$$K_{\text{sp}}[\text{La}(\text{OH})_3] = 1 \times 10^{-19}, \text{p}K_{\text{b}}(\text{NH}_3) = 4.74$$

Q.27 An important component of blood is the buffer combination of dihydrogen phosphate ion and the hydrogen phosphate ion. Consider blood with a pH of 7.44.

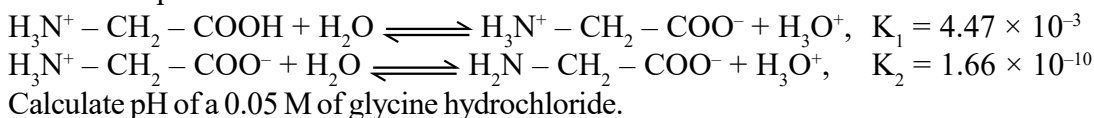
(a) What is the ratio of $\frac{[\text{H}_2\text{PO}_4^-]}{[\text{HPO}_4^{2-}]}$?

(b) What does the pH become if 25% of the hydrogen phosphate ions are converted to dihydrogen phosphate ion?

(c) What does the pH become if 15% of the dihydrogen phosphate ions are converted to hydrogen phosphate ions?

$$\begin{array}{l} \text{Given, For } \text{H}_3\text{PO}_4, \\ K_{\text{a1}} = 6.9 \times 10^{-3} \\ K_{\text{a2}} = 6.2 \times 10^{-8} \\ K_{\text{a3}} = 4.8 \times 10^{-13} \end{array}$$

Q.28 A solution of glycine hydrochloride contains the chloride ion and the glycinium ion, $^+\text{NH}_3\text{CH}_2\text{COOH}$, which is a diprotic acid.



Calculate pH of a 0.05 M of glycine hydrochloride.

Q.29 A solution of weak acid HA was titrated with base NaOH . The equivalence point was reached when 36.12 ml of 0.1 M NaOH has been added. Now 18.06 ml of 0.1 M HCl were added to titrated solution, the pH was found to be 4.92. What will be the pH of the solution obtained by mixing 10 ml of 0.2 M NaOH and 10 ml of 0.2 M HA .

Q.30 The indicator phenol red is half in the ionic form when pH is 7.2. If the ratio of the undissociated form to the ionic form is 1 : 5, find the pH of the solution. With the same pH for solution, if indicator is altered such that the ratio of undissociated form to dissociated form becomes 1 : 4, find the pH when 50% of the new indicator is in ionic form.

- Q.31** The freezing point of 3.75×10^{-2} M aqueous solution of weak acid HA is 272.9K. The molality of the solution is found to be 0.0384 molal. Find the $[H^+]$ of the solution on adding 3.75×10^{-2} moles of NaA to 1 L of the above solution. K_f of water = $1.86 \text{ K} \cdot \text{molal}^{-1}$. $T_{\text{freezing}} = 273 \text{ K}$ for water.
- Q.32** The amino acid glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, is basic because of its NH_2^- group and acidic because of its $-\text{COOH}$ group. By a process equivalent to base dissociation, glycine can acquire an additional proton to form $^+\text{NH}_3\text{CH}_2\text{COOH}$. The resulting cation may be considered to be a diprotic acid, since one proton from the $-\text{COOH}$ group and one proton from the $^+\text{NH}_3-$ group may be lost. The pK_a values for these processes are 2.35 and 9.78, respectively. In a 0.0100M solution of neutral glycine, what is the pH and what percent of the glycine is in the cationic form at equilibrium?
- Q.33** A given solution is 0.080 M in Ca^{2+} and 0.060 M in Mg^{2+} ions –
- (A) Is it possible to precipitate 99.9% of the Ca^{2+} as CaCO_3 without precipitating any MgCO_3 ?
- (B) What is the upper limit we must set on the $[\text{CO}_3^{2-}]$ in the solution in order to prevent any MgCO_3 from precipitating?
- (C) If we keep the $[\text{CO}_3^{2-}]$ at the upper limit, what is the $[\text{Ca}^{2+}]$ in the solution at the end of the separation?
- $K_{sp}(\text{CaCO}_3) = 4.8 \times 10^{-9}$, $K_{sp}(\text{MgCO}_3) = 4.0 \times 10^{-5}$
- Q.34** Saturated H_2S $[(\text{S}^{2-}) = 1.1 \times 10^{-20} \text{ M}]$ is bubbled into 0.2 M NaCN solution which is 0.02 M in each of $[\text{Ag}(\text{CN})_2^-]$ and $[\text{Cd}(\text{CN})_4^{2-}]$. Determine which sulphide precipitates first. K_{sp} for Ag_2S and CdS are 6×10^{-50} and 8×10^{-27} respectively.
- $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2^-]$, $K = 5.6 \times 10^{18}$
- $\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cd}(\text{CN})_4^{2-}]$, $K = 7.1 \times 10^{18}$
- Q.35** Consider the two equilibria
- $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^-(\text{aq})$; $K_{sp} = 4.0 \times 10^{-11}$
- $\text{F}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HF}(\text{aq}) + \text{OH}^-(\text{aq})$; $K_b(\text{F}^-) = 2.9 \times 10^{-11}$
- (a) Write the chemical equation for the overall equilibrium and determine corresponding equilibrium constant.
- (b) Determine the solubility of CaF_2 at pH = 7.0
- (c) Determine the solubility of $\text{CaF}_2(\text{s})$ at pH = 5.0
- Q.36** One of the substances sometimes responsible for the hardness of water is CaSO_4 . A particular water sample has 131 ppm CaSO_4 (131 g CaSO_4 per 10^6 g of water). If this water boiled in a tea kettle, approximately what fraction of water must be evaporated before $\text{CaSO}_4(\text{s})$ begins to deposit? Assume that solubility of CaSO_4 does not change with temperature in the range 0 to 100°C , $K_{sp}(\text{CaSO}_4) = 9.1 \times 10^{-6}$.
- Q.37** Determine the concentration of Ag^+ , $\text{Ag}(\text{S}_2\text{O}_3)^-$ and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$, $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ and $\text{S}_2\text{O}_3^{2-}$ in a solution prepared by dissolving 1.0 mole of $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ in 1.0 dm^3 of water.
- Q.38** pK_b of a weak acid is 7.09. In what ratio (in terms of volume) 0.02 M of this base and 0.02 M HCl be mixed to have 400 mL of the buffer of pH = 7?
- Q.39** What is the pH of a solution that is –
- (a) 0.0105 M HCl and 1.02 M CH_3COOH
- (b) 0.315 M CH_3COOH and 0.250 M HCOOH
- (c) 0.0030 M KOH and 0.0018 M $\text{Ca}(\text{OH})_2$
- (d) 0.55 M CH_3COOH and 0.16 M $\text{C}_6\text{H}_5\text{OH}$ (phenol)

$$K_a \left\{ \begin{array}{l} \text{CH}_3\text{COOH} = 1.8 \times 10^{-5} \\ \text{HCOOH} = 1.8 \times 10^{-4} \\ \text{C}_6\text{H}_5\text{OH} = 1.6 \times 10^{-10} \end{array} \right\}$$

- Q.40** Potassium alum is $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. As a strong electrolyte, it is considered to be 100% dissociated into K^+ , Al^{3+} , and SO_4^{2-} . The solution is acidic because of 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 11.4 g of $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in enough water to make 0.10 dm^3 of solution, calculate its $[\text{H}_3\text{O}^+]$
- (a) Considering the hydrolysis
 $\text{Al}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Al}(\text{OH})_3 + \text{H}_3\text{O}^+$ with $K_h = 1.4 \times 10^{-5} \text{ M}$
- (b) Allowing also for the equilibrium
 $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{SO}_4^{2-}$ with $K_2 = 1.26 \times 10^{-2} \text{ M}$
- Q.41** A solution is prepared by mixing one mole of HA with one mole of HB, diluting to a total volume of 1 dm^3 with water. Both HA and HB are weak acids which dissociate according to the following reversible equations.
- $$\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \quad K_1 = 1.0 \times 10^{-6} \text{ M}$$
- $$\text{HB} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{B}^- \quad K_2 = 1.0 \times 10^{-6} \text{ M}$$
- (i) Calculate the equilibrium concentrations of H_3O^+ , A^- and B^- .
- (ii) How does the presence of HB affect the dissociation of HA?
- Q.42** What is the solubility of PbS; (a) ignoring the hydrolysis of ions, and (b) including the hydrolysis of ions (assume pH of the solution to be equal to 7)? Given that $K_{\text{sp}}(\text{PbS}) = 7.0 \times 10^{-29} \text{ M}^2$, $K_{\text{b}_2}(\text{Pb}(\text{OH})^+) = 1.5 \times 10^{-8} \text{ M}$, $K_{\text{a}_1}(\text{H}_2\text{S}) = 1.0 \times 10^{-7} \text{ M}$ and $K_{\text{a}_2}(\text{HS}^-) = 1.0 \times 10^{-14} \text{ M}$.
- Q.43** Calculate the molar solubility of AgCN in water. Given :
 $K_{\text{sp}}(\text{AgCN}) = 2.3 \times 10^{-16} \text{ M}^2$ and $K_{\text{b}}(\text{CN}^-) = 1.7 \times 10^{-5} \text{ M}$
- Q.44** A $1.0 \times 10^{-3} \text{ M}$ solution of AgNO_3 is made 0.20 M in NH_3 . What are the concentration of Ag^+ , $\text{Ag}(\text{NH}_3)^+$, and $\text{Ag}(\text{NH}_3)_2^+$ in the resulting solution. Given :
- $$\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}(\text{NH}_3)^+ + \text{NH}_3 \quad K_1 = 1.4 \times 10^{-4} \text{ M}$$
- $$\text{Ag}(\text{NH}_3)^+ \rightleftharpoons \text{Ag}^+ + \text{NH}_3 \quad K_2 = 4.3 \times 10^{-4} \text{ M}$$
- Q.45** A buffer solution was prepared by dissolving 0.05 mol formic acid and 0.06 mol sodium formate in enough water to make 1.0 L of solution. K_{a} for formic acid is 1.80×10^{-4} .
- (a) Calculate the pH of the solution.
- (b) If this solution were diluted to 10 times its volume, what would be the pH?
- (c) If the solution in (b) were diluted to 10 times its volume, what would be the pH?
- Q.46** How many moles of sodium hydroxide can be added to 1.0 L of a solution 0.1 M in NH_3 and 0.1 M in NH_4Cl without changing the pOH by more than 1.00 unit? Assume no change in volume. $K_{\text{b}}(\text{NH}_3) = 1.8 \times 10^{-5}$.
- Q.47** 20 ml of a solution of 0.1 M CH_3COOH solution is being titrated against 0.1 M NaOH solution. The pH values after the addition of 1 ml and 19 ml of NaOH are $(\text{pH})_1$ and $(\text{pH})_2$, what is ΔpH ?
- Q.48** To a solution of acetic acid, solid sodium acetate is gradually added. When x grams of the salt have been added, the pH has a certain value. When y grams of the salt have been added, the pH has been further raised by 0.6 units. What is the ratio of $x : y$? If now the second solution is diluted, what happens to the pH?
- Q.49** When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl , the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.
- Q.50** A solution of chloroacetic acid, ClCH_2COOH containing 9.45 grams in 500 ml of the solution has a pH of 2.0. What is the degree of ionization of the acid.
- Q.51** A solution of ammonia bought for cleaning the windows was found to be 10% ammonia by mass, having a density of 0.935 g ml^{-1} . What is the pH of the solution., Take K_{b} for protonation of ammonia = 5.5×10^{-6} .

Q.52 The K_w of water at two different temperatures is:

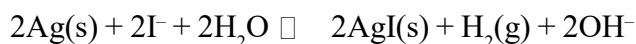
T	25°C	50°C
K_w	1.08×10^{-14}	5.474×10^{-14}

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

Q.53 A hand book states that the solubility of methylamine $\text{CH}_3\text{NH}_2(\text{g})$ in water at 1 atm pressure at 25°C is 959 volumes of $\text{CH}_3\text{NH}_2(\text{g})$ per volume of water ($pK_b = 3.39$)

- (a) Estimate the max. pH that can be attained by dissolving methylamine in water.
(b) What molarity $\text{NaOH}(\text{aq.})$ would be required to yield the same pH?

Q.54 the equilibrium constant of the reaction



is 1.2×10^{-23} at 25°C. Calculate the pH of a solution at equilibrium with the iodine ion concentration = 0.10 and the pressure of H_2 gas = 0.60 atm.

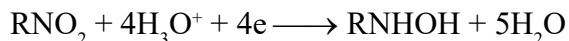
Q.55 Mixtures of solutions. Calculate the pH of the following solutions (Use data of Q.59)

- (a) 50 ml of 0.12 M H_3PO_4 + 20 ml of 0.15 M NaOH
(b) 50 ml of 0.12 M H_3PO_4 + 40 ml of 0.15 M NaOH
(c) 40 ml of 0.12 M H_3PO_4 + 40 ml of 0.18 M NaOH
(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.25 M NaOH

Q.56 Mixture of solution. Calculate the pH of the following solution (Use data of Q.59)

- (a) 50 ml of 0.050 M Na_2CO_3 + 50 ml of 0.040 M HCl
(b) 40 ml of 0.020 M Na_3PO_4 + 40 ml of 0.040 M HCl
(c) 50 ml of 0.10 M Na_2CO_3 + 50 ml of 0.10 M NaH_2PO_4 ;
(d) 40 ml of 0.10 M H_3PO_4 + 40 ml of 0.10 M Na_3PO_4

Q.57 The electrolytic reduction of an organic nitro compound was carried out in a solution buffered by acetic acid and sodium acetate. The reaction was



300 ml of a 0.0100 M solution of RNO_2 buffered initially at pH 5.00 was reduced, with the reaction above going to completion. The total acetate concentration.. $[\text{HOAc}] + [\text{OAc}^-]$, was 0.50 M. Calculate the pH of the solution after the reduction is complete.

- Q.58** (a) It is desired to prepare 100 ml of a buffer of pH 5.00. Acetic, benzoic and formic acid and their salts are available for use. Which acid should be used for maximum effectiveness against increase in pH? What acid-salt ratio should be used? pK_a values of these acids are acetic 4.74; benzoic 4.18 and formic 3.68.
(b) If it is desired that the change in pH of the buffer be no more than 0.10 unit from the addition of 1 mmol of either acid or base, what minimum concentration of the acid and salt should be used?

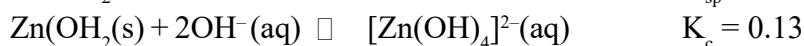
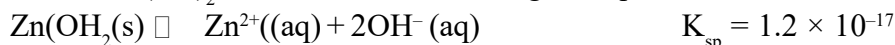
Q.59 Calculate the pH of 0.1 M solution of (i) NaHCO_3 , (ii) Na_2HPO_4 and (iii) NaH_2PO_4 . given that

$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$;	$K_1 = 4.2 \times 10^{-7} \text{ M}$
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$;	$K_2 = 4.8 \times 10^{-11} \text{ M}$
$\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^-$;	$K_1 = 7.5 \times 10^{-3} \text{ M}$
$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-}$;	$K_2 = 6.2 \times 10^{-8} \text{ M}$
$\text{HPO}_4^{2-} \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-}$;	$K_3 = 1.0 \times 10^{-12} \text{ M}$

Q.60 When a 40 mL of a 0.1 M weak base is titrated with 0.16 M HCl , the pH of the solution at the end point is 5.23. What will be the pH if 15 mL of 0.12 M NaOH is added to the resulting solution.

- Q.61** Calculate the OH^- concentration and the H_3PO_4 concentration of a solution prepared by dissolving 0.1 mol of Na_3PO_4 in sufficient water to make 1 L of solution. $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$.
- Q.62** Find the pH of 0.068 M Na_2HPO_4 solution. Use K values from the above problem if required.
- Q.63** Calculate the value of the equilibrium constants for the reactions with water of H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} as bases. Comparing the relative values of the two equilibrium constants of H_2PO_4^- with water deduce whether solutions of this ion in water are acidic or basic. Deduce whether solutions of HPO_4^{2-} are acidic or basic. Take $K_1 = 5 \times 10^{-3}$, $K_2 = 5 \times 10^{-8}$, $K_3 = 5 \times 10^{-13}$.
- Q.64** Determine the equilibrium carbonate ion concentration after equal volumes of 1.0 M sodium carbonate and 1.0 M HCl are mixed. $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-11}$.
- Q.65** K_1 and K_2 for oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, are 5.6×10^{-2} and 5.0×10^{-5} . What is $[\text{OH}^-]$ in a 0.4 m M solution of $\text{Na}_2\text{C}_2\text{O}_4$?
- Q.66** If 0.00050 mol NaHCO_3 is added to 1 litre of a buffered solution at pH 8.00, how much material will exist in each of the three forms H_2CO_3 , HCO_3^- and CO_3^{2-} ? For H_2CO_3 , $K_1 = 5 \times 10^{-7}$, $K_2 = 5 \times 10^{-13}$.
- Q.67** Hydrazine, N_2H_4 , can interact with water in two stages.
- $$\text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{N}_2\text{H}_5^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_{b1} = 8.5 \times 10^{-7}$$
- $$\text{N}_2\text{H}_5^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{N}_2\text{H}_6^{2+}(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_{b2} = 8.9 \times 10^{-16}$$
- (i) What are the concentration of OH^- , N_2H_5^+ and $\text{N}_2\text{H}_6^{2+}$ in a 0.010 M aqueous solution of hydrazine?
- (ii) What is pH of the 0.010 M solution of hydrazine?
- Q.68** How much Na_2HPO_4 must be added to one litre of 0.005 M solution of NaH_2PO_4 in order to make a 1 L of the solution of pH 6.7? $K_1 = 7.1 \times 10^{-3}$, $K_2 = 6.3 \times 10^{-8}$, $K_3 = 4.5 \times 10^{-13}$ for H_3PO_4 ?
- Q.69** A solution of volume V contains n_1 moles of QCl and n_2 moles of RCl where QOH and ROH are two weak bases of dissociation constants K_1 and K_2 respectively. Show that the pH of the solution is given by $\text{pH} = \frac{1}{2} \log \left[\left(\frac{K_1 K_2}{K_w} \right) \frac{V}{n_1 K_2 + K_1 n_2} \right]$. State assumptions, if any.
- Q.70** A buffer solution, 0.080 M in Na_2HPO_4 and 0.020 M in Na_3PO_4 , is prepared. The electrolytic oxidation of 1.00 mmol of the organic compound RNHOH is carried out in 100 mL of the buffer. The reaction is $\text{RNHOH} + \text{H}_2\text{O} \longrightarrow \text{RNO}_2 + 4\text{H}^+ + 4\text{e}^-$. Calculate the approximate pH of the solution after the oxidation is complete.
- Q.71** An organic monoprotic acid [0.1M] is titrated against 0.1 M NaOH. By how much does the pH change between one fourth and three fourth states of neutralization? If at one third stage of neutralization, the pH is 4.45 what is the dissociation constant of the acid? Between what stages of neutralisation may the pH change by 2 units.
- Q.72** 50 ml of a solution which 0.050 M in the acid HA, $\text{pK}_a = 3.80$ and 0.10 M in HB, $\text{pK}_a = 8.20$, is titrated with 0.2 M NaOH. Calculate the pH.
- (a) at the first equivalence point and (b) at the second equivalence point
- Q.73** Calculate the solubility of solid zinc hydroxide at a pH of 5, 9 and 13. Given
- $$\text{Zn(OH)}_2(\text{s}) \rightleftharpoons \text{Zn(OH)}_2(\text{aq}) \quad K_1 = 10^{-6} \text{ M} \quad (1)$$
- $$\text{Zn(OH)}_2(\text{aq}) \rightleftharpoons \text{Zn(OH)}^+ + \text{OH}^- \quad K_2 = 10^{-7} \text{ M} \quad (2)$$
- $$\text{Zn(OH)}^+ \rightleftharpoons \text{Zn}^{2+} + \text{OH}^- \quad K_3 = 10^{-4} \text{ M} \quad (3)$$
- $$\text{Zn(OH)}_2(\text{aq}) + \text{OH}^- \rightleftharpoons \text{Zn(OH)}_3^- \quad K_4 = 10^3 \text{ M}^{-1} \quad (4)$$
- $$\text{Zn(OH)}_3^- + \text{OH}^- \rightleftharpoons \text{Zn(OH)}_4^{2-} \quad K_5 = 10 \text{ M}^{-1} \quad (5)$$

Q.74 The salt Zn(OH)_2 is involved in the following two equilibria,



Calculate the pH of solution at which solubility is minimum.

Q.75 What is the solubility of AgCl in 0.20 M NH_3 ?

Given : $K_{\text{sp}}(\text{AgCl}) = 1.7 \times 10^{-10} \text{ M}^2$, $K_1 = [\text{Ag(NH}_3)^+] / [\text{Ag}^+][\text{NH}_3] = 2.33 \times 10^3 \text{ M}^{-1}$ and $K_2 = [\text{Ag(NH}_3)_2^+] / [\text{Ag(NH}_3)^+][\text{NH}_3] = 7.14 \times 10^3 \text{ M}^{-1}$.

Q.76 H_2S is bubbled into a 0.2 M NaCN solution which is 0.02 M in each Ag(CN)_2^{-} and Cd(CN)_4^{2-} . Determine which sulphide precipitates first.

$$\begin{aligned} \text{Given} \quad K_{\text{sp}}(\text{Ag}_2\text{S}) &= 1.0 \times 10^{-50} \text{ M}^3 \\ K_{\text{sp}}(\text{CdS}) &= 7.1 \times 10^{-28} \text{ M}^2 \\ K_{\text{inst}}(\text{Ag(CN)}_2^{-}) &= 1.0 \times 10^{-20} \text{ M}^2 \\ K_{\text{inst}}(\text{Cd(CN)}_4^{2-}) &= 7.8 \times 10^{-18} \text{ M}^4 \end{aligned}$$

Q.77 Predict whether or not AgCl will be precipitated from a solution which is 0.02 M in NaCl and 0.05 M in KAg(CN)_2 . Given $K_{\text{inst}}(\text{Ag(CN)}_2^{-}) = 4.0 \times 10^{-19} \text{ M}^2$ and $K_{\text{sp}}(\text{AgCl}) = 2.8 \times 10^{-10} \text{ M}^2$.

Q.78 Show that solubility of a sparingly soluble salt $\text{M}^{2+}\text{A}^{2-}$ in which A^{2-} ions undergoes hydrolysis is given by :

$$S = \sqrt{K_{\text{sp}} \left(1 + \frac{[\text{H}^+]}{K_2} + \frac{[\text{H}^+]^2}{K_1 K_2} \right)}.$$

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

MULTIPLE CHOICE ANSWER TYPE

- Q.1** An acid-base indicator has a K_a of 3.0×10^{-5} . The acid form of the indicator is red and the basic form is blue. then:
 (A) pH is 4.05 when indicator is 75% red (B) pH is 5.00 when indicator is 75% blue.
 (C) pH is 5.00 when indicator is 75% red (D) pH is 4.05 when indicator is 75% blue.
- Q.2** The equilibrium constant for the reaction
 $\text{HONO}(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{HCN}(\text{aq}) + \text{ONO}^-(\text{aq})$ is 1.1×10^{-6} . From the magnitude of this K_{eq} one can conclude that
 (A) CN^- is stronger base than ONO^- (B) HCN is a stronger acid than HONO
 (C) The conjugate base of HONO is ONO^- (D) The conjugate acid of CN^- is HCN
- Q.3** The pH of a solution of 0.10 M CH_3COOH increases when which of the following substances is added?
 (A) NaHSO_4 (B) HClO_4 (C) NH_4NO_3 (D) K_2CO_3
- Q.4** All of the following are acid-base conjugate pairs:
 (A) HONO , NO_2^- (B) H_3O^+ , OH^-
 (C) CH_3NH_3^+ , CH_3NH_2 (D) HS^- , S_2^-
- Q.5** A 50.00 mL sample of 0.0100 M $\text{Ba}(\text{OH})_2$ is titrated with 0.0100 M HCl . The solution at the equivalence point is:
 (A) 3.33×10^{-3} M BaCl_2 (C) 5.00×10^{-3} M BaCl_2
 (C) 2.50×10^{-3} M BaCl_2 (D) 1.00×10^{-2} M BaCl_2
- Q.6** A flask contains 100.00 mL of 0.100 M HOAc . To prepare a buffer with $\text{pH} = \text{p}K_a$ which of the following samples of barium acetate solution should be added to the flask?
 (A) 50.00 mL of 0.400 M $\text{Ba}(\text{OAc})_2$ (B) 25.00 mL of 0.200 M $\text{Ba}(\text{OAc})_2$
 (C) 50.00 mL of 0.200 M $\text{Ba}(\text{OAc})_2$ (D) 100.00 mL of 0.100 M $\text{Ba}(\text{OAc})_2$
- Q.7** A 50.00 mL sample of acetic acid was titrated with 0.01200 M KOH and 38.62 mL of base were required to reach the equivalence point. What was the pH of the titration mixture when 19.31 mL of base had been added? [$\text{p}K_a$ (acetic acid) = 4.74]
 (A) 2.94 (B) 3.54 (C) 4.74 (D) 5.74
- Q.8** In the following reaction:

$$\underset{\text{A}}{[\text{Cu}(\text{H}_2\text{O})_3(\text{OH})]^+} + \underset{\text{B}}{[\text{Al}(\text{H}_2\text{O})_6]^{3+}} \longrightarrow \underset{\text{C}}{[\text{Cu}(\text{H}_2\text{O})_4]^{2+}} + \underset{\text{D}}{[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{2+}}$$

 (A) A is an acid and B the base
 (B) A is a base and B the acid
 (C) C is the conjugate acid of A, and D is the conjugate base of B
 (D) C is the conjugate base of A, and D is the conjugate acid of B
- Q.9** Which does not react with NaOH or which is not acid salt?
 (A) NaH_2PO_2 (B) Na_2HPO_3 (C) Na_2HPO_4 (D) NaHCO_3

- Q.10** pH of the following solution is not affected by dilution:
 (A) 0.01 M CH_3COONa (B) 0.01 M NaHCO_3
 (C) buffer of 0.01 M CH_3COONa and 0.01 M CH_3COOH
 (D) 0.01 M $\text{CH}_3\text{COONH}_4$
- Q.11** Which of the following mixtures constitute a buffer?
 (A) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ (B) $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$
 (C) $\text{NaCl} + \text{HCl}$ (D) $\text{NH}_4\text{Cl} + (\text{NH}_4)_2\text{SO}_4$
- Q.12** Which of the following mixtures constitute a buffer?
 (A) $\text{Na}_2\text{CO}_3 + \text{HCl}$ (B) $\text{NaOH} + \text{CH}_3\text{COOH}$
 (C) $\text{NH}_3 + \text{CH}_3\text{COONH}_4$ (D) $\text{NaOH} + \text{BaCl}_2$
- Q.13** In which of the following pairs of solutions is there no effect on the pH upon dilution?
 (A) 0.1 M NH_3 and 0.1M $(\text{NH}_4)_2\text{SO}_4$ (B) 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4
 (C) 0.1 M HCl and 0.01 M NaOH (D) 0.1 M KCl and 0.1 M HCl
- Q.14** Which of the following will suppress the ionization of phthalic acid in an aqueous solution.
 (A) KCl (B) H_2SO_4 (C) HNO_3 (D) NaOH
- Q.15** Which of the following will suppress the ionization of phthalic acid in an aqueous solution?
 (A) $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ (B) $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
 (C) $\text{Na}_3\text{PO}_4 + \text{NaH}_2\text{PO}_4$ (D) $\text{NH}_3 + (\text{NH}_4)_2\text{SO}_4$
- Q.16** Which of the following mixtures can act as a buffer?
 (A) $\text{NaOH} + \text{CH}_3\text{COONa}$ (1 : 1 molar ratio)
 (B) $\text{CH}_3\text{COOH} + \text{NaOH}$ (2 : 1 molar ratio)
 (C) $\text{CH}_3\text{COOH} + \text{NaOH}$ (3 : 1 molar ratio)
 (D) $\text{CH}_3\text{COOH} + \text{NaOH}$ (1 : 1 molar ratio)
- Q.17** When $\text{HCl}(\text{g})$ is passed through a saturated solution of common salt, pure NaCl is precipitated because
 (A) HCl is highly soluble in water
 (B) the ionic product $[\text{Na}^+][\text{Cl}^-]$ exceeds its solubility product (K_{sp})
 (C) the k_{sp} of NaCl is lowered by the presence of Cl^- ions
 (D) HCl causes precipitation

REASONING TYPE

This section contains FIVE questions . Each question contains STATEMENT- 1 (Assertion) and STATEMENT - 2 (Reason). Each question has 4 choices (A), (B), (C) and (D) out of which ONLY ONE is correct.

- (A) 'S' is correct but E is wrong
 (B) 'S' is wrong but E is correct
 (C) Both 'S' and 'E' are correct and 'E' is correct explanation of 'S'.
 (D) Both 'S' and 'E' are correct but 'E' is not correct explanation of 'S'.

- Q.18 Statement-1:** The pH of an aqueous solution of acetic acid remains unchanged by the addition of sodium acetate .
Statement-2: The ionisation of acetic acid is suppressed by the addition of sodium acetate.
- Q.19 Statement-1:** The addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution, will first precipitate AgBr rather than AgCl .
Statement-2 : The value of K_{sp} of $\text{AgCl} < K_{\text{sp}}$ of AgBr .

- Q.20 Statement-1:** A bowler bowling the last crucial over in an India-Pakistan 20–20 match breathes heavily due to excitement and tension, leading to significant change in the pH of blood.
- Statement-2:** $\text{pH of blood} = \text{pK}_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$
- Q.21 Statement-1:** pH of an acidic buffer solution cannot be more than 7
- Statement-2:** Acidic buffer consists of a weak acid and its salt with a strong base.
- Q.22 Statement-1:** Addition of KCN solution to carbonyl compounds decreases the pH of solution
- Statement-2:** KCN in aqueous solution forms a basic solution due to hydrolysis of CN^- . The nucleophilic addition on carbonyl then brings in a decrease in H^+ ions or an increase in OH^- ions.
- Q.23 Statement-1:** The number of amide ions in pure liquid ammonia at -50°C is 6×10^5 per c.c
- Statement-2:** $K_{\text{NH}_3} = [\text{NH}_4^+][\text{NH}_2^-] = 10^{-30}$
- Q.24 Statement-1:** The pH of a 0.01N mono basic acid is 4.
- Statement-2:** The acid is weak
- Q.25 Statement-1:** HClO_4 acidic strength is more than that of HClO_3
- Statement-2:** In ClO_4^- negative charge density is less than that of ClO_3^-
- Q.26 Statement-1:** The solubilities of AgCl in water (S_1), 0.01M (S_2) CaCl_2 , 0.01M (S_3) NaCl are $S_1 > S_3 > S_2$
- Statement-2:** Solubility decreases with increasing common ion concentration.
- Q.27 Statement-1:** Upon dilution, degree of hydrolysis of a salt increases except in case of salt of weak acid and weak base
- Statement-2:** Upon dilution, K_h of a salt increases
- Q.28 Statement-1:** A solution of 2 : 1 molar ratio of CH_3COONa and HCl results an acidic buffer
- Statement-2:** An acidic buffer is a mixture of weak acid and its salt with strong base.

LINKED COMPREHENSION TYPE

Paragraph –I

Buffer Solutions : In general, a buffer solution is one which is resistant to change of pH upon the addition of a small amount of acid or alkali. Such solutions usually consist of a mixture of a weak acid and salt of its conjugate base, e.g. HAc and NaAc (called acidic buffers), or of a weak base and salt of its conjugate acid, e.g. NH_4OH and NH_4Cl (called basic buffers). A salt of a weak acid and a weak base, e.g. NH_4Ac , also has a buffer action.

The pH of an acidic buffer and basic buffer is expressed by Henderson-Hasselbalch equations

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]} \quad \text{pOH} = \text{pK}_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

But limitations of the above equations is that it works only for buffer solutions that fit the following criteria

- * The ratio, $[\text{conjugate base}] / [\text{weak acid}]$ has a value between 0.1 and 10.
- * Both $[\text{conjugate base}]$ and $[\text{weak acid}]$ exceed K_a by a factor of 100 or more.

The resistance to the change in pH, on the addition of an acid or alkali is called 'Buffer action'. This buffer action is measured by 'Buffer capacity' (β). It is expressed as $\beta = \frac{db}{dpH}$

where db is no. of moles of base added to one litre buffer solution and dpH is change in pH. The buffer capacity (β) is maximum when the acid and the salt are present in equal concentrations.

- Q.29** The acetate-acetic acid buffer is suitable in the pH range (assume K_b of $CH_3COO^- = 10^{-9}$)
 (A) 8 – 10 (B) 4 – 6 (C) 5 – 7 (D) 5.5 – 7.5
- Q.30** A solution of pH = 6 will be maintained by acidic buffer. Below are the few options given to a chemist. Which option will the chemist choose?
 (A) HA (0.1 M), NaA (1M) K_b of $A^- = 10^{-9}$ (B) HB (0.01 M), NaB (1 M) K_b of $B^- = 10^{-10}$
 (C) HC (1 M), NaX (0.01 M) K_b of $X^- = 10^{-6}$ (D) Any one of the above
- Q.31** pH of a mixture of 1 M benzoic acid ($pK_a = 4.20$) and 1 M C_6H_5COONa is 4.5 what is the volume of benzoic acid required to prepare a 300 ml buffer [$\log 2 = 0.3$]?
 (A) 200 ml (B) 150 ml (C) 100 ml (D) 50 ml

Paragraph –II

K_{sp} of $CdS = 8 \times 10^{-27}$, K_{sp} of $ZnS = 1 \times 10^{-21}$, K_a of $H_2S = 1 \times 10^{-21}$

- Q.32** Which metal sulphide is precipitated first when H_2S is added
 (A) ZnS (B) CdS
 (C) Both at same time (D) Both do not form ppt.
- Q.33** What $[H^+]$ must be maintained in a saturated H_2S (0.1M) to precipitate CdS but not ZnS , if $[Cd^{+2}] = [Zn^{+2}] = 0.1$ M initially
 (A) > 0.1 M (B) > 0.01 M (C) > 0.2 M (D) > 0.02 M
- Q.34** When ZnS starts precipitating. What is the concentration of Cd^{+2} is left
 (A) 8×10^{-7} (B) 0.1 (C) 4×10^{-10} (D) 2×10^{-9}

Paragraph –III

The solution whose pH or pOH is not affected by the addition of small amount of acid or base is called buffer. Buffer is a mixture of weak acid and its salt with strong base or weak base and its salt with strong acid

Acidic buffer $pH = pK_a + \log \left[\frac{\text{salt}}{\text{acid}} \right]$, Basic buffer $pOH = pK_b + \log \left[\frac{\text{salt}}{\text{base}} \right]$

- Q.35** What is the pH of the solution when 0.2M of HCl is added to one litre 1M each of CH_3COOH and acetate ion
 (A) 5.57 (B) 4.57 (C) 3.57 (D) 7.57
- Q.36** A solution of a mono basic acid was titrated with $NaOH$ solution and the end point came when 36.12ml of 0.1N $NaOH$ was added. Further 18.06ml of 0.1N HCl was added and the pH was then found to be 4.92. Find the K_a of the acid
 (A) 1.2×10^{-5} (B) 1.2×10^{-6} (C) 2.4×10^{-5} (D) 2.4×10^{-6}
- Q.37** A certain buffer solution contains equal concentrations of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is
 (A) 4 (B) 10 (C) 7 (D) 14

Passage-IV

The solubility product of a soluble salt A_xB_y is given by : $K_{sp} = [A^{y+}]^x [B^{x-}]^y$. As soon as the product of concentration of A^{y+} and B^{x-} increases than its K_{sp} , the salt starts precipitation. It may practically be noticed that $AgCl$ is more soluble in water and its solubility decreases dramatically in $0.1M$ $NaCl$ or $0.1M$ $AgNO_3$ solution. It may therefore be concluded that in presence of a common ion, the solubility of salt decreases.

Q.38 K_{sp} of SrF_2 in water is 8×10^{-10} . The solubility of SrF_2 in $0.1M$ NaF aqueous solutions is:

- (A) 8×10^{-10} (B) 2×10^{-3} (C) 2.71×10^{-10} (D) 8×10^{-8}

Q.39 The pH of a saturated solution of $Mg(OH)_2$ is ($K_{sp} Mg(OH)_2 = 1 \times 10^{-11}$) :

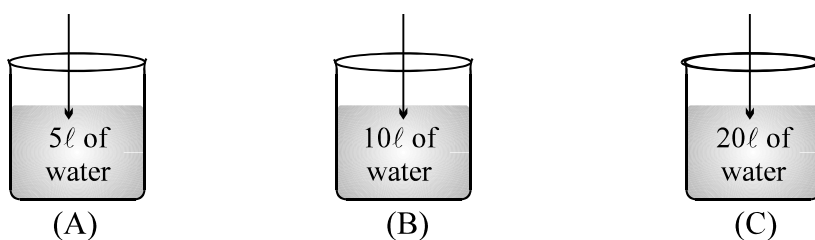
- (A) 1 (B) 3.87 (C) 10.43 (D) 5

Q.40 The volume of water needed to dissolve 1 g $BaSO_4$ ($K_{sp} = 1 \times 10^{-10}$) is :

- (A) 230 litre (B) 429 litre (C) 500 litre (D) 320 litre

Passage-V

Look at the following diagram :



There are three container A (contains 5ℓ of pure water) B (contains 10ℓ of pure water) and C (contains 20ℓ of pure water) now 1 mole each of $AgCl$, $AgBr$ and AgI are dissolved in container A, B, C respectively. If K_{sp} of $AgCl$, $AgBr$ and AgI are 10^{-10} , 1.6×10^{-13} and 8.1×10^{-17} respectively. Then—

Q.41 Moles of Ag^+ present in container A, B and C respectively are —

- (A) 10^{-5} , 4×10^{-7} , 9×10^{-9} (B) 5×10^{-5} , 4×10^{-6} , 1.8×10^{-7}
(C) 5×10^{-5} , 4×10^{-7} , 1.8×10^{-6} (D) 10^{-5} , 4×10^{-6} , 1.8×10^{-6}

Q.42 If excess of NH_3 is added in first container (A) then concentration of Cl^- in the solution will be —

- (A) 0.2 M (B) 1M (C) 10^{-5} M (D) 5×10^{-5} M

Q.43 If excess of CN^- is added in second container (B) then concentration of Br^- in the solution will be —

- (A) 1 M (B) 10^{-7} M (C) 0.1 M (D) 4×10^{-6} M

Q.44 If excess of $S_2O_3^{2-}$ is added in third container (C) then concentration of I^- in the solution will be —

- (A) 0.05 M (B) 1M (C) 9×10^{-9} M (D) 1.8×10^{-7} M

Q.45 Extra amount of pure water required to dissolve completely 1 mole of $AgCl$ present in container A (before addition of NH_3)

- (A) 10,000 ℓ (B) 10^{10} ℓ (C) 10^5 ℓ (D) 99995 ℓ

MATRIX MATCH TYPE

LEVEL-IV (Match the column)

Q.46 Match the following

- List I**
- (a) CH_3COOH
 (b) H_2SO_4
 (c) NaOH
 (d) NH_3
 (A) a-R, b-Q, c-P, d-S
 (C) a-P, b-S, c-R, d-Q

- List II**
- (P) weak base
 (Q) weak acid
 (R) strong acid
 (S) Strong base
 (B) a-Q, b-R, c-S, d-P
 (D) a-S, b-P, c-Q, d-R

Q.47 Match the following

- List I (Concentration of HCl)**
- (a) 10^{-6} M
 (b) 10^{-7} M
 (c) 10^{-8} M
 (d) 10^{-9} M
 (A) a-R, b-S, c-Q, d-P
 (C) a-Q, b-R, c-S, d-P

- List II (pH)**
- (P) 7.0
 (Q) 6.98
 (R) 6.0
 (S) 6.79
 (B) a-S, b-R, c-Q, d-P
 (D) a-P, b-Q, c-R, d-S

Q.48 Match the following

- List I**
Components present in solution
- (a) $\text{CH}_3\text{COOH} + \text{HCl}$
 (b) $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$
 (c) NH_4Cl
 (d) $\text{NH}_4\text{OH} + \text{NaOH}$
 (A) a-Q, b-R, c-S, d-P
 (C) a-Q, b-S, c-P, d-R

- List II**
Method of determination of pH
- (P) Basic buffer
 (Q) Strong base
 (R) Strong acid
 (S) Salt hydrolysis
 (B) a-R, b-S, c-P, d-Q
 (D) a-R, b-P, c-S, d-Q

Q.49 Match the following

- List I (Salt)**
- (a) HCOONa
 (b) NH_4Cl
 (c) MgSO_4
 (d) $\text{CH}_3\text{COONH}_4$
 (A) a-Q, b-P, c-R, d-P
 (C) a-R, b-Q, c-P, d-P

- List II (pH)**
- (P) 7
 (Q) < 7
 (R) > 7
 (B) a-P, b-Q, c-Q, d-R
 (D) a-R, b-R, c-Q, d-P

Q.50 A weak acid HA having $K_a = 10^{-4}$ is given 100 ml of 0.1 M acid is taken in container. Now 0.1 M NaOH is added in the container List I contains volume of NaOH added and List II contains pH. Match them.

- List I**
- (a) 10 ml NaOH solution
 (b) 25 ml NaOH solution
 (c) 75 ml NaOH solution
 (d) 100 ml NaOH solution
 (A) a-S, b-R, c-Q, d-P
 (C) a-Q, b-R, c-S, d-P

- List II**
- (P) $\frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$
 (Q) $\text{p}K_a + \log 3$
 (R) $\text{p}K_a - \log 3$
 (S) $\text{p}K_a - 2\log 3$
 (B) a-P, b-Q, c-R, d-S
 (D) a-S, b-P, c-Q, d-R

FILL IN THE BLANKS

- Q.51** In a mixture of weak acid and its salt, the ratio of concentration of salt to acid is increased ten fold. The pH of the solution would by unit.
- Q.52** The solubility of CH_3COOAg in water considering hydrolysis of CH_3COO^- ions would be then that ignoring the hydrolysis.
- Q.53** From an equimolar solution of Cl^- and Br^- ions, the addition of Ag^+ will selectively precipitates..... (K_{sp} of AgCl and AgBr are 1×10^{-10} & 1×10^{-13} respectively).
- Q.54** The solubility of AgCl in NH_3 is than the solubility in pure water because of complex ion. $[\text{Ag}(\text{NH}_3)_2]^+$ formation.
- Q.55** The hydrolytic constant K_h for the hydrolytic equilibrium
 $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4 + \text{OH}^-$ is 1.4×10^{-12}
 What is the value of ionization constant for the $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{PO}_4^- + \text{H}_3\text{O}^+$?
- Q.56** Given the equilibrium constants
 $\text{HgCl}^+ + \text{Cl}^- \rightleftharpoons \text{HgCl}_2; \quad K_1 = 3 \times 10^6$
 $\text{HgCl}_2 + \text{Cl}^- \rightleftharpoons \text{HgCl}_3^-; \quad K_2 = 8.9$
 The equilibrium constant for the disproportionation equilibrium.
 $2\text{HgCl}_2 \rightleftharpoons \text{HgCl}^+ + \text{HgCl}_3^-$ is
- Q.57** Under which set of conditions is the ionic product of water, K_w , constant at a given temperature in aqueous system?
- Q.58** If the salts M_2X , QY_2 and PZ_3 have same solubilities ($\lll 1$), their K_{sp} values are related as.....
- Q.59** K_a for an acid HA is 1×10^{-6} . K_b for A^- would be
- Q.60** An aqueous solution of K_2SO_4 has pH nearly equal to
- Q.61** The pH of a solution which is 0.1 M in sodium acetate and 0.01 M in acetic acid ($\text{p}K_a = 4.74$) would be.....
- Q.62** The conjugate acid of sulphate (SO_4^{2-}) is
- Q.63** The value of K_w with increase in temperature.
- Q.64** AgCl is soluble in aqueous sodium chloride solution than in pure water.
- Q.65** The buffer $\text{HCOOH}/\text{HCOONa}$ will have pH than 7.
- Q.66** In the reaction $\text{I}_2 + \text{I}^- \longrightarrow \text{I}_3^-$, I_2 acts as
- Q.67** An equimolar solution of NaNO_2 and HNO_2 can act as solution
- Q.68** Larger the value of $\text{p}K_a$, is the acid.
- Q.69** An aqueous solution of potash alum is in nature.
- Q.70** Salts of strong acids and weak bases undergo..... hydrolysis.
- Q.71** For salts of weak acid with weak bases, degree of hydrolysis is..... of concentration of the salt in solution.

TRUE OR FALSE

- Q.72** When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralization point, $\text{pH} = \frac{1}{2} \text{pK}_a$.
- Q.73** A solution of sodium acetate and ammonium acetate can act as a buffer
- Q.74** If the solubility of the salt $\text{L}_3\text{Na}_3(\text{AlF}_6)_2$ is x , then its solubility product would be $2916x^8$.
- Q.75** A buffer has maximum buffer capacity when the ratio of salt of acid is 10.
- Q.76** In the presence of a common ion (incapable of forming complex ion), the solubility of salt decreases.

EXERCISE

7

QUESTION FROM OTHER EXAMS

[2002]

- 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is:

(A) not a buffer solution with $\text{pH} < 7$ (B) not a buffer solution with $\text{pH} > 7$
 (C) a buffer solution with $\text{pH} < 7$ (D) a buffer solution with $\text{pH} > 7$
- Let the solubility of an aqueous solution of $\text{Mg}(\text{OH})_2$ be x then its K_{sp} is

(A) $4x^3$ (B) $108x^5$ (C) $27x^4$ (D) $9x$

[2003]

- Which one of the following statements is not true?

(A) $\text{pH} + \text{POH} = 14$ for all aqueous solutions
 (B) The pH of 1×10^{-8} M HCl is 8
 (C) 96,500 coulombs of electricity when passed through a CuSO_4 solution deposits 1 gram equivalent of copper at the cathode
 (D) The conjugate base of H_2PO_4^- is HPO_4^{2-}
- The solubility in water of a sparingly soluble salt AB_2 is $1.0 \times 10^{-5} \text{ mol L}^{-1}$. Its solubility product number will be:

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

[2004]

- The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp} . 's' is given in terms of K_{sp} by the relation:

(A) $s = (256 K_{\text{sp}})^{1/5}$ (B) $s = (128 K_{\text{sp}})^{1/4}$ (C) $s = (K_{\text{sp}}/128)^{1/4}$ (D) $s = (K_{\text{sp}}/256)^{1/5}$

[2005]

- The solubility product of a salt having general formula MX_n in water is 4×10^{-12} . The concentration of M^{2+} ions in the aqueous solution of the salt is:

(A) $4.0 \times 10^{-10} \text{ M}$ (B) $1.6 \times 10^{-4} \text{ M}$ (C) $1.0 \times 10^{-4} \text{ M}$ (D) $2.0 \times 10^{-6} \text{ M}$
- Hydrogen ion concentration in mol/L in a solution: $\text{pH} = 5.4$ will be:

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

[2006]

- Given the data at 25°C

$$\text{Ag} + \text{I}^- \longrightarrow \text{AgI} + \text{e}^- \quad E^\circ = 0.152 \text{ V}$$

$$\text{Ag} \longrightarrow \text{Ag}^+ + \text{e}^- \quad E^\circ = -0.800 \text{ V}$$
 What is the value of $\log K_{\text{sp}}$ of AgI ($2.303 \text{ RT/F} = 0.059 \text{ V}$)

(A) -37.83 (B) -16.13 (C) -8.12 (D) $+8.612$

[2007]

- The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffer solution of HA in which 50% of the acid is ionized is

(A) 7.0 (B) 4.5 (C) 2.5 (D) 9.5
- In a saturated solution of the sparingly soluble strong electrolyte AgIO_3 (molecular mass = 283) the equilibrium which sets in is $\text{AgIO}_3(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{IO}_3^-(\text{aq})$. If the solubility product constant K_{sp} of AgIO_3 at a given temperature is 1.0×10^{-8} , what is the mass of AgIO_3 contained in 100 ml of its saturated solution?

(A) $1.0 \times 10^{-4} \text{ g}$ (B) $28.3 \times 10^{-2} \text{ g}$ (C) $2.83 \times 10^{-3} \text{ g}$ (D) $1.0 \times 10^{-7} \text{ g}$

[2008]

11. Four species are listed below:

(i) HCO_3^- (ii) H_3O^+ (iii) HSO_4^- (iv) HSO_3F

Which one of the following is the correct sequence of their acid strength?

- (A) (iii) < (i) < (iv) (B) (iv) < (ii) < (iii) < (i)
(C) (ii) < (iii) < (i) < (iv) (D) (i) < (iii) < (ii) < (iv)
12. The pK_a of a weak acid, HA is 4.80, the pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be
(A) 9.22 (B) 9.58 (C) 4.79 (D) 7.01

[2009]

13. Solid $\text{Ba}(\text{NO}_3)_2$ is gradually dissolved in a $1.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$ solution. At what concentration of Ba^{2+} will a precipitate begin to form? (Given: $K_{\text{sp}} = 5.1 \times 10^{-9} \text{ M}^2$ for BaCO_3)
(A) $8.1 \times 10^{-8} \text{ M}$ (B) $8.1 \times 10^{-7} \text{ M}$ (C) $4.1 \times 10^{-5} \text{ M}$ (D) $5.1 \times 10^{-5} \text{ M}$

[2010]

14. In aqueous solution the ionization constants for carbonic acid are $K_1^\circ = 4.2 \times 10^{-7}$ and $K_2^\circ = 4.8 \times 10^{-11}$. Select the correct statement for a saturated 0.34 M solution of the carbonic acid.
(A) The concentration of H^+ is double that of CO_3^{2-}
(B) The concentration of CO_3^{2-} is 0.034 M
(C) The concentration of CO_3^{2-} is greater than of HCO_3^{2-}
(D) The concentrations of H^+ and HCO_3^- are approximately equal.
15. Solubility product of silver bromide is $5.0 \times 10^{-13} \text{ M}^2$. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is
(A) $5.0 \times 10^{-8} \text{ g}$ (B) $1.2 \times 10^{-10} \text{ g}$ (C) $1.2 \times 10^{-9} \text{ g}$ (D) $6.2 \times 10^{-5} \text{ g}$
16. At 25°C , the solubility product of $\text{Mg}(\text{OH})_2$ is $1.0 \times 10^{-11} \text{ M}^3$. At which pH will Mg^{2+} ions start precipitating in the form of $\text{Mg}(\text{OH})_2$ from a solution of 0.001 M Mg^{2+} ions ?
(A) 8 (B) 9 (C) 10 (D) 11

[OBJECTIVE]

1988

- Q.1** The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in small intestine is about 8. Aspirin will be –
 (A) unionised in the small intestine and in the stomach
 (B) completely ionised in small intestine and in the stomach
 (C) ionised in the stomach and almost unionised in the small intestine
 (D) ionised in the small intestine and almost unionised in the stomach
- Q.2** When equal volume of the following solutions are mixed, precipitation of $AgCl$ ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with –
 (A) $10^{-4} M (Ag^+)$ and $10^{-4} M (Cl^-)$ (B) $10^{-5} M (Ag^+)$ and $10^{-5} M (Cl^-)$
 (C) $10^{-6} M (Ag^+)$ and $10^{-6} M (Cl^-)$ (D) $10^{-10} M (Ag^+)$ and $10^{-10} M (Cl^-)$

1990

- Q.3** Which hydroxide will have lowest value of solubility product at normal temperature ($25^\circ C$) ?
 (A) $Mg(OH)_2$ (B) $Ca(OH)_2$ (C) $Ba(OH)_2$ (D) $Be(OH)_2$
- Q.4** The solubility product of a salt A_2B is 4×10^{-9} . Its solubility would be –
 (A) $4 \times 10^{-2} M$ (B) $2 \times 10^{-4} M$ (C) $1 \times 10^{-4} M$ (D) $1 \times 10^{-3} M$
- Q.5** At $25^\circ C$, the dissociation constants of CH_3COOH and NH_4OH in aqueous solution are almost the same. The pH of a solution of 0.01 N CH_3COOH is 4.0 at $25^\circ C$. The pH of 0.01 N NH_4OH solution at the same temperature would be –
 (A) 3.0 (B) 4.0 (C) 10.0 (D) 10.5

1992

- Q.6** Which of the following solution 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 $NaOH$
- Q.7** The following equilibrium is established when hydrogen chloride is dissolved in acetic acid :

$$HCl + CH_3COOH \rightleftharpoons Cl^- + CH_3COOH_2^+$$

 The set that characterises the conjugate acid-base pairs is
 (A) (HCl, CH_3COOH) and $(CH_3COOH_2^+, Cl^-)$ (B) $(HCl, CH_3COOH_2^+)$ and (CH_3COOH, Cl^-)
 (C) $(CH_3COOH_2^+, HCl)$ and (Cl^-, CH_3COOH) (D) (HCl, Cl^-) and $(CH_3COOH_2^+, CH_3COOH)$

1993

- Q.8** What is the decreasing order of strength of the bases OH^- , NH_2^- , $H-C \equiv C^-$ and $CH_3CH_2^-$?
 (A) $CH_3CH_2^- > NH_2^- > H-C \equiv C^- > OH^-$ (B) $H-C \equiv C^- > CH_3CH_2^- > NH_2^- > OH^-$
 (C) $OH^- > NH_2^- > H-C \equiv C^- > CH_3CH_2^-$ (D) $NH_2^- > H-C \equiv C^- > OH^- > CH_3CH_2^-$
- Q.9** Fear and excitement generally cause one to breathe rapidly and it results in the decrease of CO_2 concentration in blood. In what way will it change the pH of the blood ?
 (A) pH will decrease (B) pH will increase (C) no change (D) pH will adjust to 7

1996

- Q.10** The following acids have been arranged in the order of decreasing acid strength. Identify the correct order : $ClOH$ (I) $BrOH$ (II) IOH (III)
 (A) $I > II > III$ (B) $II > I > III$ (C) $III > II > I$ (D) $I > III > II$

1997

Q.11 If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is –

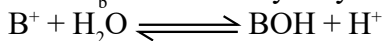
- (A) 1.74×10^{-5} (B) 3.52×10^{-3} (C) 6.75×10^{-4} (D) 5.38×10^{-2}

Q.12 The solubility of A_2X_3 is $y \text{ mol L}^{-1}$. Its solubility product is –

- (A) $6y^4$ (B) $64y^4$ (C) $36y^5$ (D) $108y^5$

1998

Q.13 If the K_b value in the hydrolysis reaction,



is 1.0×10^{-6} , then the hydrolysis constant of the salt would be :

- (a) 1.0×10^{-6} (B) 1.0×10^{-7} (C) 1×10^{-8} (D) 1.0×10^{-9}

1999

Q.14 The pH of 0.1 M solution of the following salts increases in the order of :

- (A) $\text{NaCl} < \text{NH}_4\text{Cl} < \text{NaCN} < \text{HCl}$ (B) $\text{HCl} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{NaCN}$
(C) $\text{NaCN} < \text{NH}_4\text{Cl} < \text{NaCl} < \text{HCl}$ (D) $\text{HCl} < \text{NaCl} < \text{NaCN} < \text{NH}_4\text{Cl}$

2004

Q.15 HX is weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is –

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

2005

Q.16 CH_3NH_2 (0.1 mol, $K_b = 5 \times 10^{-4}$) is mixed with 0.08 mol of HCl and the solution is diluted to 1 litre. The H^+ ion concentration of the resulting solution will be

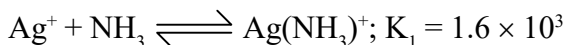
- (A) 1.6×10^{-11} (B) 8×10^{-11} (C) 3×10^{-5} (D) 1.25×10^{-4}

2006

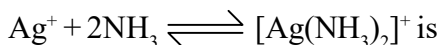
Q.17 If CO_2 be passed into water, what will remain present in solution

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

Q.18 Given:



The equilibrium constant for the reaction



- (A) 6.8×10^3 (B) 1.088×10^7 (C) 1.088×10^6 (D) 1.6×10^3

2008

Q.19 Solubility product constants (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8} , 3.2×10^{-14} and 2.7×10^{-15} , respectively. Solubilities (mol dm^{-3}) of the salts at temperature 'T' are in the order

- (A) $\text{MX} > \text{MX}_2 > \text{M}_3\text{X}$ (B) $\text{M}_3\text{X} > \text{MX}_2 > \text{MX}$
(C) $\text{MX}_2 > \text{M}_3\text{X} > \text{MX}$ (D) $\text{MX} > \text{M}_3\text{X} > \text{MX}_2$

Q.20 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) $3.7 \times 10^{-13} \text{ M}$ (B) $3.2 \times 10^{-7} \text{ M}$ (C) $3.2 \times 10^{-2} \text{ M}$ (D) $2.7 \times 10^{-2} \text{ M}$

2010

21. Aqueous solutions of HNO_3 , KOH , CH_3COOH , and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is(are)
- (A) HNO_3 and CH_3COOH (B) KOH and CH_3COONa
(C) HNO_3 and CH_3COONa (D) CH_3COOH and CH_3COONa

2011

22. In 1 L saturated solution of AgCl [$K_{\text{sp}}(\text{AgCl}) = 1.6 \times 10^{-10}$], 0.1 mole of CuCl [$K_{\text{sp}}(\text{CuCl}) = 1.0 \times 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x} . The value of 'x' is

EXERCISE

9

IIT - JEE FLASH BACK SUBJECTIVE

1986

- Q.1** A sample of hard water contains 0.005 mole of CaCl_2 per litre. What is the minimum concentration of Na_2SO_4 which must be added for removing Ca^{+2} ions from this water sample ? K_{sp} for CaSO_4 is 2.4×10^{-5} at 25°C .
- Q.2** The solubility of $\text{Mg}(\text{OH})_2$ in pure water is 9.57×10^{-3} g litre $^{-1}$. Calculate its solubility in g litre $^{-1}$ in 0.02M $\text{Mg}(\text{NO}_3)_2$.
- Q.3** The concentration of hydrogen ion in a 0.2 M solution of formic acid is 6.4×10^{-3} mole per litre. To this solution sodium formate is added so as to adjust the concentration of sodium formate one mole per litre. What will be the pH of this solution ? The dissociation constant of formic acid is 2.4×10^{-4} and the degree of dissociation of sodium formate is 0.75.
- Q.4** Calculate the approximate pH of 0.1 M aqueous H_2S solution. K_1 and K_2 for H_2S are 1.0×10^{-7} and 1.3×10^{-13} respectively at 25°C .

1987

- Q.5** How many mole of $\text{Ca}(\text{OH})_2$ must be dissolved to produced 250 ml of an aqueous solution of pH 10.65, assuming complete dissociation ?
- Q.6** What is the pH of the solution when 0.2 mole of HCl is added to one litre of a solution :
(i) 1 M each of CH_3COOH and acetate ion
(ii) 0.1 M each of CH_3COOH and acetate ion
Assume that the total volume is 1 litre
 K_a of $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$

1988

- Q.7** A certain buffer solution contains equal concentration of X^- and HX . K_b for X^- is 10^{-10} . Calculate pH of buffer.
- Q.8** How many gram mole of HCl will be required to prepare one litre of a buffer solution (containing NaCN and HCN) of pH 8.5 using 0.01 gram formula weight of NaCN ? $K_{(\text{HCN})} = 4.1 \times 10^{-10}$.
- Q.9** The pH of 0.1 M hydrocyanic acid solution is 5.2. What is the value of K_a for hydrocyanic acid ?

1989

- Q.10** Freshly precipitated Al and Mg hydroxides are stirred vigorously in a buffer solution containing 0.25 M of NH_4Cl and 0.05 M of NH_4OH . Calculate $[\text{Al}^{+3}]$ and $[\text{Mg}^{+2}]$ in solution.
 K_b for $\text{NH}_4\text{OH} = 1.8 \times 10^{-5}$. K_{sp} of $\text{Al}(\text{OH})_3 = 6 \times 10^{-32}$ and K_{sp} of $\text{Mg}(\text{OH})_2 = 8.9 \times 10^{-12}$.
- Q.11** K_{sp} of BaSO_4 is 1.5×10^{-9} . Calculate its solubility in :
(i) pure water (ii) 0.10 M BaCl_2
- Q.12** When 0.2 M acetic acid is neutralised with 0.2 M NaOH in 0.5 litre of water the resulting solution is slightly alkaline. Calculate the pH of the resulting solution. K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$.

1990

- Q.13** What is the pH of 1 M solution of acetic acid. To what volume one liter of this solution be diluted so that pH of the resulting solution will be twice of the original value ? $K_a = 1.8 \times 10^{-5}$.

- Q.14** What volume of 0.1 M sodium formate solution should be added to 50 mL of 0.05 M formic acid to produce a buffer solution of pH = 4.0. pK_a of formic acid = 3.80
- Q.15** Calculate the pH at the equivalence point when a solution of 0.1 M acetic acid is titrated with a solution of 0.1 M NaOH. K_a for acid = 1.9×10^{-5} .

1991

- Q.16** A 40 ml solution of weak base BOH is titrated with 0.1 N HCl solution. The pH of solution is found to be 10.04 and 9.14 after the addition of 5.0 ml and 20.0 ml of acid respectively. Find out K_b for weak base.
- Q.17** A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.
- Q.18** The K_{sp} of $Ag_2C_2O_4$ at $25^\circ C$ is $1.29 \times 10^{-11} \text{ mol}^3\text{L}^{-3}$. A solution of $K_2C_2O_4$ containing 0.152 mole in 500 ml water is shaken at $25^\circ C$ with excess of Ag_2CO_3 till the equilibrium is reached.
- $$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$
- At equilibrium the solution contains 0.0358 mole of K_2CO_3 . Assuming degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be same, calculate K_{sp} of Ag_2CO_3 .
- Q.19** Calcium lactate is a salt of weak acid and represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.13 mole of salt in 0.50 litre solution. The pOH of this is 5.60. Assuming complete dissociation of salt, calculate K_a of lactic acid.
- Q.20** The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate $[H^+]$ and $[OH^-]$, if K_a of HCN is 7.2×10^{-10} .

1992

- Q.21** Calculate pH for
- | | |
|-----------------------|-------------------------|
| (a) 0.001 N NaOH | (b) 0.01 N $Ca(OH)_2$ |
| (c) 0.01 M $Ca(OH)_2$ | (d) 0.0008 M $Mg(OH)_2$ |
- Assume complete ionisation of each.
- Q.22** A solution contains 0.1 M H_2S and 0.3 M HCl. Calculate the con. of S^{2-} and HS^- ions in solution. Given K_{a1} and K_{a2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.
- Q.23** Calculate the change in pH of 1 litre buffer solution containing 0.1 mol each of NH_3 and NH_4Cl up on addition of,
- (i) 0.02 mole of dissolved gaseous HCl
- (ii) 0.02 mole of dissolved NaOH.
- Assume no change in volume. $K_{NH_3} = 1.8 \times 10^{-5}$
- Q.24** The K_{sp} of $Ca(OH)_2$ is 4.42×10^{-5} at $25^\circ C$. A 500 ml of saturated solution $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated?
- Q.25** Calculate the pH at which $Mg(OH)_2$ begins to precipitate from a solution containing 0.10 M Mg^{+2} ions. K_{sp} of $Mg(OH)_2 = 1 \times 10^{-11}$.

1993

- Q.26** Nicotic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula $HNiC$. Calculate its percent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution.
- Q.27** The pH of 0.05 M aqueous solution of diethyl amine is 12.0. Calculate K_b .
- Q.28** 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 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4. K_a for H_2CO_3 in blood is 7.8×10^{-7} ?

Q.29 An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S . What is the minimum pH at which MS will precipitate? K_{sp} for MS = 6.0×10^{-21} . Concentration of saturated H_2S = 0.1 M; $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$ for H_2S .

Q.30 A solution has 0.05 M Mg^{+2} and 0.05 M NH_3 . Calculate the concentration of NH_4Cl required to prevent the formation of $Mg(OH)_2$ in solution. K_{sp} of $Mg(OH)_2$ = 9.0×10^{-12} and ionisation constant of NH_3 is 1.8×10^{-5} .

Q.31 What is the hydrogen ion concentration of 0.1 N CH_3COOH solution? The ionisation constant of CH_3COOH is 1.8×10^{-5} . What is the pH of the solution.

1994

Q.32 Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula $HSaC$. A 4×10^{-4} mole amount of saccharin is dissolved in 200 cm^3 water of pH 3. Assuming no change in volume, calculate the concentration of SaC^- ions in the resulting solution at equilibrium.

Q.33 K_a for butyric acid is 2.0×10^{-5} . Calculate pH and hydroxyl ion concentration in 0.2 M aqueous solution of sodium butyrate.

1995

Q.34 An aqueous solution contains 10% ammonia by mass and has a density of 0.99 $g\ cm^{-3}$. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for NH_4^+ = 5.0×10^{-10} M

Q.35 0.15 mole of pyridinium chloride has been added into 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in volume. (K_b for pyridine = 1.5×10^{-9} M)

Q.36 The solubility product of $AgCl$ in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M $NaCl$.

Q.37 Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation. (pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

1996

Q.38 An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M? K_a for $C_6H_5NH_3^+$ is 2.4×10^{-5} M.

Q.39 What is the pH of a 0.5 M aqueous $NaCN$ solution? pK_b of CN^- = 4.70.

Q.40 Calculate the percentage hydrolysis in 0.003 M aqueous solution of $NaOCN$. K_a for $HOCl$ = 3.33×10^{-4} .

Q.41 The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at $25^\circ C$. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at $25^\circ C$ is 3.4×10^{10} litre mol^{-1} sec^{-1} . Calculate the rate constant for proton transfer from water to NH_3 .

1997

Q.42 Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagents is 0.6 $mol\ L^{-1}$. pK_b for NH_3 = 4.7, $\log 2 = 0.30$

Q.43 The solubility product of SrF_2 in water is 8×10^{-10} . Calculate its solubility in 0.1 M NaF aqueous solution.

Q.44 A sample of $AgCl$ was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3 . The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of $AgCl$ (K_{sp} Ag_2CO_3 = 8.2×10^{-12})

Q.45 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 ($K_a = 1.0 \times 10^{-5}$)?

Q.46 K_a for ascorbic acid (HAsc) is 5×10^{-5} . Calculate the hydrogen ion concentration and percentage of hydrolysis in an aqueous solution in which the concentration of Asc^- ions is 0.02 M.

1998

Q.47 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) ?

Q.48 Given $\text{Ag}(\text{NH}_3)_2^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3$, $K_c = 6.2 \times 10^{-8}$ and K_{sp} of $\text{AgCl} = 1.8 \times 10^{-10}$ at 298 K. Calculate the concentration of the complex in 1.0 M aqueous ammonia.

Q.49 Determine the number of mole of AgI which may be dissolved in 1.0 litre of 1.0 M CN^- solution. K_{sp} for AgI and K_c for $\text{Ag}(\text{CN})_2^-$ are $1.2 \times 10^{-17} \text{ M}^2$ and $7.1 \times 10^{19} \text{ M}^{-2}$ respectively.

Q.50 0.16 g of N_2H_4 are dissolved in water and the total volume made up to 500 mL. Calculate the percentage of N_2H_4 that has reacted with water at this dilution. The K_b for N_2H_4 is $4.0 \times 10^{-6} \text{ M}$.

1999

Q.51 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? ($K_{HA} = 1.0 \times 10^{-5}$)

Q.52 The solubility of $\text{Pb}(\text{OH})_2$ in water is $6.7 \times 10^{-6} \text{ M}$. Calculate the solubility of $\text{Pb}(\text{OH})_2$ in a buffer solution of pH = 8.

Q.53 Determine the concentration of NH_3 solution whose one litre can dissolve 0.10 mole AgCl. K_{sp} of AgCl and K_f of $\text{Ag}(\text{NH}_3)_2^+$ are $1.0 \times 10^{-10} \text{ M}^2$ and $1.6 \times 10^7 \text{ M}^{-2}$ respectively.

2000

Q.54 What (H_3O^+) must be maintained in a saturated H_2S solution to precipitate Pb^{2+} , but not Zn^{2+} from a solution in which each ion is present at a concentration of 0.01 M ? ($K_{sp} \text{ H}_2\text{S} = 1.1 \times 10^{-22}$; $K_{sp} \text{ ZnS} = 1.0 \times 10^{-21}$)

Q.55 The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is $1.3653 \text{ mol litre}^{-1}$ and the $\text{p}K_a$ of H_2SO_3 is 1.92, estimate the pH of rain on that day.

2001

Q.56

(a) 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 % of that metal ion is precipitated ?

K_{sp} of AgI = 8.5×10^{-17} and K_{sp} of $\text{Hg}_2\text{I}_2 = 2.5 \times 10^{-26}$

(b) 0.01 Mol of AgNO_3 is added to 1 litre of a solution which is 0.1 M in Na_2CrO_4 and 0.005 M in NaIO_3 . Calculate the mol of precipitate formed at equilibrium and the concentrations of Ag^+ , IO_3^- and CrO_4^{2-} .

(K_{sp} values of Ag_2CrO_4 and AgIO_3 are 10^{-8} and 10^{-13} respectively.)

2002

Q.57 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C .

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

(ii) if 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is $1.75 \times 10^{-5} \text{ mol L}^{-1}$]

2003

Q.58 Will pH value of water be same at temperature 25°C and 4°C . Justify in not more than 2 or 3 sentences.

2004

Q.59 0.1 M of HA is titrated with 0.1 M NaOH, Calculate the pH at end point. Given $K_a(\text{HA}) = 5 \times 10^{-6}$ and $\alpha \ll 1$

ANSWERSHEET

Exercise - 01

1. NO_2^- , HCN , ClO_4^- , HF , H_2O , HCO_3^- , HS^-
2. BF_3 , H^+ , NH_4^+
3. F^- , HSO_4^- , CO_3^{2-}
4. NH_3 , NH_4^+ , HCOOH
7. 2.42
8. $1.7 \times 10^{-4}\text{M}$
9. $\text{F}^- = 1.5 \times 10^{-11}$, $\text{HCOO}^- = 5.6 \times 10^{-11}$, $\text{CN}^- = 2.08 \times 10^{-6}$
10. $[\text{Phenolate ion}] = 2.2 \times 10^{-6}$, $\text{pH} = 5.65$, $\alpha = 4.47 \times 10^{-5}$, pH of 0.01 M sodium phenate solution = 9.30
11. $[\text{HS}^-] = 9.54 \times 10^{-5}$, in 0.1M HCl $[\text{HS}^-] = 9.1 \times 10^{-8}\text{M}$, $[\text{S}^{2-}] = 1.2 \times 10^{-13}\text{M}$, in 0.1 M HCl $[\text{S}^{2-}] = 1.09 \times 10^{-19}\text{M}$
12. $[\text{Ac}^-] = 0.00093$, $\text{pH} = 3.03$
13. $[\text{A}^-] = 7.08 \times 10^{-5}\text{M}$, $K_a = 5.08 \times 10^{-7}$, $\text{p}K_a = 6.29$
14. (a) 2.52 (b) 11.70 (c) 2.7 (d) 11.30
15. (a) 11.65 (B) 12.21 (c) 12.57 (d) 1.87
16. $\text{pH} = 1.88$, $\text{p}K_a = 2.70$
17. $K_b = 1.6 \times 10^{-6}$, $\text{p}K_b = 5.8$
18. $\alpha = 6.53 \times 10^{-4}$, $K_a = 2.34 \times 10^{-5}$
19. (a) 0.0018 (B) 0.00018
20. $\alpha = 0.0054$
21. (a) $1.48 \times 10^{-7}\text{M}$, (b) 0.063 (c) $4.17 \times 10^{-8}\text{M}$ (d) 3.98×10^{-7}
22. (a) $1.5 \times 10^{-7}\text{M}$, (b) 10^{-5}M (c) $6.31 \times 10^{-5}\text{M}$ (d) $6.31 \times 10^{-3}\text{M}$
23. $[\text{K}^+] = [\text{OH}^-] = 0.05\text{M}$, $[\text{H}^+] = 2.0 \times 10^{-13}\text{M}$
24. $[\text{Sr}^{2+}] = 0.158\text{M}$, $[\text{OH}^-] = 0.3162\text{M}$, $\text{pH} = 13.50$
25. $\alpha = 1.63 \times 10^{-2}$, $\text{pH} = 3.09$. In presence of 0.01 M HCl, $\alpha = 1.32 \times 10^{-3}$
26. $K_a = 2.09 \times 10^{-4}$ and degree of ionization = 0.0457
27. $\text{pH} = 7.97$, degree of hydrolysis = 2.36×10^{-5}
28. $K_b = 1.5 \times 10^{-3}$
29. NaCl, KBr solutions are neutral, NaCN, NaNO_2 and KF solutions are basic and NH_4NO_3 solution is acidic.
30. (a) pH of acid solution = 1.94 (b) its salt solution = 2.87
31. $\text{pH} = 6.78$
32. (a) 11.2 (b) 7.00 (c) 3.00
33. Silver chromate $S = 0.65 \times 10^{-4}\text{M}$; Molarity of $\text{Ag}^+ = 1.30 \times 10^{-4}\text{M}$
Molarity of $\text{CrO}_4^{2-} = 0.65 \times 10^{-4}\text{M}$; Barium Chromate $S = 1.1 \times 10^{-5}\text{M}$; Molarity of Ba^{2+} and CrO_4^{2-} each is $1.1 \times 10^{-5}\text{M}$; Ferric Hydroxide $S = 1.39 \times 10^{-10}\text{M}$;
Molarity of $\text{Fe}^{3+} = 1.39 \times 10^{-10}\text{M}$; Molarity of $[\text{OH}^-] = 4.17 \times 10^{-10}\text{M}$
Lead chloride $S = 1.59 \times 10^{-2}\text{M}$; Molarity of $\text{Pb}^{2+} = 1.59 \times 10^{-2}\text{M}$
Molarity of $\text{Cl}^- = 3.18 \times 10^{-2}\text{M}$; Mercurous iodide $S = 2.24 \times 10^{-10}\text{M}$;
Molarity of $\text{Hg}_2^{2+} = 2.24 \times 10^{-10}\text{M}$ and molarity of $\text{I}^- = 4.48 \times 10^{-10}\text{M}$

34. Silver chromate is more soluble and the ratio of their molarities = 91.9
 35. No precipitate
 36. Silver benzoate is 3.317 times more soluble at lower pH
 37. The highest molarity for the solution is $2.5 \times 10^{-9} \text{ M}$
 38. 2.46 litre of water 39. Precipitation will take place in cadmium chloride solution
 40. 6.98 41. 2.62 42. $K_a = 1.0 \times 10^{-8}$ and $\text{p}K_a = 8$
 43. $\text{pH} = 2.85$ & % dissociation of $\text{HOCl} = 1.76\%$
 44. $K_b = 8.96 \times 10^{-7}$ & $\text{p}K_b = 6.04$ 45. 8.95
 46. 5.64×10^{-10} 47. 9.24 48. 7.005
 49. $1.0 \times 10^{-5} \text{ mol/L}$ 51. $2.0 \times 10^{-13} \text{ M}$

Exercise - 02

- | | | | | |
|-------|-------|-------|-------|-------|
| 1. C | 2. B | 3. C | 4. C | 5. C |
| 6. C | 7. A | 8. D | 9. C | 10. C |
| 11. D | 12. C | 13. D | 14. D | 15. D |
| 16. A | 17. A | 18. D | 19. B | |

Exercise - 03

1. 2.3 mol/lit 2. 1.5 times
 3. $[\text{H}_2\text{SO}_4] = 0 \text{ M}$, $[\text{HSO}_4^-] = 0.09 \text{ M}$, $[\text{H}^+] = 0.11 \text{ M}$
 4. $[\text{H}_2\text{S}] = 0.1 \text{ M}$, $[\text{S}^{2-}] = 1.3 \times 10^{-13} \text{ M}$, $[\text{HS}^-] = 1 \times 10^{-4} \text{ M}$, $[\text{H}^+] = 1 \times 10^{-4} \text{ M}$
 5. 1.44×10^{-4} 6. 1.63, 1.86 7. 1.2915 mg
 8. No 9. (a) $1.76 \times 10^{-4} \text{ mg/L}$, (b) $8.8 \times 10^{-5} \text{ mg/L}$, (c) 1.588 mg/L
 10. (a) $K_c = 4 \times 10^4$, (b) $K_c = 10^6$
 11. $K_c = 3.02 \times 10^{-2}$, $S = 0.123 \text{ M}$ 12. 8.7 mL
- | 0°C | 10°C | 25°C | 40°C | 50°C |
|-------|-------|-------|-------|-------|
| 7.472 | 7.267 | 7.002 | 6.767 | 6.631 |
13. 14. $K_w = 1.0 \times 10^{-14} \text{ M}^2$, $K_1 = 1.8 \times 10^{-16} \text{ M}$ 15. (i) 6.13 (ii) solution is acidic
 16. $[\text{H}_3\text{O}^+] = 1.05 \times 10^{-7} \text{ M}$, 6.98 17. (a) $3.7 \times 10^4 \text{ dm}^3$ (b) 4 dm^3
 18. 0.0528 M ; 0.0472 M ; 0.0528 M ; 0.000064 M 19. $\text{HZ} < \text{HY} < \text{HX}$, $K_a(\text{HY}) = 10^{-5} \text{ M}$, $K_a(\text{HZ}) = 10^{-9} \text{ M}$
 20. (i) $\alpha = 0.5553 \times 10^{-2}$, $K_h = 0.308 \times 10^{-4}$, $\text{pH} = 7$ (ii) $\alpha = 0.52$, $K_h = 1.208$, $\text{pH} = 4.71$
 (iii) $\alpha = 0.775$, $K_h = 11.82$, $\text{pH} = 9.79$
 21. 6.89, 7, 7.02, 7 22. 7.3 23. (a) 8.72 (b) 4.75 (c) 12.52
 24. 60.3 million 25. 8.59 26. 2.87, 1.3
 27. $1.2 \times 10^{-5} \text{ M}$, $3.2 \times 10^{-5} \text{ M}$ 28. 10.3 29. $4.11 \times 10^{-4} \text{ M}$
 30. 5.6×10^{-10} , 2.4×10^{-4} , 5.63 31. 5.68×10^{-10} 32. $K_{sp}(\text{Ag}_2\text{CrO}_4) = 4 \times 10^{-12}$
 33. 2.1×10^{-6} 34. No

35. 1.4×10^{-5} , 2.15×10^{-4} mole/litre; 15.4 time
36. $\frac{1}{2230}$ of its initial value
37. (a) 1.2×10^{-5} mole/litre (b) 9×10^{-4} mole/litre
38. (a) pH = 9.239 (b) lowered (c) pH = 4.699
39. $[H^+] = 2.5 \times 10^{-3}$

Exercise - 04

- | | | | | |
|-------|-------|-------|-------|-------|
| 1. B | 2. D | 3. C | 4. D | 5. D |
| 6. B | 7. A | 8. D | 9. C | 10. C |
| 11. C | 12. A | 13. B | 14. B | 15. C |
| 16. A | 17. A | 18. A | 19. C | 20. B |
| 21. C | 22. D | 23. C | 24. B | 25. A |
| 26. C | | | | |

Exercise - 05

1. pH = 11.22
2. pH = 11.70
3. 0.0016 mol
4. 9.55
5. $K_{sp} = 6.3 \times 10^{-21}$
6. precipitation occur
7. (i) pH = 4.35 (ii) 1.79×10^{-9} mol/lit
8. (i) 28.57% (ii) 4.11×10^{-4} mol dm⁻³
9. 10^{-8}
10. pH = 10.69
11. (a) for $Cl^- = 1.7 \times 10^{-9}$ mol dm⁻³, For $Br^- = 5 \times 10^{-3}$ mol dm⁻³, For $I^- = 8.5 \times 10^{-16}$ mol dm⁻³ (b) AgI (c) 1.7×10^{-5} mol dm⁻³ (d) 5.0×10^{-8} mol dm⁻³, 3.0×10^{-4} mol dm⁻³
12. 0.089
13. (i) 7.299×10^{-3} (ii) 4.55×10^{22} β particle
14. pH = 9.99 ; S = 2.5×10^{-9}
15. S = 8.92×10^{-5} M
16. CuS precipitate; $3.27 \times 10^{-140}\%$, MnS precipitates
17. (a) No (b) $[CH_3COO^-] = 1.7$ M
18. 1.9×10^{-5} M
19. Alkaline, pH = 8.34
20. 6.12×10^{-10} M, No
21. 5.9×10^{-5} M
22. 6.7183
23. pH = 3; 0.1 %
25. (i) pH = 9.4 (ii) pH = 4.22
26. 99.99%
27. (a) 0.59; (b) 7.16; (c) 7.55
28. 6.064
29. pH = 8.96
30. pH = 7.3
31. $[H^+] = 6.894 \times 10^{-3}$, ($K_a = 10^{-2}$)
32. pH = 6.06, % of cationic form = 0.01928 %
33. (a) yes (b) 6.7×10^{-4} (c) 7.2×10^{-6} M, 0.009%
34. Ag₂S
35. (a) $CaF_2(s) + 2H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2HF(aq) + 2OH^-(aq)$ $K_{eq} = 3.36 \times 10^{-32}$ (b) 9.44×10^{-7} M (c) 2.03×10^{-5} M
36. 67%
37. $Ag^+ = 1.38 \times 10^{-13}$ M; $Ag(S_2O_3)^- = 3.3 \times 10^{-5}$ M $Ag(S_2O_3)_2^{3-}$ & $S_2O_3^{2-} = 0.358$ M $Ag(S_2O_3)_3^{5-} = 0.642$ M
38. $V_1(\text{Acid}) = 123.8$ mL, $V_2[\text{Base}] = 276.2$ mL
39. (a) 1.92 (b) 2.15 (c) 11.82, (d) 2.51
40. (a) 1.82×10^{-3} M (b) 2.932×10^{-4} M
41. (i) 0.707×10^{-3} M (ii) presence of HB suppresses the dissociation of HA

42. (a) $8.4 \times 10^{-15} \text{ M}$ (b) $1.0146 \times 10^{-10} \text{ M}$ 43. $2.48 \times 10^{-14} \text{ M}^2$
 44. $[\text{Ag}^+] = 1.505 \times 10^{-9} \text{ M}$ $[\text{Ag}(\text{NH}_3)_3^+] = 0.7 \times 10^{-6} \text{ M}$ $[\text{Ag}(\text{NH}_3)_2^+] = 9.97 \times 10^{-4} \text{ M}$
 45. (a) pH = 3.83 (b) pH = 3.85 (c) 3.99 46. 0.0818 moles 47. pH = 2.558
 48. $x : y = 1 : 3.98$, unaltered 49. pH = 9.168
 50. $\alpha = 0.05$ 51. 11.74 52. $\Delta H_{\text{neut}} = -51.963 \text{ kJ mol}^{-1}$
 53. (a) 13.1, (b) 0.13 M 54. 1.650
 55. (a) 2.12 (b) 4.66 (c) 7.2 (d) 12 56. (a) 8.34 (b) 4.66 (c) 9.6 (d) 7.20
 57. 5.158
 58. (a) acetic acid, salt-acid molar ratio 1.8 : 1;
 (b) $[\text{HOAc}] = 0.066 \text{ m mol/mol/ml}$ and $[\text{OAc}^-] = 0.119 \text{ m mol/ml}]$
 59. 8.35, 9.60, 4.66 60. 9.168
 61. $[\text{OH}^-] = 3.73 \times 10^{-2} \text{ M}$, $[\text{H}_3\text{PO}_4] = 6 \times 10^{-18} \text{ M}$ 62. 9.7736
 63. $K_{\text{h}}(\text{H}_2\text{PO}_4^-) = 2 \times 10^{-12}$; $K_{\text{h}}(\text{HPO}_4^{2-}) = 2 \times 10^{-7}$; $K_{\text{h}}(\text{PO}_4^{3-}) = 2 \times 10^{-2}$; acidic basic
 64. $[\text{CO}_3^{2-}] = 4.9 \times 10^{-3} \text{ M}$ 65. $[\text{OH}^-] = 3 \times 10^{-7} \text{ M}$
 66. $[\text{H}_2\text{CO}_3] = 9.85 \times 10^{-6} \text{ M}$; $[\text{HCO}_3^-] = 4.9 \times 10^{-4}$ $[\text{CO}_3^{2-}] = 2.45 \times 10^{-8}$
 67. (i) $9.21 \times 10^{-5} \text{ M}$, 9.21×10^{-5} , 8.9×10^{-16} (ii) 9.96
 68. 1.6 mmol 70. 7.81
 71. 0.9542, $\text{pK}_{\text{a}} = 4.751$, $\frac{1}{11}$ th & $\frac{10}{11}$ th states of neutralization
 72. (a) 5.85 (b) 10.48 73. 10 M, $1.12 \times 10^{-6} \text{ M}$, $2 \times 10^{-4} \text{ M}$
 74. 9.99, $s = 2.6 \times 10^{-5} \text{ M}$ 75. 9.66×10^{-3}
 76. Cd^{2+} 77. Precipitation will occur

Exercise - 06

- | | | | |
|--|--|---------------------------|------------------------|
| 1. A, B | 2. A, C, D | 3. D | 4. A, C, D |
| 5. A | 6. B | 7. C | 8. B, C |
| 9. A, B | 10. B, C, D | 11. A, B | 12. A, B |
| 13. A, B | 14. B, C | 15. A, B | 16. B, C |
| 17. B, D | 18. D | 19. C | 20. D |
| 21. D | 22. C | 23. A | 24. A |
| 25. A | 26. A | 27. C | 28. A |
| 29. B | 30. A | 31. C | 32. B |
| 33. A | 34. A | 35. B | 36. A |
| 37. A | 38. D | 39. C | 40. B |
| 41. B | 42. A | 43. C | 44. A |
| 45. D | 46. B | 47. A | 48. D |
| 49. A | 50. A | 51. Increase on | 52. Greater |
| 53. Br ⁻ ion | 54. Greater | 55. 7.14×10^{-3} | 56. 3×10^{-6} |
| 57. in both dil acidic and alkaline solution | 58. $\text{M}_2\text{X} = \text{QY}_2 > \text{PZ}_3$ | 59. 10^{-8} | 60. 7 |
| 61. 5.74 | 62. HSO_4^- | 63. increase | 64. less |
| 65. less | 66. Lewis acid | 67. Buffer | 68. Weaker |
| 69. Acidic | 70. cationic | 71. independent | 72. false |
| 73. false | 74. True | 75. False | 76. True |

Exercise - 07

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1. A | 2. A | 3. B | 4. D | 5. D | 6. C |
| 7. A | 8. B | 9. D | 10. C | 11. D | 12. D |
| 13. D | 14. D | 15. C | 16. C | | |

Exercise - 08

- | | | | | | |
|-------|-------|-------|-------|-------|-------|
| 1. D | 2. A | 3. D | 4. D | 5. C | 6. D |
| 7. D | 8. A | 9. B | 10. A | 11. C | 12. D |
| 13. C | 14. B | 15. A | 16. B | 17. A | 18. B |
| 19. D | 20. D | 21. D | 22. 7 | | |

Exercise - 09

- | | | |
|--|--|---|
| 1. 4.8×10^{-3} mol/lit | 2. 8.7×10^{-4} gm/lit | 3. 4.19 |
| 4. pH = 4 | 5. 5.6×10^{-5} mole | 6. (i) 4.57 (ii) 1 |
| 7. pH = 4 | 8. 8.85×10^{-3} mol | 9. 3.98×10^{-1} |
| 10. $[Al^{+3}] = 1.28 \times 10^{-15}$ M ; $[Mg^{+2}] = 0.686$ M | | |
| 11. (i) 3.87×10^{-5} (ii) 1.5×10^{-8} M | 12. 9.02 | |
| 13. 2.3724, 2.77×10^4 lit | 14. 39.62 ml | 15. 8.71 |
| 16. 1.81×10^{-5} | 17. 10^{10} | 18. 3.97×10^{-12} mol ³ lit ⁻³ |
| 19. 8.25×10^{-4} | 20. $[H^+] = 7.2 \times 10^{-10}$ M, $[OH^-] = 1.39 \times 10^{-5}$ M | |
| 21. (a) 11 (b) 12 (c) 12.3010 (d) = 11.2041 | | |
| 22. $[S^{2-}] = 1.44 \times 10^{-20}$ M, $[HS^-] = 3.3 \times 10^{-8}$ M | | |
| 23. (i) change in pH = + 0.1761 unit; i.e. pH decreases (ii) change in pH = -0.1761; i.e. pH increases | | |
| 24. 758.2 mg | 25. 9 | 26. 1.67% |
| 27. 2.5×10^{-3} | 28. V = 78.36 ml | 29. pH = 0.9826 |
| 30. 0.067 M | 31. 1.34×10^{-3} , 2.87 | 32. 4×10^{-12} M |
| 33. $[OH^-] = 10^{-5}$, pH = 9 | 34. $[OH^-] = 1.07 \times 10^{-2}$ M, $[H^+] = 0.9268 \times 10^{-12}$ M | |
| 35. $[OH^-] = 10^{-9}$, pH = 5 | 36. 1.5×10^{-8} mol/lit | 37. 6.5 |
| 38. 0.01 M | 39. 11.5 | 40. 10^{-2} % |
| 41. 6.07×10^5 | 42. 0.2 M, 0.4 M | 43. 8×10^{-8} M |
| 44. 1.71×10^{-10} | 45. pH = 2 | 46. $[H]^+ = 5 \times 10^{-9}$; 0.01 % |
| 47. pH = 11.3010 | 48. 0.0539 | 49. 0.49 mole |
| 50. 2% | 51. 5.7033 | 52. 1.203×10^{-3} mol/lit |
| 53. 2.79 M | 54. 3.3×10^{-2} M | 55. 0.49 |
| 56. (a) $[I]^- = 5 \times 10^{-13}$ M, 99.83% (b) $[CrO_4^{2-}] = 0.0975$; $[Ag^+] = 3.2 \times 10^{-4}$ M ; $[IO_3^-] = 3.1 \times 10^{-10}$ M | | |
| 57. $\alpha = 0.000175$, pH = 1 (ii) 4.757 | 58. No | 59. 9 |