Chapter 12

IONIC EQUILIBRIUM

Ionic equilibrium is the study of equilibrium in the reactions where the formation of ions takes place in an aqueous solution.

1. ELECTROLYTES

Electrolytes are those compounds which on dissolving in polar solvents like water break into ions.

1.1 Classification of Electrolytes

Electrolytes can be classified based on their strength into two categories:

Strong electrolytes: Those electrolytes that easily break into ions and give almost complete dissociation. E.g. HCl, NaOH, NaCl, HNO_3, $HClO_4$, H_2SO_4 etc.

Weak electrolytes: Those electrolytes which dissociate partially. E.g. CH_3COOH, NH_4OH, HCN, $H_2C_2O_4$, and all organic acids and bases, etc. Electrolytes can be further classified based on the kind of compound they are- Acids, Bases, and Salts

2. CONCEPT OF ACIDS AND BASES

Different concepts have been put forward to explain acids and bases.

1. Arrhenius Concept
2. Bronsted-Lowry Concept
3. Lewis Concept

2.1 Arrhenius Concept

This theory defines acids and bases from the perspective of water as a solvent.

2.1.1 Arrhenius Acids

Those compounds which will increase H^+ ion concentration in water.

$$HA \rightarrow H^+ + A^-$$

HCl, HNO_3, H_2SO_4 are acids because they dissociate in water and give H^+ ions.

$$HNO_3(aq) \rightarrow H^+(aq) + NO^-_3(aq)$$

$$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO^{2-}_4(aq)$$

2.1.2 Arrhenius Base

A base is a substance that given hydroxyl ions in water.

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

2.1.3 Neutralization

According to Arrhenius's theory, neutralization is a process in which H^+ ions and OH^- ions combine to form a water molecule.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O$$

When acids and bases are mixed in an aqueous solution, salts and water are formed and the properties of acids and bases are destroyed.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

2.1.4 Limitations of Arrhenius Concept

Arrhenius's concept does not explain the acidic and basic behaviour of the substances in solvents other than water such as alcohol, liquid ammonia, etc.

It could not explain the acidic and basic behaviour of certain substances: CO_2, SO_2, SO_3, etc. are acids but do not contain H atom. They produce H^+ ions in the solution

$$CO_2 + H_2O \rightleftharpoons CO_3^{2-}(aq) + 2H^+(aq)$$

Similarly, NH_3, CaO, MgO, etc. are bases that do not contain the OH^- group but produce OH^- ions in solution.

$$NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$CaO + H_2O \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

2.2 Bronsted-Lowry Concept

2.2.1 Acid and Base

Acid is a substance that tends to give a proton (H^+) and a base is a substance that tends to accept a proton (H^+).

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

In the above examples, H_2O is donating proton hence acting as acid. NH_3 is accepting the proton hence acting as base.

2.2.2 Amphiprotic Species

In the following examples, H_2O acts as a base whereas SH^- and NH^+_4 ions, etc. act as acids.

$$SH^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$$

$$NH_4^+ + 2H_2O \rightleftharpoons H_3O^+ + NH_4OH$$

Water may act as an acid as well as a base and is called amphiprotic.

Amphiprotic species may be an ion or neutral molecule, for example, H_2O, SH^-, $HCO^-_{3,}$ etc.

$$HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

2.2.3 Conjugate Acid-Base Pairs

Acids and bases which differ by a proton (H^+) only are called conjugate acid-base.

The pair having one H^+ less is a conjugate base whereas the pair having one H^+ more is conjugate acid.

$$\underset{\text{Acid}-1}{HCl} + \underset{\text{Base}-1}{H_2O} \rightleftharpoons \underset{\text{Acid}-2}{H_3O^+} + \underset{\text{Base}-2}{Cl^-}$$

2.2.4 Limitations of Bronsted Lowry Concept

This concept cannot explain the reaction between acidic oxides such as CO_2, SO_2, SO_3, etc., and basic oxides such as CaO, MgO, etc. because there is no proton transfer.

$$CaO + CO_2 \rightarrow CaCO_3$$

BF_3, $AlCl_3$, $FeCl_3$ etc. behave like acids but they do not contain H-atom. Their acidic character cannot be explained by the Bronsted-Lowry concept.

2.3 Lewis Concept

2.3.1 Acid and Base

According to Lewis's concept, acid is a species that can accept a pair of electrons and base is a species that can donate a pair of electrons.

E.g. $BF_3 + NH_3 \rightleftharpoons H_3N \rightarrow BF_3$

In the above reaction, BF_3 is a Lewis acid and NH_3 is a Lewis base.

2.3.2 Types of Lewis Acids

(i) Molecules with a Central Atom Having Incomplete Octet:

All the electron-deficient molecules act as Lewis's acids e.g., BF_3, BCl_3, BI_3, $AlCl_3$, $GaCl_3$, BeF_2, etc.

(ii) Molecules with Central Atom Having Empty d-Orbitals

Molecules with central atom having empty d-orbitals : e.g., SiX_4, PX_3, PX_5, SF_4, AlF_3, $SnCl_3$, AsF_5 etc.

(iii) Cations:

Cations with noble gas configuration (e.g., Na^+, Mg^{2+}, Al^{3+}, etc.) have little affinity for an electron while ions like H^+, Ag^+, Cu^{2+}, Fe^{3+}, etc. have more affinity.

(iv) Molecules whose central atom is linked with more electronegative atom by double bond:

Example: CO_2, SO_2, SO_3

2.3.3 Types of Lewis Bases

(i) Molecules Having Lone Pair of Electrons :

Alcohols $\left(R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H\right)$, amines $\left(R\overset{\cdot\cdot}{N}H_2\right)$,

$\overset{\cdot\cdot}{N}H_3$, $\overset{\cdot\cdot}{P}H_3$, $\overset{\cdot\cdot}{P}Cl_3$, $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-R$, $H_2\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$ etc.

(ii) Molecules Containing Multiple Bonds:

$CH_2 = CH_2$, Cyclopentadienyl anion etc.

2.3.4 Limitations of Lewis Concept

It does not explain the behaviour of protonic acids such as HCl, H_2SO_4, HNO_3, etc. which do not accept electron pairs.

It does not predict the relative strength of acids and bases.

According to this concept, neutralization is treated as a coordination reaction. But coordination reaction are slow, but neutralization reaction are extremely fast.

3. DISSOCIATION OF WEAK ACIDS AND BASES

Unlike strong acids and bases, weak acids and bases dissociate partially and their comparative dissociation is expressed in terms of the degree of dissociation(a).

3.1 Degree of Dissociation

It is a measure to express the extent of dissociation of an electrolyte in solution.

Strong electrolytes have a high value of the degree of dissociation while for weak electrolytes its value is low. It is calculated as

$$\alpha = \frac{\text{Moles of electrolyte dissociated at time}}{\text{Moles of electrolyte added initially}}$$

3.2 Factors Affecting the Degree of Dissociation

3.2.1 Nature of Electrolyte

For weak electrolytes α ranges between 1-10% normally and for strong electrolytes α ranges between 90-100%.

3.2.2 Nature of the Solvent

The greater the value of the dielectric constant of the solvent, the greater is the degree of dissociation of the electrolyte.

3.2.3 Dilution or Concentrations

With the dilution of solution of a weak electrolyte α increases and at infinite dilution, dissociation is 100% (or $\alpha = 1$).

3.2.4 Temperature

Since dissociation is an endothermic process, hence, increase in temperature favours the dissociation.

3.2.5 Presence of Other Substances

The degree of dissociation of a weak electrolyte is suppressed by the presence of common ion furnished by a strong electrolyte (common ion effect).

4. OSTWALD'S DILUTION LAW

For a weak electrolyte at a constant temperature, the degree of ionization is directly proportional to the square root of the volume containing one mole of the electrolyte or inversely proportional to the square root of molar concentration.

When a weak electrolyte (AB) is dissolved in water, there exists an equilibrium between the un-ionized molecules and ions formed.

$$\left[AB \rightleftharpoons A^+ + B^-\right]$$

$$K_c = \frac{\left[A^+\right]\left[B^-\right]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} \cong C\alpha^2$$

$$\text{or}\quad \alpha = \sqrt{\frac{K_c}{C}} \Rightarrow \alpha \propto \sqrt{\frac{1}{C}}$$

If V is the volume in litre containing one mole of the weak electrolyte, then $C = \frac{1}{V}$

$$\alpha = \sqrt{K_c \times V} \Rightarrow \alpha \propto \sqrt{V}$$

Thus the degree of ionization (a) increases with dilution, or decrease in the molar concentration (C) of the weak electrolyte.

4.1 Ionization Constants of Weak Acid and Base

4.1.1 Ionization Constants of a Weak Acid

Let us consider the dissociation of a weak acid (HA).

$$HA(aq) + H_2O \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

Applying law of chemical equilibrium

$$K = \frac{\left[A^-\right]\left[H_3O^+\right]}{[HA][H_2O]}$$

As H_2O is solvent and its concentration remains almost constant (55.5 mol/L), let $K[H_2O] = K_a$.

$$K_a = \frac{\left[A^-\right]\left[H_3O^+\right]}{[HA]}$$

K_a is called the ionization or dissociation constant of the weak acid.

NOTE

Greater the value of α or H^+ ions produced at a given temperature and concentration, the greater is the acid strength. The larger the value of K_a at a given temperature, the stronger is the acid.

4.1.2 Ionization Constants of a Weak Base

Similarly, for a weak base : $BOH + aq \rightleftharpoons B^+(aq)OH^-(aq)$

$$K_b = \frac{\left[B^+\right]\left[OH^-\right]}{[BOH]}$$

K_b is called the ionization or dissociation constant of the weak base.

$$\left[OH^-\right] = C\alpha$$

or

$$\left[OH^-\right] = \sqrt{K_b \times C}$$

NOTE

Greater the value of α or OH^- ions produced at a given temperature and concentration, the greater is the basic strength. The larger the value of K_b at a given temperature, the stronger is the base.

5. SELF-IONIZATION OF WATER

5.1 Dissociation Constant of Water

In pure water, one H_2O molecule donates a proton and another water molecule accepts a proton.

$$H_2O + H_2O \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$\text{or}\quad H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$$

This ionization is called the self-ionization of water.

Applying the law of chemical equilibrium,

$$K = \frac{\left[H_3O^+\right]\left[OH^-\right]}{[H_2O]} \qquad ...(1)$$

$$\text{Or}\quad K = \frac{\left[H^+\right]\left[OH^-\right]}{[H_2O]} \qquad ...(2)$$

K is called the ionization or dissociation constant of water.

5.2 Ionic Product of Water

Water is pure liquid and its concentration remains constant, i.e.,$[H_2O] = \text{constant}$.

Equation (1) or (2) may be written as,

$$K[H_2O]=[H^+][OH^-]$$

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

Or $$K_w=[H_3O^+][OH^-]$$

K_w is called the ionic product of water.

The product of the molar concentration of H^+ and OH^- ions in an aqueous solution is constant at constant temperature and it is called the ionic product of water (K_w). Value of K_w at 25°C (298 K) is 1.0×10^{-14}.

In pure water $[H^+]=[OH^-]$,

Therefore, $[H^+]=[OH^-]=1.0\times10^{-7}$ mol/L

On increasing the temperature, more water molecules ionize to give H^+ and OH^- ions.

Therefore, K_w increases with an increase in temperature.

But at all temperatures $[H^+]=[OH^-]$.

Acidic, basic or neutral aqueous solutions always contain H^+ and OH^- ions and the product of their molar concentrations at 25°C is always 1×10^{-14}, i.e.,

$$[H^+][OH^-]=1\times10^{-14}$$

Acidic solution : $[H^+]>[OH^-], [H^+]>10^{-7}$

Neutral solution : $[H^+]=[OH^-]=1\times10^{-7}$

Basic solution : $[H^+]<[OH^-], [H^+]<10^{-7}$

5.3 Relation Between K_a & K_b of Conjugate Acid-Base Pair

Let us consider a weak acid HA and its conjugate base is A^-.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a=\frac{[H^+][A^-]}{[HA]} \qquad ...(i)$$

and $A^- + H_2O \rightleftharpoons HA + OH^-$

$$K_b=\frac{[HA][OH^-]}{[A^-]} \qquad ...(ii)$$

Multiplying the above two equations (i) and (ii)

$$K_a \times K_b=[H^+][OH^-] \qquad ...(iii)$$

Or $K_a \times K_b = K_w = 1\times10^{-14}$

By taking logarithm and multiplying both the sides with negative sign :

$$-\log K_a - \log K_b = -\log K_w$$

$$pK_a + pK_b = pK_w = 14 \text{(at 25°C)}$$

$(pK_a = -\log K_a$ and $(pK_b = -\log K_b)$

6. pH SCALE

Sorensen (1909) suggested a convenient method to express H^+ ion concentration in terms of pH. This word is derived from a Danish word potenz meaning power.

"pH is defined as the negative logarithm of the molar concentration of hydrogen ion."

$$pH=-\log[H^+]$$

Similarly, pOH is equal to negative logarithm of OH- ion concentration.

$$pOH=-\log[OH^-]$$

Relation Between pH and pOH

$$K_w=[H^+][OH^-]=1\times10^{-14}$$

(at 298 K or 25°C)

Taking logarithm and multiplying both the sides with negative:

$$\therefore\ -\log K_w = -\log[H^+]-\log[OH^-]=14$$

or $pK_w = pH + pOH$

pH and pOH of an Acidic, Basic or Neutral Solution

Acidic solution :

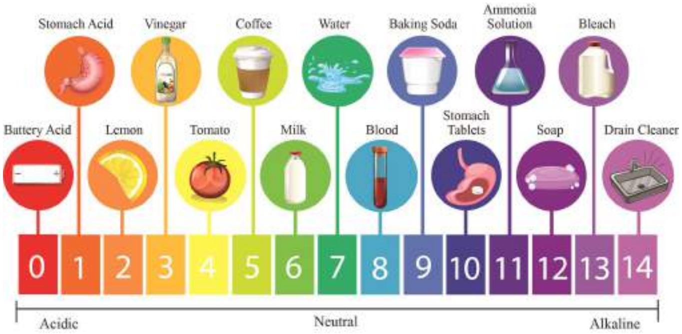
$pH<7,\ pOH>7,\ [H^+]>10^{-7},\ [OH^-]<10^{-7}$

Basic solution :

$pH>7,\ pOH<7,\ [H^+]<10^{-7},\ [OH^-]>10^{-7}$

Neutral solution :

$pH=pOH=7,\ [H^+]=[OH^-]=1\times10^{-7}$



pH of daily used items

7. pH CALCULATION OF ACIDS AND BASES

7.1 Calculation of pH for Strong Acids and Bases

1. For a strong acid : $[H^+]$ = Normality of the acid
2. For a strong base : $[OH^-]$ = Normality of the base
3. If the strength of the acid or base is given in molarity, it should be converted into normality

Normality = n × Molarity, n = 1,2,3,...

4. For monobasic acid or monoacid base :

Normality = Molarity

7.2 Calculation of pH of Weak Acids and Weak Bases

1. For a weak acid : $\left[H^+\right] = C\alpha = \sqrt{K_a \times C}$
2. For a weak base : $\left[OH^-\right] = C\alpha = \sqrt{K_b \times C}$
3. $\alpha = \sqrt{\dfrac{K_a}{C}}$ and $\alpha = \sqrt{\dfrac{K_b}{C}}$
4. $K_b \times K_a = K_w = \left[H^+\right]\left[OH^-\right] = 1 \times 10^{-14}$

$pH + pOH = 14$ (at 25°C)

7.3 pH of Mixtures of Strong Acids and Strong Bases

Equivalents (or milli-equivalents) of strong acids and strong bases are calculated. Acids and bases neutralize each other. One equivalent of acid is neutralized by one equivalent of a base. The equivalent of acid or base left is calculated. Now knowing the normality of the strong acid or strong base left, pH can be calculated.

Equivalents = Normality × Volume (in litres) and

Milli-equivalent(s) = Normality × Volume (in mL).

7.4 pH of Mixtures of Weak Acids or Weak Bases

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

K_a and C represent the dissociation constant and concentration of acid 1 and 2 respectively.

$$pH = -\log\left[H^+\right] = \frac{1}{2}pK_{a_1} + \frac{1}{2}pK_{a_2} - \frac{1}{2}\log C_1 - \frac{1}{2}\log C_2$$

For a mixture of weak bases, we use pK_{b_1} and pK_{b_2} in place of pK_{a_1} and pK_{a_2} to calculate pOH.

7.5 pH of Very Dilute Acids and Bases

When the solutions of acids or bases are concentrated, the H^+ or OH^- ions obtained from water are not considered.

It is because the ions obtained from water are negligible in comparison to ions obtained from acids or bases.

But in the case of very dilute solutions of acids or bases, ions obtained from water are not negligible in comparison to the ions obtained from acids or bases.

7.6 pH of Polyprotic Acids

A polyprotic acid is that which furnishes more than one proton per molecule in its solutions, e.g., H_2SO_4, H_3PO_4, H_2CO_3 etc.

For almost all the polyprotic acid value of K_{a1} is much larger than subsequent dissociation constants. So $[H^+]$ conc, is mainly determined by the first deprotonation constant (i.e., K_{a1}) except only for H_2SO_4 in which K_{a2} is also significant.

8. COMMON ION EFFECT

Weak electrolytes such as weak acids and weak bases dissociate to a small extent in an aqueous solution.

The dissociation of the weak electrolyte is further decreased in the presence of an ion common with the weak electrolyte.

"Suppression of dissociation of a weak electrolyte due to the presence of a strong electrolyte having a common ion is called common ion effect."

Let us consider the dissociation of CH_3COOH to which a small amount of CH_3COONa has been added.

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

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

According to Le Chatelier's principle, on increasing the concentration of CH_3COO^- ion, the equilibrium shifts in the backward direction. That is the dissociation of CH_3COOH is suppressed.

The dissociation of CH_3COOH is also suppressed in presence of HCl having H^+ common ion.

CH_3COOH is a weak acid, it dissociates partially to give CH_3COO^- and H^+ ions.

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

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]} \quad \text{or}$$

$$\left[H^+\right] = \frac{K_a\left[CH_3COOH\right]}{\left[CH_3COO^-\right]}$$

The value of the dissociation constant (K_a) is constant at a constant temperature.

In the presence of CH_3COONa, the concentration of CH_3COO^- ion increases. Therefore, the concentration of H^+ ion decreases, i.e., dissociation of CH_3COOH decreases.

9. BUFFER SOLUTIONS

"A buffer solution is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted."

9.1 Types of Buffer Solutions

Based on composition, buffer solutions are of three types:

(i) Acidic buffer: It is a mixture of a weak acid and its salt with a strong base, e. g., $CH_3COONa + CH_3COOH$, etc.

(ii) Basic buffer: It is a mixture of a weak base and its salt with a strong acid, e. g., $NH_4Cl + NH_4OH$, etc.

(iii) Salt buffer: It is a solution of a salt of a weak acid and a weak base, e. g., NH_4CN, CH_3COONH_4, etc.

9.2 Buffer Action

9.2.1 Buffer Action of Acidic Buffer

Suppose, a buffer solution contains CH_3COOH and CH_3COONa.

$$CH_3COOH \text{ and } CH_3COONa\,.$$

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

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

On adding an acid such as HCl, H_2SO_4, etc., the H^+ ions combine with CH_3COO^- ions forming weak acetic acid.

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

On adding a base such as NaOH, KOH, etc., the OH^- ions are neutralized by the H^+ ions produced by the weak acid CH_3COOH.

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

Since H^+ ions are removed from equilibrium, CH_3COOH dissociates to give more H^+ ions. The concentration of H^+ ions remains the same.

Thus the addition of strong acid or strong base does not change the pH of the buffer solution.

9.2.2 Buffer Action of Basic Buffer

Suppose, a buffer solution contains NH_4OH and NH_4Cl.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

On adding a small amount of strong acid such as HCl, the H^+ ions are neutralized by OH^- ions produced by the weak base NH_4OH.

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

Since OH^- ions are removed from equilibrium, NH_4OH dissociates to give more OH^- ions. The concentration of OH^- remains the same.

On adding a small amount of strong base such as NaOH, KOH, etc., the OH^- ions combine with NH_4^+ ions forming a weak base NH_4OH.

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

The pH of the buffer solution does not change.

Thus a buffer solution has reserve acidity and reserve basicity.

9.2.3 Buffer Action of Salt Buffer

An aqueous solution of CH_3COONH_4 is a buffer solution. It dissociates in water to produce CH_3COO^- and NH_4^+ ions.

$$CH_3COONH_4 \rightarrow CH_3COO^- + NH_4^+$$

On adding a small amount of strong acid, it is converted into weak CH_3COOH acid. Similarly, on adding a strong base, it is converted into a weak base NH_4OH. Therefore, the pH of the buffer solution does not change.

9.3 Calculation of pH of a Buffer Solution

9.3.1 pH of an Acidic Buffer Solution

pH of an acidic buffer solution is calculated from the Henderson equation.

$$\left[H^+\right] = \frac{K_a\left[\text{Acid}\right]}{\left[\text{Salt}\right]} \qquad ...(1)$$

pH may be derived by taking the logarithm of equation (1) and multiplying both sides by a minus (–).

$$-\log\left[H^+\right] = -\log K_a - \log\left[\text{Acid}\right] + \log\left[\text{Salt}\right]$$

$$\text{Or } pH = pK_a + \log\frac{\left[\text{Salt}\right]}{\left[\text{Acid}\right]} \qquad ...(2)$$

9.3.2 pH of a Basic Buffer Solution

the pH of the basic buffer solution is also calculated from the Henderson equation.

$$\left[OH^-\right] = \frac{K_b\left[\text{Base}\right]}{\left[\text{Salt}\right]} \qquad ...(3)$$

pOH may be derived by taking the logarithm of equation (3) and multiplying both sides by a minus (–).

$$pOH = pK_b + \log\frac{\left[\text{Salt}\right]}{\left[\text{Base}\right]}$$

$$pH = pK_w - pOH$$

9.4 Buffer Capacity of a Buffer Solution

The capacity of a buffer solution to keep its pH constant is called its buffer capacity.

The buffer capacity of a buffer solution is equal to the number of moles of an acid or base required to change the pH of one liter buffer solution by one unit.

$$\text{Buffer capacity} = \frac{\text{Moles of acid or base added in one litre of buffer}}{\text{Change in pH}}$$

The buffer capacity of an acidic buffer solution is maximum when [Acid] = [Salt]. For basic buffer solution: [Base] = [Salt].

9.5 Buffer Range of a Buffer Solution

For acidic buffer, buffer range is given by $pK_a \pm 1$

For basic buffer, buffer range is given by $pK_b \pm 1$

10. SALT HYDROLYSIS

"The interaction of cations/anions or both with water making the solution acidic or basic is called salt hydrolysis."

10.1 Salts of Strong Acids and Strong Bases

Salts of this type are not hydrolyzed, e.g., NaCl, KBr, $NaNO_3$, KNO_3, Na_2SO_4, $KClO_4$, etc.

It is because the cations on interaction with water produce strong bases such as NaOH, KOH, etc. and the anions on interaction with water produce strong acids (such as HCl, HNO_3, H_2SO_4, etc.) which are completely ionized in aqueous solution.

10.2 Salts of Weak Acids and Strong Bases

Salts of this type are hydrolyzed and the solution is alkaline due to the formation of OH^- ions. Hence, the pH of the solutions is more than 7.

Examples are CH_3COONa, KCN, Na_2CO_3, Na_3PO_4, K_2CO_3 etc.

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

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

In the salts of a weak acid and strong base, it is the anion that is hydrolyzed and produces weak acid. It is called anionic hydrolysis.

Suppose, the molar concentration of CH_3COONa solution is C and the salt is completely dissociated. The concentration of CH_3COO^- ion will be C mol/lit in solution. CH_3COO^- ion undergoes hydrolysis.

Suppose 'h' is the degree of hydrolysis.

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

Initial	C	0	0
At eq.	C(1 – h)	Ch	Ch

Applying law of equilibrium, the hydrolysis (K_h) is given by :

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{Ch \times Ch}{C(1-h)} = \frac{Ch^2}{(1-h)}$$

$$K_h = Ch^2 \text{ and } h = \sqrt{\frac{K_h}{C}} \qquad ...(2)$$

The weak acid (CH_3COOH) ionizes in solution,

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ...(3)$$

We know, ionic product of water

$$K_w = [H^+][OH] \qquad ...(4)$$

$$K_h = \frac{K_w}{K_a} \text{ and from equation (2)}$$

$$Ch^2 = K_h = \frac{K_w}{K_a}$$

$$\therefore \quad h = \sqrt{\frac{K_w}{K_a \times C}} \qquad ...(5)$$

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

Initial	C	0	0
At eq.	C(1 – h)	Ch	Ch

$$[OH^-] = Ch, \text{ But } [H^+] = \frac{K_w}{[OH^-]}$$

$$\therefore [H^+] = \frac{K_w}{Ch}$$

Substituting the value of h from equation (5)

$$[H^+] = \frac{K_w\sqrt{K_a C}}{C\sqrt{K_w}} = \frac{\sqrt{K_w K_a}}{C} \qquad ...(6)$$

Taking the logarithm of eq. (6) and multiplying both the sides by –1,

$$-\log[H^+] = -\log\sqrt{\frac{K_w K_a}{C}}$$

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

At 298 K, pK_w = 14, therefore, at 298 K

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

10.3 Salts of Strong Acids and Weak Bases

Salts of this type are hydrolyzed and the solution is acidic due to the formation of H^+ ions. Therefore, the pH of the solution is less than 7. Examples are NH_4Cl, $(NH_4)_2SO_4$, $CuSO_4$, $FeCl_3$, $AlCl_3$ etc.

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

In the salts of strong acid and weak base, it is the cation that is hydrolyzed and produces a weak base. It is called cationic hydrolysis.

Suppose, the concentration of NH_4^+ ion will be C mol/lit in solution. NH_4^+ ion undergoes hydrolysis. Suppose, degree of hydrolysis is 'h'.

$$\begin{array}{lcccc} & NH_4^+ + H_2O & \rightleftharpoons & NH_4OH & +H^+ \\ \text{Initial} & C & & 0 & 0 \\ \text{At eq.} & C(1-h) & & Ch & Ch \end{array}$$

Applying law of equilibrium:

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{Ch \times Ch}{C(1-h)} = Ch^2 \qquad ...(1)$$

$$h = \sqrt{\frac{K_h}{C}} \qquad ...(2)$$

The weak base (NH_4OH) ionizes in solution.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \qquad ...(3)$$

$$K_w = [H^+][OH^-] \qquad ...(4)$$

From equation (1), (3) and (4) $K_h = \dfrac{K_w}{K_b}$

and from equation (2), $Ch^2 = K_h = \dfrac{K_w}{K_b}$

$$\text{Or } h = \sqrt{\frac{K_w}{K_b \times C}} \qquad ...(5)$$

$$\begin{array}{lcccc} & NH_4^+ + H_2O & \rightleftharpoons & NH_4OH & +H^+ \\ \text{Initial} & C & & 0 & 0 \\ \text{At eq.} & C(1-h) & & Ch & Ch \end{array}$$

$\therefore [H^+] = Ch$, Substitute the value of h from equation (5).

$$[H^+] = C\sqrt{\frac{K_w}{K_b \times C}} = \sqrt{\frac{K_w \times C}{K_b}} \qquad ...(6)$$

Taking the logarithm of eq. (6) and multiplying both the sides by –1,

$$-\log[H^+] = -\frac{1}{2}[\log K_w - \log K_b + \log C]$$

$$\text{or } pH = \frac{1}{2}[pK_w - pK_b - \log C]$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C$$

10.4 Salts of Weak Acids and Weak Bases

Salts of this type are hydrolyzed. Weak acid and weak base are produced due to hydrolysis. Both cations and anions are hydrolyzed. The solution may be slightly acidic, basic, or neutral depending upon the relative strength of weak acid and weak base.

$K_a > K_b$ Solution is acidic $pH < 7$

$K_b > K_a$ Solution is basic $pH > 7$

$K_a = K_b$ Solution is neutral $pH = 7$

Examples are CH_3COONH_4, NH_4CN, $(NH_4)_2CO_3$, $(NH_4)_2S$, $AlPO_4$ etc.

Let us take the example of CH_3COONH_4. Suppose, the molar concentration of CH_3COONH_4 is C and the salt is completely dissociated in solution. The concentration of CH_3COO^- and NH_4^+ will be C. Suppose degree of hydrolysis is h.

$$\begin{array}{lccccc} & CH_3COO^- & + NH_4^+ + H_2O & \rightleftharpoons & CH_3COOH & + NH_4OH \\ \text{Initial} & C & C & & 0 & 0 \\ \text{Eq.} & C(1-h) & C(1-h) & & Ch & Ch \end{array}$$

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} \qquad ...(1)$$

$$K_h = \frac{C^2h^2}{[C(1-h)][C(1-h)]} = \frac{h^2}{(1-h)} \qquad ...(2)$$

If h is very small (1 – h) may be taken equal to 1.

$K_h = h^2$ or

$$h = \sqrt{K_h} \qquad ...(3)$$

Both CH_3COOH and NH_4OH ionize in solution.

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \qquad ...(4)$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-,$$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_4OH\right]} \qquad ...(5)$$

Ionic product of water $K_w = \left[H^+\right]\left[OH^-\right]$ . ..(6)

From equation (1), (4), (5) and (6)

$$K_h = \frac{K_w}{K_a \times K_b}$$

and from eq. (3) $K_h = h^2 = \dfrac{K_w}{K_a \times K_b}$

Or $$h = \sqrt{\frac{K_w}{K_a \times K_b}} \qquad ...(7)$$

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

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

Or $$\left[H^+\right] = \frac{K_a\left[CH_3COOH\right]}{\left[CH_3COO^-\right]} = \frac{K_aCh}{C(1-h)} = \frac{K_ah}{1-h} \qquad ...(8)$$

From the equation of the hydrolysis of CH_3COO^- and NH_4^+ ions,

$$\left[CH_3COOH\right] = Ch, \left[CH_3COO^-\right] = C(1-h)$$

But from equation (2), $\dfrac{h}{1-h} = \sqrt{K_h}$

Putting the value of $[H^+]$ from equation (8),

$$\left[H^+\right] = K_a \times \sqrt{K_h}$$

Or $$\left[H^+\right] = K_a \times \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}} \qquad ...(9)$$

Taking the logarithm of eq. (9) and multiplying both the sides by –1,

$$-\log\left[H^+\right] = -\frac{1}{2}\left[\log K_w + \log K_a - \log K_b\right]$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

11. SOLUBILITY AND SOLUBILITY PRODUCT

11.1 Solubility

The amount (or moles) of a substance dissolved in 1 litre of solution at a given temperature is termed solubility.

Based on solubility, salts are classified into three types:

I)	Soluble	Solubility > 0.1 M
II)	Slightly soluble	0.01 M $<$ solubility < 0.1 M
III)	Sparingly soluble	Solubility < 0.01 M

11.2 Solubility Product (K_{sp})

In a saturated solution of a sparingly soluble salt, there exists an equilibrium between the undissolved solid salt and the ions in the solution. Let us take the example of sparingly soluble salt $BaSO_4$.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Applying law of equilibrium,

$$K = \frac{\left[Ba^{2+}\right]\left[SO_4^{2-}\right]}{\left[BaSO_4\right]}$$

Or $K\left[BaSO_4\right] = \left[Ba^{2+}\right]\left[SO_4^{2-}\right]$

For a pure solid substance, the concentration remains constant.

$$K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right]$$

Here K_{sp} is called the solubility product.

At a given temperature, K_{sp} is equal to the product of the molar concentration of the ions in its saturated solution, each concentration raised to the power equal to the number of ions produced by the dissociation of one molecule of the electrolyte.

In general, for a sparingly soluble electrolyte A_xB_y,

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-},$$

$$K_{sp} = \left[A^{y+}\right]^x\left[B^{x-}\right]^y$$

11.3 Relation Between Solubility (S) and Solubility Product (K_{sp})

Type of salt	Expression of K_{sp}	Example
AB type	$K_{sp} = S^2$	AgCl, AgBr, $BaSO_4$
AB_2 type	$K_{sp} = 4S^2$	$CaCl_2$,PbI_2,Ag_2CO_3
AB_3 type	$K_{sp} = 27S^4$	$AlCl_3$,$FeCl_3$,Na_3PO_4
A_2B_3 type	$K_{sp} = 108S^5$	$Al_2(SO_4)_3$,$La_2(CO_3)_3$

11.4 Ionic Product

At a given temperature, the ionic product of an electrolyte in a solution is equal to the product of the molar concentration of the ions, each concentration raised to the power equal to the number of ions produced by the dissociation of one molecule of it.

K_{sp} applies to saturated solutions only whereas ionic product applies to all solutions.

Predition of Precipitation in solution

Condition	Result
$IP > K_{sp}$	Precipitation occurs
$IP > K_{sp}$	Solution is fomed
$IP > K_{sp}$	Saturated solution is formed

12. INDICATORS

12.1 Acid Base Indicators

An indicator is a substance, which is used to indicate the completion (endpoint or equivalence point) of a chemical reaction by a change in its colour.

In general, indicators are either weak acids or weak bases with a characteristic colour of unionized and ionized form.

The change in colour of an acid-base indicator occurs in a pH range. This range is different for different indicators.

pH range of indicators

Indicator	pH range	Acidic medium	Basic medium
(i) Methyl orange	3.2-4.5	Red	Yellow
(ii) Methyl red	4.2-6.5	Red	Yellow
(iii) Litmus	5.5-7.5	Red	Blue
(iv) Phenol red	6.8-8.4	Yellow	Red
(v) Phenolphthalein	8.3-10.5	Colourless	Pink

12.2 Theories of Acid-Base Indicators

12.2.1 Ostwald's Theory

According to this theory, the colour change is due to the ionization of the acid-base indicator.

The colours of the unionized indicator and ion obtained from it, are different. An acidic indicator yields a coloured anion while a basic indicator gives coloured cation.

For example, Phenolphthalein

It can be represented as HPh, it ionizes as –

$$HPh \rightleftharpoons H^+ + Ph^-$$

$$K_{in} = \frac{[H^+][Ph^-]}{[HPh]} \qquad \Rightarrow pH = pK_{in} + \log\frac{[Ph^-]}{[HPh]}$$

where K_{in} is the ionization constant of the indicator.

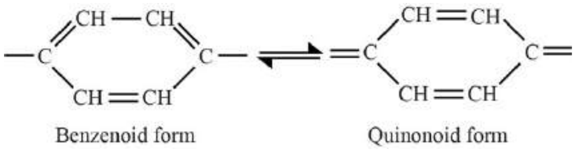
In presence of an acid, the ionization of HPh is practically negligible. Thus the solution remains colourless.

On addition of alkali, hydrogen ions are neutralized and equilibrium shifts in the forward direction and the solution becomes pink.

12.2.2 Quinonoid Theory

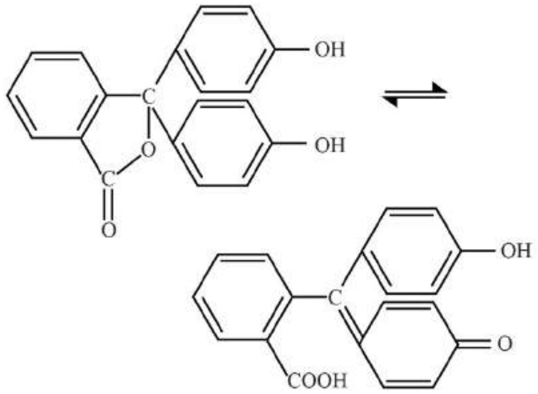
(i) All the acid-base indicators contain aromatic rings and exist in two tautomeric forms, benzenoid and quinonoid, which remain in equilibrium with each other.

(ii) The colour of the quinonoid form is usually darker than the benzenoid form. Between two forms, one is more stable in acid medium while the other is in basic medium.



Benzenoid and quinonoid forms

Benzenoid form of phenolphthalein is colourless and stable in an acidic medium. When medium changes from acidic to basic benzenoid form is converted into a quinonoid form which provides pink colour to the solution.



Benzenoid and quinonoid forms of phenolphthalein

13. ACID-BASE TITRATIONS

An acid-base titration is a method used to find the amount of an unknown acidic or basic substance through acid-base reactions.

The analyte is the solution with unknown molarity while the titrant is the solution with known molarity that is made to react with the analyte.

A suitable indicator is used to detect the endpoint of the titration reaction.

At the endpoint of the reaction, the gram equivalents of the acid consumed are always equal to the gram equivalents of the base consumed.

For example: $NaOH + HCl \rightarrow NaCl + H_2O$

Gram equivalents of HCl = Gram equivalents of NaOH

$$N_1V_1(HCl) = N_2V_2(NaOH)$$

$$n_1M_1V_1(Acid) = n_2M_2V_2(Base)$$

For example, if we have to calculate the volume of 1N HCl required to neutralize 0.5 N 100 ml KOH,

Then $N_1 = 1N$, $N_2 = 0.5\,N$ and $V_2 = 100$ ml

According to $N_1V_1 = N_2V_2$

$V_1 = 0.5 \times 100 = 50$ ml

So. 50 ml HCl is required to neutralize the given KOH.

SUMMARY

IONIC EQUILIBRIUM

Acid base concept

Arrhenius concept
Acid gives H_3O^+ and base gives OH^- in water

Bronsted-Lowry concept
Acid donates proton and base accepts proton

Lewis concept
Acid accepts electron pair and base donates electron pair

Ostwald's Dilution Law

Valid for weak electrolytes

$K_c = 3\alpha$ or $\alpha = \sqrt{\left(\frac{K_C}{C}\right)}$

So $\alpha \propto \frac{1}{\sqrt{C}}$ or $\alpha \propto \sqrt{V}$ where, V is the volume of solution at infinite dilution.

Ionic Product of Water

$H_2O(1) \rightleftharpoons H^+(aq) + OH^-(aq)$

$K_w = [H^+][OH^-] = 1 \text{ x } 10^{-14}$

$\therefore$ $[OH^-] = [H^+] = 1.0\text{x}10^{-7}$ M at 298K

$pK_w = pK_a + pK_b = 14$

pH Scale

$pH = -\log_{10}[H^+]$

$pH + pOH = pK_w = 14$ (at 25°)

For weak acid; $pH = 1/2\ (pK_a - \log C)$

For weak base; $pOH = 1/2\ (pK_b - \log C)$

For mixture of two weak acids; $[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$

Salt Hydrolysis

Salt of strong acid and strong base (e.g., NaCl)
This type of salt does not get hydrolysed.
Neutral solution with pH = 7

Salt of weak acid and strong base (e.g., CH_3COONa)
This type of salt give acidic solution on hydrolysis.
$K_h = K_w/K_a$; $pH = 7 + ½\ pK_a + ½ \log C$

Salt of strong acid and weak base (e.g., NH_4Cl)
This type of salt give basic solution on hydrolysis.
$K_h = K_w/K_b$; $pH = 7 - ½\ pK_b - ½ \log C$

Salt of weak acid and weak base (e.g., CH_3COONH_4)
This type of salt may give acidic,basic or neutral solution.
$K_h = K_w/(K_a \times K_b)$; $pH = 7 + ½\ pK_a - ½\ pK_b$

Buffer Solutions

Acidic Buffer
Example: $CH_3COOH + CH_3COONa$
$pH = pK_a + \log [Salt]/[Acid]$

Basic Buffer
Example: NH_4OH and NH_4Cl
$pOH = pK_b + \log [Salt]/[Base]$

Mixed Buffer
Example CH_3COONH_4
$pH = 7 + ½\ pK_a - ½\ pK_b$

Solubility Product

For AB type : $K_{sp} = S^2$ (Example : AgCl)

For AB_2 type : $K_{sp} = 4S^3$ (Example : $CaCl_2$)

For AB_3 type : $K_{sp} = 27S^4$ (Example : $AlCl_3$)

For A_2B_3 type : $K_{sp} = 108S^5$ (Example : $Al_2(SO_4)_3$)

SOLVED EXAMPLES

Example - 1

Calculate the pH of the following solutions:

(a) 2g of TlOH dissolved in water to give 2 litre of the solution

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of the solution

(c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.

Sol.

(a) Molar conc. of TlOH

$$= \frac{2g}{(204+16+1)g\,mol^{-1}} \times \frac{1}{2L} = 4.52 \times 10^{-3}\,M$$

$$\therefore \left[OH^-\right] = [TlOH] = 4.52 \times 10^{-3}\,M$$

$$\left[H^+\right] = 10^{-14}/(4.52 \times 10^{-3}) = 2.21 \times 10^{-12}\,M$$

$$pH = -\log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$$

(b) Molar conc. of $Ca(OH)_2 = \frac{0.3g}{(40+34)\,g\,mol^{-1}} \times \frac{1}{0.5L} = 8.11 \times 10^{-3}\,M$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-$$

$$\therefore \left[OH^-\right] = 2\left[Ca(OH)_2\right] = 2 \times (8.11 \times 10^{-3})\ M$$

$$= 16.22 \times 10^{-3}\,M$$

$$pOH = -\log(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$$

$$pH = 14 - 1.79 = 12.21$$

(c) Molar conc. of NaOH

$$= \frac{0.3g}{40g\,mol^{-1}} \times \frac{1}{0.2L} = 3.75 \times 10^{-2}\,M$$

$$\left[OH^-\right] = 3.75 \times 10^{-2}\,M$$

$$pOH = -\log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$$

$$\therefore\ pH = 14 - 1.43 = 12.57$$

(d) $M_1V_1 = M_2V_2 \therefore 13.6M \times 1mL = M_2 \times 1000mL$

$$\therefore\ M_2 = 1.36 \times 10^{-2}\,M$$

$$\left[H^+\right] = [HCl] = 1.36 \times 10^{-2}\,M.$$

$$pH = -\log(1.36 \times 10^{-2}) = 2 - 0.1335 = 1.87$$

Example - 2

The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a bromoacetic acid.

Sol. $$CH_2(Br)COOH \rightleftharpoons CH_2(Br)COO^- + H^+$$

Intial Conc	C	0	0
Conc at eqm	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$$

$$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$$

$$\left[H^+\right] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2}\,M$$

$$pH = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

Example - 3

The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate the ionization constant and pK_b.

Sol. $$Cod + H_2O \rightleftharpoons CodH^+ + OH^-$$

$$pH = 9.95 \therefore pOH = 14 - 9.95 = 4.05\ i.e.$$

$$-\log\left[OH^-\right] = 4.05$$

or $\log\left[OH^-\right] = -4.05 = \bar{5}.95$ or

$$\left[OH^-\right] = 8.913 \times 10^{-5}\,M$$

$$K_b = \frac{\left[CodH^+\right]\left[OH^-\right]}{[Cod]} = \frac{\left[OH^-\right]^2}{[Cod]} = \frac{\left(8.91 \times 10^{-5}\right)^2}{5 \times 10^{-3}}$$

$$= 1.588 \times 10^{-6}$$

$$pK_b = -\log\left(1.588 \times 10^{-6}\right) = 6 - 0.1987 = 5.8$$

Example - 4

Calculate the hydrogen ion concentration in the following biological fluids whose pH are given:

(a) Human muscle–fluid, 6.83

(b) Human stomach fluid, 1.2

(c) Human blood, 7.38

(d) Human saliva, 6.4

Sol. (a) $\log[H^+] = -pH = -6.83 = \bar{7}.17$

$\therefore [H^+] = \text{Antilog}\,\bar{7}.17 = 1.479 \times 10^{-7}\,M$

(b) $\log[H^+] = -pH = -1.2 = \bar{2}.8$

$\therefore [H^+] = \text{Antilog}\,\bar{2}.8 = 6.31 \times 10^{-2}\,M$

(c) $\log[H^+] = -pH = -7.38 = \bar{8}.62$

$\therefore [H^+] = \text{Antilog}\,\bar{8}.62 = 4.169 \times 10^{-8}\,M$

(d) $\log[H^+] = -pH = -6.4 = \bar{7}.60$

$\therefore [H^+] = \text{Antilog}\,\bar{7}.60 = 3.981 \times 10^{-7}\,M$

Example - 5

If 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentration of potassium hydrogen and hydroxyl ions. What is its pH?

Sol. $[KOH] = \frac{0.561}{56} \times \frac{1000}{200}\,M = 0.050M$

As $KOH \rightarrow K^+ + OH^-, \therefore [K^+] = [OH^-] = 0.05M$

$[H^+] = K_w / [OH^-] = 10^{-14}/0.05 = 10^{-14}/(5 \times 10^{-2})$

$= 2.0 \times 10^{-13}\,M.$

$pH = -\log[H^+] = -\log(2.0 \times 10^{-13}) = 13 - 0.3010 = 12.699$

Example - 6

The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentration of strontium and hydroxyl ions and the pH of the solution. (Atomic mass of Sr = 87.6)

Sol. Molar mass of $Sr(OH)_2 = 87.6 + 34 = 121.6\,g\,mol^{-1}$

Solubility of $Sr(OH)_2$ in moles $L^{-1} = \frac{19.23\,gL^{-1}}{121.6\,g\,mol^{-1}} = 0.1581M$

Assuming complete dissociation,

$Sr(OH)_2 \rightarrow Sr^{2+} + 2\,OH^-$

$\therefore [Sr^{2+}] = 0.1581M. [OH^-] = 2 \times 0.1581 = 0.3162M$

$pOH = -\log 0.3162 = 0.5, \therefore pH = 14 - 0.5 = 13.5$

Example - 7

The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Sol. $HCNO \rightleftharpoons H^+ + CNO^-$

pH = 2.34 means $-\log[H^+] = 2.34$ or $\log[H^+] = -2.34 = \bar{3}.66$

or $[H^+] = \text{Anti}\log\bar{3}.66 = 4.57 \times 10^{-3}\,M$

$[CNO^-] = [H^+] = 4.57 \times 10^{-3}\,M$

$$K_a = \frac{(4.57 \times 10^{-3})(4.57 \times 10^{-3})}{0.1} = 2.09 \times 10^{-4}$$

$$\alpha = \sqrt{K_a / C} = \sqrt{2.09 \times 10^{-4}/0.1} = 0.0457$$

Example - 8

The ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Sol. $[H^+] = \sqrt{K_w} = \sqrt{2.7 \times 10^{-14}} = 1.643 \times 10^{-7}\,M$

$pH = -\log[H^+] = -\log(1.643 \times 10^{-7})$

$= 7 - 0.2156 = 6.78$

Example - 9

On the basis of the equation $pH = -\log[H^+]$,the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

Sol. pH of 10^{-8} M HCl solution is not 8 because this concentration is so low that H^+ ion produced from H_2O in the solution (viz. 10^{-7}M) cannot be neglected. Total $[H^+] = 10^{-8} + 10^{-7}$ M. Solving and calculating pH, we get the value close to 7 but less than 7 as the solution is acidic.

Example - 10

pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times?

Sol. pH = 5 means $[H^+] = 10^{-5}$ M. On diluting 100 times,

$$[H^+] = \frac{10^{-5}}{100} = 10^{-7}\,M$$

This should give pH = 7 but it cannot be so because solution is acidic and pH should be less than 7. The reason is that $[H^+]$ from H_2O cannot be neglected. Thus, total $[H^+] = 10^{-7}$M (from HCl) + 10^{-7} M (from H_2O) = 2×10^{-7} M

$\therefore pH = -\log(2 \times 10^{-7}) = 7 - 0.3010 = 6.699.$

Example - 11

pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its Ionisation constant.

Sol. pH of HOCl=2.85 i.e., $-\log[H^+] = -2.85$

or $\log[H^+] = -2.85 = \bar{3}.15$

or $[H^+] = \text{antilog}\ \bar{3}.15 = 1.413 \times 10^{-3}$ M

For weak monobasic acid $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{\left[H^+\right]^2}{[HA]} = \frac{\left(1.413\times10^{-3}\right)^2}{0.08} = 2.4957 \times 10^{-5}.$$

Example - 12

Prove that the degree of dissociation of a weak monoprotic acid is given by

$\alpha = \dfrac{1}{1+10^{(pK_a - pH)}}$ where K_a is the dissociation constant of the acid.

Sol. Suppose we start with C mol L^{-1} of the weak monoprotic acid HA. Then

$$HA \rightleftharpoons H^+ + A^-$$

Initial molar conc. C $\quad$ 0 $\quad$ 0

Molar conc $\quad C - C\alpha \quad C\alpha \quad C\alpha$

after dissociation= $C(1-\alpha)$

$$\text{Thus, } K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \text{ or } C = \frac{K_a(1-\alpha)}{\alpha^2} \quad ..(i)$$

Also, $\left[H^+\right] = C\alpha$

Substituting the value of C from eqn. (i), we get

$$\left[H^+\right] = \frac{K_a(1-\alpha)}{\alpha^2} \times \alpha = \frac{K_a(1-\alpha)}{\alpha}$$

$$\therefore \quad -\log\left[H^+\right] = -[\log K_a + \log(1-\alpha) - \log\alpha]$$

or $pH = pK_a - \log(1-\alpha) + \log\alpha$

or $\log\dfrac{1-\alpha}{\alpha} = pK_a - pH$ or $\dfrac{1-\alpha}{\alpha} = 10^{pK_a - pH}$

or $\dfrac{1}{\alpha} - 1 = 10^{\,pK_a - pH}$

or $\dfrac{1}{\alpha} = 1 + 10^{pK_a - pH}$ or $\alpha = \dfrac{1}{1+10^{pK_a - pH}}$

Example - 13

Arrange the given compounds in the decreasing order of basicity on the basis of Bronsted–Lowry concept: BaO, CO_2, SO_3, B_2O_3, Cl_2O_7.

Sol. $BaO + H_2O \rightleftharpoons Ba(OH)_2$ (Basic)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strongly acidic)

$B_2O_3 + 3H_2O \rightleftharpoons 2H_3BO_3$ (Very weaky acidic)

$Cl_2O_7 + H_2O \rightleftharpoons 2HClO_4$ (Very strongly acidic)

Hence, in the decreasing order of basicity, we gave $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$.

Example - 14

What are the conjugate bases of the following?

CH_3OH, HN_3, $[Al(H_2O)_6]^{3+}$.

Sol. CH_3O^- $\quad N_3^-$ $\quad [Al(H_2O)_5OH]^{2+}$ (H$^+$ ion has been removed

methoxide ion, azide ion

from one H_2O molecule).

Example - 15

Glycine is an α–amino acid which exists in the form of Zwitter ion as $\overset{+}{N}H_3CH_2COO^-$. Write the formula of its conjugate base.

Sol. Conjugate acid =

$$\overset{+}{N}H_3CH_2COO^- + H^+ = \overset{+}{N}H_3CH_2COOH$$

Conjugate base =

$$\overset{+}{N}H_3CH_2COO^- - H^+ = NH_2CH_2COO^-$$

Example - 16

Write reaction for autoprotolysis of water. How is ionic product of water related to ionization constant of water? Derive the relationship.

Sol. Autoprotolysis of H_2O takes place as:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

For ionization of H_2O, $H_2O \rightleftharpoons H^+ + OH^-$

$$K_i = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]} = \frac{K_w}{55.55\,\text{mol}\,L^{-1}} \text{ or}$$

$$K_w = K_i \times 55.55.$$

Example - 17

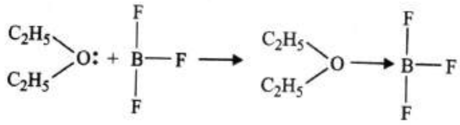
Why PO_4^{3-} ion is not amphiprotic?

Sol. An amphiprotic ion is one which can donate proton as well as accept proton. PO_4^{3-} ion can accept proton(s) but cannot donate any proton. Hence, PO_4^{3-} is not amphiprotic.

Example - 18

In the reaction between BF_3 and $C_2H_5OC_2H_5$ which one of them will act as an acid? Justify your anwer.

Sol. The reaction between BF_3 and $C_2H_5OC_2H_5$ is



As BF_3 accepts a pair of electrons, hence BF_3 is the Lewis acid.

Example - 19

Which is a stronger base in each of the following pairs and why?

(i) H_2O, Cl^- (ii) CH_3COO^-, OH^-

Sol (i) H_2O (ii) OH^-

According to Bronsted-Lowry concept H_2O and OH^- are stronger base.

Example - 20

Classify the following species as Lewis acids and Lewis bases

NH_3, BF_3, $SnCl_4$, C_5H_5N, CO, Ni^{2+}

Sol. Lewis acids: BF_3, $SnCl_4$, Ni^{2+}

Lewis bases: NH_3, C_5H_5N, CO.

Example - 21

Explain why pH of 0.1 molar solution of acetic acid will be higher than that of 0.1 molar solution of HCl?

Sol. Acetic acid is a weak electrolyte. It is not completely ionized and hence gives less H^+ ion concentration. HCl is a strong acid. It is completely ionized giving more H^+ ion concentration. As pH =—log $[H^+]$; less the $[H^+]$, greater will be the pH.

Example - 22

Calculate the approximate pH of a 0.100 M aqueous H_2S solution. K_1 and K_2 for H_2S are 1.00×10^{-7} and 1.30×10^{-13} respectively at 25°C,

Sol. $K_2 << K_1$. Hence H^+ ions are mainly from 1st dissociation, i.e. $H_2S \rightleftharpoons H^+ + HS^-$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = \frac{[H^+]^2}{[H_2S]} \text{ or } [H^+] = \sqrt{K_1[H_2S]}$$

$$\therefore \quad [H^+] = \sqrt{10^{-7} \times 10^{-1}} = 10^{-4}$$

Hence, pH=4

Example - 23

Calculate the pH at equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH solution, K_a for acetic acid = 1.9×10^{-5}

Sol. At the equivalence point, CH_3COONa is formed and its concentration = $\frac{0.1}{2} M = 0.05M$. It is a salt of weak acid and strong base. The formula for finding the pH of such a salt is

$$pH = -\frac{1}{2}[\log K_w + \log K_a - \log c]$$

$$\therefore \; pH = -\frac{1}{2}[\log 10^{-14} + \log(1.9 \times 10^{-5}) - \log(5 \times 10^{-2})]$$

$$= -\frac{1}{2}[-14 + (-5 + 0.2788) - (-2 + 0.6990)]$$

$$= \frac{1}{2}(14 + 5 - 0.2788 - 2 + 0.6990)$$

$$= \frac{17.42}{2} = 8.71$$

Example - 24

A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.

Sol. $\underset{\text{weak}}{HA} + \underset{\text{strong}}{BOH} \rightleftharpoons BA + H_2O$

or $HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$ or

$HA + OH^- \rightleftharpoons A^- + H_2O$

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

Further, for the weak acid, $HA \rightleftharpoons H^+ + A^-$,

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{......(ii)}$$

Also $K_w = [H^+][OH^-]$ .....(iii)

From eqns. (i), (ii) and (iii),

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

Example - 25

The pH of 0.05 M aqueous solution of diethylamine is 12.0. Calculate its K_b

Sol. $(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

As pH = 12, $\therefore [H^+] = 10^{-12}$ M or $[OH^-] = 10^{-2}$M,

$$[(C_2H_5)_2NH] = 0.05 - 0.01 = 0.04M$$

$$K_b = \frac{[(C_2H_5)_2NH_2^+][OH^-]}{[(C_2H_5)_2NH]} = \frac{10^2 \times 10^{-2}}{0.04} = 2.5 \times 10^{-3}$$

$$[(C_2H_5)_2NH_2^+] = [OH^-]$$

Example - 26

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

Sol. 10% ammonia by mass means 10g NH_3 are present in 100g of the solution.

$\therefore$ Molarity of the solution

$$= \frac{10}{17} \times \frac{1}{100/0.99} \times 1000 = 5.82\text{ M}$$

$$NH_3 + H_2 \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Initial conc. $\quad C \text{ mol } L^{-1}$

After dissociation $\quad C - C\alpha \quad C\alpha \quad C\alpha$

$= C(1-\alpha)$

$$[OH^-] = C\alpha = C\sqrt{\frac{K_h}{C}} = \sqrt{K_hC}$$

$$= \sqrt{\frac{K_w}{K_a} \times C} = \sqrt{\frac{10^{-14}}{5.0 \times 10^{-10}} \times 5.82} = 1.079 \times 10^{-2}\text{ M}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.079 \times 10^{-2}}$$

$= 0.9268 \times 10^{-12}$ M $= 9.268 \times 10^{-13}$ M

Example - 27

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

Sol. $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+, K_a = 5.6 \times 10^{-10}$

$$NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^-, k_b = 3.4 \times 10^{10}$$

Aim. To find k_f

We know that for a conjugate acid–base pair $K_{acid} \times K_{base} = K_w$, i.e., $K_a \times K_b = K_w$

$$\therefore K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.6 \times 10^{-10}}$$

But $K_b = \dfrac{k_f}{k_b} \therefore k_f = K_b \times k_b$

$$= \frac{10^{-14}}{5.6 \times 10^{-10}} \times 3.4 \times 10^{10} = 0.607 \times 10^6 = 6.07 \times 10^5$$

Example - 28

What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH=2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)?

Sol. pH = 2 means $[H^+] = 10^{-2}$M

pH = 12 means $[H^+] = 10^{-12}$ or $[OH^-] = 10^{-2}$ M

Thus, 200 ml of 10^{-2} M HCl are mixed with 300 ml of 10^{-2} M NaOH.

After neutralization NaOH left = 100 ml of 10^{-2} M

Total volume after mixing = 500 ml

$\therefore$ In the final solution, after mixing , $[OH^-] = \dfrac{10^{-2}}{5} = 2 \times 10^{-3}$ M or $[H^+] = \dfrac{10^{-14}}{2 \times 10^{-3}} = 5 \times 10^{-12}$

$$\therefore pH = -\log[H^+] = -\log(5 \times 10^{-12}) = 12 - 0.69 = 11.31$$

Example - 29

Calculate the degree of dissociation of 0.5 M NH_3 at 25°C in a solution of pH=12.

Sol. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Initial conc. $C \text{ mol } L^{-1} \quad 0 \quad 0$

After disso. $\quad C - C\alpha \quad C\alpha \quad C\alpha$

pH = 12 means $[H^+] = 10^{-12}$ or $[OH^-] = 10^{-2}$

$$\therefore [OH^-] = C\alpha = 10^{-2} \text{ or } \alpha = \frac{10^{-2}}{C}$$

$$= \frac{10^{-2}}{0.5} = 2 \times 10^{-2} \text{ or } 2\%.$$

Example - 30

Calculate the amount of $(NH_4)_2 SO_4$ in g which must be added to 500 mL of 0.2 M NH_3 to yield a solution of pH = 9.35. K_b for $NH_3 = 1.78\times10^{-5}$.

Sol. As it is a basic buffer, pOH

$$= pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]} = -\log K_b + \log\frac{[NH_4^+]}{[NH_4OH]}$$

As pH = 9.35, $\therefore$ pOH = 14 − 9.35 = 4.65

Millimoles of NH_4OH is solution = 0.2×500 = 100

Suppose millimoles of NH_4^+ to be added = x

$$\therefore \quad 4.65 = -\log(1.78\times10^{-5}) + \log\frac{x/500}{100/500}$$

$$= (5 - 0.2504) + \log\frac{x}{100}$$

or $\log\frac{x}{100} = -0.0996 = \bar{1}.004 \simeq 0.1$

or $\log x = 2.1$ or $x = 125.9$

$\therefore$ Millimoles of $(NH_4)_2SO_4$ to be added $= \frac{125.9}{2} = 62.95$

($\because$ 1 millimole of $(NH_4)_2\ SO_4 \equiv 2$ millimoles of NH_4^+)

$\therefore$ Mass of $(NH_4)_2SO_4$ to be added = $(62.95 \times 10^{-3}$ moles) $(132\ \text{g mol}^{-1}) = 8.3094$ g.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Theory of Electrolytes and Theory of Acids and Bases

1. Which shows weak ionisation in water

(a) H_2SO_4

(b) NaCl

(c) HNO_3

(d) NH_3

2. Which one of the following substance has the highest proton affinity

(a) H_2O

(b) H_2S

(c) NH_3

(d) PH_3

3. Which of the following is not a Lewis acid

(a) BF_3

(b) $FeCl_3$

(c) SiF_4

(d) C_2H_4

4. The conjugate base of NH_2^- is

(a) NH_3

(b) NH^{2-}

(c) NH_4^+

(d) N_3^-

5. Cl^- is the conjugate base of

(a) $HClO_4$

(b) HCl

(c) HOCl

(d) $HClO_3$

6. Which one is lewis acid

(a) Cl^-

(b) Ag^+

(c) C_2H_5OH

(d) S^{2-}

7. Which of the following is the weakest base

(a) NaOH

(b) $Ca(OH)_2$

(c) NH_4OH

(d) KOH

8. Conjugate base of NH_3 is

(a) $NH_4^{\oplus}$

(b) $NH_2^{\oplus}$

(c) $NH_2^{\ominus}$

(d) N_2

9. According to Bronsted principle, an aqueous solution of HNO_3 will contain

(a) NO_2^-

(b) NO_3^-

(c) NO_2^+

(d) NO^+

10. The conjugate acid of HPO_4^{2-} is

(a) $H_2PO_4^-$

(b) PO_4^{3-}

(c) H_3PO_4

(d) H_3PO_3

11. Review the equilibrium and choose the correct statement

$$HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$$

(a) $HClO_4$ is the conjugate acid of H_2O

(b) H_3O^+ is the conjugate base of H_2O

(c) H_2O is the conjugate acid of H_3O^+

(d) ClO_4^- is the conjugate base of $HClO_4$

12. Which of the following is the weakest acid

(a) HF

(b) HCl

(c) HBr

(d) HI

13. Among the following, the weakest Lewis base is

(a) H^-

(b) OH^-

(c) Cl^-

(d) HCO_3^-

14. Which one is the weakest acid

(a) HNO_3

(b) $HClO_4$

(c) H_2SO_4

(d) HBr

15. The correct order of acid strength is

(a) $HClO < HClO_2 < HClO_3 < HClO_4$

(b) $HClO_4 < HClO < HClO_2 < HClO_3$

(c) $HClO_2 < HClO_3 < HClO_4 < HClO$

(d) $HClO_4 < HClO_3 < HClO_2 < HClO$

16. Ammonium ion is

(a) Neither an acid nor base

(b) Both an acid and a base

(c) A conjugate acid

(d) A conjugate base

Dissociation of Weak Acids and Bases

17. Degree of dissociation of 0.1 N CH_3COOH is (Dissociation constant = 1×10^{-5})

(a) 10^{-5}

(b) 10^{-4}

(c) 10^{-3}

(d) 10^{-2}

18. The values of dissociation constants of some acids (at 25°C) are as follows. Indicate which is the strongest acid in water

(a) 1.4×10^{-2}

(b) 1.6×10^{-4}

(c) 4.4×10^{-10}

(d) 4.3×10^{-7}

19. The following equilibrium exists in aqueous solution, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ if dil HCl is added, without change in temperature, the

(a) Concentration of CH_3COO^- will increase

(b) Concentration of CH_3COO^- will decrease

(c) The equilibrium constant will increase

(d) The equilibrium constant will decrease

20. The hydrogen ion concentration in weak acid of dissociation constant K_a and concentration c is nearly equal to

(a) $\sqrt{K_a / c}$ (b) c/K_a

(c) $K_a c$ (d) $\sqrt{K_a c}$

21. 0.2 molar solution of formic acid is ionized 3.2%. Its ionization constant is

(a) 9.6×10^{-3} (b) 2.1×10^{-4}

(c) 1.25×10^{-6} (d) 4.8×10^{-5}

22. For a "c molar" concentrated solution of a weak electrolyte A_xB_y, the degree of dissociation is given as

(a) $\alpha = \sqrt{K_{eq} / c\,(x+y)}$

(b) $\alpha = \sqrt{K_{eq} c/(xy)}$

(c) $\alpha = \left(K_{eq} / c^{x+y-1} x^x y^y\right)^{1/(x+y)}$

(d) $\sqrt{K_{eq} / xyc}$

23. The pH of a 0.1 M aqueous solution of a weak acid (HA) is 3. What is its degree of dissociation ?

(a) 1% (b) 10%

(c) 50% (d) 25%

24. In which of the following dissociation of NH_4OH will be minimum

(a) NaOH (b) H_2O

(c) NH_4Cl (d) NaCl

Ostwald's Dilution Law

25. A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is

(a) 1×10^{-8} (b) 1×10^{-4}

(c) 1×10^{-6} (d) 10^{-5}

26. If α is the degree of ionization, C the concentration of a weak electrolyte and K_a the acid ionization constant, then the correct relationship between α, C and K_a is

(a) $\alpha^2 = \sqrt{\frac{K_a}{C}}$ (b) $\alpha^2 = \sqrt{\frac{C}{K_a}}$

(c) $\alpha = \sqrt{\frac{K_a}{C}}$ (d) $\alpha = \sqrt{\frac{C}{K_a}}$

27. The degree of dissociation of 0.1 M HCN solution is 0.01%. Its ionisation constant would be

(a) 10^{-3} (b) 10^{-5}

(c) 10^{-7} (d) 10^{-9}

28. For a weak acid HA, Ostwald's dilution law is represented by the equation

(a) $K_a = \frac{\alpha c}{1-\alpha^2}$ (b) $K_a = \frac{\alpha^2 c}{1-\alpha}$

(c) $\alpha = \frac{K_a c}{1-c}$ (d) $K_a = \frac{\alpha^2 c}{1-\alpha^2}$

29. Concentration CN^- in 0.1 M HCN is $[K_a = 4 \times 10^{-10}]$

(a) 2.5×10^{-6} M (b) 4.5×10^{-6} M

(c) 6.3×10^{-6} M (d) 9.2×10^{-6} M

Self-ionization of Water

30. In the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$, water is

(a) A weak base

(b) A weak acid

(c) Both a weak acid and a weak base

(d) Neither an acid nor a base

31. The unit of ionic product of water K_w are

(a) $Mol^{-1}L^{-1}$ (b) $Mol^{-2}L^{-2}$

(c) $Mol^{-2}L^{-1}$ (d) $Mol^{2}L^{-2}$

32. Autoprotolysis constant of NH_3 is

(a) $[NH_4^+][NH_3]$ (b) $[NH_2^-][NH_3]$

(c) $[NH_4^+][NH_2^-]$ (d) $[NH_4^+]/[NH_2^-]$

33. Ionic product of water increases, if

(a) Pressure is reduced (b) H^+ is added

(c) OH^- is added (d) Temperature increases

34. At 90°C, pure water has $[H_3O^+] = 10^{-6}$ mole $litre^{-1}$. What is the value of K_w at 90° C ?

(a) 10^{-6} (b) 10^{-12}

(c) 10^{-14} (d) 10^{-8}

35. $2H_2O \rightleftharpoons H_3O^+ + OH^-$, $K_w = 1 \times 10^{-14}$ at 25°C hence K_a is:

(a) 1×10^{-14} (b) 5.55×10^{-3}

(c) 18×10^{-17} (d) 1.00×10^{-7}

Calculation of pH

36. At a certain temperature the value of pK_w is 13.4 and the measured pH of soln is 7. The solution is

(a) Acidic
(b) Basic
(c) Neutral
(d) Unpredictable

37. For a pure water,

(a) pH increases and pOH decreases with increase in temperature

(b) pH decreases and pOH increases with increase in temperature

(c) both pH and pOH increase with increase in temperature

(d) both pH and pOH decrease with increase in temperature

38. What is the pH value of N/1000 KOH solution

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

39. Pure water is kept in a vessel and it remains exposed to atmospheric CO_2 which is absorbed, then its pH will be

(a) Greater than 7

(b) Less than 7

(c) 7

(d) Depends on ionic product of water

40. The pH of a solution is increased from 3 to 6; its H^+ ion concentration will be :

(a) reduced to half
(b) doubled
(c) reduced by 1000 times
(d) increased by 1000 times

41. A patient is said to suffer from acidosis when the pH of his blood

(a) falls below 7.35

(b) rises above 7.35

(c) Shows sudden fall and rise

(d) has strong basic character

42. The pH of a dilute solution of acetic acid was found to be 4.3. The addition of a small crystal of sodium acetate will cause pH to

(a) Become less than 4.3
(b) Become more than 4.3
(c) Remain equal to 4.3
(d) Unpredictable

43. The pH of a 0.001 M NaOH will be

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

44. The pH of a 10^{-9} M solution of HCl in water is

(a) 8
(b) – 8
(c) Between 7 and 8
(d) Between 6 and 7

45. A is an aqueous acid; B is an aqueous base. They are diluted separately, then

(a) pH of A increases and pH of B decreases

(b) pH of A increases and pH of B decreases till pH in each case is 7

(c) pH of A and B increase

(d) pH of B and A decrease

46. An acid solution of pH = 6 is diluted hundred times. The pH the solution becomes :

(a) 6.95
(b) 6
(c) 4
(d) 8

47. The number of H^+ ions present in 1 mL of a solution having pH = 13 is :

(a) 10^{13}
(b) 6.023×10^{13}
(c) 6.023×10^{7}
(d) 6.023×10^{10}

48. The dissociation constants of monobasic acids A, B, C and D are 6×10^{-4}, 5×10^{-5}, 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1 molar aqueous solutions are in the order :

(a) $A < B < C < D$
(b) $A > B > C > D$
(c) $A = B = C = D$
(d) None of these

49. What is the pH of a 0.015 M $Ba(OH)_2$ solution ?

(a) 1.82
(b) 1.52
(c) 12.48
(d) 12.18

50. Equal volumes of two solutions of hydrochloric acid are mixed. One solution has a pH 1 while the other has a pH 5. The pH of the resulting solution is :

(a) less than 1
(b) Between 1 and 2
(c) 3
(d) Between 4 and 5

51. Aspirin (acetyl salicyclic acid, molar mass = 180 g mol^{-1}) used as analgesic has pK_a value of 2. Two tablets of aspirin each weighing 90 mg are dissolved in 100 mL of water. The pH of the solution is

(a) 0.5
(b) 1.0
(c) 2.0
(d) 4.0

52. In a mixture of a weak acid and its salt, the ratio of concentration of acid to salt is increased ten-fold. The pH of the solution

(a) Decreases by one
(b) Increases by one-tenth
(c) Increases by one
(d) Increases ten-fold

53. The dissociation constant of HCN is 5×10^{-10}. The pH of the solution prepared by mixing 1.5 mole of HCN and 0.15 moles of KCN in water and making up the total volume to 0.5 dm^3 is

(a) 7.302
(b) 9.302
(c) 8.302
(d) 10.302

Buffer Solutions and Relationship Between K_a and K_b for a Conjugate Pair

54. Calculate the pH of a buffer prepared by mixing 0.10 mol of sodium formate and 0.05 mole of formic acid in 1.0 L of solution. [HCO_2H : $K_a = 1.8 \times 10^{-4}$]

(a) 1.8×10^{-4}
(b) 3.44
(c) 4.05
(d) 5.31

55. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and the solution diluted to one litre. The H^+ ion concentration in the solution will be

(a) 1.6×10^{-11}
(b) 8×10^{-11}
(c) 5×10^{-5}
(d) 8×10^{-2}

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

(a) 7.0
(b) 4.5
(c) 2.5
(d) 9.5

57. Buffer solutions can be prepared from mixtures of

(a) HCl and NaCl
(b) NaH_2PO_4 and Na_2HPO_4
(c) $CH_3COOH + NaCl$
(d) $NH_4OH + NH_3$

58. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be ($K_a = 10^{-5}$)

(a) 1 : 10
(b) 10 : 1
(c) 100 : 1
(d) 1 : 100

59. How many moles of HCOONa must be added to 1 L of 0.1 M HCOOH to prepare a buffer solution with a pH of 3.4 ?

(Given : K_a for HCOOH = 2×10^{-4})

(a) 0.01
(b) 0.05
(c) 0.1
(d) 0.2

60. What is the pH of a buffer solution which is 0.250 M in benzoic acid, C_6H_5COOH, and 0.150 M in sodium benzoate, C_6H_5COONa, if K_a for benzoic acid is 6.5×10^{-5} ?

(a) 3.40
(b) 3.97
(c) 4.19
(d) 4.41

61. 100 mL of a buffer solution contains 0.1 M each of weak acid HA and salt NaA. How many gram of NaOH should be added to the buffer so that its pH will be 6 ? (K_a of HA = 10^{-5}).

(a) 0.328
(b) 0458
(c) 4.19
(d) None

62. Two buffer solutions, A and B, each made with acetic acid and sodium acetate differ in their pH by one unit, A has salt : acid = x : y, B has salt : acid = y : x. If x > y, then the value of x : y is

(a) 10,000
(b) 3.17
(c) 6.61
(d) 2.10

63. K_a for HF is 3.5×10^{-4}. Calculate K_b for the fluoride ion.

(a) 3.5×10^{-4}
(b) 1.0×10^{-7}
(c) 2.9×10^{-11}
(d) 1.0×10^{-14}

Salt Hydrolysis

64. A certain buffer solution contains equal concentration of $X^{\ominus}$ and HX. The K_b for $X^{\ominus}$ is 10^{-10}. The pH of the buffer is

(a) 4
(b) 7
(c) 10
(d) 14

65. Aq. solution of sodium cyanide is

(a) Acidic
(b) Amphoteric
(c) Basic
(d) Netural

66. The solution of strong acid and weak base ($FeCl_3$) is

(a) Acidic
(b) Basic
(c) Neutral
(d) none of these

67. Which one of the following salts gives an acidic solution in water

(a) CH_3COONa
(b) NH_4Cl
(c) NaCl
(d) CH_3COONH_4

68. An aqueous solution of aluminium sulphate would show

(a) An acidic reaction
(b) A neutral reaction
(c) A basic reaction
(d) Both acidic and basic reaction

69. An aqueous solution of sodium carbonate is alkaline because sodium carbonate is a salt of

(a) Weak acid and weak base
(b) Strong acid and weak base
(c) Weak acid and strong base
(d) Strong acid and strong base

70. The aqueous solution of ammonium chloride is

(a) Neutral
(b) Basic
(c) Acidic
(d) Amphoteric

71. The aqueous solution of $FeCl_3$ is acidic due to

(a) Acidic impurities
(b) Ionisation
(c) Hydrolysis
(d) Dissociation

72. Which is the correct alternate for hydrolysis constant of NH_4CN

(a) $\sqrt{\frac{K_w}{K_a}}$
(b) $\frac{K_w}{K_a \times K_b}$
(c) $\sqrt{\frac{K_b}{c}}$
(d) $\frac{K_a}{K_b}$

73. Which of the following salt is basic ?

(a) HOCl
(b) NaOCl
(c) $NaHSO_4$
(d) NH_4NO_3

74. The pK_b of $CN^{\ominus}$ is 4.7. The pH of solution prepared by mixing 2.5 mol of KCN of 2.5 mol of HCN in water and making the total volume upto 500 mL is

(a) 10.3
(b) 9.3
(c) 8.3
(d) 4.7

75. The pH of blood is maintained by the balance between H_2CO_3 and $NaHCO_3$. If the amount of CO_2 in the blood is increased, how will it effect the pH of blood ?

(a) pH will remain same
(b) pH will be 7
(c) pH will increase
(d) pH will decrease

76. Calculate the carbonate ion concentration in a 0.10 M solution of the weak acid, carbonic acid are (H_2CO_3). The dissociation constants of carbonic acid are $K_{a1} = 4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$.

(a) 4.7×10^{-11} M
(b) 1.0×10^{-7} M
(c) 4.5×10^{-7} M
(d) 2.1×10^{-4} M

77. Which one of the following statements is true with regard to a 0.10 M H_2SO_4 solution ?

(a) $[H_2SO_4] > [H^+]$
(b) $[H^+] = [SO_4^{2-}]$
(c) $[SO_4^{2-}] > [HSO_4^-]$
(d) $[H^+] > [HSO_4^-]$

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

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

79. The pK_{a_1} and pK_{a_2} of an amino acid are 2.3 and 9.7 respectively. The isoelectric point of amino acid is :

(a) 12
(b) 7.4
(c) 6.0
(d) 3.7

80. HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_4OH is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1.0 M solutionk of NH_4CN would be :

(a) strongly acidic
(b) weakly acidic
(c) neutral
(d) weakly basic

81. K_a for hydrofluoric acid is 6.9×10^{-4}. What is the equilibrium constant K for the following reaction ?

$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$

(a) 6.9×10^{-11}
(b) 1.4×10^{-11}
(c) 2.6×10^{-9}
(d) 8.3×10^{-6}

82. To 1.0 L solution containing 0.1 mol each of NH_3 and NH_4Cl, 0.05 mol NaOH is added. The change in pH will be (pK_a for $CH_3COOH = 4.74$)

(a) 0.30
(b) –0.30
(c) 0.48
(d) –0.48

83. 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, resulting acidic buffer solution. If pH of the resulting solution is 3.9, then added volume of benzoic acid is

(a) 240 mL
(b) 150 mL
(c) 100 mL
(d) None

84. In a saturated solution of H_2S,decreasing the pH of the solution will cause

(a) the S^{2-} concentration to decrease
(b) the H_2S concentration to decrease
(c) the S^{2-} concentration to increase
(d) no change in either the H_2S or S^{2-} concentration

85. What is the pH of 0.01 M glycine solution ? For glycine $K_{a_1} = 4.5 \times 10^{-3}$ and $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K

(a) 3.0
(b) 10.0
(c) 6.1
(d) 7.2

86. The equilibrium constant for this reaction is 3.6×10^{-7}.

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

What is K_a for HOCl ?

(a) 2.8×10^{-8}
(b) 3.6×10^{-7}
(c) 6×10^{-4}
(d) 2.8×10^{-6}

Solubility and Solubility Product

87. Let the solubility of an aqueous solution of $Mg(OH)_2$ be x then its k_{sp} is

(a) $4x^3$
(b) $108x^5$
(c) $27x^4$
(d) 9x

88. The solubility of CaF_2 is a moles/litre. Then its solubility product is........

(a) s^2
(b) $4s^3$
(c) $3s^2$
(d) s^3

89. Which is the correct representation of the solubility product constant of Ag_2CrO_4

(a) $[Ag^+]^2[CrO_4^{-2}]$
(b) $[Ag^+][CrO_4^{-2}]$
(c) $[2Ag^+][CrO_4^{-2}]$
(d) $[2Ag^+]^2[CrO_4^{-2}]$

90. The correct representation for solubility product of SnS_2 is

(a) $[Sn^{4+}][S^{2-}]^2$
(b) $[Sn^{2+}][S^{2-}]^2$
(c) $[Sn^{2+}][2S^{2-}]$
(d) $[Sn^{4+}][2S^{2-}]^2$

91. K_{sp} of $Mg(OH)_2$ is 4.0×10^{-6}. At what minimum pH, Mg^{2+} ions starts precipitating 0.01 $MgCl_2$

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

92. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is

(a) 2.0×10^{-6} M
(b) 1.0×10^{-4} M
(c) 1.6×10^{-4} M
(d) 4.0×10^{-10} M

93. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol l^{-1}. Its solubility product number will be

(a) 4×10^{-15}
(b) 4×10^{-10}
(c) 1×10^{-15}
(d) 1×10^{-10}

94. Solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility in moles/litre would be

(a) 1×10^{-3}
(b) 1×10^{-9}
(c) 4×10^{-27}
(d) 1×10^{-27}

95. Solubility of AgCl will be minimum in

(a) 0.001 M $AgNO_3$
(b) Pure water
(c) 0.01 M $CaCl_2$
(d) 0.01 M NaCl

96. At 298 K, the solubility product of $PbCl_2$ is 1.0×10^{-6}. What will be the solubility of $PbCl_2$ in moles/litre

(a) 6.3×10^{-3}
(b) 1.0×10^{-3}
(c) 3.0×10^{-3}
(d) 4.6×10^{-14}

97. K_{sp} for $Ca(OH)_2$ is 5.5×10^{-6}. What is the maximum pH that can be attained in a sewage tank treated with slaked lime ?

(a) 9.35
(b) 10.35
(c) 11.35
(d) 12.35

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

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

99. The solubility product of different sparingly soluble salts are :

1. $XY = 4 \times 10^{-20}$
2. $X_2Y = 3.2 \times 10^{-11}$
3. $XY_3 = 2.7 \times 10^{-31}$

The increasing order of solubility is :

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

100. Solubility of AgCN is maximum in :

(a) acidic buffer solution
(b) basic buffer solution
(c) in pure water
(d) equal in all solution

101. The pH of an aqueous solution of $Ba(OH)_2$ is 10. If the K_{sp} of $Ba(OH)_2$ is 1×10^{-9}, then the concentration of Ba^{2+} ions in the solution in mol L^{-1} is

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

102. $CaCO_3$ and $BaCO_3$ have solubility product values 1×10^{-8} and 5×10^{-9}, respectively. If water is shaken up with both solids till equilibrium is reached, the concentration of CO_3^{2-} ion is

(a) 1.5×10^{-8}
(b) 1.225×10^{-4}
(c) 2.25×10^{-9}
(d) None of these

103. A precipitate of AgCl is formed when equal volumes of the following are mixed. [K_{sp} for AgCl = 10^{-10}]

(a) 10^{-4} M $AgNO_3$ and 10^{-7} M HCl
(b) 10^{-5} M $AgNO_3$ and 10^{-6} M HCl
(c) 10^{-5} M $AgNO_3$ and 10^{-4} M HCl
(d) 10^{-6} M $AgNO_3$ and 10^{-6} M HCl

104. The solubility of CH_3COOAg in a buffer solution with pH = 4, whose $K_{sp} = 10^{-12}$ and $K_a = \frac{10^{-4}}{3}$ is

(a) 10^{-6}
(b) 0.5×10^{-6}
(c) 5×10^{-6}
(d) 2×10^{-6}

Preferential Precipitation of Salts and Theory of Indicators

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

(a) 10^{-4} M (Ag^+) and 10^{-4}M (Cl^-)

(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)

(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

106. The pH indicators are :

(a) salts of strong acids and strong bases

(b) salts of weak acids and weak bases

(c) either weak acids or weak bases

(d) either strong acids or strong bases

107. Phenolphthalein does not act as an indicator for the titration between

(a) HCl and NH_4OH (b) $Ca(OH)_2$ and HCl

(c) NaOH and H_2SO_4 (d) KOH and CH_3COOH

108. Methyl orange gives red colour in

(a) KOH solution (b) HCl solution

(c) Na_2CO_3 solution (d) NaCl solution

109. Which acid-base indicator should be used in an aqueous solution titration which is complete at about 0.001 M H^+(aq)? The transition range in pH is given in parenthesis.

(a) Methyl violet (0.5 – 1.5)

(b) Methyl red (4.2 – 6.3)

(c) Methyl yellow (2.9 – 4.0)

(d) Phenol red (6.4 – 8.0)

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

(a) methyl orange (3 to 4)

(b) methyl red (5 to 6)

(c) bromothymol blue (6 to 7.5)

(d) phenolphthalein (8 to 9.6)

111. Which indicator is suitable for the titrations :

Titration	Indicator
(i) HCOOH/NaOH	(A) Bromothymol blue or phenolphthalein or methyl orange or thymolphthalein
(ii) HBr/KOH	(B) Methyl orange or methyl red or bromocresol green
(iii) NH_4OH/HNO_3	(C) Phenolphthalein or thymolphthalein

(a) (i) $\rightarrow$ A, (ii) $\rightarrow$ B, (iii) $\rightarrow$ C

(b) (i) $\rightarrow$ A, (ii) $\rightarrow$ C, (iii) $\rightarrow$ B

(c) (i) $\rightarrow$ B, (ii) $\rightarrow$ C, (iii) $\rightarrow$ A

(d) (i) $\rightarrow$ C, (ii) $\rightarrow$ A, (iii) $\rightarrow$ B

Acid Base Titration

112. At equivalence point, which of the following acid base reaction pH will be greater than 8 ?

(a) Acetic acid versus ammonia

(b) Acetic acid versus sodium hydroxide

(c) Hydrochloric acid versus ammonia

(d) Hydrochloric and versus sodium hydroxide

113. Why are strong acids generally used as standard solutions in acid-base titrations ?

(a)The pH at the equivalent point will always be 7

(b)They can be used to titrate both strong and weak bases

(c)Strong acids form more stable solutions than weak acids

(d)The salts of strong acid do not hydrolyze

114. In which of the following acid-base titration, pH is greater than 8 at the equivalence point ?

(a) Acetic acid vs ammonia

(b) Acetic acid vs sodium ammonia

(c) Hydrochloric acid vs ammonia

(d) Hydrochloric acid vs sodium hydroxide

115. What will be the pH of a solution formed by mixing 40 ml of 0.10 M HCl with 10 ml of 0.45 M NaOH

(a) 12 (b) 10

(c) 8 (d) 6

116. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression

(a) $\log \dfrac{[HIn]}{[In^-]} = pH - pK_{In}$

(b) $\log \dfrac{[In^-]}{[HIn]} = pH - pK_{In}$

(c) $\log \dfrac{[In^-]}{[HIn]} = pK_{In} - pH$

(d) $\log \dfrac{[HIn]}{[In^-]} = pK_{In} - pH$

117. Which of the following mixture will have the pH close to 1?

(a) 100 ml of M/10 HCl + 100 ml of M/10 NaOH

(b) 55 ml of M/10 HCl + 45ml of M/10 NaOH

(c) 10 ml of M/10 HCl + 90 ml of M/10 NaOH

(d) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

118. Consider the titratiokns listed below. In which is the pH at the equivalence point described incorrectly ?

Acid	**Base**	**pH at equiv.pt.**
(a) CH_3COOH	NaOH	> 7.00
(b) HNO_3	$Ca(OH)_2$	$= 7.00$
(c) HCl	NH_3	< 7.00
(d) HF	NaOH	< 7.00

119. 20 cm^3 of x M solution of HCl is exactly neutralised by 40 cm^3 of 0.05 M NaOH solution, the pH of HCl solution is

(a) 1.0 (b) 2

(c) 1.5 (d) 2.5

120. A sample of 50.0 mL of 0.10 M NH_3 ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.10 M HCl. Calculate the pH at the equivalence point.

(a) 6.98 (b) 2.87

(c) 7.78 (d) 5.28

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp} 's' is given in terms of K_{sp} by the relation **(2004)**

(a) $s = \left(\frac{K_{sp}}{128}\right)^{1/4}$ (b) $s = \left(\frac{K_{sp}}{256}\right)^{1/5}$

(c) $s = (256\,K_{sp})^{1/5}$ (d) $s = (128\,K_{sp})^{1/4}$

2. The conjugate base of $H_2PO_4^-$ **(2004)**

(a) PO_4^{3-} (b) HPO_4^{2-}

(c) H_3PO_4 (d) P_2O_5

3. The solubility product of a salt having general formula MX_2; in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **(2005)**

(a) 4.0×10^{-10} M (b) 1.6×10^{-4} M

(c) 1.0×10^{-4}M (d) 2.0×10^{-6}M

4. What is the conjugate base of OH^- ? **(2005)**

(a) O^{2-} (b) O^-

(c) H_2O (d) O_2

5. The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is **(2007)**

(a) 4.5 (b) 2.5

(c) 9.5 (d) 7.0

6. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is

$$AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq.)} + IO^-_{3(aq.)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution ? **(2007)**

(a) 28.3×10^{-2}g (b) 2.83×10^{-3}g

(c) 1.0×10^{-7}g (d) 1.0×10^{-4}g

7. The first and second dissociation constant of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **(2007)**

(a) 5.0×10^{-5} (b) 5.0×10^{15}

(c) 5.0×10^{-15} (d) 0.2×10^{15}

8. Four species are listed below

(i) HCO_3^- (ii) H_3O^+

(iii) HSO_4^- (iv) HSO_3F

Which of the following is the correct sequence of their acid strength ? **(2008)**

(a) iv < ii < iii < i (b) ii < iii < i < iv

(c) i < iii < ii < iv (d) iii < i < iv < ii

9. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **(2008)**

(a) 8.58 (b) 4.79

(c) 7.01 (d) 9.22

10. Solid Ba $(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{+2} will a precipitate being to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$); **(2009)**

(a) 4.1×10^{-5} M (b) 5.1×10^{-5} M

(c) 8.1×10^{-8}M (d) 8.1×10^{-7} M

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

(a) 9 (b) 10

(c) 11 (d) 8

12. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **(2010)**

(a) 1.2×10^{-10} g (b) 1.2×10^{-9} g

(c) 6.2×10^{-5} g (d) 5.0×10^{-8} g

13. In aqueous solution, the ionisation constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$ **(2010)**

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

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

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

(c) The concentration of H^+ and HCO_3^- are approximately equal

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

14. Three reactions involving $H_2PO_4^-$ are given below :

I. $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

II. $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

III. $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ?**(2010)**

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

15. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **(2011)**

(a) $\sqrt[2]{1.6\times10^{-30}}$
(b) $\sqrt[4]{1.6\times10^{-30}}$
(c) $\sqrt[4]{1.6\times10^{-30}/27}$
(d) $1.6\times10^{-30}/27$

16. An acid HA ionises as

$HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be **(2011)**

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

17. Among the following oxoacids, the correct decreasing order of acid strength is : **(2014)**

(a) $HClO_4 > HOCl > HClO_2 > HClO_3$
(b) $HClO_4 > HClO_3 > HClO_2 > HOCl$
(c) $HClO_2 > HClO_4 > HClO_3 > HOCl$
(d) $HOCl > HClO_2 > HClO_3 > HClO_4$

18. Which has the highest pH ? **(2015)**

(a) CH3COONH4
(b) Na2CO3
(c) NH4Cl
(d) NaNO3

19. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is : **(2017)**

(a) 6.9
(b) 7.0
(c) 1.0
(d) 7.2

20. Which of the following salts is the most basic in aqueous solution? **(2018)**

(a) $Pb(CH_3COO)_2$
(b) $Al(CN)_3$
(c) CH_3COOK
(d) $FeCl_3$

21. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination **(2018)**

Base	**Acid**	**End Point**
(a) Strong	Strong	Pink to colourless
(b) Weak	Strong	Colourless to pink
(c) Strong	Strong	Pinkish red to yellow
(d) Weak	Strong	Yellow to pinkish red

22. Assuming that the degree of hydrolysis is small, the pH of 0.1 M solution of sodium acetate ($K_a = 1.0 \times 10^{-5}$) will be: **(Online 2014 Set - 2)**

(a) 8.0
(b) 6.0
(c) 9.0
(d) 5.0

23. In some solutions, the concentration of H_3O^+ remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as: **(Online 2014 Set - 2)**

(a) Buffer solutions
(b) True solutions
(c) Ideal solutions
(d) Colloidal solutions

24. The conjugate base of hydrazoic acid is: **(Online 2014 Set - 3)**

(a) N_2^-
(b) N_3^-
(c) N^{-3}
(d) HN_3^-

25. Zirconium phosphate $[Zr_3(PO_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ? **(Online 2014 Set - 4)**

(a) $S = \{K_{sp}/(6912)^{1/7}\}$
(b) $S = (K_{sp}/6912)^{1/7}$
(c) $S = \{K_{sp}/144\}^{1/7}$
(d) $S = \{K_{sp}/6912\}^{7}$

26. Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is 10^{+5}, the ratio of salt to acid concentration in the buffer solution will be : **(Online 2017 Set - 1)**

(a) 4 : 5
(b) 1 : 10
(c) 10 : 1
(d) 5 : 4

27. 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be : **(Online 2017 Set - 2)**

(a) 3.75
(b) 4.75
(c) 8.25
(d) 9.25

28. The minimum volume of water required to dissolve 0.1 g lead(II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2\times10^{-8}$; atomic mass of Pb =207u) is : **(Online 2018 Set - 1)**

(a) 0.36 L
(b) 17.98 L
(c) 0.18 L
(d) 1.798 L

29. Which of the following is a Lewis acid ? **(Online 2018 Set - 1)**

(a) PH_3 (b) $B(CH_3)_3$

(c) NaH (d) NF_3

30. Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? **(Online 2018 Set - 2)**

(1) $100\,mL\frac{M}{10}HCl+100\,mL\frac{M}{10}NaOH$

(2) $75\,mL\frac{M}{5}HCl+25\,mL\frac{M}{5}NaOH$

(3) $60\,mL\frac{M}{10}HCl+40\,mL\frac{M}{10}NaOH$

(4) $55\,mL\frac{M}{10}HCl+45\,mL\frac{M}{10}NaOH$

31. The pH of rain water, is approximately: **(2019-01-09/Shift-2)**

(a) 5.6 (b) 7.5

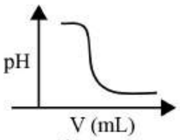
(c) 7.0 (d) 6.5

32. If K_{sp} of Ag_2CO_3 is 8 x 10^{-12}, the molar solubility of Ag_2CO_3 in 0.1 M $AgNO_3$ is: **(2019-01-12/Shift-2)**

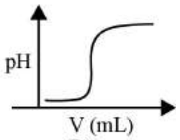
(a) 8 x 10^{-12} M (b) 8 x 10^{-11} M

(c) 8 x 10^{-10} M (d) 8 x 10^{-13} M

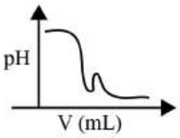
33. In an acid base titration, 0.1 M HCl solution was added to the NaOH solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment? **(2019-04-09/Shift-2)**



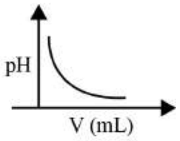
(A)



(B)



(C)



(D)

(a) (B) (b) (A)

(c) (C) (d) (D)

34 Consider the following statements

(I) The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

(II) Ionic product of water is temperature dependent.

(III) A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%

(IV) The Le Chatelier's principle is not applicable to common-ion effect.

The correct statements are: **(2019-04-10/Shift-1)**

(a) I, II, III (b) I, II, IV

(c) II, III (d) I, II

35. The pH of a 0.02 M NH_4 Cl solution will be [given $K_b(NH_4OH) = 10^{-5}$ and log 2 = 0.301]**(2019-04-10/Shift-2)**

(a) 2.65 (b) 4.35

(c) 4.65 (d) 5.32

36 What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3 = 2.4 \times 10^{-24}$: **(2019-04-12/Shift-1)**

(a) 3 x 10^{-19} (b) 12 x 10^{-21}

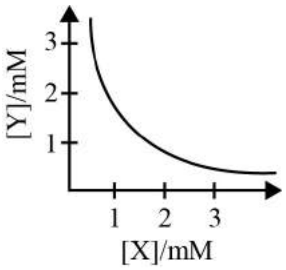
(c) 3 x 10^{-22} (d) 12 x 10^{-23}

37 The molar solubility of $Cd(OH)_2$ is 1.84 x 10^{-5} M in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is: **(2019-04-12/Shift-2)**

(a) $1.84\times10^{-9}\,M$ (b) $\frac{2.49}{1.84}\times10^{-9}\,M$

(c) $6.23\times10^{-11}\,M$ (d) $2.49\times10^{-10}\,M$

38. The stoichiometry and solubility product of a salt with the solubility curve given below is, respectively: **(2020-01-08/Shift-1)**



(a) $X_2Y, 2\times10^{-9}\,M^3$ (b) $XY_2, 1\times10^{-9}\,M^3$

(c) $XY_2, 4\times10^{-9}\,M^3$ (d) $XY, 2\times10^{-6}\,M^3$

39. The K_{sp} for the following dissociation is = 1.6×10^{-5}.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

Which of the following choices is correct for a mixture of 300 mL 0.134 M $Pb(NO_3)_2$ and 100 mL 0.4 M NaCl? **(2020-01-09/Shift-1)**

(a) $Q > K_{sp}$ (b) $Q < K_{sp}$

(c) $Q = K_{sp}$ (d) Not enough data provided

40. The solubility product of $Cr(OH)_3$ at 298 K is 6×10^{-31}. The concentration of hydroxide ions in a saturated solution of $Cr(OH)_3$ will be: **(2020-01-09/Shift-2)**

(a) $\left(18\times10^{-31}\right)^{1/4}$ (b) $\left(18\times10^{-31}\right)^{1/2}$

(c) $\left(2.22\times10^{-31}\right)^{1/4}$ (d) $\left(4.86\times10^{-29}\right)^{1/4}$

41. An acidic buffer is obtained on mixing: **(2020-09-03/Shift-1)**

(a) 100 mL of 0.1 M HCl and 200 mL of 0.1 M CH_3COONa

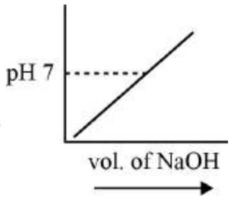
(b) 100 mL of 0.1 M HCl and 200 mL of 0.1 M NaCl

(c) 100 mL of 0.1 M CH_3COOH and 100 mL of 0.1 M NaOH

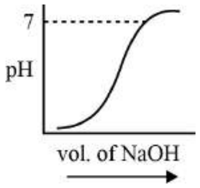
(d) 100 mL of 0.1 M CH_3COOH and 200 mL of 0.1 M NaOH

42. 100 mL of 0.1 M HCl is taken in a beaker and to it 100 mL of 0.1 M NaOH is added in steps of 2 mL and the pH is continuously measured. Which of the following graphs correctly depicts the change in pH? **(2020-09-03/Shift-2)**

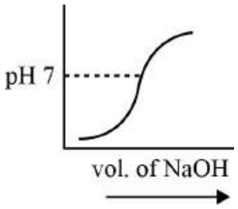
(a)



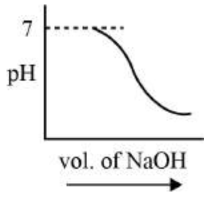
(b)



(c)



(d)



43. Arrange the following solutions in the decreasing order of pOH: **(2020-09-06/Shift-1)**

(A) 0.01 M HCl, (B) 0.01 M NaOH

(C) 0.01 M CH_3COONa, (D) 0.01 M NaCl

(a) (A) > (C) > (D) > (B) (b) (B) > (D) > (C) > (A)

(c) (B) > (C) > (D) > (A) (d) (A) > (D) > (C) > (B)

44. The solubility of AgCN in a buffer solution of pH = 3 is x. The value of x is:

[Assume: No cyno complex is formed;

$K_{sp}[AgCN] = 22 \times 10^{-16}$ and $K_a(HCN) = 6.2 \times 10^{-10}$] **(2021-02-25/Shift-1)**

(a) 1.9×10^{-5} (b) 2.2×10^{-16}

(c) 1.6×10^{-6} (d) 0.625×10^{-6}

45. The solubility of $Ca(OH)_2$ in water is:

[Given: The solubility product of $Ca(OH)_2$ in water = 5.5×10^{-6}] **(2021-02-25/Shift-2)**

(a) 1.11×10^{-6} (b) 1.77×10^{-6}

(c) 1.77×10^{-2} (d) 1.11×10^{-2}

46. A solution is 0.1 M in Cl^- and 0.001 M in CrO_4^{2-}. Solid $AgNO_3$ is gradually added to it. Assuming that the addition does not change in volume and

$$K_{sp}(AgCl) = 1.7\times10^{-18}\,M^2 \text{ and}$$

$$K_{sp}(Ag_2CrO_4) = 1.9\times10^{-12}\,M^3$$

Select correct statement form the following: **(2021-07-20/Shift-2)**

(a) AgCl precipitates first because its K_{sp} is high

(b) Ag_2CrO_4 precipitates first as its K_{sp} is low

(c) Ag_2CrO_4 precipitates first because the amount of Ag^+ needed is low

(d) AgCl will precipitates first at the amount of Ag^+ needed to precipitate is low

Numerical Value Type Questions

47. Two solutions A and B each of 100 L was made by dissolving 4g of NaOH and 9.8g of H_2SO_4 in water, respectively. The pH of the resulting solution obtained from mixing 40 L of solution A and 10 L of solution B is: **(2020-01-07/Shift-1)**

48. 3 grams of acetic acid is added to 250 mL of 0.1 M HCl and the solution is made up to 500 mL. To 20 mL of this solution mL of 5 M NaOH is added. The pH of this solution is____.

(Giving: log 3 = 0.4771, pK_a of acetic acid = 4.74, molar mass of acetic acid = 60 g/mole). **(2020-01-07/Shift-2)**

49. The photoelectric current from Na (Work function, $w_0 = 2.3$ eV) is stopped by the output voltage of the cell Pt(s) H_2 (g, 1 Bar) HCl (aq. pH = 1) | AgCl(s) | Ag(s).

The pH of aq. HCl required to stop the photoelectric current from K($w_0 = 2.25$ eV), all other conditions remaining the same, is ……. x 10^{-2} (to the nearest integer).

Given, $2.303\frac{RT}{F} = 0.06V; E^\circ_{AgCl|Ag|Cl^-} = 0.22V$

(2020-09-03/Shift-1)

50. A soft drink was bottled with a partial pressure of CO_2 of 3 bar over the liquid at room temperature. The partial pressure of CO_2 over the solution approaches a value of 30 bar when 44g of CO_2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is ….. x 10^{-1}.

(First dissociation constant of

$H_2CO_3 = 4.0 \times 10^{-7}$; log 2 = 0.3;

density of the soft drink = 1 g mL^{-1})**(2020-09-07/Shift-1)**

51. If the solubility product of AB_2 is 3.20 x 10^{-11} M^3, then the solubility of AB_2 in pure water is….. x 10^{-4} mol L^{-1} [Assuming that neither kind of ion reacts with water].

(2020-09-06/Shift-2)

52. The solubility product of PbI_2 is 8.0 x 10^{-9}. The solubility of lead iodide in 0.1 molar solution of lead nitrate is $x \times 10^{-6}$ mol/L. The value of x is ____. (Rounded off to the nearest integer) [Given $\sqrt{2} = 1.41$]

(2021-02-24/Shift-2)

53. The pH ammonium phosphate solution, if pK_a of phosphoric acid and pK_b of ammonium hydroxide are 5.23 and 4.75 respectively, is_____. **(2021-02-26/Shift-2)**

Given 4.99

54. Two salts A_2X and MX have the same value of solubility product of 4.0 x 10^{-12}. The ratio of their molar solubilities i.e. $\frac{S(A_2X)}{S(MX)} =$ _____. (Round off to the Nearest integer).

(2021-03-16/Shift-1)

55. Sulphurous acid (H_2SO_3) has $Ka_1 = 1.7 \times 10^{-2}$ and $Ka_2 = 6.4 \times 10^{-8}$. The pH of 0.588 M H_2SO_3 is ___. (Round off to the Nearest integer). **(2021-03-16/Shift-2)**

56. 0.01 moles of a weak acid HA ($K_a = 2.0$ x 10^{-6}) is dissolved in 1.0 L of 0.1 M HCl solution. The degree of dissociation of HA is ….. x 10^{-5} (Round off to the Nearest integer). [Neglect volume change on adding HA. **(2021-03-17/Shift-1)**

Assume degree of dissociation << 1]

57. In order to prepare a buffer solution of pH 5.74, sodium acetate is added to acetic acid. If the concentration of acetic acid in the buffer is 1.0 M, the concentration of sodium acetate in the buffer is…… M. (Round off to the Nearest integer).

[Given: pK_a (acetic acid) = 4.74] **(2021-03-18/Shift-1)**

58. The solubility of $CdSO_4$ in water is 8.0 x 10^{-4} mol L^{-1}. Its solubility in 0.01 M H_2SO_4 solution is …… x 10^{-6} mol L^{-1}. (Round off to the Nearest integer).

(Assume that solubility is much less than 0.01 M)

(2021-03-18/Shift-2)

59. The OH^- concentration in a mixture of 5.0 mL of 0.0504 M NH_4Cl and 2 mL of 0.0210 M NH_3 solution is X x 10^{-6} M. The value of x is _____. (Nearest integer)

[Given $K_w = 1$ x 10^{-14} and $K_b = 1.8$ x 10^{-5}]

(2021-08-26/Shift-1)

60. A_3B_2 is a sparingly soluble salt of molar mass M (g mol^{-1}) and solubility x gL^{-1}. The solubility product satisfies $K_{sp} = a\left(\frac{x}{M}\right)^5$. The value of a is _____. (Integer Answer)

(2021-08-31/Shift-1)

61. The pH of a solution obtained by mixing 50 mL of 1 M HCl and 30 mL of 1 M NaOH is $x \times 10^{-4}$. The value of x is _____. (Nearest integer) [log 2.5 = 0.3979]

(2021-08-31/Shift-2)

62. The molar solubility of $Zn(OH)_2$ in 0.1 M NaOH solution is $x \times 10^{18}$ M. The value of x is ….. (Nearest integer)

(Given: The solubility product of $Zn(OH)_2$ is 2×10^{-20})

(2021-09-01/Shift-2)

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

63. For the following assertion and reason, the correct option is: **(2020-01-08/Shift-2)**

Assertion (A) : The pH of water increases with increase in temperature.

Reason (R) : The dissociation of water into H^+ and OH^- an exothermic reaction.

(a) Both assertion and reason are false.

(b) Assertion is not true, but reason is true.

(c) Both assertion and reason are true and the reason is the correct explanation for the assertion.

(d) Both assertion and reason are true, but the reason is not the correct explanation for the assertion.

64 For the following Assertion and Reason, the correct option is **(2020-01-08/Shift-2)**

Assertion (A): When Cu (II) and sulphide ions are mixed, they react together extremely quickly to give a solid.

Reason (R): The equilibrium constant of $Cu^{2+}(aq) + S^{2-}(aq) \rightleftharpoons CuS(s)$ is high because the solubility product is low.

(a) (A) is false and (R) is true.

(b) Both (A) and (R) are false

(c) Both (A) and (R) are true but (R) is not the explanation for (A).

(d) Both (A) and (R) are true but (R) is the explanation for (A)

65. Given below are two statements. **(2021-08-26/Shift-1)**

Statement I: In the titration between strong acid and weak base methyl orange is suitable as an indicator.

Statement II: For titration of acetic acid with NaOH phenolphthalein is not a suitable indicator.

In the light of the above statements, choose the most appropriate answer from the options given below.

(a) Statement I is false, but Statement II is true

(b) Statement I is true, but Statement II is false

(c) Both Statement I and Statement II are true

(d) Both Statement I and Statement II are false

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

Objective Questions I [Only one correct option]

1. In the following reaction :

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

Which two substances are Bronsted bases ?

(a) CO_3^{2-} and H_3O^+ (b) HCO_3^- and H_3O^+

(c) HCO_3^- and CO_3^{2-} (d) CO_3^{2-} and H_2O

2. The equilibrium constant for this reaction is approximately 10^{-3}.

$$HPO_4^{2-}(aq.) + HCO_3^-(aq.) \rightleftharpoons H_2PO_4^-(aq.) + CO_3^{2-}(aq.)$$

Which is the strongest conjugate base in this reaction ?

(a) $HPO_4^{2-}(aq.)$ (b) $HCO_3^-(aq.)$

(c) $H_2PO_4^-(aq.)$ (d) $CO_3^{2-}(aq.)$

3. Arrange the following acids in increasing order of their acid strength :

I. $HClO_4$ II. H_2SO_4 III. H_3PO_4

(a) III < II < I (b) I < II < III

(c) II < III < I (d) III < I < II

4. Consider the following reaction which proceeds predominantly from

$$HSO_4^- + NH_3 \rightleftharpoons NH_4^+ + SO_4^{2-}$$

From the information given it is clear that

(a) HSO_4^- is a stronger acid than NH_4^+.

(b) NH_3 is a weaker base than SO_4^{2-}

(c) HSO_4^- is a stronger base than NH_4^+

(d) NH_3 is a weaker base than NH_4^+

5. A mixture of weak acid is 0.1 M in HCOOH ($K_a = 1.8 \times 10^{-4}$) and 0.1 M in HOCN ($Ka = 3.1 \times 10^{-4}$). Hence, $[H_3O^{\oplus}]$ is

(a) 7.0×10^{-3} M (b) 4.1×10^{-4} M

(c) 0.20 M (d) 4.1×10^{-3} M

6. Like water, ammonia (NH_3) is an amphoteric substance that can be used as a solvent for acid base reactions. The phase label (am) means solvated by ammonia (ammoniated). Which statement is correct, extrapolating from your knowledge of acid base reactions in water ?

(a) Auto-ionization of ammonia is described by

$$2NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$$

(b) The strongest acid that can exist in ammonia solution is H_3O^+ (am).

(c) The strongest base, which can exist in ammonia solution, is NH_4^+ (am).

(d) The addition of an acid to an ammonia solution will increase the concentration of NH_2^- (am).

7. The concentration of NaOH solution is 10^{-8} M. Find out the (OH^-) concentration

(a) 10^{-8} (b) Greater than 10^{-6}

(c) 10^{-6} (d) Lies between 10^{-6} and 10^{-7}

8. The charge balance equation of species in 0.1 M CH_3COOH solution is given by :

(a) $[H^+] = [OH^-]$

(b) $[H^+] = [CH_3COO^-]$

(c) $[H^+] = [OH^-] + [CH_3COO^-]$

(d) $2[H^+] = [OH^-] + [CH_3COO^-]$

9. A solution of 2M formic acid (HCOOH) is 0.95% ionized. What is the K_a of formic acid ?

(a) 1.9×10^{-2} (b) 1.8×10^{-4}

(c) 9×10^{-5} (d) 4.5×10^{-5}

10. What is the K_b of a weak base that produces one OH^- per molecule if a 0.05 M solution is 2.5% ionized ?

(a) 7.8×10^{-8} (b) 1.6×10^{-6}

(c) 3.2×10^{-5} (d) 1.2×10^{-3}

11. The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be :

(a) unionised in the small intestine and in the stomach

(b) completely ionized in the small intestine and in the stomach

(c) ionised in the stomach and almost unionised in the small intestine

(d) ionised in the small intestine and almost unionised in the stomach

12. In our body, carbon dioxide (CO_2) combines with water (H_2O) to form carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbonic acid undergoes dissociation as,

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

During the physical and mental stress, the rate of respiration increses, which results in the decrease in concentration of CO_2 in the blood. What will be the effect on pH of human blood during the stress ?

(a) Decreases (b) Remains same

(c) Increases (d) Cannot be predicted

13. What is the pH of a solution at 25°C that is 0.010 M in HCl and 0.025 M in HNO_3 ?

(a) 1.49 (b) 1.60

(c) 1.82 (d) 3.60

14. If 112 mL of HCl(g) at S.T.P. conditions become the solute in 500 mL of water solution, what will be the pH of this mixture ?

(a) 0.5 (b) 1.0

(c) 1.5 (d) 2.0

15. Why is it necessary to take the acid-base properties of water into account when computing the hydronium ion concentration of very dilute solutions of strong acids ?

(a) The hydroxide ion produced from the dissociation of water reacts with most of the H^+ ion produced from the acid.

(b) The dissociation constant for water is larger in dilute rather than in concentrated solutions of acids.

(c) The amount of H^+ ion produced by the dissociation of water is significant compared to that produced by the acid.

(d) The conjugate base of the strong acid reacts with the hydroxide ion produced from the dissociation of water.

16. When one drop of a concentrated HCl is added to 1 L of pure water at 25°C, the pH drops suddenly from 7 to 4. When the second drop of the same acid is added, the pH of the solution further drops to about

(a) 0 (b) 1.0

(c) 2.0 (d) 3.7

17. The pH of 10^{-5} M HCl solution if 1 ml of it is diluted to 1000 ml is :

(a) 5 (b) 8

(c) 7.02 (d) 6.98

18. On diluting a buffer solution, its pH :

(a) increases (b) decreases

(c) remains same (d) can't say

19. Calculate the $[NH_3]/[NH_4^+]$ ratio in an ammonia-ammonium chloride buffer with a pH of 9.00. ($K_b = 1.8 \times 10^{-5}$ for ammonia)

(a) 0.56 : 1.00 (b) 0.74 : 1.00

(c) 0.86 : 1.00 (d) 1.12 : 1.00

20. A buffer solution of pH = 9.00 is made by dissolving ammonium chloride and ammonia in water. How many moles of ammonium chloride must be added to 1.0 L of 0.25 M ammonia to prepare this buffer ?

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^-(aq) + OH^-(aq);\ K_b = 1.8 \times 10^{-5}$$

(a) 0.25 mol (b) 0.45 mol

(c) 0.65 mol (d) 2.2 mol

21. Which of these aqueous solutions are buffers ?

1. A solution that is 0.1 M HNO_3 and 0.1 M HCl.
2. A solution that is 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4.
3. A solution made by mixing 10 mL of 0.1 M HF and 5.0 mL of 0.1 M NaOH.
4. A solution made by mixing 10 mL of 0.1 M KOH and 20 mL of 0.1 M HCl.

(a) 1 and 2 (b) 2 and 3

(c) 3 and 4 (d) 1 and 4

22. A solution was prepared by mixing 10.0 mL of 0.50 M NaOH with 10.0 mL of 1.00 M acetic acid, $K_a = 1.8 \times 10^{-5}$. Find the pH of solution.

(a) 2.45 (b) 1.67

(c) 2.37 (d) 4.74

23. What volume of 0.40 M NH_3 solution must be added to 1.0 L of 0.10 M NH_4Cl solution to give a buffer having pH of 10.00 ? For NH_3, $K_b = 1.8 \times 10^{-5}$

(a) 1.4 L (b) 1.1 L

(c) 0.97 L (d) 0.61 L

24. For the overall reaction

$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$, the value of K_a is 1×10^{-22}. The K_{sp} for ZnS is 1.2×10^{-23}. What would be the maximum concentration of $Zn^{+2}(aq)$ ion in a 0.01 M solution of H_2S that has its pH adjusted to 5 by mixing a strong acid with the H_2S ?

(a) 1.2×10^{-9} M (b) 2.4×10^{-6} M

(c) 3.8×10^{-4} M (d) 1.8×10^{-1} M

25. For the overall reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$, the value of K_a is 1×10^{-22}. The K_{sp} for FeS is 4×10^{-19}. What would be the maximum concentration of Fe^{+2} (aq) ion in a 0.1 M solution of H_2S that has has its pH adjusted to 2 by mixing a strong acid with the H_2S ?

(a) 4×10^{-38} M (b) 6×10^{-10} M

(c) 6×10^{-6} M (d) 4.0 M

26. $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-\ ;\ pK_1 = 2.15$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}\ \ pK_2 = 7.20$

Hence pH of 0.01 M NaH_2PO_4 is :

(a) 9.35 (b) 4.675

(c) 2.675 (d) 7.350

27. Calculate the molar concentrations of H_3O^+, HSO_4^-, and SO_4^{2-} in a 0.250 M solution of H_2SO_4. Assume K_{a_1} is very large ; $K_{a_2} = 1.20 \times 10^{-2}$.

$[H_3O^+]$, M	$[HSO_4^-]$, M	$[SO_4^{2-}]$, M
(a) 0.250	0.250	0.000
(b) 0.250	0.250	0.0120
(c) 0.500	0.000	0.500
(d) 0.261	0.239	0.0110

28. What is the equilibrium [OH^-] in 0.1413 M H_2CO_3 ?

$$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^- \ (K_a = 4.30 \times 10^{-7})$$

(a) 7.07×10^{-14} M (b) 2.46×10^{-4} M

(c) 4.16×10^{-11} M (d) 6.84×10^{-6} M

29. A 100 mL portion of water is added to each of the following two solutions.

(i) 100 mL of 0.02 M KCl (ii) 100 mL of 0.02 M HCl

Which of the following statements is correct ?

(a) There will be no change in pH of solution (i) and (ii)

(b) The pH of solution (i) will remain the same but pH of solution (ii) will increase

(c) The pH of solution (i) will remain same but of solution (ii) will decrease

(d) The pH of solution (ii) will remain same but of solution (i) will increase

30. The correct order of increasing [H_3O^+] in the following aqueous solution is :

(a) 0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_3$

(b) 0.01 M NaCl < 0.01 M $NaNO_3$ < 0.01 M H_2S < 0.01 M H_2SO_4

(c) 0.01 M H_2S < 0.01 M $NaNO_3$ = 0.01 M NaCl < 0.01 M H_2SO_4

(d) 0.01 M H_2S < 0.01 M $NaNO_3$ < 0.01 M NaCl < 0.01 M H_2SO_4

31. pH of water is 7. When a substance Y is dissolved in water, the pH becomes 11. The substances Y is a salt of :

(a) weak acid and weak base

(b) strong acid and strong base

(c) strong acid and weak base

(d) weak acid and strong base

32. Calcium lactate is a salt of weak acid i.e., lactic acid having general formula $Ca(Lac)_2$. Aqueous solution of salt has 0.3 M concentration. pOH of solution is 5.60. If 90% of the salt is dissociated then what will be the value of pK_a ?

(a) 2.8 – log (0.54) (b) 2.8 + log (0.54)

(c) 2.8 + log (0.27) (d) None of these

33. If 0.1 mol of salt is added to 1 L water, which of these salts is expected to produce the most acidic solution ?

(a) $NaC_2H_3O_2$ (b) NH_4NO_3

(c) $CuSO_4$ (d) $AlCl_3$

34. Hydrolysis constants of two salts KA and KB of weak acids HA and HB are 10^{-8} and 10^{-6}. If the dissociation constant of third acid HC is 10^{-2}. The order of acidic strengths of three acids will be :

(a) HA > HB > HC (b) HB > HA > HC

(c) HC > HA > HB (d) HA = HB = HC

35. Which of the following are Lewis acids?

(a) PH_3 and BCl_3 (b) $AlCl_3$ and $SiCl_4$

(c) PH_3 and $SiCl_4$ (d) BCl_3 and $AlCl_3$

36. A solution of 0.1 M NaZ has pH = 8.90. The K_a of HZ is

(a) 6.3×10^{-11} (b) 6.3×10^{-10}

(c) 1.6×10^{-5} (d) 1.6×10^{-6}

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

(a) 1.74×10^{-5} (b) 3.52×10^{-3}

(c) 6.75×10^{-4} (d) 5.38×10^{-2}

38. The solubility of silver benzoate (C_6H_5COOAg) in H_2O and in a buffer solution of pH = 2, 3, and 4 are S_1, S_2, S_3 and S_4 respectively. The decreasing order of solubility is

(a) $S_1 > S_2 > S_3 > S_4$ (b) $S_4 > S_3 > S_2 > S_1$

(c) $S_2 > S_3 > S_4 > S_1$ (d) $S_3 > S_2 > S_4 > S_1$

39. K_{sp} of Mg $(OH)_2$ is 1 × 10^{-12}. 0.01 M $MgCl_2$ will be precipitating at the limiting pH :

(a) 8 (b) 9

(c) 10 (d) 12

40. The solubility products of MA, MB, MC and MD are 1.8×10^{-10}, 4×10^{-3}, 4×10^{-8} and 6×10^{-5} respectively. If a 0.01 M solution of MX is added dropwise to a mixture containing A^-, B^-, C^- and D^- ions then the one to be precipitated first will be :

(a) MA (b) MB

(c) MC (d) MD

41. Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately :

(a) $10^9\left(\frac{W}{M}\right)^5$ (b) $10^7\left(\frac{W}{M}\right)^5$

(c) $10^5\left(\frac{W}{M}\right)^5$ (d) $10^3\left(\frac{W}{M}\right)^5$

42. How many grams of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will dissolve in 1.0 L of 6.0 M NH_3 ($K_b = 1.8 \times 10^{-5}$). The $K_{formation}$ for $Ag(NH_3)_2^+$ is 1.7×10^7.

(a) 0.0013 g (b) 43 g

(c) 1.3 g (d) 12 g

43. For Ag_2CO_3, K_{sp} = 6.2 × 10^{-12}, For AgCl, K_{sp} = 2.8 ×10^{-10}. Solid Ag_2CO_3 and solid AgCl are added to a beaker containing 1.00 M Na_2CO_3(aq). Under these conditions the [CO_3^{2-}] = 1.00 M. Calculate the [Cl^-] in solution when equilibrium is established.

(a) 1.1×10^{-4} (b) 1.26×10^{-6}

(c) 0.15 (d) 2.8×10^{-6}

44. Given the following K_{sp} values : for $M(OH)_4$, $K_{sp}(M) = 4.0 \times 10^{-19}$; for $Z(OH)_2$, $K_{sp}(Z) = 1.0 \times 10^{-14}$. One mole of each of the above solids is placed in a beaker containing 1 (one) litre of pure water. These solids go into equilibrium with their ions. Calculate the pH required for the metal ion concentrations to be equal, $[M^{4+}] = [Z^{2+}]$.

(a) 12.6
(b) 9.6
(c) 6.7
(d) 11.8

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

(a) pK_{a_1} and pK_{a_2}

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

(c) pK_a and $(pK_{a_1} + pK_{a_2})$

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

46. 0.2 g sample of benzoic acid, C_6H_5COOH is titrated with 0.12 M Ba $(OH)_2$ solution. What volume of $Ba(OH)_2$ solution is required to reach the equivalence point ?

Molar mass of benzoic acid is 122 g mol^{-1}

(a) 6.82 mL
(b) 13.6 mL
(c) 17.6 mL
(d) 35.2 mL

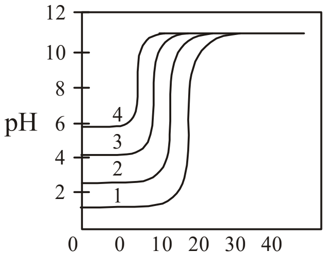
47. How many milliliters (mL) of a 0.0500 M NaOH (a strong base) solution should be added to 1.00 L of 0.100 M H_3PO_4, solution to produce a buffer of pH = 2.00 ? For H_3PO_4,

$K_{a_1} = 6.67 \times 10^{-3}$

Given : $H_3PO_4 + OH^-$ (from NaOH) $\rightarrow H_2PO_4^- + H_2O$

(a) 200
(b) 400
(c) 600
(d) 800

48. Following figure represents simulated titration curves for solutions of four acids titrated with the same standard base solution. Based on these titration curves, we can accurately predict that



(a) Curve 4 represents the smallest concentration and the weakest acid.

(b) Curve 1 represents the largest concentration and the strongest acid.

(c) The dissociation constant for the acid represented by curve 3 is about 1×10^{-4} (i.e., $K_a = 1 \times 10^{-4}$).

(d) All the responses above are correct.

Objective Questions II

[One or more than one correct option]

49. Which among the following represent the conjugate acid/base pairs ?

(a) H_3O^+/H_2O

(b) H_2SO_4/SO_4^{2-}

(c) HCO_3^-/CO_3^{2-}

(d) All are conjugate acid/base pairs

50. At 25ºC, pH of a 0.01 M solution of a monobasic acid (HA) is 4. The correct statement(s) regarding HA and its given solution is (are)

(a) HA is a weak acid

(b) The ionization constant (K_a) of acid is approximately 10^{-6} at 25ºC

(c) Increasing the temperature of solution would cause the pH to decrease

(d) Addition of 0.1 M HCl solution would lower pH by increasing degree of ionization.

51. Choose the correct statement :

(a) pH of acidic buffer solution decreases if more salt is added

(b) pH of acidic buffer solution increases if more salt is added

(c) pH of basic buffer decreases if more salt is added

(d) pH of basic buffer increases if more salt is added

52. Which of the following will function as buffer ?

(a) NaCl + NaOH
(b) Borax + Boric acid
(c) $NaH_2PO_4 + NaHPO_4$
(d) $NH_4Cl + NH_4OH$

53. Which of the following mixtures is (are) buffer ?

(a) 10 mL 0.1 M NH_4Cl + 10 mL 0.08 M NaOH

(b) 20 mL 0.22 M CH_3COOH + 30 mL 0.15 M NaOH

(c) A 0.10 M $NaHCO_3$ solution

(d) 15 mL 0.12 M CH_3NH_2 + 10 mL 0.07 M HCl

54. Degree of hydrolysis for a salt of strong acid and weak base is :

(a) independent of dilution

(b) increase with dilution

(c) increase with decrease in K_b of the bases

(d) decreases with decrease in temperature

55. A 0.1 M sodium acetate solution was prepared. The $K_h = 5.6 \times 10^{-10}$

(a) The degree of hydrolysis is 7.48×10^{-5}

(b) The $[OH^-]$ concentration is 7.48×10^{-3} M

(c) The $[OH^-]$ concentration is 7.48×10^{-6} M

(d) The pH is approximately 8.88

56. Which among the following salts will give basic solution on hydrolysis ?

(a) NaH_2PO_4 (b) NH_4Cl

(c) NaCl (d) K_2CO_3

57. A solution containing a mixture of 0.05 M NaCl and 0.05 M NaI is taken. (K_{sp} of AgCl = 10^{-10} and K_{sp} of AgI = 4×10^{-16}). When $AgNO_3$ is added to such a solution:

(a) the concentration of Ag^+ required to precipitate Cl^- is 2×10^{-9} mol/L

(b) the concentration of Ag^+ required to precipitate I^- is 8×10^{-15} mol/L

(c) AgCl and AgI will be precipitate together

(d) first AgI will be precipitated

58. Which of the following is (are) correct when 0.1 L of 0.0015 M $MgCl_2$ and 0.1L of 0.025 M NaF are mixed together ? (K_{sp} of $MgF_2 = 3.7 \times 10^{-8}$)

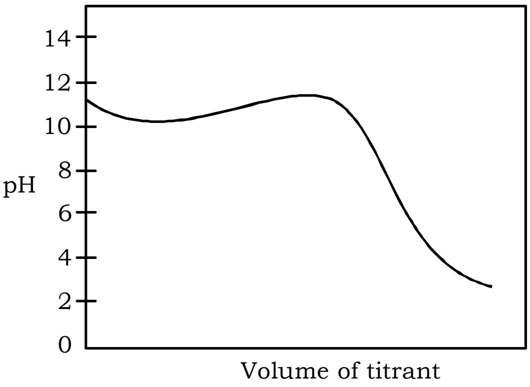
(a) MgF_2 remains in solution

(b) MgF_2 precipitates out

(c) $MgCl_2$ precipitates out

(d) Cl^- ions remain in solution

59. The titration curve given below involves 1.0 M solutions of an acid and a base.



Which of the following is/are correct for the given curve ?

(a) The solution being titrated is a base and the titrant is an acid

(b) The pH at the equivalence point must be less than 7

(c) The titrated solution is strong acid

(d) The titrated solution is strong base

60. The percentage ionization of a weak base is given by

(a) $\left(\sqrt{\frac{K_a}{c}}\right)\times 100$ (b) $\left(\frac{1}{1+10^{pK_b - pOH}}\right)\times 100$

(c) $\left(\sqrt{\frac{K_b}{c}}\right)\times 100$

(d) $\left(\sqrt{\frac{K_w}{c \times K_a \text{ of conjugate acid}}}\right)\times 100$

61. Which of the following statements is/are correct about the ionic product of water ?

(a) K_a (equilibrium constant of water) < K_w (ionic product of water)

(b) $pK_a > pK_w$

(c) At 100°C, K_w of water becomes 10^{-12}

(d) Ionic product of water at 25°C is 10^{-14}

62. A solution is prepared by mixing 100 mL 0.50 M hydrazoic acid (HN_3), whose $K_a = 3.6 \times 10^{-4}$, with 400 mL of 0.10M cyanic acid (HOCN), whose $K_a = 8 \times 10^{-4}$. Which of the following is (are) true regarding

(a) $[H^+] = 10^{-2}$ M (b) $[N_3^-] = 3.6 \times 10^{-3}$

(c) $[OCN^-] = 4.57 \times 10^{-3}$ (d) $[OH^-] = 7.14 \times 10^{-13}$

63. Which of the following is (are) correct for buffer solution ?

(a) Acidic buffer will be effective within in the pH range $(pK_a \pm 1)$

(b) Basic buffer will be effective within the pH range $(pK_w - pK_b \pm 1)$

(c) $H_3PO_4 + NaH_2PO_4$ is not a buffer solution

(d) Buffer behaves most effectively when the [Salt]/[Acid] ratio equal to one

64. The equilibrium constant (K_c) for the reaction of a weak acid HA with strong base NaOH is 10^9 at 25°C. Which of the following are correct deduction ?

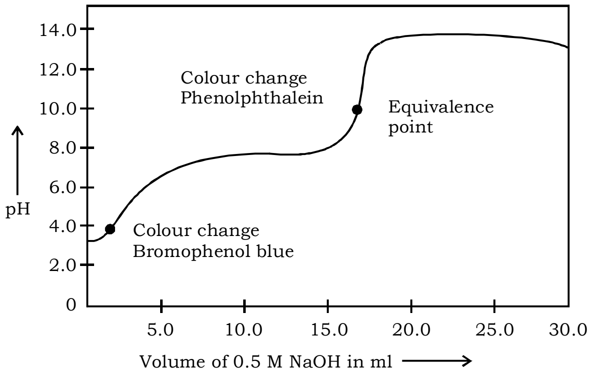
(a) The ionization constant (K_a) at 25°C is 10^{-5} for HA.

(b) pH of a 0.01 M aqueous solution of HA at 25°C will be 3.5

(c) pH of a 0.10 M aqueous solution of NaA at 25°C will be 9.

(d) If K_b of a weak base BOH is 10^{-4} at 25°C, equilibrium constant for neutralization of HA with BOH at 25°C will be 10^{-5}

65. Titration curve for a weak acid with a strong base is



Which of the following s/are correct for the above curve ?

(a) At the half-neutralization point pH = pK_a

(b) The pH is greater than 7 at the equivalence point

(c) The colour change in basic medium

(d) The solution at the half neutralization is buffer solution

Numerical Value Type Questions

66. A buffer solution is formed by mixing 100 mL 0.01 M CH_3COOH with 200 mL 0.02 M CH_3COONa. If this buffer solution is made to 1.0 L by adding 700 mL of water, pH will change by a factor of

67. If the equilibrium constant of the reaction of a weak acid HA with a strong base is 10^9, then pH of a 0.10 M NaA solution is

68. $M(OH)_x$ has K_{sp} of 4×10^{-9} and its solubility of 10^{-3} M. The value of x is _______ .

69. Solubility product constant of a springly soluble salt MCl_2 is 4×10^{-12} at 25°C. Also, at 25°C, solubility of MCl_2 is an aqueous solution of $CaCl_2$ is 4×10^8 times less compared to its solubility in pure water. Hence, concentration (molarity) of $CaCl_2$ solution is

70. The solubility product constant of a metal carbonate MCO_3 is 2×10^{-12} at 25°C. A solution is 0.1 M in $M(NO_3)_2$ and it is saturated with 0.01 M CO_2. Also the ionization constant of CO_2 are $K_{a_1} = 4 \times 10^{-7}$ and $K_{a_2} = 5 \times 10^{-11}$ at 25°C. The minimum pH that must be maintained to start any precipitation is

71. The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.5 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid ? (in 10^{-6})

72. How much AgBr could dissolve in 1.0 L of 0.4 M NH_3 ? Assume that Ag $(NH_3)_2^+$ is the only complex formed .

Given : The dissociation constant for

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

$K_d = 6.0 \times 10^{-8}$ and K_{sp} (AgBr) = 5.0×10^{-13}.

73. When a 40 mL of a 0.1 M weak base, BOH is titrated with 0.10 M HCl, the pH of the solution at the end point is 5.5. What will be the pH if 10 mL of 0.10 M NaOH is added to the resulting solution ?

Assertion Reason

(A) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion.

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

74. **Assertion (A) :** $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.

Reason (R) : Size of $[Al(H_2O)_6]^{3+}$ smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge.

(a) A (b) B

(c) C (d) D

75. **Assertion (A) :** Water acts as leveling solvent for various acids.

Reason (R) : Leveling effect of water is due to high dielectric constant and strong proton accepting tendency.

(a) A (b) B

(c) C (d) D

76. **Assertion (A) :** Addition of HCl(aq.) to HCOOH(aq.) decreases the ionization of HCOOH.

Reason (R) : Common ion effect of H^+ ion, reduces the ionization of HCOOH.

(a) A (b) B

(c) C (d) D

77. **Assertion (A) :** pH of HCl solution is less than that of acetic acid of the same concentration.

Reason (R) : In equimolar solutions, the number of titrable protons present in HCl in less than that present in acetic acid.

(a) A (b) B

(c) C (d) D

78. **Assertion (A) :** pH of water increases with an increase in temperature.

Reason(R): K_w of water increases with increase in temperature.

(a) A (b) B

(c) C (d) D

79. **Assertion (A) :** pH of 10^{-8} M HCl lies between 6 and 7.

Reason (R) : For very dilute solutions of acids, H^+ ion contribution from water is also taken into consideration.

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

80. **Assertion (A) :** If Ka of HA is 10^{-3} and Ka of HB is 10^{-4} at 25°C, pH of an aqueous solution of HB will be one unit greater than pH of equimolar solution of HA.

Reason (R) : For weak acids, both concentration and ionization constant affects the pH.

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

81. **Assertion (A) :** Increasing the temperature of an aqueous acetic acid solution decreases pH.

Reason (R) : Ionization of acetic acid is endothermic in nature.

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

82. **Assertion (A) :** pH value of HCN solution decreases when NaCN is added to it

Reason (R) : NaCN provides a common ion CN^- to HCN.

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

83. **Assertion (A) :** An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) : Acetic acid is a weak acid and NH_4OH is a weak base.

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

84. **Assertion (A) :** Aqueous solution of ammonium carbonate is basic.

Reason (R) : Acidic or Basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b of the acid and base forming it.

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

85. **Assertion (A) :** H_3BO_3 is aprotic acid.

Reason (R) : Borax is salt of H_3BO_3 and NaOH ; its aqueous solution is alkaline in nature.

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

86. **Assertion (A) :** When aqueous, solution of CH_3COONH_4 is diluted, then its degree of hydrolysis increases.

Reason (R) : Ammonium acetate is the salt of weak acid and weak base, its degree of hydrolysis does not depend on the concentration.

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

87. **Assertion (A) :** If HA and HB are two weak non-basic acids with $K_a(HA) < K_b(HB)$, then, the aqueous solution of NaA will have higher pH than pH of aqueous solution of NaB of same concentration.

Reason (R) : Conjugate base of a weaker acid is stronger than the same of stronger acid.

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

88. **Assertion (A) :** On mixing 500 mL of 10^{-6} M Ca^{2+} ion and 500 mL of 10^{-6} M F^- ion, the precipitate of CaF_2 will be obtained K_{sp} $(CaF_2) = 10^{-18}$.

Reason (R) : If K_{sp} is less than ionic product, precipitate will be obtained.

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

89. **Assertion (A) :** The pH of the solution at the mid point of the weak acid strong base titration becomes equal to the pK_a of the acid.

Reason (R) : The molar concentrations of proton acceptor and proton donor become equal at mid point of a weak acid.

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

Match the Following

Each question has two columns. Four options are given representing matching of elements from Column-I and Column-II.

90. Match the Column-I with Column-II :

	Column - I		Column - II
(A)	Degree of hydrolysis for salts of strong acid and weak base	(p)	the hydrolysis of anion which is irreversible.
(B)	Hydrolysis constant	(q)	is not possible because of the reaction of strong base with strong acid.
(C)	Na_2O in water is basic due to	(r)	is affected when temperature is changed and concentration is changed.
(D)	$Na^+ + H_2O \rightleftharpoons NaOH + H^+$	(s)	is independent of volume of solution taken but depends upon temperature

91. Match the Column-I with Column-II :

Column - I	**Column - II**
(Salt)	**(Nature of hydrolysis)**
(A) NH_4CN	(p) Only cation hydrolysis
(B) CH_3COONa	(q) Only anion hydrolysis
(C) $NaClO_4$	(r) Both cation and anion hydrolysis
(D) $Fe(NO_3)_2$	(s) No hydrolysis

92. Match the Column-I with Column-II :

Column - I	**Column - II**
(A) $[A^{+Y}]^X [B^{-X}]^Y > K_{sp}$	(p) Precipitation just starts
(B) $[A^{+Y}]^X [B^{-X}]^Y < K_{sp}$	(q) Buffer capacity
(C) $[A^{+Y}]^X [B^{-X}]^Y = K_{sp}$	(r) The solid AXB_4 will precipitate out
(D) d(n)/dpH	(s) No precipitation

93. Match the Column-I with Column-II :

Column - I	**Column - II**
(A) has highest pH at end point when titrated against standard NaOH	(p) CH_3COOH $K_a = 1.8 \times 10^{-5}$
(B) has lowest pH at the end point when titrated against standard NaOH	(q) HCN $K_a = 5 \times 10^{-10}$
(C) release maximum heat when neutralized with NaOH	(r) HF $K_a = 5 \times 10^{-4}$
(D) release equal amount of heat when neutralized with strong acid or base	(s) NH_4OH $K_b = 1.8 \times 10^{-5}$

94. Match the Column-I with Column-II :

Column - I	**Column - II**
(Titration)	**(Indicator used)**
(A) Strong acid versus strong base	(p) Methyl orange (3 – 4.4)
(B) Weak acid versus strong base	(q) Methyl red (4.3 – 6.3)
(C) Strong acid versus weak base	(r) Phenolphthalein (8 – 10)
(D) Weak acid versus weak base	(s) No suitable indicator

95. Match the Column-I with Column-II :

Column-I	**Column-II**
(A) NH_4Cl	(p) No hydrolysis
(B) NaCl	(q) $h = \sqrt{K_h / C}$
(C) CH_3COONa	(r) $h = \sqrt{\dfrac{K_w}{CK_b}}$
(D) CH_3COONH_4	(s) $h = \sqrt{K_h}$

where, C = Concentration of Salt ; K_h = hydrolysis constant K_w = Ionic product of water ; K_b = Dissociation constant of weak base

Paragraph Type Questions

Use the following passage, to solve Q. 96 to Q. 97

Passage

The concentration of hydrogen ion is a measure of acidity or alkalinity of a solution.

For mono basic acids :

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

$$\alpha = \sqrt{\frac{K_a}{C}}$$

where, K_a = Dissociation constant of acid

C = molarity of acid

$$[H^+] = C\alpha, [H^+] = \frac{K_a}{\alpha}, \; [H^+] = \sqrt{CK_a}$$

pH of a weak acid can be calculated using $[H^+]$ by any of above methods.

$[H^+]_{Total} = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$ (When two weak acids are mixed)

$[H^+]$ of polyprotic acid (weak, H_3A) (has dissociation constants $K_{a_1} >> K_{a_2} >> K_{a_3}$); will be contributed by first dissociation at the most.

96. What will be the value of $[H^+]$ of 10^{-6} M CH_3COOH ? ($K_a = 1.8 \times 10^{-5}$)

(a) 4.24×10^{-6} M
(b) 10^{-6} M
(c) 9.5×10^{-7} M
(d) 10^{-8} M

97. What will be sulphide ion concentration of a dilute solution that has been saturated with 0.1 M H_2S if the pH of the solution is 3 ?

$$K_{a_1} = 1\times10^{-7} \; ; \; K_{a_2} = 1.3\times10^{-13}$$

(a) 1.25×10^{-11}
(b) 1.3×10^{-13}
(c) 1.45×10^{-9}
(d) 1.30×10^{-15}

Use the following passage, to solve Q. 98 to Q. 100

Passage

Hydrogen carbonate and phosphate buffers in the blood prevent excess hydrogen ions $[H^+]$ produced by metabolic activity, from decreasing the pH of the blood. Carbon dioxide released into the blood during respiration is regulated by this system and prevented from causing changes in plasma pH prior to its excretion from the lungs. Excessive change in blood chemistry which would change the plasma pH from its normal level 7.4. This excretes hydrogen ions and retains hydrogen carbonate ions and retains hydrogen ions if the pH rises. This may produce change in the pH of the urine from 4.5 to 8.5. A fall in pH also stimulates the kidney cells to produce the base ion ammonia (NH_4^+) which combines with acids brought to the kidney and is then excreted as ammonium salts.

98. The normal pH of blood is

(a) 4.5 (b) 8.5

(c) 7.32 (d) 7.4

99. Which of the following buffer present in the blood ?

(a) $HCO_3^- + H_2CO_3$ and $PO_4^{3-} + HPO_4^{2-}$

(b) $HCO_3^- + CO_3^{2-}$ and $HPO_4^{2-} + H_2PO_4^-$

(c) $HCO_3^- + H_2CO_3$ and $PO_4^{3-} + H_3PO_4$ (d) None of these

100. Assuming that the buffer in blood is $CO_2 - HCO_3^-$. Calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH.

(K_1 of $H_2CO_3 = 4.2 \times 10^{-7}$)

(a) 15 (b) 16

(c) 14 (d) 11

Use the following passage, to solve Q. 101 to Q. 102

Passage

H_3PO_4 is a tribasic acid with pK_{a_1}, pK_{a_2} and pK_{a_3} 2.12, 7.21, and 12.32, respectively. It is used in fertiliser productions and its various salts are used in food, detergent, toothpaste, and in metal treatment.

Small quantities of H_3PO_4 are used in imparting the sour or tart taste to soft drinkes, such as Coca Cola, and beers, in which H_3PO_4 in present 0.05% by weight (density = 1.0 g mL^{-1}).

10^{-3} M H_3PO_4 (pH = 7) is used in fertilisers as an aqueous soil digesting. Plants can absorb zinc in water soluble form only. Zinc phosphate is the source of zinc and PO_4^{3-} ions in the soil. K_{sp} of zinc phosphate = 9.1×10^{-33}.

101. $[PO_4^{3-}]$ ion in the soil with pH = 7, is

(a) 10^{-3} M (b) 1.2×10^{-4} M

(c) 2.2×10^{-4} M (d) 1.1×10^{-10} M

102. $[Zn^{2+}]$ ion in the soil is

(a) 2.9×10^{-11} M (b) 4.0×10^{-10} M

(c) 3.0×10^{-6} M (d) 9.1×10^{-5} M

Use the following passage, to solve Q. 103 to Q. 105

Passage

Solubility of a salt is defined as the maximum amount of a salt which can be dissolved in a given amount of solvent at a particular temperature. Unit of solubility is mole per litre of solution. The solubility of a salt of weak acid with strong base (CH_3COOAg) in acidic buffer can be calculated as

$$\underset{S-X}{CH_3COOAg} \rightleftharpoons \underset{S}{CH_3COO^-(aq)} + Ag^+(aq)$$

S = Solubility of salt

$$\underset{(S-X)}{CH_3COO^-(aq)} + \underset{\text{(from acidic buffer)}}{H^+} \rightleftharpoons \underset{X}{CH_3COOH}$$

$$K_{sp} = [Ag^+][CH_3COO^-] = S(S-X)$$

Dissociation constant of weak acid

$$(K_a) = \frac{(S-X)[H^+]}{X}$$

103. The solubility of LiOH in a solution with pH = 8 is ($K_{sp} = 1.8 \times 10^{-12}$)

(a) 1.8×10^{-18} (b) 1.8×10^{-6}

(c) 10^{-6} (d) 1.8×10^{-4}

104. The solubility of AgCl is maximum in

(a) 0.1 M NaCl (b) 0.1 M $CaCl_2$

(c) 55.5 M H_2O (d) None of these

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

(a) 4.9×10^{-10} (b) 5.9×10^{-5}

(c) 6.9×10^{-10} (d) 8.3×10^{-5}

Use the following passage, to solve Q. 106 to Q. 108

Passage

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product K_{sp}.

(i) When $K_{ip} = K_{sp}$, the solution is just saturated and no precipitation takes place.

(ii) When $K_{ip} < K_{sp}$, the solution is unsaturated and precipitation will not take place.

(iii) When $K_{ip} > K_{sp}$, the solution is supersaturated and precipitation takes place.

106. Which of the following is most soluble ?

(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$) (b) MnS ($K_{sp} = 7 \times 10^{-16}$)

(c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)

107. The concentration of Ag^+ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} g ion per litre. The solubility product of AgCl is :

(a) 0.353×10^{-10} (b) 0.530×10^{-10}

(c) 1.12×10^{-10} (d) 2.12×10^{-10}

108. If the solubility of $Li_3Na_3(AlF_6)_2$ is x mol L^{-1}, then its solubility product is equal to :

(a) $12x^3$ (b) $18x^3$

(c) x^8 (d) $2916x^8$

Use the following passage, to solve Q. 109 to Q. 111

Passage

The solubility product constant of AgCN is 2.5×10^{-16}. The acid dissociation constant of HCN is 6.2×10^{-10}. Now solid AgCN is dissolved in a buffer solution of pH 3.

Answer the following questions :

109. The concentration ratio of HCN to CN^- in the solution is

(a) 6.25×10^{-7} (b) 1.6×10^{6}

(c) 1.6×10^{9} (d) 6.2×10^{-10}

110. The solubility of AgCN (mol-L^{-1}) in the above solution is

(a) S (b) $S^{1/2}$

(c) S^2 (d) S^3

111. The factor by which the solubility of AgCN is increased in the above solution as compared to its solubility in pure water is

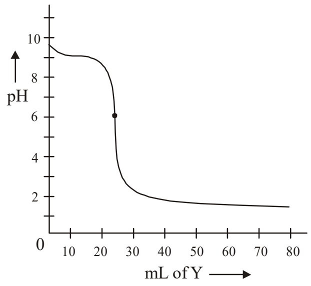
(a) 10 (b) 100

(c) 1250 (d) 5000

Use the following passage, to solve Q. 112 to Q. 115

Passage

100 mL of a solution of X is titrated with a 0.1 M solution of Y giving the following titration curve :



Answer the following four questions based on the information provided.

112. Y is a

(a) strong acid (b) strong base

(c) weak base (d) weak acid

113. X is a

(a) strong acid (b) strong base

(c) weak base (d) weak acid

114. The initial concentration of X is

(a) 0.10 M (b) 0.02 M

(c) 0.05 M (d) 0.01 M

115. The approximate value of ionization constant (K_a/K_b) of X is

(a) 5×10^{-9} (b) 5×10^{-6}

(c) 2×10^{-4} (d) 3×10^{-5}

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTIONS

Objective Questions I [Only one correct option]

1. The pH of 10^{-8} M solution of HCl in water is **(1981)**

(a) 8
(b) –8
(c) between 7 and 8
(d) between 6 and 7

2. At 90ºC, pure water has $[H_3O^+]$ as 10^{-6} mol L^{-1}. What is the value of K_w at 90ºC ? **(1981)**

(a) 10^{-6}
(b) 10^{-12}
(c) 10^{-14}
(d) 10^{-8}

3. Of the given anions, the strongest base is **(1981)**

(a) ClO^-
(b) ClO_2^-
(c) ClO_3^-
(d) ClO_4^-

4. An acidic buffer solution can be prepared by mixing the solution of **(1981)**

(a) solution of acetate and acetic acid
(b) ammonium chloride and ammonium hydroxide
(c) sulphuric acid and sodium sulphate
(d) sodium chloride and sodium hydroxide

5. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained, when equal volumes of the following are mixed **(1982)**

(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-
(b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(c) 10^{-5} M Ca^{2+} + 10^{-3} M F^-
(d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

6. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is **(1984)**

(a) 4
(b) 7
(c) 10
(d) 14

7. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is **(1984)**

(a) 1.0×10^{-4}
(b) 1.0×10^{-10}
(c) 1.0×10^{10}
(d) 1.0×10^{-14}

8. An example of a reversible reaction is **(1985)**

(a) $Pb(NO_3)_2\,(aq) + 2NaI\,(aq) = PbI_2\,(s) + 2NaNO_3\,(aq)$
(b) $AgNO_3\,(aq) + HCl\,(aq) = AgCl\,(s) + HNO_3\,(aq)$
(c) $2Na\,(s) + 2H_2O(l) = 2\,NaOH\,(aq) + H_2(g)$
(d) $KNO_3\,(aq) + NaCl\,(aq) = KCl\,(aq) + NaNO_3\,(aq)$

9. The best indicator for detection of end point in titration of a weak acid and a strong base is **(1985)**

(a) methyl orange (3 to 4)
(b) methyl red (5 to 6)
(c) bromothymol blue (6 to 7.5)
(d) phenophthalein (8 to 9.6)

10. The compound that is not a Lewis acid is **(1985)**

(a) BF_3
(b) $AlCl_3$
(c) $BeCl_2$
(d) $SnCl_4$

11. The conjugate acid of NH_2^- is **(1985)**

(a) NH_3
(b) NH_2OH
(c) NH_4^+
(d) N_2H_4

12. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be **(1988)**

(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine in the small intestine
(c) ionised in the stomach and almost unionised in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

13. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with **(1988)**

(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)
(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)
(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)
(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

14. Which of the following is the strongest acid ? **(1989)**

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$

(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

15. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25ºC) is **(1990)**

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$

(c) $Ba(OH)_2$ (d) $Be(OH)_2$

16. Which of the following solutions will have pH close to 1.0 ? **(1992)**

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

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

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

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

17. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is **(1997)**

(a) $6y^4$ (b) $64y^4$

(c) $36y^5$ (d) $108y^5$

18. The pH of 0.1 M solution of the following salts increase in the order **(1999)**

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$

19. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is **(2001)**

(a) $L_s = S^{p+q} . p^p .q^q$

(b) $L_s = S^{p+q} . p^q .q^p$

(c) $L_s = S^{pq} . p^p .q^q$

(d) $L_s = S^{pq} . (p.q)^{(p+q)}$

20. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium **(2002)**

(a) $CuS > ZnS > Na_2S$

(b) $ZnS > Na_2S > CuS$

(c) $Na_2S > CuS > ZnS$

(d) $Na_2S > ZnS > CuS$

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

(a) FeS (b) MgS

(c) HgS (d) ZnS

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

(a) 0.01% (b) 0.0001%

(c) 0.1% (d) 0.5%

23. A weak acid HX has the dissociation constant 1×10^{-5}M. It forms a salt NaX on reaction with alkali. The percentage hydrolysis of 0.1 M solution of NaX ? **(2004)**

(a) 0.0001% (b) 0.01%

(c) 0.1% (d) 0.15%

24. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is **(2004)**

(a) 25% (b) 50%

(c) 75% (d) 85%

25. CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is **(2005)**

(a) 1.6×10^{-11} (b) 8×10^{-11}

(c) 5×10^{-5} (d) 8×10^{-2}

26. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+ ;\ K_1 = 3.5 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ ;\ K_2 = 1.7 \times 10^{-3}$

then the formation constant of $[Ag(NH_3)_2]^+$ is **(2006)**

(a) 6.08×10^{-6} (b) 6.08×10^{6}

(c) 6.08×10^{-9} (d) None of these

27. The species present in solution when CO_2 is dissolved in water are **(2006)**

(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$

(b) H_2CO_3, CO_3^{2-}

(c) HCO_3^-, CO_3^{2-}

(d) CO_2, H_2CO_3

28. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition ? **(2006)**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction

(b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent

(c) The catalyst will increase the rate of forward reaction by β

(d) Catalyst will not alter the rate of either of the reaction.

29. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol, dm^{-3}) of the salts at temperature 'T' are in the order **(2008)**

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

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

30. 2.5 mL of $\frac{2}{5}$ M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$ M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) **(2008)**

(a) 3.7×10^{-13} M (b) 3.2×10^{-7} M

(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

31. Passing H_2S gas into a mixture of Mn^{2+}, Ni^{2+}, Cu^{2+} and Hg^{2+} ions in an acidified aqueous solution precipitates. **(2011)**

(a) CuS and HgS (b) MnS and CuS

(c) MnS and NiS (d) NiS and HgS

32. The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298 K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1 M $AgNO_3$ solution is **(2013)**

(a) 1.1×10^{-11} (b) 1.1×10^{-10}

(c) 1.1×10^{-12} (d) 1.1×10^{-9}

33. When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 °C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt.2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt.1) where a temperature rise of 5.6 °C was measured.

(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

The pH of the solution after Expt.2 is **(2015)**

(a) 2.8 (b) 4.7

(c) 5.0 (d) 7.0

Objective Questions II

[One or more than one correct option]

34. Which of the following statement (s) is (are) correct ? **(1998)**

(a) The pH of 1.0×10^{-8} M solution of HCl is 8

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

(c) Autoprotolysis constant of water increases with temperature

(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = $\left(\frac{1}{2}\right) pK_a$

35. A buffer solution can be prepared from a mixture of **(1999)**

(a) sodium acetate and acetic acid in water

(b) sodium acetate and HCl in water

(c) ammonia and ammonium chloride in water

(d) ammonia and sodium hydroxide in water

36. Aqueous solutions of HNO_3, KOH, CH_3COOH and CH_3COONa of identical concentrations are provided. The pair(s) of solutions which form a buffer upon mixing is (are) **(2010)**

(a) HNO_3 and CH_3COOH (b) KOH and CH_3COONa

(c) HNO_3 and CH_3COONa (d) CH_3COOH and CH_3COONa

Numerical Value type Questions

37. The concentration of hydrogen ions in a 0.20 M solution of formic acid is 6.4×10^{-3} mol/L. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution ? The dissociation constant of formic acid is solution ? The dissociation constant of formic acid is 2.4×10^{-4} and the degree of dissociation of sodium formate is 0.75. **(1985)**

38. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $Mg(NO_3)_2$ solution. **(1986)**

39. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated ? **(1992)**

40. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which in 2 M in H_2CO_3, in order to maintain a pH of 7.4 ? (K_a for H_2CO_3 in blood is 7.8×10^{-7}) **(1993)**

41. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate ?

K_{sp} for MS $= 6.0 \times 10^{-21}$, conc. of saturated $H_2S = 0.1$ M and $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S. **(1993)**

42. For the reaction,

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

The equilibrium constant, at 25°C, is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$. **(1994)**

43. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissciation

(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

(1995)

44. What is the pH of a 0.50 M aqueous NaCN solution ?

(pK_b of CN^- = 4.70) **(1996)**

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

(1996)

46. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- ions per litre. Calculate the solubility product of AgCl. **(1997)**

[K_{sp} (Ag_2CO_3) = 8.2×10^{-12}]

47. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.36653 mol/L and pK_a of H_2SO_3 is 1.92, Estimate the pH of rain on that day. **(2000)**

48. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point, Given, K_a (HA) $= 5 \times 10^{-6}$ and $\alpha << 1$. **(2004)**

49. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of 0.01 M solution of its sodium salt is **(2009)**

50. In 1 L saturated solution AgCl [K_{sp}(AgCl) = $1.6 \text{ x } 10^{-10}$], 0.1 mol of CuCl [K_{sp}(CuCl) = $1.0 \text{ x } 10^{-6}$] is added. The resultant concentration of Ag^+ in the solution is $1.6 \text{ x } 10^{-x}$. The value of "x" is **(2011)**

51. The solubility of a salt of weak acid (AB) at pH = 3 is

$Y \text{ x } 10^{-3}$ mol L^{-1}. The value of Y is _____.

(Given that the value of solubility product of AB

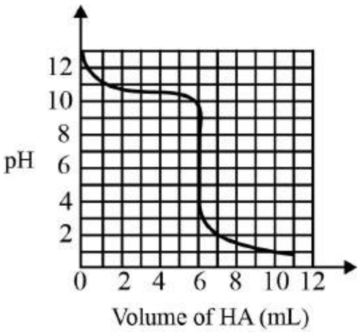
(K_{sp}) = $2 \text{ x } 10^{-10}$ and the value of ionization constant of HB

(K_a) = $1 \text{ x } 10^{-8}$) **(2018)**

52. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base?

The neutralization reaction is given by

$B + HA \rightarrow BH^+ + A^-$ **(2020)**



53. An acidified solution of 0.05 M Zn^{2+} is saturated with 0.1 M H_2S. What is the minimum molar concentration (M) of H^+ required to prevent the precipitation of ZnS? Use $K_{sp}(ZnS) = 1.25 \times 10^{-22}$ and overall dissociation constant of $H_2S, K_{NET} = K_1K_2 = 1 \times 10^{-21}$ **(2020)**

Match the Following

Each question has two columns. Four options are given representing matching of elements from Column-I and Column-II.

54. Dilution processes of different aqueous solutions, with water, are given in LIST–I. The effects of dilution of the solutions on $[H^+]$ are given in LIST–II. (Note: Degree of dissociation (a) of weak acid and weak base is << 1: degree of hydrolysis of salt << 1: $[H^+]$ represents the concentration of H^+ ions) **(2018)**

LIST– I	LIST– II
P. (10 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 60 mL	1. the value of $[H^+]$ does not change on dilution
Q. (20 mL of 0.1 M NaOH + 20 mL of 0.1 M acetic acid) diluted to 80 mL	2. the value of $[H^+]$ changes to half of its initial value on dilution
R. (20 mL of 0.1 M HCl + 20 mL of 0.1 M ammonia solution) diluted to 80 mL	3. the value of $[H^+]$ changes to two times of its initial value on dilution.
S. 10 mL saturated solution of $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is diluted to 20 mL (solid $Ni(OH)_2$ is still present after dilution).	4. the value of $[H^+]$ changes to $\frac{1}{\sqrt{2}}$ times of its initial value on dilution
	5. the value of $[H^+]$ changes to $\sqrt{2}$ times of its initial value on dilution

Match each process given in LIST–I with one or more effect(s) in LIST–II. The correct option is

(a) P – 4; Q – 2; R – 3; S – 1 (b) P – 4; Q – 3; R – 2; S – 3

(c) P – 1; Q – 4; R – 5; S – 3 (d) P – 1; Q – 5; R – 4; S – 1

Paragraph Type Questions

Use the following passage,to solve Q. 55 to Q. 56

Passage

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

(Consider heat capacity of all solutions as 4.2J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

55. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is

(a) 1.0 (b) 10.0

(c) 24.5 (d) 51.4

56. The pH of the solution after Expt. 2 is

(a) 2.8 (b) 4.7

(c) 5.0 (d) 7.0

Subjective Type Questions

57. How many moles of sodium propionate should be added to 1 L of an aqueous solution containing 0.020 moles of propionic acid to obtain a buffer solution of pH 4.75 ? What will be pH if 0.010 moles of HCl are dissolved in the above buffer solution ? Compare the last pH value with the pH of 0.010 M HCl solution. Dissociation constant of propionic acid, K_a at 25°C is 1.34×10^{-5}. **(1981)**

58. 20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid solution to give 70 mL of the solution. What is the pH of this solution ? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. (Ionisation constant of $CH_3COOH = 1.8 \times 10^{-5}$). **(1982)**

59. Give reason for the statement that “the pH of an aqueous solution of sodium acetate is more than seven”. **(1982)**

60. The dissociation constant of a weak acid HA is 4.9×10^{-8}. After making the necessary approximations, calculate :

(i) pH

(ii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7. **(1983)**

61. A solution contains a mixture of Ag^+ (0.10 M) and Hg^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion and which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated ? **(1984)**

$K_{sp} : AgI = 8.5 \times 10^{-17}, \; HgI_2 = 2.5 \times 10^{-26}$

62. What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing

(i) 1 M each of acetic acid and acetate ion ?

(ii) 0.1 M each of acetic acid and acetate ion ?

Assume the total volume is one litre. K_a for acetic acid $= 1.8 \times 10^{-5}$. **(1987)**

63. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide. Calculate the concentration of alminimum and magnesium ions in solution **(1989)**

$K_b[NH_4OH] = 1.8 \times 10^{-5}$ $\quad K_{sp}[Mg(OH)_2] = 8.9 \times 10^{-12}$

$K_{sp}[Al(OH)_3] = 6 \times 10^{-32}$

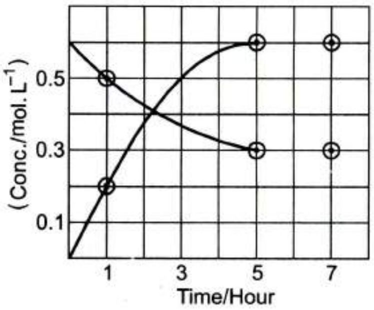
64. What is the pH of 1.0 M solution of acetic acid ? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value ? Given : $K_a = 1.8 \times 10^{-5}$. **(1990)**

65. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3L^{-3}. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached

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

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. **(1991)**

66. The progress of reaction, $A \rightleftharpoons nB$ with time, is represented in fig. given below. Determine



(i) the value of n

(ii) the equilibrium constant, K and

(iii) the initial rate of conversion of A. **(1994)**

67. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ? ($K_a = 1.0 \times 10^{-5}$) **(1997)**

Fill in the Blanks

68. The conjugate base of HSO_4^- in aqueous solution is .... **(1982)**

69. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .... **(1984)**

70. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy. **(1987)**

71. In the reaction $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is .... **(1997)**

72. $(CH_3OH_2)^+$ is .... acidic than $(CH_3NH_3^+)$. **(1997)**

True / False

73. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(1982)**

74. Solubility of sodium hydroxide increases with increase in temperature. **(1985)**

75. The following species are in increasing order of their acidic property : ZnO, Na_2O_2, P_2O_5, MgO **(1985)**

Answer Key

CHAPTER -12 | IONIC EQUILIBRIUM

EXERCISE - 1 :
BASIC OBJECTIVE QUESTIONS

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

EXERCISE - 2 :
PREVIOUS YEAR JEE MAINS QUESTIONS

1.	(b)	**2.**	(b)	**3.**	(c)	**4.**	(a)	**5.**	(c)
6.	(b)	**7.**	(c)	**8.**	(c)	**9.**	(c)	**10.**	(b)
11.	(b)	**12.**	(b)	**13.**	(c)	**14.**	(a)	**15.**	(c)
16.	(a)	**17.**	(b)	**18.**	(b)	**19.**	(a)	**20.**	(c)
21.	(d)	**22.**	(c)	**23.**	(a)	**24.**	(b)	**25.**	(b)
26.	(c)	**27.**	(d)	**28.**	(c)	**29.**	(b)	**30.**	(b)
31.	(a)	**32.**	(c)	**33.**	(b)	**34.**	(a)	**35.**	(d)
36.	(c)	**37.**	(d)	**38.**	(c)	**39.**	(a)	**40.**	(a)
41.	(a)	**42.**	(c)	**43.**	(d)	**44.**	(a)	**45.**	(d)
46.	(d)	**47.**	(10.6)			**48.**	(5.23)		
49.	(58.00)			**50.**	(37.00)				
51.	(2.00)			**52.**	(141.0)				
53.	(7.00)			**54.**	(50.00)				
55.	(1.00)			**56.**	(2.00)				
57.	(10.00)			**58.**	(64.00)				
59.	(3.00)			**60.**	(108.0)				
61.	(6021.00)			**62.**	(2.00)				
63.	(a)	**64.**	(c)	**65.**	(b)				

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EXERCISE - 3 :
ADVANCED OBJECTIVE QUESTIONS

1. (d) **2.** (d) **3.** (a) **4.** (a) **5.** (a)
6. (a) **7.** (d) **8.** (c) **9.** (b) **10.** (c)
11. (d) **12.** (c) **13.** (a) **14.** (d) **15.** (c)
16. (d) **17.** (d) **18.** (c) **19.** (a) **20.** (b)
21. (a) **22.** (d) **23.** (a) **24.** (a) **25.** (d)
26. (b) **27.** (d) **28.** (c) **29.** (b) **30.** (b)
31. (d) **32.** (a) **33.** (b) **34.** (c) **35.** (d)
36. (c) **37.** (c) **38.** (c) **39.** (b) **40.** (a)
41. (b) **42.** (b) **43.** (a) **44.** (d) **45.** (b)
46. (a) **47.** (d) **48.** (d) **49.** (a,c)
50. (a,b,c) **51.** (b,c)
52. (b,c,d) **53.** (a,c,d)
54. (b,c,d) **55.** (a,c,d)
56. (a,d) **57.** (a,b,d)
58. (b,d) **59.** (a,b,c)
60. (b,c,d) **61.** (a,b,c,d)
62. (a,b) **63.** (a,b,d)
64. (a,b,c,d) **65.** (a,b,c,d)
66. (0.00) **67.** (9.00)
68. (2.00) **69.** (2.00) **70.** (4.00) **71.** (4.00)
72. (0.001) **73.** (9.00) **74.** (a) **75.** (a)
76. (a) **77.** (c) **78.** (d) **79.** (a) **80.** (d)
81. (a) **82.** (d) **83.** (b) **84.** (a) **85.** (b)
86. (d) **87.** (a) **88.** (d) **89.** (a)
90 $(A \rightarrow r); (B \rightarrow s); (C \rightarrow p); (D \rightarrow q)$
91. $(A \rightarrow r); B \rightarrow r); (C \rightarrow s); (D \rightarrow p)$
92 $(A \rightarrow r); (B \rightarrow s); (C \rightarrow p); (D \rightarrow q)$
93. $(A \rightarrow q); (B \rightarrow r); (C \rightarrow r); (D \rightarrow p,s)$
94. $(A \rightarrow p,q,r); (B \rightarrow r); (C,p,q); (D \rightarrow s)$
95. $(A \rightarrow q,r); (B \rightarrow p); (C \rightarrow q); (D \rightarrow s)$
96. (a) **97.** (d) **98.** (d) **99.** (a)
100. (d) **101.** (c) **102.** (a) **103.** (b)
104. (c) **105.** (a) **106.** (b) **107.** (c)
108. (d) **109.** (b) **110.** (c) **111.** (c)
112. (a) **113.** (c) **114.** (b) **115.** (c)

EXERCISE - 4 :
PREVIOUS YEAR JEE ADVANCED QUESTIONS

1. (d) **2.** (b) **3.** (a) **4.** (a) **5.** (b)
6. (a) **7.** (c) **8.** (d) **9.** (d) **10.** (c)
11. (a) **12.** (d) **13.** (a) **14.** (a) **15.** (d)
16. (d) **17.** (d) **18.** (b) **19.** (a) **20.** (d)
21. (c) **22.** (a) **23.** (b) **24.** (c) **25.** (b)
26. (a) **27.** (a) **28.** (b) **29.** (d) **30.** (d)
31. (a) **32.** (b) **33.** (b) **34.** (b,c)
35. (a,b,c) **36.** (c,d) **37.** (4.20)
38. (8.7×10^{-4}) **39.** (747.4)
40. (80.00) **41.** (1.00)
42. (7.50×10^{-18}) **43.** (6.5)
44. (11.5) **45.** (6.12×10^{5})
46. (2×10^{-8}) **47.** (4.86)
48. (9.00) **49.** (8.00)
50. (7.00) **51.** (4.47)
52. (3.00) **53.** (0.20)
54. (d) **55.** (a)
56. (b) **68.** (SO_4^{2-})
69. (Amphoteric) **70.** (Hydration)
71. (I_2) **72.** (More)
73. False **74.** False **75.** False