6

IONIC EQUILIBRIUM

Arrhenius Theory

When dissolved in water, the substances which releases

(i) H^+ ions are called acids *e.g.* HNO_3, $HClO_4$, CH_3COOH,

(ii) OH^- ions are called bases, *e.g.* NaOH, KOH, NH_4OH

Bronsted - Lowry Protonic Concept : acid is H^+ donor and base is H^+ acceptor

Conjugate acid and base

To get conjugate acid of a given species add H^+ to it. *e.g.* conjugate acid of N_2H_4 is $N_2H_5^+$.

To get conjugate base of any species subtract H^+ from it. *e.g.* Conjugate base of NH_3 is NH_2^-.

HCl is an acid while its conjugate ion Cl^- is a base.

HCO_3^- can donate proton as well as can accept proton hence amphiprotic.

Lewis Concept : Acids are substances which accept a lone pair of electrons to form a coordinate bond and bases are the substances which donate a lone pair of electrons to form a coordinate bond.

- Lewis-acid is lone pair acceptor ; Lewis-base is lone-pair donor.

Ostwald dilution law: Applicable for weak electrolytes (weak acids/bases)

If α is negligiable with respect to 1 ($\alpha < 0.5$), than for mono basic acid and mono acidic base.

$$\therefore \qquad K_C = C\alpha^2 \qquad \text{or} \qquad \alpha = \sqrt{\left(\frac{K_C}{C}\right)}$$

$$\text{So} \qquad \alpha \propto \frac{1}{\sqrt{C}} \qquad \text{or} \qquad \alpha \propto \sqrt{V}$$ where, V is the volume of solution

at infinite dilution α reaches its maximum value, unity.

Presence of other solute (Common ion effect)

Degree of ionisation of a weak electrolyte is suppressed by the addition of a substance having an ion common to weak electrolyte is known as common ion effect.

Ionic Product of Water

Pure water is weak electrolyte and dissociated as:

$$\begin{array}{lccccc} & H_2O & \rightleftharpoons & H^+ & + & OH^- \\ \text{Before dissociation} & C & & 0 & & 0 \\ \text{After dissociation} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$K_{eq.} = \frac{[H^+][OH^-]}{[H_2O]}$$

where, K_{eq} is dissociation constant or equilibrium constant of water. Since, dissociation of water is too less and undissociated H_2O can be taken as constant, therefore

$$K_{eq}[H_2O] \rightleftharpoons [H^+]\,[OH^-]$$

$$K_w = [H^+][OH^-]$$

The new constant K_w is known as ionic product of water. The numerical value of K_w increases considerably with temperature. It is 1.0×10^{-14} at 25°C. The variation of ionic product of water with temperature is given by

$$\ln\frac{K_{w_2}}{K_{w_1}} = \frac{\Delta_r H}{R}\frac{[T_2 - T_1]}{T_1 T_2}$$

pH CONCEPT

S. Sorenson used a new term pH to express the hydrogen ion concentration.

$$pH = -\log[H^+] \quad \text{or} \quad pH = -\log[H_3O^+] \quad \text{or} \quad [H^+] = 10^{-pH}$$

For simplicity hydrogen ions are simply written as H^+, with the understanding that H^+ ions in solution are always solvated.

- Ionic product (auto ionisation constant) of water
  $K_w = 1 \times 10^{-14} = [H_3O^+][OH^-]$ at 298 K
- K_w increases with increase in T
- $pH + pOH = pK_w = 14$ (at 298 K)
- For weak acid and its conjugate base

$$K_a K_b = K_w$$

or $$pK_a + pK_b = pK_w = 14 \quad \text{(at 298 K)}$$

pH calculation of weak acid (HA)

$$\begin{array}{lccccc} & HA(aq) & \rightleftharpoons & H^+(aq) & + & A^-(aq) \\ \text{Initial conc.} & C & & - & & - \\ \text{Conc. at eq.} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

if $\alpha << 1$; $K_a \approx C\alpha^2$

pH calculation of weak base (BOH)

$$\begin{array}{lccccc} & BOH(aq) & \rightleftharpoons & B^+(aq) & + & OH^-(aq) \\ \text{Initial conc.} & C & & & & \\ \text{Conc. at eq.} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$K_b = \frac{C\alpha^2}{1-\alpha}$$

if $\alpha << 1$; $K_b \approx C\alpha^2$

$$[H^+] = C\alpha = \sqrt{K_aC}$$

$$\therefore \quad pH = \frac{1}{2}(pK_a - \log C)$$

α = Degree of ionisation

K_a = ionisation constant of weak acid

$$[OH^-] = C\alpha = \sqrt{K_bC}$$

$$\therefore \quad pOH = \frac{1}{2}(pK_b - \log C)$$

α = Degree of ionisation

K_b = ionisation constant of weak base

pH Calculation of mixture of two weak acid *HA* and *HB* :

- $[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$; if α_1 and α_2 of both acids are negligiable w.r.t. unity.

K_{a_1} and K_{a_2} are ionization constant of HA and HB respectively.
C_1 and C_2 are concentration of HA and HB respectively.

pH calculation of mixture of two weak base *A*OH and *B*OH.

$[OH^-] = \sqrt{K_{b_1}C_1 + K_{b_2}C_2}$; if α_1 and α_2 of both bases are negligiable w.r.t. unity.

K_{b_1} and K_{b_2} are ionization constant of *A*OH and *B*OH respectively.
C_1 and C_2 are concentration of *A*OH and *B*OH respectively.

Salt Hydrolysis

- Hydrolysis is the interaction of cation/anion/both ions of the salt with H_2O
- Salt of strong acid (SA) and strong base (SB) is not hydrolysed ; solution is neutral, pH = 7 at 25°C.
- Salt of SA and weak base (WB) is acidic due to hydrolysis of cation

$$h = \text{degree of hydrolysis} = \sqrt{\frac{K_w}{K_bC}} = \sqrt{\frac{K_h}{C}}, \quad K_h \text{ (hydrolysis constant)} = \frac{Ch^2}{(1-h)}$$

$$pH = 7 - \frac{1}{2}(pK_b + \log C) \qquad \text{At } 25°C$$

- Salt of weak acid (WA) and SB is alkaline due to hydrolysis of anion

$$h = \sqrt{\frac{K_w}{K_aC}} = \sqrt{\frac{K_h}{C}}$$

$$pH = 7 + \frac{1}{2}(pK_a + \log C) \qquad \text{At } 25°C$$

- Salt of WA and WB is neutral ($K_a = K_b$), acidic ($K_a > K_b$) and basic ($K_b > K_a$) due to hydrolysis of both

$$h = \sqrt{\frac{K_w}{K_aK_b}} = \sqrt{K_h} \quad ; \quad pH = 7 + \frac{1}{2}(pK_a - pK_b) \qquad \text{At } 25°C$$

- For amphiprotic salt like HS^-, HCO_3^-, $pH = \frac{pK_1 + pK_2}{2}$ or $[H^+] = \sqrt{K_1K_2}$

(K_1 = first ionisation constant, K_2 = second ionisation constant of acid)

Buffer Solutions are the solutions whose pH does not change significantly on adding a small quantity of strong base or strong acid.

In general buffer solutions are simple (salts of weak acid and weak base), or mixed buffer.

Mixed buffer are of two types :

(A) Acidic buffer solutions : weak acid with its conjugate base :

made by mixing a weak acid with its conjugate base. *e.g.*, CH_3COOH with CH_3COONa, $NaHCO_3$ and H_2CO_3, H_3PO_4 and NaH_2PO_4.

(B) Basic buffer solutions : weak base with its conjugate acid :

$NH_3(aq)$ with $NH_4Cl(aq)$, $RNH_2(aq.)$ and $RNH_3Cl(aq.)$ etc,

If K_a for acid (or K_b for base) is not too high, we may write :

Henderson's Equation

For acidic buffer solution : $pH = pK_a + \log([salt]/[acid])$

For basic buffer solution : $pOH = pK_b + \log([salt]/[base])$

- For good buffer capacity, [salt] : [acid] ratio should be as close to one as possible. In such a case,

  $pH = pK_a$. (This also is the case at midpoint of titration)
- Buffer capacity $= \dfrac{\text{No. of moles of acid (or base) added per litre of buffer solution}}{\text{Change in pH}}$

Maximum Buffer Capacity

It can be proved that maximum buffer capacity is achieved when the salt and acid or base concentration is equal.

Indicators : Indicator is a substance which indicates the point of equivalence in a titration by undergoing a change in its colour. They are weak acids or weak bases.

Theory of Indicators : The ionized and unionized forms of indicators have different colours. If 90 % or more of a particular form (ionised or unionised) is present, then its colour can be distinctly seen. In general, for an indicator which is weak acid, $HIn \rightleftharpoons H^+ + In^-$, the ratio of ionized to unionized form can be determined from

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

So, for detectable colour change, $pH = pK_a \pm 1$

This roughly gives the range of indicators. Ranges for some popular indicators are

Indicators	pH range	Colour	
		Acid medium	Basic medium
Methyl orange	3.1 – 4.4	red	yellow
Methyl red	4.2 – 6.3	red	yellow
Phenolphathlene	8.3 – 10	colourless	pink

Equivalence point: The point at which exactly equivalent amounts of acid and base have been mixed.

Acid Base Titration : For choosing a suitable indicator titration curves are of great help. In a titration curve, change in pH is plotted against the volume of alkali to a given acid. Four cases arise.

- **Strong acid *vs* strong base :** The curve is almost vertical over the pH range 3.5-10. This abrupt change corresponds to equivalence point. Any indicator suitable.
- **Weak acid *vs* strong base :** Final solution is basic 9 at equivalence point. Vertical region (not so sharp) lies in pH range 6.5-10. So, phenolphathlene is suitable.

- **Strong acid *vs* weak base :** Final solution acidic. Vertical point in pH range 3.8-7.2. Methyl red or methyl orange suitable.
- **Weak acid *vs* weak base :** No sharp change in pH. No suitable indicator.

Note : *at midpoint of titration,* $pH = pK_a$*, thus by pH measurements,* K_a *for weak acids (or* K_b *for weak bases) can be determined.*

Polyprotic acids and bases : K_2, K_3 etc. can be safely neglected. If $K_1 >> K_2 >> K_3$ and only K_1 plays a significant role in pH calculation.

Solubility (S) and Solubility Product (K_{sp})

This is generally used for sparingly soluble salts,

Let the salt is $A_x\ B_y$, present in water. Let the solubility of A_xB_y, is S

$$\begin{array}{lccc} & A_xB_y(s) \rightleftharpoons & xA^{y+}(aq) + & yB^{x-}(aq) \\ & - & xS & yS \\ \therefore & \multicolumn{3}{l}{K_{sp} = (xS)^x \cdot (yS)^y = x^x y^y \cdot (S)^{x+y}} \end{array}$$

e.g., For sparingly soluble salts (*e.g.*, $Ag_2C_2O_4$) an equilibrium which exists as

$$Ag_2C_2O_4(s) \rightleftharpoons 2Ag^+(aq.) + C_2O_4^{2-}(aq.)$$

Then $$K_{sp} = [Ag^+]^2[C_2O_4^{2-}]$$

Ionic product (*Q*) : It is defined as product of concentration of all the ions of a sparingly soluble salt at time '*t*'.

- **Case-1 :** If $Q < K_{sp}$ then solution is unsaturated no precipitation takes place.
- **Case-2 :** If $Q = K_{sp}$ then solution is saturated.
- **Case-3 :** If $Q > K_{sp}$ solution is super saturated, precipitation takes place.

Common ion effects : Suppression of dissociation by adding an ion common with dissociated products. *e.g.*, Solubility of AgCl decreases in presence of NaCl (Cl^- ion common) OR in presence of $AgNO_3$(Ag^+ ion common)

$$\begin{array}{lccc} & AgCl(s) \rightleftharpoons & Ag^+(aq) \quad + & Cl^-(aq) \\ \text{Solubility in water At eq.:} & - & S & S \\ \text{Solubility in 0.01} M \text{ NaCl At eq.:} & - & S' & (S'+0.01) \end{array}$$

$$K_{sp} = [Ag^+][Cl^-]_{Total}$$

$$K_{sp} = S'(S'+0.01) \qquad \text{where} \qquad S' < S$$

Simultaneous solubility : When two sparingly soluble salts are present in water with atleast a common ion, then solubility of both salts decreases *e.g.*, AgCl and AgBr, $SrSO_4$ and $BaSO_4$

e.g. Calculate simultaneous solubility of AgCl and AgBr in the solution.

If simultaneous solubility of AgCl and AgBr are x and y respectively.

$$\begin{array}{lccc} & AgCl(s) \rightleftharpoons & Ag^+(aq.) + & Cl^-(qq.) \\ \text{At eq.} & - & (x+y) & x \end{array}$$

$$K_{sp_1}(AgCl) = [Ag^+]_{Total}[Cl^-]$$

$$K_{sp_1} = (x+y)x$$

$$\begin{array}{lccc} & AgCl(s) \rightleftharpoons & Ag^+(aq.) + & Cl^-(qq.) \\ \text{At eq.} & - & (x+y) & y \end{array}$$

$$K_{sp_2}(AgBr) = [Ag^+]_{Total}[Br^-]$$

$$K_{sp_2} = (x+y)y$$

Effect of complex formation and hydrolysis on solubility : Solubility increases due to complex formation and hydrolysis of anion (cation/anion)

Solubility of AgBr in aq. sol. of NH_3.

Let solubility of AgBr is x

$$\begin{array}{lllll}
 & AgBr(s) \rightleftharpoons & Ag^+(aq) + & Br^-(qq) & ; \ K_{sp} \\
\text{At eq.} & - & (x-y) & x & \\
 & Ag^+(aq) + & 2NH_3(aq) \rightleftharpoons & Ag(NH_3)_2^+(aq) & ; \ K_f \\
\text{At eq.} & (x-y) & (z-2y) & y & \\
\hline
\text{Overall} & AgBr(s) + & 2NH_3(aq) \rightleftharpoons & Ag(NH_3)_2^+(aq) + & Br^-(aq) \\
\text{Reaction at eq.} & - & (z-2y) & y & x
\end{array}$$

Due to very large value of K_f we can assume $y \approx x$

$$K_{sp} \cdot K_f = \frac{x^2}{(z-2x)^2}$$

Level 1

1. Morphine ($C_{17}H_{19}NO_3$), which is used medically to relieve pain is a base. What is its conjugate acid?

(a) $C_{17}H_{18}NO_3^+$ (b) $C_{17}H_{18}NO_3$ (c) $C_{17}H_{20}NO_3^-$ (d) $C_{17}H_{20}NO_3^+$

2. The conjugate base of $H_2PO_4^-$ is :

(a) H_3PO_4 (b) $H_2PO_4^-$ (c) HPO_4^{2-} (d) PO_4^{3-}

3. The strongest Bronsted base in the following anion is:

(a) CN^- (b) Cl^- (c) I^- (d) Br^-

4. Which salt can furnish H^+ in its aqueous solution?

(a) NaH_2PO_2 (b) Na_2HPO_3 (c) Na_2HPO_4 (d) All of these

5. Which is the set of amphiprotic species?

(a) H_3O^+, HPO_4^{2-}, HCO_3^- (b) H_2O, HPO_3^{2-}, $H_2PO_2^-$

(c) $H_2PO_4^-$, $H_2PO_3^-$, H_2O (d) All of these

6. The K_a values for HPO_4^{2-} and HSO_3^- are 4.8×10^{-13} and 6.3×10^{-8} respectively. Therefore, it follows the HPO_4^{2-} is a .... acid than HSO_3^- and PO_4^{3-} is a .... base than SO_3^{2-}.

(a) weaker, stronger (b) stronger, weaker (c) weaker, weaker (d) stronger, stronger

7. Given the following K_a values, determine which species is the strongest base.

$HSO_4^- = 1.2 \times 10^{-2}$, $H_2PO_4^- = 6.3 \times 10^{-8}$, $HCO_3^- = 4.7 \times 10^{-11}$

(a) CO_3^{2-} (b) H_2SO_4

(c) SO_4^{2-} (d) HPO_4^{2-}

8. Given that K_w for water is $10^{-13}\ M^2$ at 62°C, compute the sum of pOH and pH for a neutral aqueous solution at 62°C :

(a) 7.0 (b) 13.30

(c) 14.0 (d) 13.0

9. The value of the ion product constant for water, (K_w) at 60°C is $9.6 \times 10^{-14}\ M^2$. What is the $[H_3O^+]$ of a neutral aqueous solution at 60°C and an aqueous solution with a pH = 7.0 at 60°C are respectively?

(a) 3.1×10^{-8}, acidic (b) 3.1×10^{-7}, neutral

(c) 3.1×10^{-8}, basic (d) 3.1×10^{-7}, basic

10. For pure water :

(a) pH increases while pOH decreases with rise in temperature

(b) pH decreases while pOH increases with rise in temperature

(c) both pH and pOH decreases with rise in temperature

(d) both pH and pOH increases with rise in temperature

11. A beer has a pH of 4.30. What is the $[H_3O^+]$?

(a) 3.0×10^{-4} (b) 2.0×10^{-4} (c) 2.0×10^{-5} (d) 5.0×10^{-5}

12. The hydrogen ion concentration of the oceans is about $2 \times 10^{-9} M$. What is the pH?
(a) 8.85 (b) 9.3 (c) 7.85 (d) 8.7

13. The hydroxide ion concentration of a wine is $8 \times 10^{-11} M$. What is the pH of the wine?
(a) 2.10 (b) 2.9 (c) 3.9 (d) 4.9

14. The pH of a solution is 5. To this solution acid was added so that its pH value becomes 2.0. The increase in H^+ concentration is :
(a) 100 times (b) 5 times (c) 2.5 times (d) 1000 times

15. A solution has a pH = 9, it is 1000 times more basic than the original solution. What was the pH of the original solution?
(a) 12 (b) 6 (c) 9 (d) 10

16. Equal volumes of two HCl solutions of pH = 3 and pH = 5 were mixed. What is the pH of the resulting solution?
(a) 3.5 (b) 4.0 (c) 4.5 (d) 3.3

17. pOH of 0.002 M HNO_3 is :
(a) $11 + \log 2$ (b) $11 - \log 2$ (c) $-3 + \log 2$ (d) None of these

18. Number of equivalents of HCl present in 100 mL of its solution whose pH is 4 :
(a) 10^{-4} (b) 10^{-3} (c) 10^{-2} (d) 10^{-5}

19. To a 10 mL of 10^{-3} N H_2SO_4 solution water has been added to make the total volume of one litre. Its pOH would be :
(a) 3 (b) 12 (c) 9 (d) 5

20. The pH of a solution of H_2SO_4 is 1. Assuming complete ionisation, find the molarity of H_2SO_4 solution :
(a) 0.1 (b) 0.2 (c) 0.05 (d) 2.0

21. pH of a strong diprotic acid (H_2A) at concentrations :
(i) 10^{-4} M, (ii) $10^{-4} N$
are respectively :
(a) 3.7 and 4.0 (b) 4 and 3.7 (c) 4 and 4 (d) 3.7 and 3.7

22. Calcium hydroxide is a strong base. Compute $[Ca^{2+}]$ and $[OH^-]$ for a solution that is prepared by dissolving 0.60 g of $Ca(OH)_2$ in enough water to make a 1500 mL of solution.
[Atomic weights : Ca = 40, O = 16, H = 1]
(a) $5.4 \times 10^{-3}, 9.1 \times 10^{-13}$ (b) $5.4 \times 10^{-3}, 1.08 \times 10^{-2}$
(c) $5.4 \times 10^{-3}, 5.4 \times 10^{-3}$ (d) $8.1 \times 10^{-3}, 8.1 \times 10^{-3}$

23. pH of 10^{-6} M HCl(*aq.*) is :
(a) just less than 6 (b) exactly equal to 6
(c) just greater than 6 (d) just less than 7

24. 10^{-5} M NaOH solution at 25°C is diluted 1000 times. The pH of the resultant solution will :
(a) be equal to 8 (b) lie between 7 and 8
(c) lie between 6 and 7 (d) remain unchanged

25. 4.0 g of NaOH and 4.9 g of H_2SO_4 are dissolved in water and volume is made upto 250 mL. The pH of this solution is:
(a) 7.0 (b) 1.0 (c) 2.0 (d) 12.0

26. A 25.0 mL sample of 0.10 M HCl is titrated with 0.10 M NaOH. What is the pH of the solution at the points where 24.9 and 25.1 mL of NaOH have been added?
(a) 3.70, 10.70 (b) 3.30, 10.30 (c) 3.70, 10.30 (d) 3.0, 11.0

27. What is the pH of a solution in which 25.0 mL of 0.1 M NaOH is added to 25 mL of 0.08 M HCl and final solution is diluted to 500 mL?
(a) 3 (b) 11 (c) 12 (d) 13

28. What is the pH of a solution in which 10.0 mL of 0.010 M $Sr(OH)_2$ is added to 10.0 mL of 0.010 M HCl?
(a) 2.30 (b) 1.50 (c) 11.70 (d) 7.00

29. At 90°C, pure water has $[H^+] = 10^{-6}$ M, if 100 mL of 0.2 M HCl is added to 200 mL of 0.1 M KOH at 90°C then pH of the resulting solution will be :
(a) 5 (b) 6 (c) 7 (d) None of these

30. What change will occur for the following reaction if the hypochlorous acid solution is diluted from 0.1 to 0.01 M?

$$HOCl(aq.) + H_2O(l) \rightleftharpoons OCl^-(aq.) + H_3O^+(aq.)$$

(a) a decrease in the fraction of acid ionized
(b) an increase in the fraction of acid ionized
(c) no change in the fraction of acid ionized
(d) we can not predict

31. Given K_a values of 5.76×10^{-10} and 4.8×10^{-10} for NH_4^+ and HCN respectively. What is the equilibrium constant for the following reaction?

$$NH_4^+(aq.) + CN^-(aq.) \rightleftharpoons NH_3(aq.) + HCN(aq.)$$

(a) 0.83 (b) 1.2 (c) 8.0×10^{-11} (d) 27.6×10^{-10}

32. Which is the strongest acid (pK_a value is given)?
(a) HCOOH [3.77] (b) C_6H_5COOH [4.22]
(c) CH_3COOH [4.7] (d) CH_3CH_2COOH [4.88]

33. Given : Enthalpy of ionization of two acids :
$\Delta H^\circ(HCN) = 45.2$ kJ mol^{-1}
$\Delta H^\circ(CH_3COOH) = 2.1$ kJ mol^{-1}

which relationship for the two acids is true
(a) $pK_a(HCN) = pK_a(CH_3COOH)$ (b) $pK_a(HCN) > pK_a(CH_3COOH)$
(c) $pK_a(HCN) < pK_a(CH_3COOH)$ (d) $pK_a(HCN) = \frac{45.2}{2.1} pK_a(CH_3COOH)$

34. What is the hydronium ion concentration of a 0.25 M HA solution? ($K_a = 4 \times 10^{-8}$)
(a) 10^{-4} (b) 10^{-5} (c) 10^{-7} (d) 10^{-10}

35. What is the percent ionization (α) of a 0.01 M HA solution? ($K_a = 10^{-4}$)
(a) 9.5% (b) 1% (c) 10.5% (d) 17%

36. Given the two concentration of HCN ($K_a = 10^{-9}$) are 0.1 M and 0.001 M respectively. What will be the ratio of degree of dissociation?
(a) 1 (b) 0.1 (c) 0.003 (d) 0.01

37. A 0.10 *M* solution of HF is 8.0% ionized. What is the K_a?
(a) 6.4×10^{-4} (b) 8.8×10^{-4} (c) 6.95×10^{-4} (d) 7.6×10^{-4}

38. A weak base *M*OH of 0.1 *N* concentration shows a pH value of 9. What is the percentage degree of ionization of the acid?
(a) 0.01% (b) 0.001% (c) 0.1% (d) 0.02%

39. 0.01 *M* H*A* (*aq.*) is 2% ionized; $[OH^-]$ of solution is :
(a) 2×10^{-4} (b) 10^{-8} (c) 5×10^{-11} (d) 5×10^{-12}

40. If degree of ionization is 0.01 of decimolar solution of weak acid H*A* then pK_a of acid is :
(a) 2 (b) 3 (c) 5 (d) 7

41. What concentration of $HCOO^-$ is present in a solution of 0.01 *M* HCOOH ($K_a = 1.8\times10^{-4}$) and 0.01 *M* HCl?
(a) 1.8×10^{-3} (b) 10^{-2} (c) 1.8×10^{-4} (d) 10^{-4}

42. Chose the correct code

	Column-I		**Column-II**
(P)	pK_b of X^- (K_a of $HX = 10^{-6}$)	**(1)**	6.9
(Q)	pK_b of $10^{-8} M$ HCl	**(2)**	8
(R)	pH of $10^{-2} M$ acetic solution (Take K_a of acetic acid $= 1.6\times10^{-5}$)	**(3)**	10.7
(S)	pOH of a solution obtained by mixing equal volumes of solution with pH 3 and 5.	**(4)**	3.4

Codes :

	P	Q	R	S
(a)	1	2	4	3
(b)	4	3	2	1
(c)	2	1	4	3
(d)	1	2	3	4

43. How much water must be added to 300 mL of 0.2 *M* solution of CH_3COOH ($K_a = 1.8\times10^{-5}$) for the D.O.I. (α) of the acid to double?
(a) 600 mL (b) 900 mL (c) 1200 mL (d) 1500 mL

44. What is $[NH_4^+]$ in a solution that contain 0.02 *M* NH_3 ($K_b = 1.8\times10^{-5}$) and 0.01 *M* KOH?
(a) 9×10^{-6} (b) 1.8×10^{-5} (c) 3.6×10^{-5} (d) None of these

45. A hand book states that the solubility of $RNH_2(g)$ in water at 1 atm and 25°C is 22.41 volumes of $RNH_2(g)$ per volume of water. (pK_b of $RNH_2 = 4$) Find the max. pOH that can be attained by dissolving RNH_2 in water :
(a) 1 (b) 2 (c) 4 (d) 6

46. The $[H^+]$ of a resulting solution that is 0.01 M acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.01 M in benzoic acid ($K_a = 6.3 \times 10^{-5}$) :

(a) 9×10^{-4} (b) 81×10^{-4} (c) 9×10^{-5} (d) 2.8×10^{-3}

47. 6.0 g weak acid HA (mol. wt. = 60 g/mol.) is dissolved in water and formed 10 m^3 solution. If $K_{a(HA)} = 10^{-9}$, then pOH of solution is : [Given : log 4 = 0.6]

(a) 6.7 (b) greater than 6.7 and less than 7.0

(c) greater than 7.0 and less than 7.3 (d) greater than 7.3

48. Carbonic acid (H_2CO_3), a diprotic acid has $K_{a_1} = 4.0 \times 10^{-7}$ and $K_{a_2} = 7.0 \times 10^{-11}$. What is the $[HCO_3^-]$ of a 0.025 M solution of carbonic acid?

(a) 7.8×10^{-3} (b) 6.6×10^{-4} (c) 10^{-10} (d) 1.0×10^{-4}

49. Carbonic acid (H_2CO_3), a diprotic acid has $K_{a_1} = 4.0 \times 10^{-7}$ and $K_{a_2} = 7.0 \times 10^{-11}$. What is the $[CO_3^{2-}]$ of a 0.025 M solution of carbonic acid?

(a) 5.5×10^{-9} (b) 5.5×10^{-8} (c) 7.0×10^{-9} (d) 7.0×10^{-11}

50. Selenious acid (H_2SeO_3), a diprotic acid has $K_{a_1} = 3.0 \times 10^{-3}$ and $K_{a_2} = 5.0 \times 10^{-8}$. What is the $[OH^-]$ of a 0.30 M solution of a selenious acid?

(a) 2.85×10^{-3} (b) 5.0×10^{-6} (c) 3.5×10^{-12} (d) 3.5×10^{-13}

51. Which of the hydrated species can exist?

I : $H_5O_2^+$ II : H_3O^+ III : $H_3O_2^-$ IV : $H_7O_3^+$

Select alternate from :

(a) II only (b) I and II (c) I, II and IV (d) I, II, III and IV

52. Consider the following salts. Which one(s) when dissolved in water will produce an acidic solution?

1. NH_4Cl 2. $KHSO_4$ 3. NaCN 4. KNO_3

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

53. Consider the following salts. Which one(s) when dissolved in water will produce a basic solution?

1. $RbClO_4$ 2. $NaNO_2$ 3. NH_4Cl 4. NaCl

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

54. At 25°C dissociation constants of acid HA and base BOH in aqueous solution are same. The pH of 0.01 M solution of HA is 5. The pOH of 10^{-4} M solution of BOH at the same temperature is:

(a) 3.5 (b) 4 (c) 6 (d) None of these

55. Which of the following solutions has the highest pH?

(a) 0.2 M $HClO_4$ (b) 0.20 M CH_3COOH

(c) 0.020 M HCl (d) 0.2 M NaCl

56. From separate solutions of four sodium salts NaW, NaX, NaY and NaZ had pH 7.0, 9.0, 10.0 and 11.0 respectively, when each solution was 0.1 M, the weakest acid is :

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

57. The pH values 0.1 M solution of HCOONa (I), HCOOH (II), CH_3COONH_4 (III), NaOH (IV), HCl (V), will be in the order :

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

58. pH of an aqueous NaCl solution at 50°C should be :
(a) 7 (b) > 7 (c) < 7 (d) 0

59. Upon hydrolysis of sodium carbonate, the reaction takes place between:
(a) Na^+ and water (b) Na^+ and OH^- (c) CO_3^{2-} and water (d) CO_3^{2-} and H^+

60. The solution of blue vitrol in water is acidic because:
(a) $CuSO_4$ reacts with water (b) Cu^{2+} reacts with water
(c) SO_4^{2-} reacts with water (d) $CuSO_4$ removes OH^- ions from water

61. 1 mL of 0.1 *N* HCl is added to 999 mL solution of NaCl. The pH of the resulting solution will be :
(a) 7 (b) 4 (c) 2 (d) 1

62. If a salt of strong acid and weak base hydrolyses appreciably ($\alpha = 0.1$), which of the following formula is to be used to calculate degree of hydrolysis 'α'?
(a) $\alpha = \sqrt{\frac{K_w}{K_a \cdot a}}$ (b) $\alpha = \sqrt{\frac{K_w}{K_b \cdot a}}$ (c) $\alpha = \sqrt{\frac{K_w}{K_a \cdot K_b}}$ (d) None of these

63. The correct formula to calculate the hydroxyl ion concentration of an aqueous solution of NH_4NO_3 is :
(a) $\sqrt{\frac{C \times K_w}{K_b}}$ (b) $\sqrt{\frac{K_w \times K_b}{C}}$ (c) $\sqrt{\frac{C \times K_w}{K_a}}$ (d) $\sqrt{\frac{K_a \times K_w}{C}}$

64. $[H^+] = \sqrt{\frac{K_w K_a}{C}}$ is suitable for
(a) NaCl, NH_4Cl (b) CH_3COONa, NaCN
(c) CH_3COONa, $(NH_4)_2SO_4$ (d) CH_3COONH_4, $(NH_4)_2CO_3$

65. What is the hydrolysis constant of the OCl^- ion? The ionization constant of HOCl is 3.0×10^{-8}.
(a) 3.33×10^{-8} (b) 3.33×10^{-7} (c) 3.0×10^{-7} (d) 3.33×10^{-6}

66. What is the pH of a 0.10 *M* $C_6H_5O^-$ solution? The K_a of C_6H_5OH is 1.0×10^{-10}.
(a) 10.51 (b) 11.04 (c) 11.50 (d) 12

67. Calculate the $[OH^-]$ in 0.01 *M* aqueous solution of NaOCN (K_b for $OCN^- = 10^{-10}$) :
(a) 10^{-6} *M* (b) 10^{-7} *M* (c) 10^{-8} *M* (d) None of these

68. What is the ionization constant of an acid if the hydronium ion concentration of a 0.40 *M* solution is 1.40×10^{-4} *M*?
(a) 1.96×10^{-8} (b) 1.22×10^{-9} (c) 4.90×10^{-8} (d) 1.40×10^{-6}

69. The degree of hydrolysis of 0.1 RNH_3Cl solution is 1.0%. If the concentration of RNH_3Cl is made 0.4 *M*, what is the new degree of hydrolysis (in percentage)?
(a) 0.01 (b) 0.001 (c) 0.2 (d) 0.5

70. % hydrolysis of 0.1*M* CH_3COONH_4, when $K_a(CH_3COOH) = K_b(NH_4OH) = 1.8 \times 10^{-5}$ is:
(a) 0.55 (b) 7.63 (c) 0.55×10^{-2} (d) 7.63×10^{-3}

71. The enthalpy of neutralisation of four acids HA, HB, HC and HD with NaOH are –13, –12, –11, –10 kcal/mol. Which salt has maximum degree of hydrolysis?
(a) 1*M* Na*A* (b) 1*M* Na*B* (c) 1*M* Na*C* (d) 1*M* Na*D*

72. Calculate $[H^+]$ at equivalent point between titration of 0.1 *M*, 25 mL of weak acid HA ($K_{a(HA)} = 10^{-5}$) with 0.05 *M* NaOH solution :
(a) 3×10^{-9} (b) 1.732×10^{-9} (c) 8 (d) 10

73. When a salt of weak acid and weak base is dissolved in water at 25°C, the pH of the resulting solution will always :
(a) be 7 (b) be greater than 7
(c) be less than 7 (d) depend upon K_a and K_b values

74. What will be the pH of an aqueous solution of 1.0 *M* ammonium formate?
Given : $pK_a = 3.8$ and $pK_b = 4.8$
(a) 7.5 (b) 3.4 (c) 6.5 (d) 10.2

75. What will be the pH and % α (degree of hydrolysis) respectively for the salt *BA* of 0.1 *M* concentration? Given : K_a for $HA = 10^{-6}$ and K_b for $BOH = 10^{-6}$
(a) 5, 1% (b) 7, 10% (c) 9, 0.01% (d) 7, 0.01%

76. The percentage degree of hydrolysis of a salt of weak acid (HA) and weak base (BOH) in its 0.1 *M* solution is found to be 10%. If the molarity of the solution is 0.05 *M*, the percentage hydrolysis of the salt should be :
(a) 5% (b) 10% (c) 20% (d) None of these

77. What is the hydronium ion concentration of a 0.02 *M* solution of Cu^{2+} solution of copper(II) perchlorate? The acidity constant of the following reaction is 5×10^{-9}.

$$Cu^{2+}(aq.) + 2H_2O(l) \rightleftharpoons Cu(OH)^+(aq.) + H_3O^+(aq.)$$

(a) 1×10^{-5} (b) 7×10^{-4} (c) 5×10^{-4} (d) 1×10^{-4}

78. What is the acidity constant for the following reaction given that the hydronium ion concentration of a 0.04 *M* solution of Ni^{2+} solution of nickel(II) perchlorate is 4.5×10^{-6}?

$$Ni^{2+}(aq.) + 2H_2O(l) \rightleftharpoons Ni(OH)^+(aq.) + H_3O^+(aq.)$$

(a) 2×10^{-12} (b) 4×10^{-6} (c) 5×10^{-12} (d) 5×10^{-10}

79. Calculate the pH at 25°C of a solution that is 0.10 *M* in $Fe(NO_3)_3$. The acid dissociation constant for the reaction given below is 1.0×10^{-3}.

$$[Fe(H_2O)_6]^{3+} + H_2O(l) \rightleftharpoons H_3O^+(aq.) + [Fe(H_2O)_5(OH)]^{2+}$$

(a) 2.00 (b) 2.02 (c) 2.30 (d) 2.50

80. Approximate pH of 0.01 *M* NaHA is calculated by :
($K_{a_1} = 10^{-6}$ and $K_{a_2} = 10^{-8}$ are ionization constants of H_2A)
(a) $pH = 7 + \frac{pK_{a_1}}{2} + \frac{\log C}{2}$ (b) $pH = 7 - \frac{pK_{a_1}}{2} - \frac{\log C}{2}$
(c) $pH = \frac{pK_{a_1} + pK_{a_2}}{2}$ (d) None of these

81. H_3PO_4 is a weak triprotic acid; approximate pH of 0.1 M $Na_2HPO_4(aq.)$ is calculated by :

(a) $\frac{1}{2}[pK_{a_1} + pK_{a_2}]$ (b) $\frac{1}{2}[pK_{a_2} + pK_{a_3}]$ (c) $\frac{1}{2}[pK_{a_1} + pK_{a_3}]$ (d) $pK_{a_1} + pK_{a_2}$

82. Which of the following is a buffer solution?

(a) 500 mL of 0.1 N CH_3COOH + 500 mL of 0.1 N NaOH

(b) 500 mL of 0.1 N CH_3COOH + 500 mL of 0.1 N HCl

(c) 500 mL of 0.1 N CH_3COOH + 500 mL of 0.2 N NaOH

(d) 500 mL of 0.2 N CH_3COOH + 500 mL of 0.1 N NaOH

83. If 20 mL of 0.1 M NaOH is added to 30 mL of 0.2 M CH_3COOH ($pK_a = 4.74$), the pOH of the resulting solution is :

(a) 4.44 (b) 9.56 (c) 8.96 (d) 9.26

84. $H_2CO_3 + NaHCO_3$ found in blood helps in maintaining pH of the blood close to 7.4. An excess of acid entering the blood stream is removed by:

(a) HCO_3^- (b) H_2CO_3 (c) H^+ ion (d) CO_3^{2-} ion

85. 100 mL of 0.02M benzoic acid ($pK_a = 4.20$) is titrated using 0.02M 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

86. What is the pH of a solution of 0.28 M acid and 0.84 M of its conjugate base if the ionization constant of acid is 4×10^{-4}?

(a) 3.88 (b) 3.34 (c) 7 (d) 10.12

87. The toxic compound 2,4-dinitrophenol has $K_a = 10^{-4}$ M. In an experiment, a buffer solution of 2,4-dinitrophenol was prepared with the pH adjusted to 5. Calculate the ratio of the concentrations of the dissociated ion to the undissociated acid :

(a) 0.01 (b) 0.1 (c) 10 (d) 100

88. Equilibrium constant for the following reaction is 1×10^{-9} :

$$C_5H_5N(aq.) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq.) + OH^-(aq.)$$

Determine the mole of pyridinium chloride ($C_5H_5N.HCl$) that should be added to 500 mL solution of 0.4 M pyridine (C_5H_5N) to obtain a buffer solution of pH = 5 :

(a) 0.1 mole (b) 0.2 mole (c) 0.3 mole (d) 0.4 mole

89. Which one of the following mixture does not act as a buffer solution?

(a) Boric acid and borax

(b) Sodium phosphate & disodium hydrogen phosphate

(c) Sodium propionate and propionic acid

(d) Sod. acetate and sodium propionate

90. The acid dissociation constant of uric acid is $K_a = 4.0 \times 10^{-6}$ M. The pH of a sample is 6.0. What is the ratio of urate ion to uric acid in the urine?

(a) 2.0 (b) 4.0 (c) 6.0 (d) 0.25

91. CH_3NH_2 (1.2 mole, $pK_b = 3.3$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting pH of solution is :

(a) 10.7 (b) 3.6 (c) 10.4 (d) 11.3

92. An aqueous solution at room temperature is 0.1 M with respect to ammonium chloride and 0.01 M with respect to NH_4OH ($pK_b = 5$), the pH of the solution is :
(a) 7.5 (b) 6.8 (c) 6.5 (d) 8.0

93. Which of the following will decrease with dilution at a given temperature?
(a) pH of 10^{-3} M acetic acid solution
(b) pH of 10^{-3} M aniline solution
(c) degree of dissociation of 10^{-3} M acetic acid
(d) degree of dissociation of 10^{-3} M aniline solution

94. A 1 L solution contains 0.2 M NH_4OH and 0.2 M NH_4Cl. If 1.0 mL of 0.001 M HCl is added to it. What will be the $[OH^-]$ of the resulting solution ($K_b = 2\times 10^{-5}$)
(a) 2×10^{-5} (b) 5×10^{-10} (c) 2×10^{-3} (d) None of these

95. 0.1 M formic acid solution is titrated against 0.1 M NaOH solution. What would be the difference in pH between 1/5 and 4/5 stages of neutralization of acid ?
(a) 2 log 3/4 (b) 2 log 1/5 (c) log 1/3 (d) 2 log 4

96. In the neutralization process of H_3PO_4 and NaOH, the number of buffers formed will be:
(a) 3 (b) 1 (c) 2 (d) 4

97. A buffer solution is made up of acetic acid [$pK_a = 5$] having conc. = 1.5 M and sodium acetate having conc. = 0.15 M. What is the number of OH^- ions present in 1 litre solution?
(a) $10^{-10}\ N_A$ (b) $10^{-4}\ N_A$ (c) $10^{-3}\ N_A$ (d) $10^{-6}\ N_A$

98. 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) KNO_3 (d) K_2CO_3

99. H^+ ion concentration of water does not change by adding :
(a) CH_3COONa (b) $NaNO_3$ (c) NaCN (d) Na_2CO_3

100. pK_a of NH_4^+ is 9.26. Hence, effective range for $NH_4OH - NH_4Cl$ buffer is about pH :
(a) 8.26 to 10.26 (b) 4.74 to 5.74 (c) 3.74 to 5.74 (d) 8.26 to 9.26

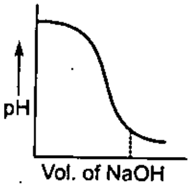
101. 1.0 L solution is prepared by mixing 61 gm benzoic acid ($pK_a = 4.2$) with 72 gm of sodium benzoate and then 300 mL 1.0 M HBr solution was added. The pH of final solution is:
(a) 3.6 (b) 3.8 (c) 4.2 (d) 4.8

102. The pH of a solution containing 0.4 M HCO_3^- and 0.2 M CO_3^{2-} is :
$[K_{a_1}\ (H_2CO_3) = 4\times10^{-7};\ K_{a_2}\ (HCO_3^-) = 4\times10^{-11}]$
(a) 10.4 (b) 10.1 (c) 6.1 (d) 10.7

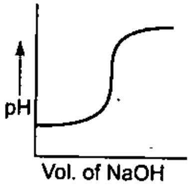
103. The pH of the resultant solution of 20 mL of 0.1 M H_3PO_4 and 20 mL of 0.1 M Na_3PO_4 is :
(a) $pK_{a_1} + \log 2$ (b) pK_{a_1} (c) pK_{a_2} (d) $\dfrac{pK_{a_1} + pK_{a_2}}{2}$

104. Which one of the following curves represents the graph of pH during the titration of NaOH and HCl(*aq.*)?

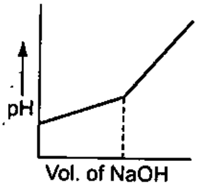
(a)



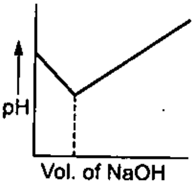
(b)



(c)

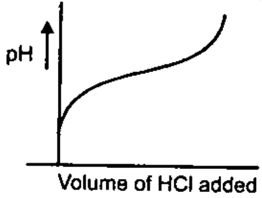


(d)

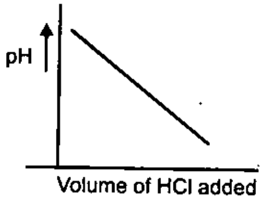


105. When 100 mL of 0.1 M NaCN solution is titrated with 0.1 M HCl solution the variation of pH of solution with volume of HCl added will be :

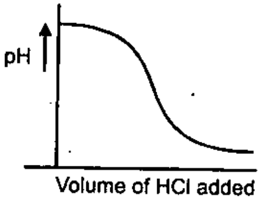
(a)



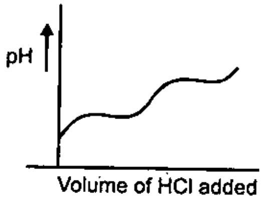
(b)



(c)



(d)



106. The best indicator for the detection of end point in titration of a weak acid and a strong base is :

(a) Methyl orange (3.1 to 4.4)
(b) Methyl red (4.2 to 6.3)
(c) Bromothymol blue (6 to 7.6)
(d) Phenolphthalein (8.2 to 10)

107. Select the best indicator from the given table for titration of 20 mL of 0.02 M CH_3COOH with 0.02 M NaOH. Given pK_a (CH_3COOH) = 4.74

	Indicator	**pH range**
(I)	Bromothymol blue	6.0–7.6
(II)	Thymolphthalein	9.3–10.5
(III)	Malachite green	11.4–13
(IV)	M-Cresol purple	7.4–9.0

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

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

(a) 40
(b) 85.7
(c) 14.3
(d) 60

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

(a) $8 \times 10^{-5}\ M$ (b) $9 \times 10^{-5}\ M$ (c) $1 \times 10^{-5}\ M$ (d) $3 \times 10^{-4}\ M$

110. An acid-base indicator which is a weak acid has a pK_a value = 5.45. At what concentration ratio of sodium acetate to acetic acid would the indicator show a colour half-way between those of its acid and conjugate base forms ? [pK_a of acetic acid = 4.75]

(a) 4 : 1 (b) 6 : 1 (c) 5 : 1 (d) 3 : 1

111. A 20.0 mL sample of a 0.20 M solution of the weak diprotic acid H_2A is titrated with 0.250 M NaOH. The solution of the second equivalent point is :

(a) 0.10 M NaHA (b) 0.153 M Na_2A (c) 0.10 M Na_2A (d) 0.0769 M Na_2A

112. During the titration of a weak diprotic acid (H_2A) against a strong base (NaOH), the pH of the solution half-way to the first equivalent point and that at the first equivalent point are given respectively by :

(a) pK_{a_1} and $pK_{a_1} + pK_{a_2}$ (b) $\sqrt{K_{a_1}C}$ and $\frac{pK_{a_1} + pK_{a_2}}{2}$

(c) pK_{a_1} and $\frac{pK_{a_1} + pK_{a_2}}{2}$ (d) pK_{a_1} and pK_{a_2}

113. In which of the following cases is the solution of AgCl unsaturated?

(a) $[Ag^+][Cl^-] < K_{sp}$ (b) $[Ag^+][Cl^-] > K_{sp}$ (c) $[Ag^+][Cl^-] = K_{sp}$ (d) $[Ag^+][Cl^-] \le K_{sp}$

114. When equal volumes of the following solutions are mixed, the precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur with :

(a) $10^{-4}\ M\ (Ag^+)$ and $10^{-4}\ M\ (Cl^-)$ (b) $10^{-5}\ M\ (Ag^+)$ and $10^{-5}\ M\ (Cl^-)$

(c) $10^{-5}\ M\ (Ag^+)$ and $10^{-6}\ M\ (Cl^-)$ (d) $10^{-10}\ M\ (Ag^+)$ and $10^{-10}\ M\ (Cl^-)$

115. Choose the correct set of True/False for following statements:

(i) Silver chloride is more soluble in very concentrated sodium chloride solution than in pure water.

(ii) The pH of a buffer solution does not change on addition of small amount of an acid or a base.

(iii) Addition of NH_4Cl does not affect the pH of a solution of NH_4OH

(iv) Degree of hydrolysis of ammonium acetate does not depend upon the concentration of ammonium acetate solution.

(v) A mixture of acetic acid and sodium acetate can act as buffer solution.

(a) TTFTT (b) FTTTF (c) TFTF (d) FFTTT

116. A 1 litre solution containing NH_4Cl and NH_4OH has hydroxide ion concentration of 10^{-6} mol/litre. Which of the following hydroxides could be precipitated when the solution is added to 1 litre solution of 0.1 M metal ions?

(I) $Ba(OH)_2$ ($K_{sp} = 5 \times 10^{-3}$) (II) $Ni(OH)_2$ ($K_{sp} = 1.6 \times 10^{-16}$)

(III) $Mn(OH)_2$ ($K_{sp} = 2 \times 10^{-13}$) (IV) $Fe(OH)_2$ ($K_{sp} = 8 \times 10^{-16}$)

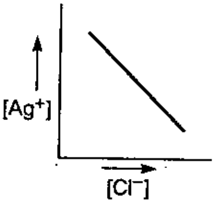
(a) I, II, IV (b) IV (c) II and IV (d) II, III, IV

117. 150 mL of 0.0008 M ammonium sulphate is mixed with 50 mL of 0.04 M calcium nitrate. The ionic product of $CaSO_4$ will be : ($K_{sp} = 2.4 \times 10^{-5}$ for $CaSO_4$)

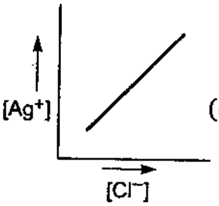
(a) $< K_{sp}$ (b) $> K_{sp}$ (c) $\approx K_{sp}$ (d) None of these

118. In a saturated solution of AgCl, NaCl is added gradually. The concentration of Ag^+ is plotted against the concentration of Cl^-. The graph appears as :

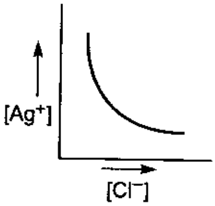
(a)



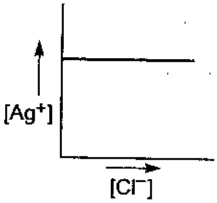
(b)



(c)



(d)



119. K_{sp} of AgCl is 1×10^{-10}. Its solubility in $0.1 M$ KNO_3 will be :

(a) 10^{-5} moles/litre (b) $> 10^{-5}$ moles/litre (c) $< 10^{-5}$ moles/litre (d) None of these

120. 50 mL of a solution containing 10^{-3} mole of Ag^+ is mixed with 50 mL of a 0.1 M HCl solution. How much Ag^+ remains in solution? (K_{sp} of AgCl $= 1.0 \times 10^{-10}$)

(a) 2.5×10^{-9} (b) 2.5×10^{-7} (c) 2.5×10^{-8} (d) 2.5×10^{-10}

121. The solubility of a sparingly soluble salt A_xB_y in water is 'S' moles per litre. The solubility product has the value :

(a) S^2 (b) $x^y y^x \cdot S^{x+y}$ (c) $x^x y^y S^{x+y}$ (d) S^{x+y}

122. What is the molarity of a saturated solution of $CaCO_3$? ($K_{sp} = 2.8 \times 10^{-9}$)

(a) 2.6×10^{-5} (b) 2.8×10^{-9} (c) 5.2×10^{-5} (d) 5.6×10^{-9}

123. K_{sp} of $Zr_3(PO_4)_4$ in terms of solubility (S) is :

(a) $108\,S^7$ (b) $4\,S^3$ (c) $6912\,S^7$ (d) None of these

124. The solubility of electrolytes MX_1, MX_2 and MX_3 is 1×10^{-3} moles per litre. Hence their respective solubility products are :

(a) 10^{-6}, 4×10^{-9}, 27×10^{-12} (b) 10^{-9}, 4×10^{-9}, 32×10^{-12}

(c) 10^{-9}, 8×10^{-8}, 32×10^{-12} (d) None of these

125. A saturated solution of $Ca_3(PO_4)_2$ has $[Ca^{2+}] = 2 \times 10^{-8} M$ and $[PO_4^{3-}] = 1.6 \times 10^{-5}$ M K_{sp} of $Ca_3(PO_4)_2$ is :

(a) 3.2×10^{-13} (b) 3.2×10^{-34} (c) 2.048×10^{-33} (d) None of these

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

(a) $Ba_3(PO_4)_2$ ($K_{sp} = 6 \times 10^{-39}$) (b) ZnS ($K_{sp} = 7 \times 10^{-16}$)

(c) $Fe(OH)_3$ ($K_{sp} = 6 \times 10^{-38}$) (d) $Ag_3(PO_4)$ ($K_{sp} = 1.8 \times 10^{-18}$)

127. Silver ions are added to a solution with $[Br^-] = [Cl^-] = [CO_3^{2-}] = [AsO_4^{3-}] = 0.1M$. Which compound will precipitate with lowest $[Ag^+]$?

(a) AgBr ($K_{sp} = 5 \times 10^{-13}$) (b) AgCl ($K_{sp} = 1.8 \times 10^{-10}$)

(c) Ag_2CO_3 ($K_{sp} = 8.1 \times 10^{-12}$) (d) Ag_3AsO_4 ($K_{sp} = 1 \times 10^{-22}$)

128. The solubility of different sparingly soluble salts are given as under :

S. No.	Formula Type	Solubility product
1.	AB	4.0×10^{-20}
2.	A_2B	3.2×10^{-11}
3.	AB_3	2.7×10^{-31}

The correct increasing order of solubility is :
(a) 1, 3, 2 (b) 2, 1, 3 (c) 1, 2, 3 (d) 3, 1, 2

129. If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of this substance in mole per m^3 is :
(a) 8×10^{-3} (b) 6.4×10^{-5} (c) 8×10^{-6} (d) None of these

130. The solubility of $Ba_3(AsO_4)_2$ (formula weight = 690) is 6.9×10^{-2} g/100 mL. What is the K_{sp} ?
(a) 1.08×10^{-11} (b) 1.08×10^{-13} (c) 1.0×10^{-15} (d) 6.0×10^{-13}

131. The solubility of $AgBrO_3$ (formula weight = 236) is 0.0072 g in 1000 mL. What is the K_{sp} ?
(a) 2.2×10^{-8} (b) 3.0×10^{-10} (c) 3.0×10^{-5} (d) 9.3×10^{-10}

132. The solubility of PbF_2 (formula weight = 245) is 0.46 g/L. What is the solubility product?
(a) 1.1×10^{-10} (b) 2.6×10^{-8} (c) 1.1×10^{-7} (d) 6.8×10^{-9}

133. How many grams of MgC_2O_4 (formula weight = 112) will dissolve in 1.5 L of water? ($K_{sp} = 8.1 \times 10^{-5}$)
(a) 1.0 (b) 1.29 (c) 1.512 (d) 4.65

134. What is the molarity of F^- ions in a saturated solution of BaF_2? ($K_{sp} = 1.0 \times 10^{-6}$)
(a) 1.0×10^{-2} (b) 1.0×10^{-3} (c) 1.26×10^{-2} (d) 6.3×10^{-3}

135. What is the molarity of F^- in a saturated solution of InF_3? ($K_{sp} = 7.9 \times 10^{-10}$)
(a) 2.3×10^{-3}. (b) 8.3×10^{-3} (c) 1.0×10^{-3} (d) 7.0×10^{-3}

136. What is the pH of a saturated solution of $Cu(OH)_2$? ($K_{sp} = 2.6 \times 10^{-19}$)
(a) 6.1 (b) 7.30 (c) 8.42 (d) 7.90

137. The solubility product of AgCl is $10^{-10}\ M^2$. The minimum volume (in m^3) of water required to dissolve 14.35 mg of AgCl is approximately :
(a) 0.01 (b) 0.1 (c) 100 (d) 10

138. What is the molar solubility of $Fe(OH)_2$ ($K_{sp} = 8.0 \times 10^{-16}$) at pH 13.0?
(a) 8.0×10^{-18} (b) 8.0×10^{-15} (c) 8.0×10^{-17} (d) 8.0×10^{-14}

139. What is the minimum pH necessary to cause a precipitate of $Pb(OH)_2$ ($K_{sp} = 1.2 \times 10^{-5}$) to form in a 0.12 M $PbCl_2$ solution?
(a) 12.4 (b) 10.8 (c) 12.0 (d) 11.1

140. Which of the following would increase the solubility of $Pb(OH)_2$:
(a) Add hydrochloric acid
(b) Add a solution of $Pb(NO_3)_2$
(c) Add a solution of NaOH
(d) None of the above–the solubility of a compound is constant at constant temperature

141. What is the molar solubility of Ag_2CO_3 ($K_{sp} = 4 \times 10^{-13}$) in 0.1 M Na_2CO_3 solution?
(a) 10^{-6} (b) 10^{-7} (c) 2×10^{-6} (d) 2×10^{-7}

142. What is the concentration of Pb^{2+} when $PbSO_4$ ($K_{sp} = 1.8 \times 10^{-8}$) begins to precipitate from a solution that is 0.0045 M in SO_4^{2-}?
(a) $4.0 \times 10^{-8}\ M$ (b) $1.0 \times 10^{-6}\ M$ (c) $2.0 \times 10^{-8}\ M$ (d) $4.0 \times 10^{-6}\ M$

143. What is the concentration of Ba^{2+} when BaF_2 ($K_{sp} = 1.0 \times 10^{-6}$) begins to precipitate from a solution that is 0.30 M F^-?
(a) 9.0×10^{-7} (b) 3.3×10^{-5} (c) 1.1×10^{-5} (d) 3.0×10^{-7}

144. Solubility of AgCl in 0.2 M NaCl is x and that in 0.1 M $AgNO_3$ is y then which of the following is correct?
(a) $x = y$ (b) $x > y$ (c) $x < y$ (d) We cannot predict

145. What is the molarity of $Fe(CN)_6^{4-}$ in a saturated solution of $Ag_4[Fe(CN)_6]$? ($K_{sp} = 1.6 \times 10^{-41}$)
(a) 1.6×10^{-8} (b) 5.2×10^{-8} (c) 2.0×10^{-8} (d) 2.3×10^{-9}

146. At 25°C, K_{sp} for $PbBr_2$ is equal to 8×10^{-5}. If the salt is 80% dissociated, what is the solubility of $PbBr_2$ in mol/litre?
(a) $\left[\frac{10^{-4}}{1.6 \times 1.6}\right]^{1/3}$ (b) $\left[\frac{10^{-5}}{1.6 \times 1.6}\right]^{1/3}$ (c) $\left[\frac{10^{-4}}{0.8 \times 0.8}\right]^{1/3}$ (d) $\left[\frac{10^{-5}}{1.6 \times 1.6}\right]^{1/2}$

147. What is the molar solubility of $Mn(OH)_2$($K_{sp} = 4.5 \times 10^{-14}$) in a buffer solution containing equal amounts of NH_4^+ and NH_3 ($K_b = 1.8 \times 10^{-5}$)?
(a) 3.0×10^{-4} (b) 1.38×10^{-4} (c) 1.38×10^{-3} (d) 7.3×10^{-4}

148. Find moles of NH_4Cl required to prevent $Mg(OH)_2$ from precipitating in a litre of solution which contains 0.02 mole of NH_3 and 0.001 mole of Mg^{2+} ions.

Given : K_b $(NH_3) = 10^{-5}$; K_{sp} $[Mg(OH)_2] = 10^{-11}$.

(a) 10^{-4} (b) 2×10^{-3} (c) 0.02 (d) 0.1

149. What mass of AgI will dissolve in 1.0 L of 1.0 M NH_3? Neglect change in conc. of NH_3.
[Given : K_{sp} (AgI) $= 1.5 \times 10^{-16}$; K_f $[Ag(NH_3)_2^+] = 1.6 \times 10^7$]; (At. wt. Ag = 108; I = 127)
(a) 4.9×10^{-5} g (b) 0.0056 g (c) 0.035 g (d) 0.011 g

150. Consider the following statement and select correct option :
(I) K_{sp} of $Fe(OH)_3$ in aqueous solution is 3.8×10^{-38} at 298 K. The concentration of Fe^{3+} will increase when $[H^+]$ ion concentration decreases.
(II) In a mixture of NH_4Cl and NH_4OH in water, a further amount of NH_4Cl is added. The pH of the mixture will decreases.
(III) An aqueous solution of each of the following salts (NH_4I, HCOOK) will be basic, acidic respectively.
(a) only I is correct (b) only II is correct
(c) only III is correct (d) II and III are correct

Level 2

1. Equilibrium constants of T_2O (T or ${}_1H^3$ is an isotope of ${}_1H^1$) and H_2O are different at 298 K. Let at 298 K pure T_2O has pT (like pH) is 7.62. The pT of a solution prepared by adding 10 mL of 0.2 *M* TCl to 15 mL of 0.25 *M* NaOT is :
(a) 2 – log 7 (b) 14 + log 7 (c) 13.24 – log 7 (d) 13.24 + log 7

2. Liquid NH_3 ionises to a slight extent. At a certain temp. it's self ionization constant $K_{SIC(NH_3)} = 10^{-30}$. The number of NH_4^+ ions are present per 100 cm^3 of pure liquid are :
(a) 10^{-15} (b) 6.022×10^8 (c) 6.022×10^7 (d) 6.022×10^6

3. To what volume of 10 litre of 0.5 *M* CH_3COOH $(K_a = 1.8 \times 10^{-5})$ be diluted in order to double the hydroxide ion concentration :
(a) 20 L (b) 30 L (c) 40 L (d) None of these

4. 20 mL of 0.1 *M* weak acid *HA* $(K_a = 10^{-5})$ is mixed with solution of 10 mL of 0.3 *M* HCl and 10 mL of 0.1 *M* NaOH. Find the value of $[A^-]/([HA] + [A^-])$ in the resulting solution :
(a) 2×10^{-4} (b) 2×10^{-5} (c) 2×10^{-3} (d) 0.05

5. What concentration of FCH_2COOH $(K_a = 2.6 \times 10^{-3})$ is needed so that $[H^+] = 2 \times 10^{-3}$?
(a) 2×10^{-3} *M* (b) 2.6×10^{-3} *M* (c) 5.2×10^{-3} *M* (d) 3.53×10^{-3} *M*

6. Calculate the ratio of $HCOO^-$ and F^- in a mixture of 0.2 *M* HCOOH $(K_a = 2 \times 10^{-4})$ and 0.1 *M* HF $(K_a = 6.6 \times 10^{-4})$:
(a) 1 : 6.6 (b) 1 : 3.3 (c) 2 : 3.3 (d) 3.3 : 2

7. If first dissociation of $X(OH)_3$ is 100% where as second dissociation is 50% and third dissociation is negligible then the pH of 4×10^{-3} *M* $X(OH)_3$ is :
(a) 11.78 (b) 10.78 (c) 2.5 (d) 2.22

8. H_3A is a weak triprotic acid $(K_{a_1} = 10^{-5}, K_{a_2} = 10^{-9}, K_{a_3} = 10^{-13})$
What is the value of pX of 0.1 *M* H_3A (*aq.*) solution? where $pX = -\log X$ and $X = \dfrac{[A^{3-}]}{[HA^{2-}]}$
(a) 7 (b) 8 (c) 9 (d) 10

9. Calcium lactate is a salt of weak organic acid and strong base represented as $Ca(LaC)_2$. A saturated solution of $Ca(LaC)_2$ contains 0.6 mole in 2 litre solution. pOH of solution is 5.60. If 90% dissociation of the salt takes place then what is pK_a of lactic acid?
(a) 2.8 – log (0.54) (b) 2.8 + log (0.54) (c) 2.8 + log (0.27) (d) None of these

10. What is the concentration of $CH_3COOH(aq.)$ in a solution prepared by dissolving 0.01 mole of $NH_4^+CH_3COO^-$ in 1 L H_2O? $[K_{a(CH_3COOH)} = 1.8 \times 10^{-5}; K_{b(NH_4OH)} = 1.8 \times 10^{-5}]$
(a) 5.55×10^{-5} (b) 0.10 (c) 6.4×10^{-4} (d) 5.55×10^{-3}

11. K_a for the reaction; $Fe^{3+}(aq.) + H_2O(l) \rightleftharpoons Fe(OH)^{2+}(aq.) + H_3O^+(aq.)$ is 6.5×10^{-3}. What is the max. pH value which could be used so that at least 80% of the total iron (III) in a dilute solution exists as Fe^{3+}?
(a) 2 (b) 2.41 (c) 2.79 (d) 1.59

12. $Fe(OH)_2$ is diacidic base has $K_{b_1} = 10^{-4}$ and $K_{b_2} = 2.5 \times 10^{-6}$

What is the concentration of $Fe(OH)_2$ in 0.1 *M* $Fe(NO_3)_2$ solution?

(a) 4×10^{-9} (b) 2.5×10^{-6} (c) 10^{-10} (d) 10^{-14}

13. How many gm of solid KOH must be added to 100 mL of a buffer solution? Which is 0.1 *M* each w.r.t. acid *HA* and salt K *A* to make the pH of solution 6.0. [Given : pK_a (HA) = 5]

(a) 0.458 (b) 0.327 (c) 5.19 (d) None of these

14. Fixed volume of 0.1 *M* benzoic acid ($pK_a = 4.2$) solution is added into 0.2 *M* sodium benzoate solution and formed a 300 mL, resultant acidic buffer solution. If pH of this buffer solution is 4.5 then find added volume of benzoic acid :

(a) 100 mL (b) 150 mL (c) 200 mL (d) None of these

15. A 1.025 g sample containing a weak acid *HX* (mol. wt. = 82) is dissolved in 60 mL water and titrated with 0.25 *M* NaOH. When half of the acid was neutralised the pH was found to be 5.0 and at the equivalence point the pH is 9.0. Calculate weight percentage of *HX* in sample :

(a) 50% (b) 75% (c) 80% (d) None of these

16. Which of the following expression for % ionization of a monoacidic base (*B*OH) in aqueous solution at appreciable concentration is not correct?

(a) $100 \times \sqrt{\frac{K_b}{c}}$ (b) $\frac{1}{1 + 10\,(pK_b - pOH)}$

(c) $\frac{K_w [H^+]}{K_b + K_w}$ (d) $\frac{K_b}{K_b + [OH^-]}$

17. A solution of weak acid *HA* was titrated with base NaOH. The equivalent point was reached when 40 mL of 0.1 *M* NaOH has been added. Now 20 mL of 0.1 *M* HCl were added to titrated solution, the pH was found to be 5.0. What will be the pH of the solution obtained by mixing 20 mL of 0.2 *M* NaOH and 20 mL of 0.2 *M* *HA*?

(a) 7 (b) 9 (c) 11 (d) None of these

18. A buffer solution 0.04 *M* in Na_2HPO_4 and 0.02 *M* in Na_3PO_4 is prepared. The electrolytic oxidation of 1.0 milli-mole of the organic compound *R*NHOH is carried out in 100 mL of the buffer. The reaction is

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

The approximate pH of solution after the oxidation is complete is :
[Given : for H_3PO_4, $pK_{a_1} = 2.2$; $pK_{a_2} = 7.20$; $pK_{a_3} = 12$]

(a) 6.90 (b) 7.20 (c) 7.5 (d) None of these

19. When a 20 mL of 0.08 *M* weak base *B*OH is titrated with 0.08 HCl, the pH of the solution at the end point is 5. What will be the pOH if 10 mL of 0.04 *M* NaOH is added to the resulting solution?
[Given : log 2 = 0.30 and log 3 = 0.48]

(a) 5.40 (b) 5.88 (c) 4.92 (d) None of these

20. Calculate approximate pH of the resultant solution formed by titration of 25 mL of 0.04 M Na_2CO_3 with 50 mL of 0.025 M HCl. [Given : $pK_{a_1} = 6.4$ and $pK_{a_2} = 10.3$ for H_2CO_3]

(a) 5.92 (b) 6.88 (c) 6.4 (d) 5.88

21. In the titration of a solution of a weak acid HA and NaOH, the pH is 5.0 after 10 mL of NaOH solution has been added and 5.60 after 20 mL NaOH has been added.
What is the value of pK_a for HA?

(a) 5.15 (b) 5.3 (c) 5.6 (d) None of these

22. 50 mL of 0.05 M Na_2CO_3 is titrated against 0.1 M HCl. On adding 40 mL of HCl, pH of the solution will be [Given : For H_2CO_3, $pK_{a_1} = 6.35$, $pK_{a_2} = 10.33$; $\log 3 = 0.477$, $\log 2 = 0.30$]

(a) 6.35 (b) 6.526 (c) 8.34 (d) 6.173

23. 10 mL of 0.1 M tribasic acid H_3A is titrated with 0.1 M NaOH solution. What is the ratio of $\frac{[H_3A]}{[A^{3-}]}$ at 2nd equivalence point? [Given : $K_{a_1} = 10^{-3}$, $K_{a_2} = 10^{-8}$, $K_{a_3} = 10^{-12}$]

(a) $\simeq 10^{-4}$ (b) $\simeq 10^{+4}$ (c) $\simeq 10^{-7}$ (d) $\simeq 10^{+6}$

24. A_3B_2 is a sparingly soluble salt of molar mass M (g mol^{-1}) and solubility x g litre^{-1}. The ratio of the molar concentration of B^{3-} to the solubility product of the salt is :

(a) $108\frac{x^5}{M^5}$ (b) $\frac{1}{108}\frac{M^4}{x^4}$ (c) $\frac{1}{54}\frac{M^4}{x^4}$ (d) None of these

25. A solution is 0.10 M $Ba(NO_3)_2$ and 0.10 M $Sr(NO_3)_2$. If solid Na_2CrO_4 is added to the solution, what is $[Ba^{2+}]$ when $SrCrO_4$ begins to precipitate?
[K_{sp} $(BaCrO_4) = 1.2 \times 10^{-10}$; K_{sp} $(SrCrO_4) = 3.5 \times 10^{-5}$]

(a) 7.4×10^{-7} (b) 2.0×10^{-7} (c) 6.1×10^{-7} (d) 3.4×10^{-7}

26. A solution is 0.01 M KI and 0.1 M KCl. If solid $AgNO_3$ is added to the solution, what is the $[I^-]$ when AgCl begins to precipitate?
[K_{sp} (AgI) $= 1.5 \times 10^{-16}$; K_{sp} (AgCl) $= 1.8 \times 10^{-10}$]

(a) 3.5×10^{-7} (b) 6.1×10^{-8} (c) 2.2×10^{-7} (d) 8.3×10^{-8}

27. A solution of 0.1 M in Cl^- and 10^{-4} M CrO_4^{-2}. If solid $AgNO_3$ is gradually added to this solution, what will be the concentration of Cl^- when Ag_2CrO_4 begins to precipitate?

$$[K_{sp}\ (AgCl) = 10^{-10}\ M^2;\ K_{sp}\ (Ag_2CrO_4) = 10^{-12}\ M^3]$$

(a) 10^{-6} M (b) 10^{-4} M (c) 10^{-5} M (d) 10^{-9} M

28. If 500 mL of 0.4 M $AgNO_3$ is mixed with 500 mL of 2M NH_3 solution then what is the concentration of $Ag(NH_3)^+$ in solution?
Given : $K_{f_1}[Ag(NH_3)^+] = 10^3$; $K_{f_2}[Ag(NH_3)_2^+] = 10^4$

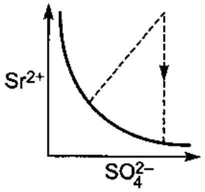
(a) $3.33 \times 10^{-7} M$ (b) $3 \cdot 33 \times 10^{-5} M$ (c) $3 \times 10^{-4} M$ (d) $10^{-7} M$

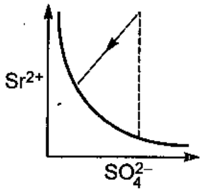
29. The simultaneous solubility of AgCN ($K_{sp} = 2.5 \times 10^{-16}$) and AgCl ($K_{sp} = 1.6 \times 10^{-10}$) in 1.0 M $NH_3(aq.)$ are respectively : [Given : K_f $[Ag(NH_3)_2^+] = 10^7$]

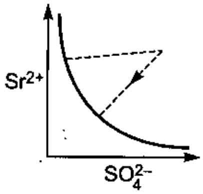
(a) 0.037, 5.78×10^{-8} (b) 5.78×10^{-8}, 0.037

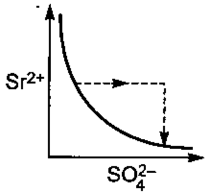
(c) 0.04, 6.25×10^{-8} (d) 1.58×10^{-3}, 1.26×10^{-5}

30. There exist an equilibrium between solid $SrSO_4$ and Sr^{2+} and SO_4^{2-} ion in aqueous medium. The possible equilibrium states are shown in figure as thick line. Now, if equilibrium is disturbed by addition of (a) $Sr(NO_3)_2$ and (b) K_2SO_4 and dotted line represent approach of system towards equilibrium. Match the columns given below :

(iii)


(iv)


(v)


(vi)


(I) addition of $Sr(NO_3)_2$ (II) addition of K_2SO_4

(a) (I) (iii), (II) (iv) (b) (I) (iv), (II) (v)

(c) (I) (vi), (II) (v) (d) (I) (iv), (II) (vi)

31. Solubility of AgCN is maximum in :

(a) acidic buffer solution (b) basic buffer solution

(c) in pure water (d) equal in all solution

32. $AgBr(s) + 2S_2O_3^{2-}(aq.) \rightleftharpoons Ag(S_2O_3)_2^{3-}(aq.) + Br^-(aq.)$

[Using : K_{sp} (AgBr) $= 5 \times 10^{-13}$ K_f $(Ag(S_2O_3)_2^{3-}) = 5 \times 10^{13}$]

What is the molar solubility of AgBr in 0.1 M $Na_2S_2O_3$?

(a) 0.5 M (b) 0.45 M (c) 0.045 M (d) None of these

33. What is $[Ag^+]$ in a solution made by dissolving both Ag_2CrO_4 and $Ag_2C_2O_4$ until saturation is reached with respect to both salts?

$$[K_{sp}\ (Ag_2C_2O_4) = 2 \times 10^{-11},\quad K_{sp}\ (Ag_2CrO_4) = 2 \times 10^{-12}]$$

(a) 2.80×10^{-4} (b) 7.6×10^{-5} (c) 6.63×10^{-6} (d) 3.52×10^{-4}

34. What is the minimum pH required to prevent the precipitation of ZnS in a solution that is 0.01 M $ZnCl_2$ and saturated with 0.10 M H_2S?

[Given : $K_{sp} = 10^{-21}, K_{a_1} \times K_{a_2} = 10^{-20}$]

(a) 0 (b) 1 (c) 2 (d) 4

35. The salt $Al(OH)_3$ is involved in the following two equilibria,

$$Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq.) + 3OH^-(aq.);\ K_{sp}$$

$$Al(OH)_3(s) + OH^-(aq.) \rightleftharpoons Al(OH)_4^-(aq.);\ K_c$$

Which of the following relationship is correct at which solubility is minimum?

(a) $[OH^-] = \left(\dfrac{K_{sp}}{K_c}\right)^{1/3}$ (b) $[OH^-] = \left(\dfrac{K_c}{K_{sp}}\right)^{1/4}$

(c) $[OH^-] = \sqrt{\left(\dfrac{K_{sp}}{K_c}\right)^{1/4}}$ (d) None of these

Level 3

PASSAGE 1

Solution of an acid and it's anion (that is, it's conjugate base) or of a base and it's common cation are buffered. When we add a small amount of acid or base to any one of them, the pH of solution changes very little. pH of buffer solution can be computed as

for acidic buffer : $\text{pH} = \text{p}K_a + \log \dfrac{[\text{Conjugate base}]}{[\text{Acid}]}$

for basic buffer : $\text{pOH} = \text{p}K_b + \log \dfrac{[\text{Conjugate acid}]}{[\text{Base}]}$

It is generally accepted that a solution has useful buffer capacity (pH change resisting power) provided that the value of [salt or conjugate base]/[acid] for acidic buffer lies within the range of 1 : 10 to 10 : 1. Buffer capacity is max. when [conjugate base] = [acid]

1. One litre of an aqueous solution contain 0.15 mole of CH_3COOH ($\text{p}K_a = 4.8$) and 0.15 mole of CH_3COONa. After the addition of 0.05 mole of solid NaOH to this solution, the pH will be :
(a) 4.5 (b) 4.8 (c) 5.1 (d) 5.4

2. Calculate the pH of a solution made by adding 0.01 mole of HCl in 100 mL of a solution which is 0.2 *M* in NH_3 ($\text{p}K_b = 4.74$) and 0.3 *M* in NH_4^+ :

(Assuming no change in volume)
(a) 5.34 (b) 8.66 (c) 7.46 (d) None of these

3. Useful buffer range of weak acid *HA* ($K_a = 10^{-5}$) is :
(a) 5 to 7 (b) 4 to 6 (c) 3 to 5 (d) None of these

4. Select correct statement :
(a) When we add small amount of NaOH in acidic buffer solution, pOH of solution is increases
(b) When we add small amount of NaOH in basic buffer solution, pH of solution is increases
(c) When we add small amount of water in acidic buffer solution, pH of solution is decreases
(d) When 100 mL of 0.2 *M* CH_3COOH react with 200 mL of 0.1 *M* NaOH buffer solution is formed

PASSAGE 2

Hydrolysis is an acid-base reaction of a cation or anion or both ions of a salt with water. Resultant solution of hydrolysis may be acidic, basic or neutral. The anion A^- which is a weaker base than OH^- and which has it's conjugate acid *HA* stronger than water but weaker than H_3O^+ shows the phenomenon of hydrolysis Ex. : CH_3COO^-, CN^-, NO_2^-, etc.

The cation B^+ which is a weaker acid than H_3O^+ and which has it's conjugate base *BOH* stronger than water but weaker than OH^- shows the phenomenon of hydrolysis Ex. : NH_4^+, $C_6H_5NH^+$, $N_2H_5^+$ etc.

The hydrolysis constant of anion and cation are given by

$A^-(aq.) + H_2O(l) \rightleftharpoons HA(aq.) + OH^-(aq.)$

$$K_h = \frac{K_w}{K_a} \Rightarrow \frac{[HA(aq.)][OH^-(aq.)]}{[A^-(aq.)]}$$

$B^+(aq.) + H_2O(l) \rightleftharpoons BOH(aq.) + H^+(aq.)$

$$K_h = \frac{K_w}{K_b} \Rightarrow \frac{[BOH(aq.)][H^+(aq.)]}{[B^+(aq.)]}$$

1. Which of the following statement is true?
(a) Weaker the acid, greater will be hydrolysis of its anion
(b) Weaker the base, greater will be hydrolysis of its cation
(c) Both (a) and (b)
(d) None of these

2. Select the correct statement :
(a) KCl undergoes hydrolysis
(b) $K_h = K_b(A^-)$ and $K_h = K_a(B^+)$
(c) 0.1 M solution of NaCN is acidic
(d) resultant solution of equal volume of 0.1 M NH_3 and 0.1 M HCl is basic

3. When pure ammonium chloride is dissolved in pure water, the pH of the resulting solution is not 7. This is because :
(a) ammonium ions accept protons from water molecules leaving free OH^- ions in solution
(b) ammonium ions donate protons to water molecules forming H_3O^+ ions in solution
(c) ammonium ions combine with water molecule to give the weak base, ammonium hydroxide
(d) chloride ion made the solution acidic

4. Calculate percentage degree of hydrolysis in a 0.1 M solution of CH_3COONa.
(K_a of $CH_3COOH = 10^{-5}$)
(a) 0.1 (b) 0.01 (c) 10^{-4} (d) None of these

PASSAGE 3

Acid-base indicators are either weak organic acids or weak organic bases. Indicator change colour in dilute solution when the hydronium ion concentration reaches a particular value. For example, phenolphthalein is a colourless substance in any aqueous solution with a pH less than 8.3. In between the pH range 8.3 to 10, transition of colour (colourless to pink) takes place and if pH of solution is greater than 10 solution is dark pink. Considering an acid indicator HIn, the equilibrium involving it and it's conjugate base In^- can be represented as :

$$\underset{\text{acidic form}}{HIn} \rightleftharpoons H^+ + \underset{\text{basic form}}{In^-}$$

pH of solution can be computed as :

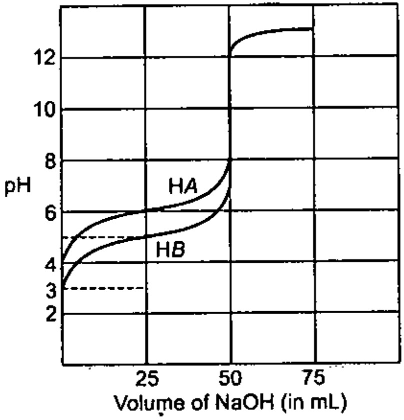
$$pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$$

In general, transition of colour takes place in between the pH range $pK_{In} \pm 1$.

1. An indicator is a weak acid and pH range is 4.0 to 6.0. If indicator in 50% ionized in a given solution then what is the ionization constant of the acid?
(a) 10^{-4} (b) 10^{-5} (c) 10^{-6} (d) None of these

2. Select the correct statement(s) :
(a) At midway in the transition of an acidic indicator, $pH = pK_{In}$
(b) Methyl orange (3.1 to 4.4) is a suitable indicator for titration of weak acid and strong base
(c) Bromothymol blue (6.0 to 7.6) is a good indicator for titration of HCl and NaOH
(d) Thymol blue (1.2 to 2.8) is a very good indicator for titration of 100 mL of 0.1 *M* NH_4OH ($pK_b = 4.74$) and 0.1 *M* HCl

3. Following is the titration curve of two acids *HA* and *HB* (5 milli-moles each) titrated against strong base NaOH (0.1 *M*)



What is pK_a for *HB* acid?
(a) 3 (b) 4 (c) 5 (d) 6

4. What is the equilibrium constant for the reaction

$$HB(aq.) + NaA(aq.) \rightleftharpoons HA(aq.) + NaB(aq.)?$$

(a) 10 (b) 0.1 (c) 10^{-7} (d) 10^{-11}

5. Calculate the pH at equivalent point when *HB* is titrated with NaOH.
(a) 8.75 (b) 8.85 (c) 9.0 (d) None of these

6. Which of the following indicator is most suitable for titration of *HB* with strong base :
(a) Phenolphthalein (8.3 – 10) (b) Bromothymol blue (6 – 7.6)
(c) Methyl red (4.2 – 6.3) (d) Malachite green (11.4 – 13)

PASSAGE 4

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as

$$AgCl(s) \rightleftharpoons Ag^+(aq.) + Cl^-(aq.); \quad K_{sp} = [Ag^+(aq.)][Cl^-(aq.)]$$

Where K_{sp} is called the solubility product constant or simply the solubility product. In general, the solubility product of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

For concentrations of ions that do not necessarily correspond to equilibrium conditions we use the reaction quotient (Q) which is called the ion or ionic product (Q), to predict whether a precipitate will form. Note that Q has the same form as K_{sp}.

The possible relationships between Q and K_{sp} are

$Q < K_{sp}$ Unsaturated solution
$Q = K_{sp}$ Saturated solution
$Q > K_{sp}$ Supersaturated solution; precipitate will form

1. Will a precipitate form if 50 cm^3 of 0.01 M $AgNO_3$ and 50 cm^3 of 2×10^{-5} M NaCl are mixed? [Given : K_{sp} (AgCl) $= 10^{-10}$ M^2]

(a) Yes
(b) No
(c) Ionic product is less than solubility product, hence precipitate will form
(d) Data insufficient

2. Will a precipitate form if 1 volume of 0.1 M Pb^{2+} ion solution is mixed with 3 volume of 0.3 M Cl^- ion solution? [Given : K_{sp} ($PbCl_2$) $= 1.7 \times 10^{-5}$ M^3]

(a) Yes
(b) No
(c) Ionic product is less than solubility product, hence precipitate will form
(d) Data insufficient

3. At 25°C, will a precipitate of $Mg(OH)_2$ form when a 0.0001 M solution of $Mg(NO_3)_2$ is adjusted to a pH of 9.0? At what minimum value of pH will precipitation start? [Given : K_{sp} ($Mg(OH)_2$) $= 10^{-11}$ M^3]

(a) No, pH = 3.5 (b) No, pH = 10.5 (c) No, pH = 6.0 (d) Yes, pH = 8.5

4. Determine the molar solubility of MgF_2 from it's solubility product $K_{sp} = 4 \times 10^{-9}$:

(a) 10^{-3} (b) 6.32×10^{-5} (c) 2×10^{-5} (d) None of these

5. The solubility product of ferric hydroxide in aqueous solution is 6×10^{-38} at 298 K. The solubility of Fe^{3+} ion will increase when the :

(a) pH is increased
(b) pH is 7.0
(c) pH is decreased
(d) saturated solution is exposed to the atmosphere

ONE OR MORE ANSWERS IS/ARE CORRECT

1. Which is/are wrong statement(s)?
(a) Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases
(b) All Lewis bases are Bronsted bases
(c) All Bronsted acids are Lewis acids
(d) Conjugate base of a strong acid is weak

2. Which of the following are conjugate acid-base pairs :
(a) HCO_3^-, CO_3^{2-} (b) $C_6H_5\overset{+}{N}H_3, C_6H_5NH_2$
(c) $H_2C_2O_4, HC_2O_4^-$ (d) OH^-, H^+

3. Which are the set of amphiprotic species?
(a) $H_2O, H_2PO_4^-, HPO_4^{2-}$ (b) HPO_4^{2-}, HCO_3^-
(c) $H_2PO_2^-, H_2PO_3^-, HC_2O_4^-$ (d) $HPO_3^{2-}, H_2O, CO_3^{2-}$

4. Which of the following statements is/are not correct?
(a) A substance which can provide OH^- in aqueous medium is a base
(b) A substance which can accept a pair of electron is a base
(c) A substance which can accept a proton in aqueous medium is a base
(d) A substance which can donate a pair of electron is a base

5. If degree of ionization (α) of a weak electrolyte *AB* is very less then α is :
(a) directly proportional to the square root of volume of solution
(b) inversely proportional to the dilution
(c) inversely proportional to the square root of concentration
(d) directly proportional to concentration

6. Factor influencing the degree of ionization of a weak electrolyte is :
(a) dilution (b) temperature
(c) presence of other ions (d) nature of solvent

7. Which of the following statement(s) is/are correct about the ionic product of water?
(a) K_i (ionization constant of water) $< K_w$ (ionic product of water)
(b) $pK_i > pK_w$
(c) At 25°C, $K_i \doteq 1.8 \times 10^{-14}$
(d) Ionic product of water at 10°C is 10^{-14}

8. Which among the following statement is/are correct?
(a) $pH = -\log_{10}[H_3O^+]$ for dilute solution
(b) pH of H_2O decreases with increase of temperature
(c) pH can not more than 14
(d) If a solution is diluted ten times, its pH always increases by 1

9. If concentration of two weak acids are different and D.O.I. (α) are very less then their relative strength can be compared by :
(a) $\frac{[H^+]_1}{[H^+]_2}$ (b) $\frac{\alpha_1}{\alpha_2}$ (c) $\frac{C_1\alpha_1}{C_2\alpha_2}$ (d) $\frac{K_{a_1}C_1}{K_{a_2}C_2}$

10. If concentration of two weak bases are same and D.O.I. (α) are very less then their relative strength can be compared by :

(a) $\frac{[OH^-]_1}{[OH^-]_2}$ (b) $\frac{K_{b_1}}{K_{b_2}}$ (c) $\frac{\alpha_1}{\alpha_2}$ (d) $\frac{\sqrt{K_{b_1}}}{\sqrt{K_{b_2}}}$

11. Which of the following expressions is/are true?

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

(b) $[OH^-] < \sqrt{K_w}$ for an acidic solution

(c) pH + pOH = 14 at all temperature

(d) $[OH^-] = 10^{-7}$ M at 25°C

12. If K_{a_1}, K_{a_2} and K_{a_3} be the first, second and third ionization constant of H_3PO_4 and $K_{a_1} >> K_{a_2} >> K_{a_3}$ which is/are correct :

(a) $[H^+] \simeq \sqrt{K_{a_1}[H_3PO_4]}$ (b) $[H^+] \simeq [HPO_4^{2-}]$

(c) $K_{a_2} \simeq [HPO_4^{2-}]$ (d) $[HPO_4^{2-}] = [PO_4^{3-}]$

13. Which of the following mixtures constitute a buffer?

(a) HCOOH + HCOONa (b) $Na_2CO_3 + NaHCO_3$

(c) NaCl + HCl (d) $NH_4Cl + (NH_4)_2SO_4$

14. Which of the following mixtures can act as a buffer?

(a) NaOH + HCOONa (1 : 1 molar ratio) (b) HCOOH + NaOH (2 : 1 molar ratio)

(c) NH_4Cl + NaOH (2 : 1 molar ratio) (d) HCOOH + NaOH (1 : 1 molar ratio)

15. Which of the following will function as buffer?

(a) NaCl + NaOH (b) Borax + boric acid

(c) $NaH_2PO_4 + Na_2HPO_4$ (d) $NH_4Cl + NH_4OH$

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

(a) The conjugate acid of NH_2^- is NH_3

(b) Solubility product constant increases with increase in concentration of ions

(c) On diluting a buffer solution pH change is negligible

(d) In alkaline buffer solution, if some HCl is added, it's $[OH^-]$ will increase

17. Degree of hydrolysis (α) for a salt of strong acid and weak base is :

(a) independent of dilution (b) increases with dilution

(c) increases with decrease in K_b (d) increases with increase in temperature

18. The compound whose 0.1 M solution is acidic :

[pK_a of HCOOH = 3.75, pK_b of NH_4OH = 4.74]

(a) Ammonium formate (b) Ammonium sulphate

(c) Ammonium chloride (d) Sodium formate

19. Formic acid is a weak acid and hydrochloric acid is a strong acid. It follows that the :

(a) $[OH^-]$ of 0.01 M HCl (*aq.*) will be less than that of 0.01 M HCOOH (*aq.*)

(b) solution containing 0.1 M NaOH (*aq.*) and 0.1 M HCOONa (*aq.*) is a buffer solution

(c) pH of 10^{-9} M HCl (*aq.*) will be approximately 7 at 25°C

(d) pH of a solution formed by mixing equimolar quantities of HCOOH and HCl will be less than that of a similar solution formed from HCOOH and HCOONa

20. If you have a saturated solution of CaF_2, then :

(a) $[Ca^{2+}] = (K_{sp}/4)^{1/3}$ (b) $2 \times [Ca^{2+}] = [F^-]$

(c) $[Ca^{2+}] = 2[F^-]$ (d) $[Ca^{2+}] = \sqrt{K_{sp}}$

21. Which is/are correct statement(s) about the solubility of AgCl(*s*).?

Given : $K_{sp(AgCl)} = 10^{-10}; K_f[Ag(NH_3)_2^+] = 10^8$.

(a) Solubility of AgCl in pure water is 10^{-5} gm/litre

(b) Solubility of AgCl in $2M$ KBr is 10^{-5} mol/litre

(c) Solubility of AgCl in $2M$ $AgNO_3$ is $5 \times 10^{-11} M$

(d) Solubility of AgCl in $2M$ NH_3 is $0.182M$

22. H_2A is a weak diprotic acid. If the pH of $0.1M$ H_2A solution is 3 and concentration of A^{2-} is 10^{-12} at 25°C.

Select correct statement(s)

(a) $[H^+]_{total} \approx [H^+]$ from first step of ionisation of acid H_2A

(b) Concentration of OH^- in solution is $10^{-3} M$

(c) The value of K_{a_1} is nearly 10^{-5}

(d) $pK_{a_2} - pK_{a_1} = 9$

23. Which is/are correct statement(s)?

(a) CH_3COONH_4 have greater degree of hydrolysis in $0.2 M$ solution in comparison of $0.4M$ solution.

(b) Anion have lesser basic strength than OH^-, does not hydrolysis

(c) The CH_3COO^- have greater degree of hydrolysis in comparision of $HCOO^-$ when their salt solution have equal conc.

(d) SO_4^{2-} does hydrolysis but HSO_4^- does not undergo hydrolysis

24. $0.01M$ NH_4Cl (*aq*) solution at 25°C has:

(a) $[Cl^-(aq)] < 10^{-2}M$ (b) $[NH_4^+(aq)] < 10^{-2}M$

(c) pOH > 7 (d) $[H^+] > 10^{-7} M$

25. In an acidic indicator HIn has ionisation constant is 10^{-8}. The acid form of indicator is yellow and alkaline form is red. Which is correct statement:

(Given : log2 = 0.3, log3 = 0.48)

(a) The pH range of indicator is 7 to 9

(b) Change in pH is 0.96 when 75% yellow colour change to 75% red colour

(c) This indicator is suitable for the titration of strong acid Vs strong base

(d) pH of indicator is 8.3 when ratio of acid form to alkaline form is 2.

MATCH THE COLUMN

Column-I and **Column-II** contains four entries each. Entries of Column-I are to be matched with some entries of Column-II. One or more than one entries of Column-I may have the matching with the same entries of Column-II.

1.

Column-I	Column-II
(A) HCl	(P) Bronsted base
(B) NH_3	(Q) Bronsted acid
(C) H_2O	(R) Arrhenius acid
(D) CN^-	(S) Lewis base in adduct displacement reaction

2.

Column-I	Column-II
(A) Conjugate acid-base pair	(P) Bronsted-Lowry concept
(B) Acid-base adduct	(Q) Lewis concept
(C) An acid-base reaction	(R) Arrhenius concept
(D) Proton donation	(S) $K_a \cdot K_b = K_w$

3.

Column-I	Column-II
(A) $Fe(NO_3)_2(aq.)$	(P) Only cationic hydrolysis
(B) $KClO_4(aq.)$	(Q) Only anionic hydrolysis
(C) $HCOONa(aq.)$	(R) Both cationic as well as anionic hydrolysis
(D) $NH_4CN(aq.)$	(S) No hydrolysis

4.

Column-I	Column-II
(A) Salt of weak acid and weak base	(P) $pH = 1/2\,[pK_w + pK_a + \log C]$
(B) Salt of weak acid and strong base	(Q) $pH = 1/2\,[pK_w + pK_a - pK_b]$
(C) Salt of strong acid and strong base	(R) $pH = 1/2\,[pK_w - pK_b - \log C]$
(D) Salt of strong acid and weak base	(S) $pH = 1/2\,[pK_w]$

5.

Column-I	**Column-II**
(A) Salt of weak acid and weak base ($pK_a = pK_b$)	(P) pH of solution at 25°C less than 7
(B) Salt of weak acid and strong base	(Q) pH of solution at 25°C greater than 7
(C) Salt of strong acid and strong base	(R) pH of solution at 25°C equal to 7
(D) Salt of strong acid and weak base	(S) pH cannot be find until the value of K_a/K_b is given

6.

Column-I	**Column-II**
(A) pH of 0.1 M HA ($pK_a = 5$) and 0.01 M NaA	(P) 4
(B) pH of 0.1 M BOH ($pK_b = 6$) and 0.1 M BCl	(Q) 7
(C) pH of 0.1 M salt of weak acid ($pK_a = 5$) and weak base ($pK_b = 7$)	(R) 6
(D) pH of 500 litre of 0.02 M HNO_3 and 500 litre 0.01 M $Sr(OH)_2$	(S) 8

7.

Column-I	**Column-II**
(A) CH_3COOH ($pK_a = 4.74$, 0.1 M) + CH_3COONa (0.1 M)	(P) Acidic buffer at it's maximum capacity
(B) CH_3COOH (0.1 M) + HCl (0.1 M)	(Q) Buffer solution
(C) CH_3COOH ($pK_a = 4.74$, 0.1 M) + NH_4OH ($pK_b = 4.74$, 0.1 M)	(R) pH < 7 at 25°C
(D) CH_3COONa (300 mL of 0.1 M) + HCl (100 mL of 0.1 M)	(S) pH = 7 at 25°C

8.

Column-I	**Column-II**
(A) Titration of a strong acid with strong base	(P) Methyl orange (3.1 – 4.4)
(B) Titration of weak acid with strong base	(Q) Methyl red (4.2 – 6.3)
(C) Titration of strong acid with weak base	(R) Phenolphthalein (8.3 – 10)
(D) Titration of weak acid with weak base	(S) No general indicator is suitable

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

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

10.

Column-I	Column-II
(A) Mercurous iodide	(P) $108\,S^5$
(B) Aluminium phosphate	(Q) $4\,S^3$
(C) Calcium phosphate	(R) S^2
(D) Zirconium phosphate	(S) $6912\,S^7$

ASSERTION-REASON TYPE QUESTIONS

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason).
Examine the statements carefully and mark the correct answer according to the instructions given below :

(A) If both the statements are TRUE and STATEMENT-2 is the correct explanation of STATEMENT-1
(B) If both the statements are TRUE but STATEMENT-2 is NOT the correct explanation of STATEMENT-1
(C) If STATEMENT-1 is TRUE and STATEMENT-2 is FALSE
(D) If STATEMENT-1 is FALSE and STATEMENT-2 is TRUE

1. STATEMENT-1 : All strong monoprotic acid with same concentration in dilute solution show same pH.
STATEMENT-2 : Water shows levelling effect.

2. STATEMENT-1 : If water is heated to 50°C then pH will increase.
STATEMENT-2 : K_w increases with increase in temperature.

3. STATEMENT-1 : Addition of HCl(*aq.*) to HCOOH(*aq.*) decrease the ionization of HCOOH(*aq.*)
STATEMENT-2 : Due to common ion effect of H^+, ionization of HCOOH decrease.

4. STATEMENT-1 : pH of $10^{-7}\,M$ HCl is less than 7 at 25°C.
STATEMENT-2 : At very low concentration of HCl, contribution of H^+ from water is considerable.

5. **STATEMENT-1 :** The ionization constants of weak diprotic acid are in the order of $K_{a_1} > K_{a_2}$.

STATEMENT-2 : Removal of H^+ from anion is difficult as compare to neutral atom.

6. **STATEMENT-1 :** When 0.1 M weak diprotic acid H_2A dissociates with its dissociation constants $K_{a_1} = 10^{-3}$ and $K_{a_2} = 10^{-8}$, then $[A^{-2}]$ is almost equal to 10^{-3} M.

STATEMENT-2 : Since $K_{a_2} << K_{a_1}$ for 0.1 M H_2A, so $[A^{-2}]$ is negligible w.r.t. $[HA^-]$.

7. **STATEMENT-1 :** pH value of acidic buffer solution change, if buffer solution is diluted upto very larger extent.

STATEMENT-2 : $[H^+]$ decrease due to change in concentration as well as α and decrease in concentration is more as compare to increase in α.

8. **STATEMENT-1 :** In a titration of weak acid with strong base, the pH at the half equivalence point is pK_a.

STATEMENT-2 : At half equivalence point, it will form acidic buffer at it's maximum capacity where [acid] = [salt].

9. **STATEMENT-1 :** In the titration of Na_2CO_3 with HCl using methyl orange indicator, the volume of the acid required at the equivalence point is twice that of the acid required using phenolphthalein as indicator.

STATEMENT-2 : Two moles of HCl are required for the complete neutralisation of one mole of Na_2CO_3.

10. **STATEMENT-1 :** In the acid-base titration involving strong base and weak acid, methyl red can be used as an indicator.

STATEMENT-2 : Methyl red changes its colour in the pH range 4.2 to 6.3.

11. **STATEMENT-1 :** Sparingly soluble salts AB and XY_2 with the same solubility product, will have different solubility.

STATEMENT-2 : Solubility of sparingly soluble salt depend upon solubility product.

12. **STATEMENT-1 :** Solubility product of BaF_2 will increase on dilution.

STATEMENT-2 : Solubility of BaF_2 will change on changing temperature.

13. **STATEMENT-1 :** Solubility of sparingly soluble salt decreases due to common ion effect.

STATEMENT-2 : Solubility product constant does not depend on common ion effect.

14. **STATEMENT-1 :** Solubility of AgCl in $NH_3(aq.)$ is greater than in pure water.

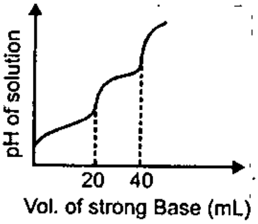
STATEMENT-2 : When AgCl dissolve in $NH_3(aq.)$, complex ion formation $Ag(NH_3)_2^+$ takes place and solubility equilibria of AgCl shifted in forward direction.

15. **STATEMENT-1 :** Solubility of AgCN in acidic solution is greater than that in pure water.

STATEMENT-2 : Solubility equilibria of AgCN in water is shifted in forward direction due to formation of HCN.

SUBJECTIVE PROBLEMS

1. Calculate pOH of $0.1 M$ aq. solution of weak base BOH ($K_b = 10^{-7}$) at 25°C.
2. pH of $0.01 M$ aq. solution of HA is 4. Find the value of pK_a of HA at 25°C.
3. Calculate approximate pH of $10^{-10} M$ NaOH at 25°C.
4. Calculate pH of a resultant solution of 25 mL of $0.1 M$ HCl, 50 mL of $0.02 M$ HNO_3 and 25 mL of $0.1 M$ NaOH.
5. Calculate pH of a resultant solution of $0.1 M$ HA ($K_a = 10^{-6}$) and $0.45 M$ HB ($K_a = 2 \times 10^{-6}$) at 25°C.
6. 0.16g N_2H_4 ($K_b = 4 \times 10^{-6}$) 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 in this solution
7. Calculate pH of a buffer solution that contains $0.1 M$ NH_4OH ($K_b = 10^{-5}$) and $0.1 M$ NH_4Cl.
8. Calculate the ratio of sodium formate and formic acid ($K_a = 2 \times 10^{-4}$) in a buffer solution of pH = 4.3.
9. What is the pOH of 0.1 KB (salt of weak acid and strong base) at 25°C ? (Given : pK_b of $B^- = 7$)
10. A certain weak acid has $K_a = 10^{-5}$. If the equilibrium constant for its reaction with a strong base is represented as $y \times 10^{10}$ then find the value of y.
11. If solubility of AgCl in $0.2 M$ solution of $AgNO_3$ is represented as $y \times 10^{-10}$ then find the value of y.
    (Given : $K_{sp(AgCl)} = 10^{-10}$)
12. When one litre of a saturated solution of $PbCl_2$ (mol. wt. = 278) is evaporated, the residue is found to weight 2.78g. If K_{sp} of $PbCl_2$ is represented as $y \times 10^{-6}$ then find the value of y.
13. A solution is saturated in $SrCO_3$ and SrF_2. The CO_3^{2-} was found to be 10^{-3} mol/L.
    If the concentration of F^- in solution is represented as $y \times 10^{-2} M$ then what is the value of y ?
    [Given : $K_{sp}(SrCO_3) = 2.5 \times 10^{-10}$; $K_{sp}(SrF_2) = 10^{-10}$]
14. 10 mL of H_2A (weak diprotic acid) solution is titrated against $0.1 M$ NaOH. pH of the solution is plotted against volume of strong base added and following observation is made.



If pH of the solution at first equivalence point is pH_1 and at second equivalence point is pH_2. Calculate the value of $(pH_2 - pH_1)$ at 25°C
Given: For H_2A, $pK_{a_1} = 4.6$ and $pK_{a_2} = 8$, $\log 25 = 1.4$

15. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is:

NaCN	KCl	CH_3COONH_4	NaH_2PO_4	$ZnCl_2$	Na_3PO_4
$Fe(NO_3)_3$	Na_2CO_3	NH_4Cl	$NaHCO_3$	$Na_2C_2O_4$	Na_2HPO_4

Given:

Acid	Ka_1	Ka_2	Ka_3
H_3P_4	10^{-3}	10^{-8}	10^{-12}
H_2CO_3	10^{-6}	10^{-11}	–
$H_2C_2O_4$	10^{-2}	10^{-5}	–

ANSWERS

Level 1

1. (d)	2. (c)	3. (a)	4. (c)	5. (c)	6. (a)	7. (a)	8. (d)	9. (d)	10. (c)
11. (d)	12. (d)	13. (c)	14. (d)	15. (b)	16. (d)	17. (a)	18. (d)	19. (c)	20. (c)
21. (a)	22. (b)	23. (a)	24. (b)	25. (a)	26. (c)	27. (b)	28. (c)	29. (b)	30. (b)
31. (b)	32. (a)	33. (b)	34. (a)	35. (a)	36. (b)	37. (c)	38. (a)	39. (c)	40. (c)
41. (c)	42. (c)	43. (b)	44. (c)	45. (b)	46. (a)	47. (c)	48. (d)	49. (d)	50. (d)
51. (d)	52. (b)	53. (b)	54. (c)	55. (d)	56. (d)	57. (b)	58. (c)	59. (c)	60. (b)
61. (b)	62. (d)	63. (b)	64. (b)	65. (b)	66. (c)	67. (a)	68. (c)	69. (d)	70. (a)
71. (d)	72. (b)	73. (d)	74. (c)	75. (b)	76. (b)	77. (a)	78. (d)	79. (b)	80. (c)
81. (b)	82. (d)	83. (a)	84. (a)	85. (c)	86. (a)	87. (c)	88. (b)	89. (d)	90. (b)
91. (c)	92. (d)	93. (b)	94. (a)	95. (d)	96. (a)	97. (a)	98. (d)	99. (b)	100. (a)
101. (a)	102. (b)	103. (c)	104. (b)	105. (c)	106. (d)	107. (d)	108. (b)	109. (a)	110. (c)
111. (d)	112. (c)	113. (a)	114. (a)	115. (a)	116. (c)	117. (a)	118. (c)	119. (a)	120. (a)
121. (c)	122. (c)	123. (c)	124. (a)	125. (c)	126. (d)	127. (a)	128. (a)	129. (d)	130. (b)
131. (d)	132. (b)	133. (c)	134. (c)	135. (d)	136. (d)	137. (a)	138. (d)	139. (c)	140. (a)
141. (a)	142. (d)	143. (c)	144. (c)	145. (d)	146. (a)	147. (b)	148. (b)	149. (d)	150. (b)

Level 2

1. (d)	2. (c)	3. (c)	4. (a)	5. (d)	6. (c)	7. (a)	8. (d)	9. (a)	10. (a)
11. (d)	12. (c)	13. (a)	14. (b)	15. (c)	16. (c)	17. (b)	18. (c)	19. (b)	20. (b)
21. (b)	22. (d)	23. (c)	24. (c)	25. (d)	26. (d)	27. (a)	28. (b)	29. (a)	30. (b)
31. (a)	32. (c)	33. (d)	34. (b)	35. (d)					

Level 3

Passage-1: 1. (c) 2. (b) 3. (b) 4. (b)

Passage-2: 1. (c) 2. (b) 3. (b) 4. (b)

Passage-3: 1. (b) 2. (a,c) 3. (c) 4. (a) 5. (b) 6. (a)

Passage-4: 1. (a) 2. (a) 3. (b) 4. (a) 5. (c)

One or More Answer is/are Correct

1. (b,c) 2. (a,b,c) 3. (a,b) 4. (b) 5. (a,c) 6. (a,b,c,d) 7. (a,b) 8. (a,b)
9. (a,c) 10. (a,c,d) 11. (a,b,d) 12. (a,c) 13. (a,b) 14. (b, c) 15. (b, c, d) 16. (a, c)
17. (b, c, d) 18. (b, c) 19. (a, c, d) 20. (a, b) 21. (b,c,d) 22. (a,c) 23. (c,d) 24. (b,c,d)
25. (a,b,c)

Match the Column

1. A → Q, R; B → P, S; C → P Q, S; D → P, S
2. A → P, S; B → Q; C → P, Q, R; D → P; R
3. A → P; B → S; C → Q; D → R
4. A → Q; B → P; C → S; D → R
5. A → R; B → Q, S; C → R; D → P, S
6. A → P; B → S; C → R; D → Q
7. A → P, Q, R; B → R; C → Q, S; D → Q, R
8. A → P, Q, R; B → R; C → P, Q; D → S
9. A → S; B → P; C → R; D → Q
10. A → Q; B → R; C → P; D → S

Assertion-Reason Type Questions

1. (A) 2. (D) 3. (A) 4. (A) 5. (A) 6. (D) 7. (A) 8. (A) 9. (B) 10. (D)
11. (B) 12. (D) 13. (B) 14. (A) 15. (A)

Subjective Problems

1. 4 2. 6 3. 7 4. 2 5. 3 6. 2 7. 9 8. 4 9. 4 10. 9
11. 5 12. 4 13. 2 14. 4 15. 6

Hints and Solutions

Level 1

4. (c) H_3PO_2 and H_3PO_3 are mono and dibasic acids. Hence, NaH_2PO_2 and Na_2HPO_3 are normal salts. While Na_2HPO_4 is acid-salt as one proton is there in the compound.

16. (d) When equal volumes are taken, the concentration becomes half.

$$\therefore \quad [H^+] = \frac{1}{2}(10^{-3} + 10^{-5})$$

$$= 505 \times 10^{-6}$$

$$\therefore \quad pH = 3.3$$

17. (a) $[H^+] = 0.002\,M$

$$pH = \log 2 \times 10^{-3}$$

$$= 3 - \log 2$$

$$\therefore \quad pOH = 11 + \log 2$$

18. (d) pH = 4, $\quad [H^+] = 10^{-4}$ mol/litre

Equivalent of HCl in 100 mL solution

$$= \frac{10^{-4} \times 100}{1000} = 10^{-5}$$

19. (c)

$$N_1V_1 = N_2V_2$$

$$10^{-3} \times 10 = N_2 \times 1000$$

$$\Rightarrow \quad N_2 = 10^{-5}$$

$$\therefore \quad pH = 5$$

and pOH = 14 − 5 = 9

22. (b) $[Ca(OH)_2(aq.)] = \frac{0.60}{74} \times \frac{1000}{1500}$

$$= 5.40 \times 10^{-3}$$

$$Ca(OH)_2(aq.) \longrightarrow Ca^{2+}(aq.) + 2OH^-(aq.)$$

$$[Ca^{2+}] = 5.40 \times 10^{-3}$$

$$[OH^-] = 2 \times 5.40 \times 10^{-3} = 1.08 \times 10^{-2}$$

27. (b) Milli-equivalents of HCl = 25 × 0.08 = 2

Milli-equivalents of NaOH = 2.5

remaining $[OH^-] = \frac{2.5 - 2}{500} = 10^{-3}$

$$\therefore \quad [H^+] = 10^{-11} \text{ or } pH = 11$$

29. (b) 20 meq. of HCl reacts completely with 20 meq. of KOH. Hence, the final solution is neutral. Thus, at 90°C, pH = 6.

32. (a) ∵ Strength of acid $\propto \frac{1}{pK_a}$

∴ Formic acid will be the strongest acid.

35. (a)

$$\begin{array}{lccc} & HA(aq.) & \rightleftharpoons H^+(aq.) + & A^-(aq.) \\ \text{at equilibrium} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{C\alpha^2}{1 - \alpha}$$

$$\Rightarrow \quad 10^{-4} = \frac{(0.01)\,\alpha^2}{1 - \alpha}$$

$$\Rightarrow \quad \alpha = 0.095$$

$$\Rightarrow \quad \%\,\alpha = 9.5$$

38. (a) pH = 9; $[OH^-] = 10^{-5}$; $C\alpha = 10^{-5}$

$$\therefore \; \alpha = 10^{-4}$$

% ionization = $10^{-4} \times 100 = 0.01\%$

40. (c) α is negligible w.r.t. 1 so $K_a = C\alpha^2$.

$$\Rightarrow 0.1 \times (0.01)^2 \Rightarrow 10^{-5}$$

$$\therefore \quad pK_a = 5$$

41. (c)

$$\begin{array}{ccc} HCOOH \rightleftharpoons & H^+ & + HCOO^- \\ C - x & x + 0.01 & x \end{array}$$

$$K_a = \frac{(x + 0.01)\,x}{0.01 - x}$$

neglect x w.r.t. 0.01 due to common ion effect

$$K_a = x$$

$$\therefore \quad x = [HCOO^-] = 1.8 \times 10^{-4}$$

43. (b) ∵ α is negligible w.r.t. 1

$$K_a = C_1\alpha_1^2 = C_2\alpha_2^2$$

$$\therefore \quad C_2 = C_1\left(\frac{\alpha_1}{\alpha_2}\right)^2$$

$$= 0.2 \times \frac{1}{4} = 0.05$$

$$C_1V_1 = C_2V_2$$

$\Rightarrow \quad 300 \times 0.2 = 0.05 \times V_2$

$\Rightarrow \quad V_2 = 1200 \text{ mL}$

Volume of H_2O added $= 1200 - 300$

$= 900$ mL

44. (c) Due to low value of K_b and common ion effect we can neglect x w.r.t. 0.01 when $x = c\alpha$

$$K_b = \frac{x \times 0.01}{0.02}$$

$\therefore \quad x = [NH_4^+] = 3.6 \times 10^{-5}$

45. (b) $n_{RNH_2(g)} = \frac{1 \times 22.41}{0.0821 \times 273} = 1$

$$[RNH_2(aq.)] = \frac{n_{RNH_2}}{\text{Volume of solution}} = 1$$

α is negligible w.r.t. 1 so

$$pOH = \frac{1}{2}[pK_b - \log C] = 2$$

46. (a) α is negligible w.r.t. 1 for both acid so

$$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$$

$$= \sqrt{1.8 \times 10^{-5} \times 0.01 + 6.3 \times 10^{-5} \times 0.01}$$

$$[H^+] = \sqrt{81 \times 10^{-8}} = 9 \times 10^{-4}$$

47. (c) $[HA] = \frac{\left(\frac{6}{60}\right)}{10000} \Rightarrow 10^{-5} M$

$$\alpha = \frac{\sqrt{10^{-9}}}{10^{-5}} \Rightarrow 0.01 \text{ (negligible w.r.t. 1)}$$

$\therefore \ [H^+] = \sqrt{10^{-9} \times 10^{-5}} \Rightarrow \sqrt{10^{-14}}$

$\Rightarrow \quad 10^{-7} M, \quad \because [H^+] < 10^{-6} M$

So we should consider $[H^+]$ from $H_2O \Rightarrow [H^+]_{total} = 2 \times 10^{-7}$ without considering common ion effect pH $= 6.7$, so pOH $= 7.3$ but due to C.I. effect H^+ from H_2O will be less

so pH > 6.7

$\therefore$ pOH of solution is exist between 7.0 and 7.3.

48. (d) and 49. (d)

$$K_{a_1} = \frac{[H^+]_{total}[HCO_3^-]}{[H_2CO_3]}$$

$\because K_{a_1} >> K_{a_2}$ and concentration is appreciable so we can neglect α w.r.t. 1

$\therefore \quad [H^+]_{total} \simeq [HCO_3^-]$;

$[HCO_3^-] = \sqrt{4 \times 10^{-7} \times 0.025} \Rightarrow 10^{-4}$

and $\quad [CO_3^{2-}] \simeq K_{a_2}$

50. (d) $[H^+]_{total} \simeq [H^+]$ from first step

$\therefore \quad K_{a_1} = \frac{C\alpha^2}{(1-\alpha)}$; α is not negligible w.r.t. 1 so

after solving quadratic equation $\alpha = 0.095$

$$\therefore \quad [OH^-] = \frac{10^{-14}}{0.95 \times 0.3}$$

$\Rightarrow \quad 3.5 \times 10^{-13}$

54. (c) $\quad pH = \frac{1}{2}pK_a - \frac{1}{2}\log C$

$\Rightarrow \quad 5 = \frac{1}{2}pK_a + \frac{1}{2} \times 2$

$pK_a = 8 \quad \Rightarrow \quad pK_b = 8;$

$pOH = \frac{1}{2}pK_b - \frac{1}{2}\log C = 4 + 2 = 6$

67. (a) $K_{a(HOCN)} = \frac{10^{-14}}{10^{-10}} = 10^{-4}$

$K_h = K_{b(OCN^-)} = 10^{-10}$

$$\alpha = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-10}}{0.01}} = 10^{-4}$$

$\because \ \alpha << 0.1; \ \therefore K_h = c\alpha^2$

$[OH^-] = c\alpha; \ [OH^-] = 0.01 \times 10^{-4} = 10^{-6} M$

69. (d) $\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{C_2}{C_1}} \Rightarrow \frac{0.01}{\alpha_2} = \sqrt{\frac{0.4}{0.1}}$

$\alpha_2 = 0.005$ or $\% \ \alpha_2 = 0.5$

71. (d) $h = \sqrt{\frac{K_w}{K_a C}}$

|Enthalpy of neutralisation| $\downarrow K_a \downarrow h \uparrow$

72. (b) $[NaA] = \frac{25 \times 0.1}{25 + 50} = \frac{2.5}{75}$

$$[H^+] = \sqrt{\frac{K_w \cdot K_a}{C}} = 1.732 \times 10^{-9}$$

74. (c) $pH = \frac{1}{2}(pK_w + pK_a - pK_b) = 6.5$

75. (b) $\because \quad pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7$

and $\alpha = \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{10^{-14}}{10^{-12}}} = 0.1$

or $\% \quad \alpha = 10$

76. (b) α does not depend on concentration in this case.

77. (a) $\alpha=\sqrt{\frac{K_h}{C}}$; $[H_3O^+]=C\alpha$

$$=\sqrt{K_h\times C}=\sqrt{0.02\times5\times10^{-9}}=10^{-5}$$

79. (b) α is not negligible w.r.t. 1 so after solving quadratic equation $\alpha=0.095$

$[H^+]=C\alpha=0.0095$; $pH=2.02$

83. (a)

	CH_3COOH	+ $NaOH$	$\longrightarrow$ CH_3COONa	+ H_2O
initial milli-moles	6	2	—	—
after reaction	4	—	2	—

$$pH=pK_a+\log\frac{[CH_3COO^-]}{[CH_3COOH]}=4.44$$

91. (c)

	CH_3NH_2	+ HCl	$\longrightarrow$ CH_3NH_3Cl
initial milli-moles	1.2	0.08	
after reaction	0.04	—	0.08

$$pOH=pK_b+\log\frac{[CH_3NH_3^+]}{[CH_3NH_2]}$$

$$=3.3+\log\frac{0.08}{0.04}=3.6$$

$\therefore\quad pH=10.4$

92. (d) $pOH=pK_b+\log\frac{[NH_4^+]}{[NH_4OH]}=6$

$\therefore\quad pH=14-6=8.0$

97. (a) Henderson equation is

$$pH=pK_a+\log\frac{[salt]}{[acid]}=4$$

$\therefore pOH=10$, $[OH^-]=10^{-10}$

Number of OH^- ions $=10^{-10}N_A$;

where N_A = Avogadro's number.

101 (a) Mol of $C_6H_5COOH=\frac{61}{122}=0.5$;

Mol of $C_6H_5COONa=\frac{72}{144}=0.5$

$$pH=pK_a+\log\frac{(C_6H_5COONa)}{(C_6H_5COOH)};$$

$$pH=4.2+\log\frac{0.2}{0.8}=3.6$$

102. (b) $pH=pK_{a_2}+\log\frac{[CO_3^{2-}]}{[HCO_3^-]}$

$$=(11-\log 4)+\log\left(\frac{0.2}{0.4}\right)=10.1$$

103. (c)

	H_3PO_4	+ PO_4^{3-}	$\longrightarrow$ $H_2PO_4^-$	+ HPO_4^{2-}
initial milli moles	20×0.1	20×0.1		
after reaction	—	—	2	2

Buffer solution of $H_2PO_4^-$ (acid) and HPO_4^{2-} (conjugate base) is formed;

$$pH=pK_{a_2}+\log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}=pK_{a_2}$$

107. (d) At equivalent point

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

$$=\frac{1}{2}[14+4.74-2]=8.37$$

Where $[Salt]=\frac{\text{milli-moles of acid}}{\text{Total volume}}$

$$=\frac{20\times0.02}{20+20}=0.01$$

For best indicator pH at equivalent point should lie between colour transition range of indicator.

109. (a) $HIn \rightleftharpoons In^-+H^+$; $K_{In}=\frac{[H^+][In^-]}{[HIn]}$

red blue

Case I : $3\times10^{-5}=\frac{[H^+]_1\times0.25}{0.75}$

Case II : $3\times10^{-5}=\frac{[H^+]_2\times0.75}{0.25}$

$[H^+]_1=9\times10^{-5}\,[H^+]_2=10^{-5}$

Change in $[H^+]=8\times10^{-5}$

116. (c) When 1 litre each solution are mixed

$[OH^-]=10^{-6}M$ (Buffer solution)

$M^{n+}=0.05M$

for $Q=[0.5][10^{-6}]^2=5\times10^{-14}$

$Q>K_{sp}$ for Fe^{2+} and Ni^{2+}

So $Fe(OH)_2$ and $Ni(OH)_2$ are ppt.

117. (a) For $[Ca^{+2}]$, $M_1V_1=M_2V_2$

$0.04\times50=M_2\times200\Rightarrow M_2=0.01$

Similarly, for $[SO_4^{-2}]$

$$0.0008\times150=M_2\times200$$

$\Rightarrow\quad M_2=0.0006$

ionic product $(Q)=[Ca^{+2}]\times[SO_4^{-2}]$

$=6\times10^{-8}$ So $Q<K_{sp}$

120. (a) $$[Ag^+] = \frac{10^{-3}}{50+50}\times 1000 = 0.01$$

$$[Cl^-] = \frac{0.1\times 50}{50+50} = 0.05$$

$$Q = [Ag^+][Cl^-] = 5\times 10^{-4}$$

$$\because\ Q > K_{sp}$$

$$\begin{array}{lccc} & Ag^+(aq.) & + Cl^-(aq.) & \longrightarrow AgCl(s) \\ \text{at given condition} & 0.01 & 0.05 & \\ \text{after precipitation} & x & \simeq 0.04 & \end{array}$$

$$K_{sp} = [Ag^+][Cl^-];\quad 10^{-10} = x\times 0.04$$

$$x = [Ag^+] = 2.5\times 10^{-9}$$

124. (a) The corresponding values of solubility products of the given electrolytes are :

$$\begin{array}{ccc} MX_1 & MX_2 & MX_3 \\ S^2 = 10^{-6}, & 4S^3 = 4\times 10^{-9}, & 27S^4 = 27\times 10^{-12} \end{array}$$

128. (a) Solubility of $AB = \sqrt{K_{sp}} = 2\times 10^{-10}$

Solubility of $A_2B = \sqrt[3]{\frac{K_{sp}}{4}} = 2\times 10^{-4}$

Solubility of $AB_3 = \left[\frac{K_{sp}}{27}\right]^{1/4} = 10^{-8}$

129. (d) $HgSO_4(s) \rightleftharpoons Hg^{2+}(aq.) + SO_4^{2-}(aq.)$

$$S = \sqrt{6.4\times 10^{-5}} = 8\times 10^{-3}\ \text{mol/L}$$
$$= 8\ \text{mol/m}^3$$

134. (c) $$\underset{}{BaF_2(s)} \rightleftharpoons \underset{S}{Ba^{2+}(aq.)} + \underset{2S}{2F^-(aq.)}$$

$$K_{sp} = 4S^3;\quad S = \left(\frac{10^{-6}}{4}\right)^{1/3} = 0.63\times 10^{-2}$$

Molarity of $F^- = 2S = 2\times 0.63\times 10^{-2}$
$= 1.26\times 10^{-2}$

136. (d) $$Cu(OH)_2(s) \rightleftharpoons \underset{S}{Cu^{2+}(aq.)} + \underset{2S}{2OH^-(aq.)}$$

$$K_{sp} = 4S^3$$

$$\therefore\quad S = 4\times 10^{-7}$$

$$[OH^-] = 2S = 8\times 10^{-7}$$

$$pOH = 6.1\quad \therefore\ pH = 7.90$$

137. (a) $[Ag^+]$ or $S = \sqrt{K_{sp}} = 10^{-5}\ M$

$$10^{-5} = \frac{\dfrac{14.35\times 10^{-3}}{143.5}}{V\ (\text{in litre})}$$

$$V = 10\ \text{litre}\quad \text{or}\quad 0.01\ \text{m}^3$$

141. (a) Let solubility of Ag_2CO_3 in presence of Na_2CO_3 is x,

$$Ag_2CO_3(s) \rightleftharpoons \underset{2x}{2Ag^+(aq.)} + \underset{(x+0.1)\simeq 0.1}{CO_3^{2-}(aq.)}$$

$$K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

$$\Rightarrow\quad 4\times 10^{-13} = (2x)^2\times 0.1$$

$$\Rightarrow\quad x = 10^{-6}$$

146. (a) $$PbBr_2(s) \rightleftharpoons \underset{0.8S}{Pb^{+2}(aq.)} + \underset{2\times 0.8\times S}{2Br^-(aq.)}$$

$$K_{sp} = [Pb^{+2}][Br^-]^2$$

$$\Rightarrow\quad 8\times 10^{-5} = (0.8S)(1.6S)^2$$

$$\Rightarrow\quad S = \left[\frac{10^{-4}}{1.6\times 1.6}\right]^{1/3}$$

147. (b) For basic buffer solution

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

$$\therefore\quad [OH^-] = 1.8\times 10^{-5}$$

$$K_{sp} = [Mn^{2+}][OH^-]^2$$

$$[Mn^{2+}] = 1.38\times 10^{-4}\ M$$

148. (b) $$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{10^{-11}}{10^{-3}}} = 10^{-4}$$

$$pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_3]}$$

$$\Rightarrow\quad 4 = 5 + \log\frac{[NH_4Cl]}{[NH_3]}$$

$$\Rightarrow\quad 0.10 = \frac{[NH_4Cl]}{[NH_3]}$$

moles of NH_4Cl required $= 0.1\times 0.02$
$= 2\times 10^{-3}$

149. (d) Due to higher value of K_f, mostly Ag^+ converted into complex.

$$AgI(s) \rightleftharpoons Ag^+(aq.) + I^-(aq.);\ K_{sp}$$

$$\underline{Ag^+(aq.) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.);\ K_f}$$

overall reaction is

$$AgI(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + I^-(aq.)$$

$$K_{eq} = K_{sp}\cdot K_f$$

$$K_{sp}\cdot K_f = \frac{x^2}{1^2}$$

$$\therefore\quad x = 4.9\times 10^{-5}\ \text{mol/litre}$$

So mass of AgI required is

$$= 4.9\times 10^{-5}\times 235 = 0.011\ g$$

Level 2

1. (d)

$$\begin{array}{lcccccccc} & \text{TCl} & + & \text{NaOT} & \longrightarrow & \text{NaCl} & + & \text{T}_2\text{O} \\ \text{Initial milli-moles} & 2 & & 3.75 & & & & \end{array}$$

milli-moles of remaining NaOT = 1.75

$$\therefore \quad [\text{OT}^-] = \frac{1.75}{25} = 7 \times 10^{-2} \text{ moles}$$

$$\text{pOT} = 2 - \log 7$$

$$\text{pT} + \text{pOT} = 7.62 \times 2$$

$$\therefore \quad \text{pT} = 15.24 - 2 + \log 7$$

$$= 13.24 + \log 7$$

2. (c) $2\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{NH}_2^-;$ $\quad [\text{NH}_4^+] = \sqrt{K_{SIC}}$

$$K_{\text{SIC}} = [\text{NH}_4^+][\text{NH}_2^-]$$

$$\therefore \quad [\text{NH}_4^+] = 10^{-15}\, M$$

$\because$ Number of NH_4^+ ions in 1000 cm^3

$$= 10^{-15} \times 6.022 \times 10^{23}$$

$\therefore$ Number of NH_4^+ ions in 100 cm^3

$$= 10^{-15} \times 6.022 \times 10^{23} \times \frac{100}{1000}$$

$$= 6.022 \times 10^7$$

3. (c) α is very less so $[\text{H}^+] = \sqrt{K_a \times C} = 3 \times 10^{-3}$

$$\text{Now } [\text{H}^+] = \frac{3 \times 10^{-3}}{2} = 1.5 \times 10^{-3}$$

$$(1.5 \times 10^{-3}) = \sqrt{K_a \cdot C_2}$$

$$\Rightarrow \quad C_2 = 0.125$$

milli-moles of acid remain constant

$$C_1V_1 = C_2V_2$$

$$10 \times 0.5 = 0.125 \times V_2$$

$$\Rightarrow \quad V_2 = 40 \text{ litre}$$

4. (a) $[\text{H}^+] = \dfrac{10 \times 0.3 - 10 \times 0.1}{10 + 10 + 20} = 0.05$

$$[\text{H}A] = \frac{20 \times 0.1}{20 + 20} = 0.05$$

$$\begin{array}{ccccc} \text{H}A & \rightleftharpoons & \text{H}^+ & + & A^- \\ 0.05 - x & & 0.05 + x & & x \end{array}$$

Due to common ion effect neglect x w.r.t. 0.05

$$K_a = \frac{(0.05 + x) \cdot x}{(0.05 - x)} \simeq x$$

$$\therefore \quad x = 10^{-5}$$

$$\therefore \quad \frac{[A^-]}{[\text{H}A] + [A^-]} = \frac{x}{x + 0.05} = 2 \times 10^{-4}$$

5. (d)

$$\begin{array}{lccccc} & \text{FCH}_2\text{COOH}(aq.) & \rightleftharpoons & \text{FCH}_2\text{COO}^-(aq.) & + & \text{H}^+(aq.) \\ \text{at eqm.} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$K_a = \frac{[\text{H}^+][\text{FCH}_2\text{COO}^-]}{[\text{FCH}_2\text{COOH}]}$$

$$\Rightarrow \quad 2.6 \times 10^{-3} = \frac{(2 \times 10^{-3})^2}{[\text{FCH}_2\text{COOH}]}$$

at eqm. $[\text{FCH}_2\text{COOH}] = 1.53 \times 10^{-3}$

Total concentration $= 2 \times 10^{-3} + 1.53 \times 10^{-3}$

$$= 3.53 \times 10^{-3}$$

6. (c)

$$\begin{array}{ccccc} \text{HCOOH}(aq.) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{HCOO}^-(aq.) & + & \text{H}_3\text{O}^+(aq.) \\ C_1 - x & & x & & x + y \end{array}$$

$$\begin{array}{ccccc} \text{HF}(aq.) + \text{H}_2\text{O}(l) & \rightleftharpoons & \text{F}^-(aq.) & + & \text{H}_3\text{O}^+(aq.) \\ C_2 - y & & y & & x + y \end{array}$$

$\because$ α is very less for both acid so

$$K_a\,(\text{HCOOH}) = \frac{x\,(x + y)}{C_1};$$

$$K_a\,(\text{HF}) = \frac{y\,(x + y)}{C_2}$$

$$\therefore \quad \frac{x}{y} = \frac{K_a\,(\text{HCOOH})\,C_1}{K_a\,(\text{HF})\,C_2}$$

$$\frac{[\text{HCOO}^-]}{[\text{F}^-]} = \frac{x}{y}$$

$$= \frac{2 \times 10^{-4} \times 0.2}{6.6 \times 10^{-4} \times 0.1} = \frac{2}{3.3}$$

7. (a) First dissociation

$$X(\text{OH})_3 \longrightarrow X(\text{OH})_2^+ + \text{OH}^-$$

Second dissociation :

$$X(\text{OH})_2^+ \longrightarrow X(\text{OH})^{2+} + \text{OH}^-$$

$$\text{Total } [\text{OH}^-] = 4 \times 10^{-3} + 2 \times 10^{-3} = 6 \times 10^{-3}$$

$$\text{pOH} = 3 - \log 6 \simeq 2.22$$

$$\therefore \quad \text{pH} = 11.78$$

8. (d) α is negligible w.r.t. 1

$[\text{H}^+]$ mainly from first step

$$[\text{H}^+] = \sqrt{K_{a_1} \times C} = \sqrt{10^{-5} \times 0.1} = 10^{-3}$$

$$\therefore \quad K_{a_3} = \frac{[\text{H}^+][A^{3-}]}{[\text{H}A^{2-}]} = 10^{-13} = \frac{10^{-3}[A^{3-}]}{[\text{H}A^{2-}]}$$

$$X = \frac{[A^{3-}]}{[\text{H}A^{2-}]} = 10^{-10};$$

$$\therefore \quad \text{p}X = 10$$

9. (a) $Ca(LaC)_2 \longrightarrow Ca^{2+} + 2LaC^-$

Initial concentration $0.6/2 = 0.3\ M$

After dissociation $[LaC^-] = 2 \times 0.3 \times 0.9 = 0.54\ M$

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

$$14 - 5.6 = \frac{1}{2}[14 + pK_a + \log(0.54)]$$

$$pK_a = 2.8 - \log(0.54)$$

10. (a) $CH_3COO^-(aq.) + NH_4^+(aq.) + H_2O(l) \rightleftharpoons CH_3COOH(aq.) + NH_4OH(aq.)$

at equilibrium $C(1-\alpha)$ $\quad C(1-\alpha)$ $\quad C\alpha$ $\quad C\alpha$

$$K_h = \frac{K_w}{K_aK_b} = \frac{\alpha^2}{(1-\alpha)^2}$$

$$\frac{10^{-14}}{(1.8 \times 10^{-5})^2} = \frac{\alpha^2}{(1-\alpha)^2}$$

$$\frac{10^{-2}}{1.8} = \frac{\alpha}{1-\alpha};\ \alpha = 5.55 \times 10^{-3}$$

$$[CH_3COOH] = C\alpha = 0.01 \times 0.0055 = 5.55 \times 10^{-5}$$

11. (d) $Fe^{3+}(aq.) + H_2O(l) \rightleftharpoons Fe(OH)^{2+}(aq.) + H_3O^+(aq.)$

$$K_a = \frac{[Fe(OH)^{2+}][H_3O^+]}{[Fe^{3+}]}$$

$$\Rightarrow 6.5 \times 10^{-3} = \frac{0.20}{0.80} \times [H_3O^+]$$

$$\Rightarrow [H_3O^+] = 2.6 \times 10^{-2};\ pH = 1.59$$

12. (c) Due to larger difference between K_{h_1} and K_{h_2} and common ion effect we can assume that y is negligible w.r.t. x

$Fe^{2+} + H_2O \rightleftharpoons Fe(OH)^+ + H^+$

at equilibrium $C - x$ $\quad x - y$ $\quad x + y$

$Fe(OH)^+ + H_2O \rightleftharpoons Fe(OH)_2 + H^+$

at equilibrium $x - y$ $\quad y$ $\quad y + x$

$$K_{h_2} = \frac{K_w}{K_{b_1}} = \frac{10^{-14}}{10^{-4}} = 10^{-10} = \frac{y(x+y)}{(x-y)} \Rightarrow y$$

$$\therefore\ K_{h_2} = y \Rightarrow Fe(OH)_2 = 10^{-10}$$

13. (a) Let x milli-moles of NaOH is added

$$6 = 5 + \log\left[\frac{s+x}{a-x}\right];\ \frac{s+x}{a-x} = 10$$

or $\frac{10+x}{10-x} = 10 \Rightarrow x = 8.18$

$\therefore$ wt $= 8.18 \times 10^{-3} \times 56 = 0.458$ gm

14. (b) $pH = pK_a + \log\frac{[C_6H_5COO^-]}{[C_6H_5COOH]}$

$$\therefore\ \frac{[C_6H_5COO^-]}{[C_6H_5COOH]} = 2$$

Let volume of acid is V mL

$$\frac{0.2 \times (300 - V)}{0.1 \times V} = 2 \Rightarrow V = 150\ \text{mL}$$

15. (c) When half acid is neutralized $pH = pK_a$

& At the equivalent point

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

$$= 9 = \frac{1}{2}[14 + 5 + \log C] = C = 0.1$$

Let V mL of NaOH is used in titration

milli eq. of NaOH $= 0.25 \times V =$ milli eq. of salt formed

$$\therefore\ \frac{0.25 \times V}{V + 60} = 0.1 = V = 40\ \text{mL}$$

milli equivalent or milli-moles of acid = 10

wt. of acid $= 10 \times 10^{-3} \times 82 = 0.82$ gm

wt. % of acid $= \frac{0.82}{1.025} \times 100 = 80\%$

16. (c) $BOH(aq.) \rightleftharpoons B^+(aq.) + OH^-(aq.)$

At equilibrium : $c(1-\alpha)$ $\quad c\alpha$ $\quad c\alpha$

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \Rightarrow \frac{c\alpha^2}{(1-\alpha)};$$

neglect α w.r.t. 1 as concentration is appreciable, $\%\ \alpha = 100 \times \sqrt{\frac{K_b}{c}}$

Total dissolved base present in solution as BOH and B^+

So $\alpha = \frac{[B^+]}{[B^+] + [BOH]}$

$$\Rightarrow \frac{1}{1 + \frac{[BOH]}{[B^+]}} = \frac{1}{1 + \frac{[OH^-]}{K_b}}$$

$$\Rightarrow \frac{K_b}{K_b + [OH^-]} \Rightarrow \frac{K_b \cdot [H^+]}{K_b[H^+] + K_w}$$

also $pOH = -\log[OH^-]$; $[OH^-] = 10^{-pOH}$;

$$K_b = 10^{-pK_b}$$

$$\alpha = \frac{1}{1 + \frac{10^{-pOH}}{10^{-pK_b}}} \Rightarrow \frac{1}{1 + 10^{(pK_b - pOH)}}$$

17. (b) $HA + NaOH \longrightarrow NaA + H_2O$

milli-moles of salt NaA or $A^- = 40 \times 0.1 = 4$

Now $A^- + H^+ \longrightarrow HA$

	A^-	H^+	HA
Initial milli-moles	4	2	
Final milli-moles	2	—	2

Acidic buffer solution is formed and $[A^-] = [HA]$

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \Rightarrow pK_a = 5$$

Now $HA + NaOH \longrightarrow NaA + H_2O$

hydrolysis of A^- will takes place

$$[NaA] = \frac{\text{milli moles of acid}}{\text{Total volume}} = \frac{20 \times 0.2}{20 + 20} = 0.1$$

$$pH = \frac{1}{2}(pK_w + pK_a + \log C) = \frac{1}{2}[14 + 5 - 1] = 9$$

18. (c) Moles of H^+ produced $= 4 \times 10^{-3}$

$$\therefore \quad [H^+] = \frac{4 \times 10^{-3}}{0.1} = 0.04\ M$$

$$PO_4^{3-}(aq.) + H^+(aq.) \longrightarrow HPO_4^{2-}(aq.)$$

	PO_4^{3-}	H^+	HPO_4^{2-}
Initial milli-moles	0.02	0.04	
Final milli-moles	—	0.02	0.02

$$HPO_4^{2-}(aq.) + H^+(aq.) \longrightarrow H_2PO_4^-(aq.)$$

	HPO_4^{2-}	H^+	$H_2PO_4^-$
Initial milli-moles	0.06	0.02	0.02
Final milli-moles	0.04	—	0.02

Finally buffer solution of $H_2PO_4^-$ (acid) and HPO_4^{2-} (conjugate base) is formed

$$pH = pK_{a_2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.2 + \log \frac{0.04}{0.02} = 7.5$$

19. (b) $BOH + HCl \longrightarrow BCl + H_2O$

at equilibrium point $N_1V_1 = N_2V_2$; $V_2 = 20$ mL

$$\therefore \quad [BCl] = \frac{20 \times 0.08}{20 + 20} = 0.04$$

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

$$\therefore \quad pK_b = 5.4$$

$$B^+ + OH^- \longrightarrow BOH; \text{ Basic Buffer is formed}$$

	B^+	OH^-	BOH
Initial milli-moles	1.6	0.4	
Final milli-moles	1.2	—	0.4

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

$$= 5.4 + \log\left(\frac{1.2}{0.4}\right) = 5.4 + 0.48$$

$$\text{pOH} = 5.88$$

20. (b)

$$\begin{array}{lcccccl} & CO_3^{2-} & + & H^+ & \longrightarrow & HCO_3^- & \text{acidic buffer is formed.} \\ \text{Initial milli-moles} & 25 \times 0.04 & & 50 \times 0.25 & & 1 & \\ \text{Final milli-moles} & — & & 0.025 & & & \end{array}$$

$$\begin{array}{lcccc} & HCO_3^- & + \; H^+ & \longrightarrow & H_2CO_3 \\ \text{Initial milli-moles} & 1 & 0.25 & & \\ \text{Final milli-moles} & 0.75 & — & & 0.25 \end{array}$$

$$\text{pH} = \text{p}K_{a_1} + \log\frac{[HCO_3^-]}{[H_2CO_3]} = 6.4 + \log\left(\frac{0.75}{0.25}\right) = 6.88$$

21. (b) Let a is initial milli-moles of HA and molarity of NaOH solution is x

$$HA + NaOH \longrightarrow NaA + H_2O$$

In both case solution is acidic, so acidic buffer solution is formed.

$$5 = \text{p}K_a + \log\frac{10x}{a - 10x}$$

$$\Rightarrow \quad 5.60 = \text{p}K_a + \log\frac{20x}{a - 20x}$$

$$\Rightarrow \quad 0.60 = \log\frac{20x}{(a - 20x)} \times \frac{(1 - 10x)}{10x}$$

$$\Rightarrow \quad 4 = \frac{2(a - 10x)}{(a - 20x)} \Rightarrow a = 30x$$

$$\therefore \quad 5 = \text{p}K_a + \log\frac{10x}{20x}$$

$$\text{or} \quad \text{p}K_a = 5.3$$

22. (d)

$$\begin{array}{lccccc} & CO_3^{2-} & + & H^+ & \longrightarrow & HCO_3^- \\ \text{Initial milli-moles} & 50 \times 0.05 & & 40 \times 01 & & — \\ \text{Final milli-moles} & — & & 1.5 & & 2.5 \end{array}$$

$$\begin{array}{lcccc} & HCO_3^- & + \; H^+ & \longrightarrow & H_2CO_3 \\ \text{Initial milli-moles} & 2.5 & 1.5 & & — \\ \text{Final milli-moles} & 1 & — & & 1.5 \end{array}$$

$$\text{pH} = \text{p}K_{a_1} + \log\frac{[HCO_3^-]}{[H_2CO_3]} = 6.173$$

23. (c) At second equivalence point the only species present at appreciable concentration is HA^{2-}

So, $$\text{pH} = \frac{\text{p}K_{a_2} + \text{p}K_{a_3}}{2} = \frac{8 + 12}{2} = 10$$

$$[H^+] = 10^{-10}$$

and $$\frac{[H_3A]}{[A^{3-}]} = \frac{[H^+]^3}{K_{a_1}K_{a_2}K_{a_3}} = 10^{-7}$$

24. (c) Solubility $S = \dfrac{x}{M}$

$$\begin{array}{ccc} A_3B_2(s) \rightleftharpoons & 3A^{2-}(aq.) + & 2B^{3-}(aq.) \\ & 3S & 2S \end{array}$$

$$K_{sp} = (3S)^3 (2S)^2 = 108S^5$$

$$\frac{[B^{3-}]}{K_{sp}} = \frac{2S}{108S^5} = \frac{1}{54}\frac{M^4}{x^4}$$

25. (d) $K_{sp}\,(SrCrO_4) = [Sr^{2+}][CrO_4^{2-}]$

$$[CrO_4^{2-}] = \frac{3.5\times10^{-5}}{0.1} = 3.5\times10^{-4}$$

$K_{sp}\,(BaCrO_4) = [Ba^{2}][CrO_4^{2-}]$

$[CrO_4^{2-}]_{total} \simeq [CrO_4^{2-}]$ from $SrCrO_4$

$$[Ba^{2+}] = \frac{1.2\times10^{-10}}{3.5\times10^{-4}} = 3.4\times10^{-7}$$

27. (a) $[Ag^+]$ required for precipitation of AgCl

$$[Ag^+] = \frac{K_{sp}\,(AgCl)}{[Cl^-]} = 10^{-9}$$

$[Ag^+]$ required for precipitation of Ag_2CrO_4

$$= \sqrt{\frac{K_{sp}\,(Ag_2CrO_4)}{[CrO_4^{2-}]}} = \sqrt{\frac{10^{-12}}{10^{-4}}} = 10^{-4}$$

At this point, the concentration of Cl^- ion in the solution can be calculated from K_{sp} (AgCl)

$$\therefore \quad [Cl^-] = \frac{K_{sp}\,(AgCl)}{[Ag^+]} = \frac{10^{-10}}{10^{-4}} = 10^{-6}\,M$$

28. (b) After mixing $[Ag^+] = 0.2\,M$; $[NH_3] = 1\,M$

Due to very high value of K_f; Ag^+ mainly converted into complex

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

Initial concentration $\quad 0.2 \quad 1$

At equilibrium $\quad x \quad 0.6 \quad \simeq 0.2$

$$Ag(NH_3)_2^+(aq.) \rightleftharpoons Ag(NH_3)^+(aq.) + NH_3(aq.)$$

At equilibrium $\quad 0.2 - y \quad y \quad 0.6 + y$

$\quad \simeq 0.2 \quad \simeq 0.6$

$$\frac{1}{K_{f_2}} = \frac{y\times0.6}{0.2} \Rightarrow \frac{0.1}{10^4};\ y = [Ag(NH_3)^+] \Rightarrow 3.33\times10^{-5}M$$

29. (a)

$$AgCl(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + Cl^-(aq.)$$

$$K_1 = 1.6\times10^{-10}\times10^7 = 1.6\times10^{-3}$$

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

$$AgCN(s) + 2NH_3(aq.) \rightleftharpoons Ag(NH_3)_2^+(aq.) + CN^-(aq.)$$

$$K_2 = 2.5\times10^{-16}\times10^7 = 2.5\times10^{-9}$$

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

$$\frac{[Cl^-]}{[CN^-]} = \frac{1.6\times10^{-3}}{2.5\times10^{-9}} = 6.4\times10^5$$

$$K_1 = \frac{x^2}{(1-2x)^2} \quad \Rightarrow \quad \frac{x}{1-2x} = 0.04$$

$$x = 0.037$$

$$\therefore \quad [\mathrm{CN^-}] = \frac{0.037}{6.4 \times 10^5} = 5.78 \times 10^{-8}$$

32. (c)

$$\mathrm{AgBr}(s) \rightleftharpoons \mathrm{Ag^+}(aq.) + \mathrm{Br^-}(aq.);\ K_{sp}$$

$$\mathrm{Ag^+}(aq.) + 2\mathrm{S_2O_3^{2-}}(aq.) \rightleftharpoons \mathrm{Ag(S_2O_3)_2^{3-}}(aq.);\ K_f$$

$$\underset{0.1-2x}{\mathrm{AgBr}(s) + 2\mathrm{S_2O_3^{2-}}(aq.)} \rightleftharpoons \underset{x}{\mathrm{Ag(S_2O_3)_2^{3-}}(aq.)} + \underset{x}{\mathrm{Br^-}(aq.)};\ K_{sp} \cdot K_f = 25$$

Value K_f is very higher so we can assume almost $\mathrm{Ag^+}$ converts into complex

33. (d)

$$\mathrm{Ag_2CrO_4}(s) \rightleftharpoons \underset{2x+2y}{2\mathrm{Ag^+}(aq.)} + \underset{x}{\mathrm{CrO_4^{2-}}(aq.)}$$

$$\mathrm{Ag_2C_2O_4}(s) \rightleftharpoons \underset{2y+2x}{2\mathrm{Ag^+}(aq.)} + \underset{y}{\mathrm{C_2O_4^{2-}}(aq.)}$$

$$\frac{K_{sp_1}}{K_{sp_2}} = \frac{x}{y} = \frac{2 \times 10^{-12}}{2 \times 10^{-11}} \Rightarrow \frac{x}{y} = 0.1$$

$$2 \times 10^{-11} = (2x + 2y)^2 \cdot y$$

$$2 \times 10^{-11} = 4.84y^3$$

$$y = 1.6 \times 10^{-4};$$

$$\therefore \quad x = 0.16 \times 10^{-4}$$

$$\text{Total } [\mathrm{Ag^+}] = 2x + 2y$$

$$= (2 \times 0.16 + 2 \times 1.6) \times 10^{-4}$$

$$= 3.52 \times 10^{-4}$$

34. (b) $K_{sp} = [\mathrm{Zn^{2+}}][\mathrm{S^{2-}}]$

$$[\mathrm{S^{2-}}] = \frac{10^{-21}}{0.01} = 10^{-19}$$

$$\text{for } K_{a_1} \cdot K_{a_2} = \frac{[\mathrm{H^+}]^2[\mathrm{S^{2-}}]}{[\mathrm{H_2S}]}$$

$$10^{-20} = \frac{[\mathrm{H^+}]^2 \times 10^{-19}}{0.1} \Rightarrow [\mathrm{H^+}] = 0.1$$

or $\quad \mathrm{pH} = 1$

35. (d) Dissolved $\mathrm{Al(OH)_3}$ present in solution as $\mathrm{Al^{3+}}(aq.)$ as well as $\mathrm{Al(OH)_4^-}(aq.)$

$$\therefore \quad S = [\mathrm{Al^{3+}(aq.)}] + [\mathrm{Al(OH)_4(aq.)}]$$

$$S = \frac{K_{sp}}{[\mathrm{OH^-}]^3} + K_c \cdot [\mathrm{OH^-}]$$

for minimum solubility

$$\frac{dS}{d(\mathrm{OH^-})} = 0$$

$$\text{or} \quad -\frac{K_{sp} \times 3}{[\mathrm{OH^-}]^4} + K_c = 0$$

$$[\mathrm{OH^-}] = \left(\frac{3K_{sp}}{K_c}\right)^{1/4}$$

Level 3

Passage-1

2. (b) $[\mathrm{HCl}] = \dfrac{0.01}{0.1} = 0.1\,M$

$$\mathrm{pOH} = 4.74 + \log\left(\frac{0.3+0.1}{0.2-0.1}\right) = 5.34$$

$$\therefore \quad \mathrm{pH} = 14 - 5.34 = 8.66$$

Passage-3

3. (c) When acid is half neutralized $\mathrm{pH} = \mathrm{p}K_a$

$\therefore \quad \mathrm{p}K_a = 5$

4. (a) $K_{\mathrm{eq}} = \dfrac{K_a\,(\mathrm{HB})}{K_a\,(\mathrm{HA})} = \dfrac{10^{-5}}{10^{-6}} = 10$

5. (b) When $V_{\mathrm{NaOH}} = 0$ mL; $\mathrm{pH} = 3$

or $\quad [\mathrm{H^+}] = 0.001$

$$K_{a(\mathrm{HB})} = \frac{C\alpha^2}{(1-\alpha)} = \frac{(0.001)\,\alpha}{1-\alpha} = 10^{-5}$$

$$\alpha = 0.01$$

$$C = \frac{0.001}{0.01} = 0.1$$

$$C = \frac{n_{\mathrm{HB}}}{V}$$

$$0.1 = \frac{5}{V};\ V = 50 \text{ mL}$$

$$\therefore \quad [\text{Na}B] = \frac{\text{milli-moles of acid}}{\text{total volume}} = \frac{5}{50+50} = 0.05$$

$$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$$

$$= \frac{1}{2}[14 + 5 + \log(0.05)]$$

$$= 8.85$$

6. (a) For best indicator, pH $\simeq$ $\text{p}K_{\text{In}}$ of an indicator as well as pH transition range of the indicator must coincide with the steep portion of the titration curve.

One or More Answers is/are Correct

21. (b,c,d)

(a) $S = \sqrt{K_{sp}} = 10^{-5}\ \text{mol lit}^{-1}$

(b) $s = 10^{-5}\ \text{mol lit}^{-1}$

(c) $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

$$S+2 \quad S$$

$$10^{-10} = (S+2)S \Rightarrow S = \frac{10^{-10}}{2} = 5\times10^{-11}$$

(d)

$$\text{AgCl}(s) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$$

$$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^2 + \text{Cl}^-$$

$$\text{AgCl}(s) + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+ + \text{Cl}^-$$

$$K = \frac{[\text{Ag}(\text{NH}_3)_2]^+[\text{Cl}^-]}{[\text{NH}_3]^2} = K_{sp}\times K_f$$

$$\frac{S^2}{(2-S)^2} = 10^{+8}\times10^{-10} = 10^{-2}$$

$$\frac{S^2}{(2-S)^2} = 10^{-1}$$

$$10S = 2-S$$

$$S = \frac{2}{11} = 0.182\ M$$

22. (a,c)

$$\text{H}_2A \rightleftharpoons \text{H}^+ + \text{H}A^-;$$

At equation $\quad C-X \quad x+y \quad x-y$

At equation $\quad \text{H}A^- \rightleftharpoons \text{H}^+ + A^{2-}$

$$x-y \quad x+y \quad y$$

$pK_{a_2} - pK_{a_1} = 12-5 = 7$

$\because$ y is very less so $x+y \approx x$

$x-y \approx x$

$K_{a_2} = y = 10^{-12};\quad pK_{a_2} = 12$

$$\therefore K_{a_1} = \frac{x^2}{c-x}$$

$$\text{pH} = \frac{1}{2}[\text{p}K_{a_1} - \log c]$$

$$3 = \frac{1}{2}[pK_{a_1} + 1] \qquad pK_{a_1} = 5$$

25. (a,b,c)

$$pH_1 = 8 \log \frac{25}{75} = 8 + \log \frac{1}{3}$$

$$pH_2 = 8 + \log \frac{75}{25} = 8 + \log 3$$

$$\text{Change in pH} = \log 3 - \log \frac{1}{3} = 2 \log 3$$

Subjective Problems

13. Let's assume simultaneous solubility of $SrCO_3$ as $x\,M$ while SrF_2 as $y\,M$

$$SrCO_3(s) \rightleftharpoons Sr^{2+}(aq) + CO_3^{2-}(aq)$$

At eq. $\quad (x+y)M \quad xM \qquad ; K_{sp_1} = (x+y)x$

$$SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq) \quad ; 2.5 \times 10^{-10} = (x+y)x \qquad \ldots(1)$$

At eq. $\quad (y+x)M \quad 2yM \qquad ; K_{sp_2} = (x+y)(2y)^2$

$$10^{-10} = 4y^2(x+y) \qquad \ldots(2)$$

$$2.5 = \frac{x}{4y^2}$$

$$10y^2 = x = 10^{-3}$$

$$10y^2 = x = 10^{-3}$$

$$y^2 = 10^{-4}$$

$$y = 10^{-2}M \qquad \therefore\ [F^-] = 2y = 2 \times 10^{-2}\,M$$

14. $H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O$

$$pH_1 = \frac{1}{2}(pK_{a_1} + pK_{a_2}) = \frac{1}{2}(4.6 + 8) = 6.3$$

$$N_1V_1 = N_2V_2$$

$$N_1 \times 10 = 0.1 \times 20$$

$$N_1 = 0.2$$

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

$$c = \frac{2m\text{ mole}}{50\text{ mL}} = \frac{1}{25}M$$

$$pH_2 - pH_1 = 10.3 - 6.3 = 4$$

15. $NaCN$; Na_3PO_4; Na_2CO_3; $NaHCO_3$; $Na_2C_2O_4$; Na_2HPO_4