DAY TEN

Ionic Equilibrium

Learning & Revision for the Day

- Weak and Strong Electrolytes
- Degree/Dissociation
- Various concepts of Acids and Bases and their Ionisation
- Ionisation of Water
- pH Scale
- Solubility of Sparingly Soluble Salts
- Buffer Solution

The equilibrium concept also extends to ionic reactions. There it is known as **ionic equilibrium** and applied as equilibrium between dissociated and undissociated form of an ionic reaction of weak acid, weak base, hydrolysis reaction etc.

Weak and Strong Electrolytes

1. **Weak electrolytes** dissociate partially in the solutions and such solutions are poor conductor of electricity. e.g. CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, HCN etc.
2. **Strong electrolytes** dissociate completely into their ions in solution and such solutions are very good conductor of electricity. e.g. HCl, H_2SO_4, NaOH, KOH, NaCl, KCl etc.

Ionisation of Electrolytes

Separation of an electrolyte into their ions either on fusion or dissolution is called **ionisation** or **dissociation.**

$$\mathrm{NaCl}(aq) \longrightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

(Usually the term dissociation is used for weak electrolyte and ionisation for strong electrolyte).

The solution of weak electrolytes contain ions, which are in equilibrium with unionised molecules.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

This equilibrium is known as **ionic equilibrium** and is dynamic in nature.

Degree/Dissociation

- The fraction of total number of moles undergoing ionisation is called degree of ionisation or dissociation (α). Alternately, the fraction of the amount of an electrolyte present in the solution as free ions is called degree of ionisation (α).

$$\alpha = \frac{\text{number of moles of electrolyte dissociated ionized as ions}}{\text{total number of moles of electrolyte dissolved}}$$

- The extent of ionisation depends upon the strength of bond and extent of solution of ions obtained.

  Various factors influencing degree of ionisation/dissociation are as follows:

  (i) For strong electrolyte, $\alpha = 1$ at normal dilution while for most of the polar covalent compounds, i.e. weak electrolytes, $\alpha <<< 1$.

  (ii) Degree of ionisation of an electrolyte increases with polarity of the solvent.

  (iii) The degree of ionisation of an electrolyte decreases with increase in concentration of the electrolyte.

  (iv) The degree of ionisation rises with raise in temperature of the solution.

  (v) The addition of species possessing a common ion to that of weak electrolyte causes a decrease in the degree of dissociation of weak electrolyte.

Ostwald's Dilution Law

It states that degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration or directly proportional to the square root of volume containing one mole of the solute.

$$\alpha \propto \frac{1}{\sqrt{C}}, \ \alpha = \sqrt{\frac{K}{C}} = \sqrt{KV}$$

where, α = degree of dissociation
V = volume containing 1 mole of weak electrolyte
K = dissociation constant

NOTE Ostwald's dilution law is applicable only to weak electrolytes because for strong electrolytes,

$$\alpha \simeq 1, \ \text{i.e.} \ K_a \to \infty$$

Various applications of Ostwald's dilution law are as follows:

- To calculate the value of dissociation constant (K) of the weak acids and weak bases, by determining the degree of dissociation (α) from conductance measurement $\left(\frac{\lambda_V}{\lambda_\infty}\right)$ at any concentration C.
- To calculate the degree of dissociation, α of weak acids and bases by knowing the value of K.
  For weak acid, put $[A^+] = [H^+]$ and $K = K_a$
  Similarly for weak bases,
  $$[B^-] = [OH^-] \quad \text{and} \quad K = K_b$$
- This law holds good only in case of weak electrolytes. The value of K can be calculated only in dilute solutions of weak electrolytes.

Various Concept of Acids and Bases and their Ionisation

An acid is that whose aqueous solution tastes sour, turns blue litmus red, neutralises bases and so on. On the other hand, the aqueous solution of a base tastes bitter, turns red litmus blue, neutralises acid and so on.

1. Arrhenius Theory

According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions OH^- (aq).

Limitations of Arrhenius theory are as follows:

(i) Free H^+ and OH^- ions do not exist in water.

(ii) The concept is limited to aqueous solutions only.

(iii) It cannot explain the acidic character of certain substances which don't contain free H^+ ions like, $AlCl_3$, BF_3 and basic character of substances which don't contain free OH^- ions. NH_3, PH_3.

2. Bronsted-Lowry Concept

According to Bronsted-Lowry concept, acids are proton donors while bases are proton acceptors. A conjugate pair of acid and a base differs by a proton.

Conjugate base

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \longrightarrow H_3O^+ + Cl^-$$

Conjugate acid

The substances which behave both as an acid and a base are called **amphiprotic**. e.g. H_2O, HSO_3^-, HS^- etc.

Conjugate base of weak acid is strong or *vice-versa*.

NOTE
- The strength of acid depends upon the nature of solvent. e.g. H_2SO_4, $HClO_4$, HNO_3 and HCl, all have same strength in water due to levelling effect of water.
- In acetic acid solvent, the order of their acidic strength is $HClO_4 > H_2SO_4 > HCl > HNO_3$.

Limitations of Bronsted-Lowry concept are as follows:

(i) The protonic definition cannot be used to explain the reactions occurring in the non-protonic solvents such as $COCl_2, SO_2, N_2O_4$ etc.

(ii) This concept cannot explain the reactions between some acidic oxides (such as CO_2, SO_2, SO_3) and basic oxides (such as CaO, BaO, MgO) which take place even in the absence of the solvent, e.g. $CaO + SO_3 \longrightarrow CaSO_4$

(iii) $BF_3, AlCl_3$ etc., do not have any hydrogen and hence, cannot give a proton but are known to behave as acids.

3. Lewis Concept

According to Lewis concept acids are the substances which accept a pair of electrons to form a coordinate bond and bases are the substances which donate a pair of electrons to form coordinate bond.

Following species can act as Lewis acids are

(i) Molecules in which central atom has incomplete octet e.g. BF_3, $AlCl_3$, $FeCl_3$ etc.

(ii) Molecules in which the central atom is either non-metal cation or metal cation with empty *d*-orbital. (*d*-block elements)
e.g. SiX_4, GeX_4, PX_3, $TiCl_4$, H^+, Ag^+etc.

Lewis bases should satisfy following conditions are

(a) Octet should be complete and central atom should be more electronegative.

(b) Lone pair/pairs should be present, e.g. $\ddot{\text{N}}\text{H}_3$, $\text{H}_2\underset{\cdot\cdot}{\ddot{\text{O}}}$, $R—\underset{\cdot\cdot}{\ddot{\text{O}}}\text{H}$, $R—\underset{\cdot\cdot}{\ddot{\text{O}}}R$ etc.

(c) Negatively charged species, e.g. CN^-, OH^-, Cl^- etc.

Limitations of Lewis concept are as follows:

(i) The strength of Lewis acids and bases is found to depend on the type of reaction, it is not possible to arrange them in any order of their relative strength.

(ii) It does not explain the behaviour of protonic acids which do not form coordinate bond such as HNO_3, HCl, H_2SO_4 etc.

(iii) Catalytic activity of Lewis acid cannot be explained because the catalytic activity of many acids is due to their tendency to furnish H^+. Lewis acid does not do so.

Relative Strength of Mono Acidic Bases

Relative strength of mono acidic bases (or mono basic acids) of equimolar concentrations can be given as

$$\frac{\text{Strength of base }(B\text{OH})_1}{\text{Strength of base }(B\text{OH})_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}} = \frac{\alpha_1}{\alpha_2}$$

$$\frac{\text{Strength of acid }(\text{H}A)_1}{\text{Strength of acid }(\text{H}A)_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}} = \frac{\alpha_1}{\alpha_2}$$

where, K_a and K_b are the dissociation constants of acid and base respectively.

Ionisation of Water

- Pure water is a weak electrolyte and is ionised according to following equation.

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

At 25°C, for pure water $[H_3O^+] = [OH^-] = 10^{-7}$ mol/L

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$

Here, K_w is called the **ionic product** of water and is defined as the product of molar concentration of H^+ ions and OH^- ions

$$K = \frac{K_w}{55.55}$$

where, K = ionisation constant

- Value of K_w depends upon temperature as it is equilibrium constant. If temperature increases, value of K_w also increases.
- For dissociation of weak acids in water, K_a is called **acid ionisation constant**.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \ ;$$

$$K_a = \frac{[CH_3COO^-]\ [H_3O^+]}{(CH_3COOH)}$$

- Similarly, for a weak base, K_b is called base ionisation constant.

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-;\ K_b = \frac{[NH_4^+][OH^-]}{(NH_4OH)}$$

Relation between K_a and K_b

- Relation between acid dissociation (K_a) and base dissociation (K_b) constants is

$$K_a \times K_b = K_w$$

where, $pK_a = -\log K_a$, $pK_b = -\log K_b$ and $pK_w = -\log K_w$

- Many acids are capable of furnishing more than one protons in water. Such acids are called **polybasic** or **polyprotic** acids, e.g. H_2SO_4, H_3PO_4 etc.
- The first ionisation constant (K_{a_1}) is always greater than the second ionisation constant (K_{a_1}).

pH Scale

It is used to express and compare the acidic and basic strength of a solution. pH is defined as the negative logarithm of H_3O^+ ion concentration (in moles per litre) present in it.

Thus, $\text{pH} = -\log[H_3O^+]$

Similarly, $\text{pOH} = -\log[OH^-]$

$$\text{pH} + \text{pOH} = 14$$

Relation between pK_a and pK_b is given as:

$$pK_a + pK_b = 14 = pK_w$$

pH scale range is 0 to 14 and it depends upon the value of K_w. As temperature increases, value of pH decreases at 25°C.

Following observations are seen with solutions:

(i) pH of very dilute ($\sim 10^{-8}$ M or lower) acids or bases is nearly 7 but not 7 (i.e. not simply – log [acid or base]) due to ionisation of water.

(ii) pH of strong acids with concentration > 1 M is never negative, it is zero only.

NOTE Greater the value of K_a or K_b smaller is the value of pK_a and pK_b and stronger is acid or base.

pH of Mixtures of Acid and Bases

The rules for determining the pH of mixtures of acids and bases are as follows:

(i) If strong acid or strong base remains unused, calculate the concentration or molarity of H^+ ions and OH^- ions left in the solution and then calculate the pH or pOH accordingly.

(ii) If weak acid or weak base is left behind or remains unused, a buffer (acidic or basic) is formed. Calculate the concentration of salt formed (millimoles of salt formed/volume of solution) and the concentration of weak acid or weak base left behind. Use the buffer equation to calculate the pH of the solution.

(iii) If acids or bases are completely neutralised, then salt is formed. Calculate the concentration of the salt formed and use the hydrolysis equation to calculate the pH of the solution.

NOTE
- pH value of a solution decreases on heating because ionisation of water is an endothermic process. pH of boiling water is 6.5625, although it is neutral.
- When pH decreases by one unit, H^+ ion concentration increases by a factor of 10. Similarly, when pH decreases by two units, H^+ ion concentration increases by a factor of 100.

Hydrolysis of Salts and pH of their Solutions

- The process of salt hydrolysis is actually the reverse process of neutralisation. The reaction of an anion or cation of the salt with water accompanied to produce acidic and basic solution is called **salt hydrolysis**. Salt hydrolysis affects the pH of the solution.
- **Salts of strong acids and strong bases** (i.e. neutral salts) do not undergo hydrolysis are called **neutral salt**, e.g. NaCl, $CaSO_4$ etc. If such salt is dissolved in water, pH of the solution remains 7.
- **Salt of a strong acid and weak base**, e.g. NH_4Cl are called **acidic salts**. Such salts undergo cationic hydrolysis. pH of acidic salt solution will be less than 7.

For such salts, $[H_3O^+] = \sqrt{K_h \times C}$

$$K_h = \frac{K_w}{K_b} \quad \text{or} \quad \text{pH} = 7 - \frac{1}{2}\,[\,\text{p}K_b + \log C] \text{ at } 25°\text{C}$$

where, K_h = hydrolysis constant

K_b = ionisation constant for weak base

C = molar concentration of salt.

- **Salt of strong base and weak acid**, e.g. $NaNO_2$, NaCN, CH_3COONa are termed as **basic salts**. Such salts undergo anionic hydrolysis. pH of basic salt solution will be more than 7.

For basic salts, $[OH^-] = \sqrt{K_h \times C}$ or $K_h = \dfrac{K_w}{K_a}$

$$\text{pH} = 7 + \frac{1}{2}\,[\,\text{p}K_a + \log C] \text{ at } 25°\text{C}$$

- The salts other than halides, sulphates, nitrates of metals fall into salts of weak acid and base category, e.g. CH_3COONH_4 etc.

For such salts, $K_h = \dfrac{K_w}{K_a \times K_b}$, $\text{pH} = 7 + \dfrac{1}{2}\,[\text{p}K_a - \text{p}K_b]$

NOTE There is no effect of dilution on the hydrolysis of salts of weak acid and weak base because pH and K_h are all independent of concentration, C.

Solubility of Sparingly Soluble Salts

Lattice enthalpy and solvation enthalpy play an important role in deviding the solubility of the salts in particular solvent. For a salt to be able to dissolve in a particular solvent, the solvation enthalpy must be higher than its lattice enthalpy.

Solubility Product

It is defined as the product of molar concentration of its ions in a saturated solution, each concentration terms raised to the power equal to the number of ions produced on dissociation of one molecule of electrolyte.

$$A_x B_y \rightleftharpoons x\,A^+ + yB^-$$

$$\therefore \quad K_{sp} = [A^+]^x\,[B^-]^y$$

e.g. $$A_2X_3 \longrightarrow \underset{2S}{2A^{3+}} + \underset{3S}{3X^{2-}}$$

$$K_{sp} = [A^{3+}]^2[X^{2-}]^3$$

$$K_{sp} = (2S)^2(3S)^3$$

$$\therefore \quad K_{sp} = 108\,S^5$$

$$\text{BaSO}_4(s) \underset{\text{in water}}{\overset{\text{Saturated solution}}{\rightleftharpoons}} \underset{S}{\text{Ba}^{2+}}\,(aq) + \underset{S}{\text{SO}_4^{-}}(aq)$$

$$K_{sp} = [S]\,[S]$$

$$K_{sp} = S^2$$

where, S = molar solubility, K_{sp} = solubility product

NOTE If the ionic product exceeds the value of the solubility product of a sparingly soluble salt then precipitation will occur.

Common Ion Effect

- It states that if to the solution of a weak electrolyte, a solution of strong electrolyte is added which furnishes an ion common to that furnished by the weak electrolyte, the ionisation of the weak electrolyte is suppressed.

e.g. $$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

- If NH_4Cl or NaOH is added to NH_4OH solution, the above equilibrium will shift to the left due to high concentration of common ion and therefore, the ionisation of NH_4OH is further suppressed.
- In IInd group of qualitative analysis, H_2S is passed in the presence of HCl. This is due to the fact that HCl suppresses the ionisation of weakly dissociated H_2S. Due to this only

sulphides of II group radicals are precipitated. Sulphides of III, IV etc., groups are not precipitated because of their high solubility product.

- The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation.

Buffer Solution

The solution, which maintains its pH constant or reserve acidic or basic nature even upon addition of small amounts of acid or base is called **buffer solution**. The ability of buffer solution to resist changes in pH on addition of acid or base is called **buffer action**.

A buffer solution should exhibit following characteristics:

(i) Buffer solutions possess a definite pH value.

(ii) Their pH value remains constant on keeping long or dilution.

(iii) The pH value is not changed on the addition of a strong acid in acidic buffer and a strong base in basic buffer.

Two types of buffer are as follows:

(a) A buffer solution pH of which is less than 7 is called **acidic buffer**. Weak acid with its salt of strong base gives acidic buffer.
e.g. $CH_3COOH + CH_3COONa$; HCN + NaCN

(b) A buffer solution having pH more than 7 is called **basic buffer**. Weak base with its salt of strong acid gives basic buffer.
e.g. $NH_4OH + NH_4Cl$, $C_6H_5NH_2 + C_6H_5NH_3^+Cl^-$

Henderson's Equation for Buffer Solution

For acidic buffer; $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

For basic buffer; $\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}$

Buffer Capacity

Buffer capacity is quantitatively defined as the number of moles of acid or base added to 1 L in of buffer solution to change the pH by unity.

$$\text{Buffer capacity} = \frac{\text{number of moles of acid / base added to 1 L of buffer}}{\text{change in pH}}$$

Buffer capacity is maximum when

(a) $[\text{salt}] = [\text{acid}]$, $\text{pH} = \text{p}K_a$ for acidic buffer

(b) $[\text{salt}] = [\text{base}]$, $\text{pH} = \text{p}K_b$ for basic buffer

Greater the buffer capacity, larger is its capacity to resist the change in pH value.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Of the given anions, the strongest Bronsted base is

(a) ClO^- (b) ClO_3^- (c) ClO_2^- (d) ClO_4^-

2 Four species are listed below:

I. HCO^{3-} II. H_3O^+ III. HSO_4^- IV. HSO_3F

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

(a) IV<II<III<I (b) II<III<I<IV

(c) I<III< II<IV (d) III<I<IV<II

3 Three reactions involving $H_2PO_4^-$ are given below:

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

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

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

In which of the above does $H_2PO_4^-$ act as an acid?

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(a) Only II (b) Both I and II

(c) Only III (d) Only I

4 The pK_w of a neutral solution at 50°C is 13.36, what would be the pH of the solution at this temperature?

(a) 7.63 (b) 7.00 (c) 6.68 (d) 7.96

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

(a) 7.0 (b) 5.98 (c) 6.78 (d) 4.58

6 Dissociation constant of a weak acid is 1×10^{-4}. Equilibrium constant of its reaction with strong base is

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

7 The pH of the neutralisation point of 0.1 N ammonium hydroxide with 0.1 N HCl is

(a) 8 (b) 6 (c) 7 (d) 9

8 NaOH is a strong base. What will be pH of 5.0×10^{-2}M NaOH solution ? (log 2 = 0.3) → JEE Main (Online) 2013

(a) 14.00 (b) 13.70 (c) 13.00 (d) 12.70

9 What is the pH of a 10^{-4}M OH^- solution at 330 K, if K_w at 330 K is $10^{-13.6}$? → JEE Main (Online) 2013

(a) 4 (b) 9.0 (c) 10 (d) 9.6

10 How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? → JEE Main (Online) 2013

(a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L

11 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionisation constant, K_a of the acid is ➞ AIEEE 2012

(a) 3×10^{-1} (b) 1×10^{-3} (c) 1×10^{-5} (d) 1×10^{-7}

12 Values of dissociation constant, K_a are given as follows:

Acid	K_a
HCN	6.2×10^{-10}
HF	7.2×10^{-4}
HNO_2	4.0×10^{-4}

Correct order of increasing base strength of the base CN^-, F^- and NO_2^- will be ➞ JEE Main (Online) 2013

(a) $F^- < CN^- < NO_2^-$ (b) $NO_2^- < CN^- < F^-$
(c) $F^- < NO_2^- < CN^-$ (d) $NO_2^- < F^- < CN^-$

13 An acid HA ionises as $HA \rightleftharpoons H^+ + A^-$

The pH of 1.0 M solution is 5. Its dissociation constant would be ➞ AIEEE 2011

(a) 1×10^{-10} (b) 5.0 (c) 5×10^{-8} (d) 1×10^{-5}

14 What will be the degree of ionisation of 0.05 M acetic acid if its pK_a value is 4.74 ?

(a) 0.019% (b) 1.9% (c) 3.0% (d) 4.74%

15 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

(a) 0.01% (b) 0.0001% (c) 0.1% (d) 0.5%

16 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 ➞ JEE Main 2017

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

17 Number of $(OH)^-$ in 1 mL solution of pH $= 13$ is

(a) 1×10^{-13} (b) 6.00×10^{7}
(c) 6.00×10^{13} (d) 6.02×10^{19}

18 pH of 0.005 M calcium acetate (pK_a of $CH_3COOH = 4.7$) is

(a) 7.04 (b) 9.37 (c) 9.26 (d) 8.37

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

(a) 7.01 (b) 9.22 (c) 9.58 (d) 4.79

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

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

21 The solubility of $PbCl_2$ is

(a) $\sqrt{K_{sp}}$ (b) $(K_{sp})^{1/3}$
(c) $(K_{sp}/4)^{1/3}$ (d) $(8\,K_{sp})^{1/2}$

22 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?

(a) FeS (b) MgS (c) HgS (d) ZnS

23 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

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

24 The solubility product of $BaSO_4$ is 1.5×10^{-9}. The precipitation in a 0.01 M Ba^{2+} solution will start on adding H_2SO_4 of concentration.

(a) 10^{-9} M (b) 10^{-8} M (c) 10^{-7} M (d) 10^{-6} M

25 Solid $Ba(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At which concentration of Ba^{2+}, precipitate of $BaCO_3$ begins to form?
(K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) ➞ AIEEE 2012

(a) 5.1×10^{-5} M (b) 7.1×10^{-5} M
(c) 4.1×10^{-5} M (d) 8.1×10^{-2} M

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

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

27 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 1 L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is ➞ AIEEE 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

28 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? ➞ AIEEE 2010

(a) 9 (b) 10 (c) 11 (d) 8

29 The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained when equal volumes of the following are mixed

(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^- (b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-
(c) Both (a) and (b) (d) None of these

30 The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is ➞ AIEEE 2012

(a) $\sqrt[2]{1.6 \times 10^{-30}}$ (b) $\sqrt[4]{1.6 \times 10^{-30}}$
(c) $\sqrt[4]{1.6 \times 10^{-30}/27}$ (d) $1.6 \times 10^{-30}/27$

31 Which one of the following arrangements represents the correct order of solubilities of sparingly soluble salts Hg_2Cl_2, $Cr_2(SO_4)_3$, $BaSO_4$ and $CrCl_3$ respectively? ➞ JEE Main (Online) 2013

(a) $\left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}$

(b) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{108}\right)^{1/5}$

(c) $(K_{sp})^{1/2}, \left(\frac{K_{sp}}{108}\right)^{1/5}, \left(\frac{K_{sp}}{27}\right)^{1/4}, \left(\frac{K_{sp}}{4}\right)^{1/3}$

(d) $\left(\frac{K_{sp}}{4}\right)^{1/3}, \left(\frac{K_{sp}}{108}\right)^{1/5}, (K_{sp})^{1/2}, \left(\frac{K_{sp}}{27}\right)^{1/4}$

32 The solubility of $AgBrO_3$ in an aqueous solution of $NaBrO_3$ (as compared to that in water) is

(a) the same
(b) more
(c) less
(d) unpredictable due to a new chemical reaction

33 The solubility of AgI in NaI solution is less than that in pure water because

(a) AgI forms complex with NaI
(b) of common ion effect
(c) solubility product of AgI is less
(d) the temperature of the solution decreases

34 How do we differentiate between Fe^{3+} and Cr^{3+} in group III?

(a) By taking excess of NH_4OH
(b) By increasing NH_4^+ ion concentration
(c) By decreasing OH^- ion concentration
(d) Both (b) and (c)

35 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and diluted to one litre. What will be the H^+ concentration in the solution?

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

36 Which of the following will produce a buffer solution when mixed in equal volumes?

(a) 0.1 mol dm^{-3} NH_4OH and 0.1mol dm^{-3} HCl
(b) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(c) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(d) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

37 What would be the pH of a solution obtained by mixing 5g of acetic acid and 7.5 g of sodium acetate and making the volume equal to 500 mL?

($K_a = 1.75 \times 10^{-5}, pK_a = 4.76$) ➞ JEE Main (Online) 2013

(a) pH = 4.70
(b) pH < 4.70
(c) pH of solution will be equal to pH of acetic acid
(d) 4.76 < pH < 5.0

38 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 ionised is

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

39 An aqueous solution of 1 M NaCl and 1 M HCl is

(a) not a buffer but pH < 7
(b) not a buffer but pH > 7
(c) a buffer with pH < 7
(d) a buffer with pH > 7

Direction (Q. Nos. 40-44) *In the following questions assertion followed reason is given. Choose the correct answer out of the following choices.*

(a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
(b) Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.
(c) Assertion is true but Reason is false.
(d) Assertion and Reason both are wrong.

40 **Assertion** (A) When HCl gas passes through saturated solution of NaCl, a solid NaCl separates out from the solution.

Reason (R) HCl decreases the solubility product of NaCl.

41 **Assertion** (A) The addition of Ag^+ ions to a mixture of an aqueous solution of NaCl and NaBr causes precipitation of AgBr, instead of AgCl.

Reason (R) Solubility product of AgCl is less than that of AgBr.

42 **Assertion** (A) The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) Hydrogen sulphide is a weak acid.

43 **Assertion** (A) According to the principle of common ion effect, the solubility of HgI_2 is expected to be less in aqueous solution of KI than in water. But HgI_2 dissolves in an aqueous solution of KI to form a clear solution.

Reason (R) Iodide ion (I^-) is highly polarisable.

44 **Assertion** (A) A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amounts of acid or alkali.

Reason (R) A solution containing a mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75.

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1. The pH values of 0.1 M solution of HCl, CH_3COOH, NH_4Cl and CH_3COONa will have the order

(a) $HCl < CH_3COOH < NH_4Cl < CH_3CO\overset{-}{O}\overset{+}{N}a$
(b) $CH_3COONa < NH_4Cl < CH_3COOH < HCl$
(c) $NH_4Cl < CH_3COONa < CH_3COOH < HCl$
(d) All will have same pH value

2 Which one of the following statements is not true?

(a) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}
(b) pH + pOH = 14 for all aqueous solutions
(c) The pH of 1×10^{-8} M HCl is 8
(d) $\alpha = \sqrt{K_v}$ for a weak electrolyte

3 What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH? ($K_a = 1.74 \times 10^{-5}$) [log 4.17 = 0.6201]

(a) 3.4 (b) 3.6 (c) 3.9 (d) 3.0

4 A weak acid (H*A*) is 4% ionised at 1 M. Per cent ionisation is 1% in the presence of A^-. The concentration of A^- is

(a) 0.04 M (b) 0.16 M (c) 0.02 M (d) 0.10 M

5 An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+}? ➞ **JEE Main 2018**

(a) 5×10^{-9} M (b) 2×10^{-9} M
(c) 1.1×10^{-9} M (d) 1.0×10^{-10} M

6 Hydroxyl ion concentration $[OH^-]$ in the case of sodium acetate can be expressed as (where, K_a is dissociation constant of CH_3COOH and C is the concentration of sodium acetate)

(a) $[OH^-] = (CK_w\ K_a)^{1/2}$ (b) $[OH^-] = C \cdot K_w \sqrt{K_a}$
(c) $[OH^-] = \left(\frac{C \cdot K_w}{K_a}\right)^{1/2}$ (d) $[OH^-] = C \cdot K_a \cdot K_w$

7 The silver ion in a solution is precipitated by addition of chloride ion. The final volume of solution is 500 mL. What should be the concentration of Cl^- ion if not more than 0.10 mg of Ag^+ ion remains unprecipitated? ($K_{sp}(AgCl) = 1.0 \times 10^{-10}$)

(a) 5.4×10^{-5} M (b) 1.9×10^{-6} M
(c) 5.4×10^{-4} M (d) 1.9×10^{-7} M

8 The degree of ionisation of 1.0 M weak acid, H*A* is 0.5%. If 2 mL of 1.0 M H*A* solution is diluted to 32 mL, the degree of ionisation of the acid and H_3O^+ ion concentration in the resulting solution will be respectively.

(a) 0.02 and 3.125×10^{-4} (b) 0.02 and 1.25×10^{-3}
(c) 1.25×10^{-3} and 0.02 (d) 0.02 and 8.0×10^{-12}

9 1 dm^3 solution containing 10^{-5} moles each of Cl^- ions and CrO_4^{2-} ions is treated with 10^{-4} moles of silver nitrate. Which one of the following observation is made? ($K_{sp}Ag_2CrO_4 = 4 \times 10^{-12}$), ($K_{sp}$ AgCl $= 1 \times 10^{-10}$)

(a) Precipitation does not occur
(b) Silver chromate gets precipitated first
(c) Silver chloride gets precipitated first
(d) Both silver chromate and silver chloride start precipitating simultaneously

10 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283), the equilibrium sets as $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$. 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?

(a) 28.3×10^{-2} g (b) 2.83×10^{-3} g
(c) 1.0×10^{-7} g (d) 1.0×10^{-4} g

11 A solution of monoprotic weak acid has ionisation constant K_a. What is the minimum concentration C in terms of K_a, such that the concentration of the undissociated acid can be equated to C within a 10% limit of error. [Assume that activity coefficient correction are negligible.]

(a) $45K_a$ (b) $10K_a$
(c) $90K_a$ (d) $80K_a$

12 What will be the pH of a buffer solution prepared by dissolving 30 g of Na_2CO_3 in 500 mL of an aqueous solution containing 150 mL of 1 M HCl?
[K_a for $HCO_3^- = 5.63 \times 10^{-11}$]

(a) 10.197 (b) 8.089
(c) 9.858 (d) 6.400

13 2.5 mL of 2/5 M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with 2/15 M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C)

(a) 3.7×10^{-13}M (b) 3.2×10^{-7}M
(c) 3.2×10^{-2}M (d) 2.7×10^{-2}M

14 1 M NH_4OH and 1M HCl are mixed to make total volume of 300 mL. If pH of the mixture is 9.26 and pK_a $[NH_4^+] = 9.26$ then volume ratio of NH_4OH and HCl will be

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

ANSWERS

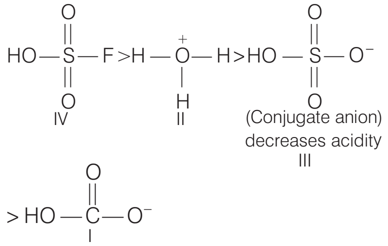
SESSION 1	**1** (a)	**2** (c)	**3** (a)	**4** (c)	**5** (c)	**6** (b)	**7** (b)	**8** (d)	**9** (d)	**10** (d)
	11 (c)	**12** (c)	**13** (a)	**14** (b)	**15** (a)	**16** (b)	**17** (d)	**18** (d)	**19** (a)	**20** (d)
	21 (c)	**22** (c)	**23** (d)	**24** (d)	**25** (a)	**26** (d)	**27** (b)	**28** (b)	**29** (b)	**30** (c)
	31 (d)	**32** (c)	**33** (b)	**34** (d)	**35** (b)	**36** (c)	**37** (d)	**38** (c)	**39** (a)	**40** (b)
	41 (c)	**42** (b)	**43** (b)	**44** (a)						
SESSION 2	**1** (a)	**2** (c)	**3** (a)	**4** (b)	**5** (c)	**6** (c)	**7** (a)	**8** (b)	**9** (c)	**10** (b)
	11 (c)	**12** (a)	**13** (c)	**14** (c)						

Hints and Explanations

SESSION 1

1 HClO is the weakest acid, hence its conjugate base, i.e. ClO^- is the strongest Bronsted base.

2 Acidity order is as follows:



$$\underset{\text{IV}}{HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-F} > \underset{\text{II}}{H-\overset{+}{\underset{\underset{\displaystyle H}{|}}{O}}-H} > \underset{\substack{\text{(Conjugate anion)}\\ \text{decreases acidity}\\ \text{III}}}{HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-O^-} > \underset{\text{I}}{HO-\overset{\overset{\displaystyle O}{\|}}{C}-O^-}$$

3 Only in reaction (ii) $H_2PO_4^-$, gives H^+ to H_2O thus, behaves as an acid. In other two reactions it accept H^+ and thus behaves as a base.

4 $pK_w = pH + pOH$

But $[H^+] = [OH^-] \Rightarrow pH = pOH$,

$\therefore$ $pK_w = 2\,pH$

$$pH = \frac{pK_w}{2} = \frac{13.36}{2} = 6.68$$

5 $K_w = [H^+][OH^-] = 2.7 \times 10^{-14}$

But $[H^+] = [OH^-]$, therefore,

$$K_w = [H^+]^2$$

$$[H^+] = \sqrt{K_w} = \sqrt{2.7 \times 10^{-14}}$$

$$= 1.643 \times 10^{-7}\ M$$

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

$$= -\log[1.643 \times 10^{-7}] = 6.78$$

6 $HA \rightleftharpoons H^+ + A^-$

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

$$HA + NaOH \rightleftharpoons ANa + H_2O$$

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

$$K_C = \frac{[A^-]\,[H_2O]}{[HA][OH^-]} \qquad \text{...(ii)}$$

Also, $K_w = [H^+][OH^-] = 10^{-14}$ ...(iii)

From equations (i), (ii) and (iii)

$$K_C = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = 1 \times 10^{10}$$

7 NH_4OH (weak base) + HCl (strong acid) forms NH_4Cl, which gives acidic solution with $pH < 7$.

8 $5.0 \times 10^{-2}\ M\ NaOH \equiv [OH^-]$

$$= 5 \times 10^{-2} M$$

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

$$[H^+] \cdot 5 \times 10^{-2} = 1 \times 10^{-14}$$

$$[H^+] = \frac{1 \times 10^{-14}}{5 \times 10^{-2}}$$

$$= 2 \times 10^{-13}$$

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

$$= -\log(2 \times 10^{-13})$$

$$= 12.69 \approx 12.70$$

9 At 330 K,

$$[H^+][OH^-] = K_w = 1 \times 10^{-13.6}$$

$$[H^+](10^{-4}\ M) = 1 \times 10^{-13.6}$$

$$[H^+] = \frac{1 \times 10^{-13.6}}{10^{-4}} = 10^{-9.6}$$

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

$$= -\log(10^{-9.6}) = 9.6$$

10 $pH = 1 \ \therefore [H^+] = 10^{-1} = 0.1 M$

$pH = 2 \ \therefore \ [H^+] = 10^{-2} = 0.01 M$

For dilution of HCl, $M_1V_1 = M_2V_2$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10\ L$$

Volume of water to be added

$$= 10 - 1 = 9\ L$$

11 $pH = 3 \Rightarrow H^+ = 10^{-3}\ M = \alpha C$

$$\alpha = \frac{10^{-3}}{C} = \frac{10^{-3}}{0.1} = 0.01 << 1$$

According to Ostwald dilution law

$\therefore$ $K_a = \alpha^2 C$

$$= (0.01)^2 \times 0.1$$

$$= 1 \times 10^{-5}$$

12 We know that acidic strength $\propto K_a$ value.

Thus, on the basis of K_a value, order of acidic strength is

$$HCN < HNO_2 < HF.$$

Conjugate base of a strong acid is weak.

Therefore, the order of base strength of conjugate base is

$$F^- < NO_2^- < CN^-.$$

13

$$\begin{array}{lccccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ \text{At } t=0 & 1 & & 0 & & 0 \\ \text{At } t=t & (1-10^{-5}) & & (10^{-5}) & & (10^{-5}) \end{array}$$

$$[A^-] = [H^+]$$

$$\Rightarrow \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[10^{-5}][10^{-5}]}{[1-10^{-5}]}$$

Since, $1 >>> 10^{-5}$, therefore, $(1-10^{-5}) \approx 1$.

$\therefore$ $K_a = 1 \times 10^{-10}$

14

$$\begin{array}{lccc} & CH_3COOH \rightleftharpoons & CH_3COO^- & + H^+ \\ \text{Initially} & 1 & 0 & 0 \\ \text{After ionisation} & 1-\alpha & \alpha & \alpha \end{array}$$

$$pK_a = -\log K_a = 4.74$$

$\therefore$ $K_a = 1.82 \times 10^{-5}$

From, $K_a = \dfrac{C\alpha^2}{(1-\alpha)} = C\alpha^2 \qquad (\because 1-\alpha \approx 1)$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.82 \times 10^{-5}}{0.05}} = 0.019 \text{ or } 1.9\%$$

15 $NaX + H_2O \rightleftharpoons NaOH + HX$

HX is a weak acid, so Na X is a salt of weak acid and strong base.

Hydrolysis constant of Na X,

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{10^{-5}} = 1 \times 10^{-9}$$

Again, $K_h = \dfrac{h^2}{V} = Ch^2$

(where, h = degree of hydrolysis)

$$1 \times 10^{-9} = 0.1 \times h^2$$

$$h^2 = \frac{1 \times 10^{-9}}{0.1} = 1 \times 10^{-8} \quad \Rightarrow$$

$h = 1 \times 10^{-4}$

% of degree of hydrolysis of NaX salt

$$= 1 \times 10^{-4} \times 100 = 1 \times 10^{-2} = 0.01\%$$

16 For a salt of weak acid and weak base,

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

Given, $pK_a\ (HA) = 3.2$, $pK_a\ (BOH) = 3.4$

$$\therefore \quad pH = 7 + \frac{1}{2}(3.2) - \frac{1}{2}(3.4)$$

$$= 7 + 1.6 - 1.7 = 6.9$$

17 $pH = 13$, $pOH = 1$

$[OH^-] = 10^{-1}\ M$

mole of $(OH)^- = \dfrac{1 \times 0.1}{1000} = 1 \times 10^{-4}$ mol

$= 1 \times 10^{-4} \times 6.02 \times 10^{23}\ OH^-$ ions per mL

$= 6.02 \times 10^{19}$

18 $\underset{(0.005\ M)}{(CH_3COO)_2Ca} \rightarrow Ca^{2+} + \underset{(2 \times 0.005 = 0.01)}{2CH_3COO^-}$

$[CH_3COO^-] = 0.01\ M$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \underset{\text{Alkaline}}{OH^-}$$

$$\text{pH} = 7 + \frac{\text{p}K_a}{2} + \frac{\log C}{2}$$
$$= 7 + 2.37 + \frac{\log 0.01}{2}$$
$$= 7 + 2.37 - 1 = 8.37$$

19 For salt of a weak acid and weak base,

$$\text{pH} = 7 + \frac{1}{2}[\text{p}K_a - \text{p}K_b]$$
$$= 7 + \frac{1}{2}[4.80 - 4.78]$$
$$= 7 + \frac{1}{2}(0.02)$$
$$= 7.01$$

20 $AB_2 \longrightarrow A^{2+} + 2B^-$

$$K_{sp} = [A^{2+}][2B^-]^2$$
$$= (1.0 \times 10^{-5})(2 \times 1.0 \times 10^{-5})^2$$
$$= 4 \times 10^{-15}$$

21 Let the solubility of $PbCl_2 = x$ mol

$$\underset{x\,\text{mol/L}}{PbCl_2} \rightleftharpoons \underset{x}{Pb^{2+}} + \underset{2x}{2Cl^-}$$

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

or $= (x) \times (2x)^2$ or $= 4x^3$

$$\therefore \quad x = \sqrt[3]{\frac{K_{sp}}{4}} = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

22 The one with lowest value of K_{sp}, i.e. HgS will precipitate out first.

23

Salt	**Solubility product**	**Solubility**
MX	$S_1^2 = 4.0 \times 10^{-8}$	$S_1 = 2 \times 10^{-4}$
MX_2	$4S_2^3 = 3.2 \times 10^{-14}$	$S_2 = 2 \times 10^{-5}$
M_3X	$27S_3^4 = 2.7 \times 10^{-15}$	$S_3 = 1 \times 10^{-4}$

Thus, order of solubilities

$$= MX > M_3X > MX_2$$

24 K_{sp} of $BaSO_4 = 1.5 \times 10^{-9}$,

$$Ba^{2+} = 0.01\text{ M}$$
$$SO_4^{2-} > \frac{1.5 \times 10^{-9}}{0.01} > 1.5 \times 10^{-7}$$

i.e. $SO_4^{2-} > 10^{-6}$ M

25 Concentration of CO_3^{2-} ions

$$= 1.0 \times 10^{-4}\text{ M}$$

For precipitation $K_{sp} \le [Ba^{2+}][CO_3^{2-}]$

Given, $K_{sp} = 5.1 \times 10^{-9}$

Hence, minimum concentration of Ba^{2+} ions should be

$$= \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}} = 5.1 \times 10^{-5}\text{ M}$$

26 For the solute, $A_xB_y \rightleftharpoons xA + yB$

$$K_{sp} = x^x y^y (s)^{x+y}$$

Thus, $Mx_4 \rightleftharpoons M^{4+} + 4x^-$, $x = 1$, $y = 4$

$$K_{sp} = (1)^1 (4)^4 (S)^{(1+4)} = 256\,S^5$$
$$S = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

27 $K_{sp} = [Ag^+][Br^-] = 5.0 \times 10^{-13}$

$$[Ag^+] = 0.05\text{ M}$$
$$Br^- = \frac{5 \times 10^{-13}}{0.05} = 1 \times 10^{-11}\text{M}$$

Moles of KBr $= 1 \times 10^{-11} \times 1 = 1 \times 10^{-11}$

Weight of KBr $= 1 \times 10^{-11} \times 120$

$$= 1.2 \times 10^{-9}\text{g}$$

28 $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$
$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = 10^{-4}$$

pOH = 4 and pH = 10.

29 When ionic product is greater than K_{sp}, then precipitation occurs.

$\therefore K_{sp} <$ Ionic product.

This happens in option (b) where

$$1.7 \times 10^{-10} < (10^{-2})(10^{-3})$$
$$1.7 \times 10^{-10} < 10^{-6}$$

30 $\underset{S}{Ca(OH)_3(s)} \rightleftharpoons \underset{S}{Cr^{3+}(aq)} + \underset{3S}{3OH^-(aq)}$

$$K_{sp} = [Cr^{3+}][OH^-]^3$$
$$1.6 \times 10^{-30} = (S)(3S)^3$$
$$1.6 \times 10^{-30} = 27(S)^4$$
$$\therefore \quad S^4 = \frac{1.6 \times 10^{-30}}{27}$$
$$S = \sqrt[4]{\frac{1.6 \times 10^{-30}}{27}}$$

31 (i) $\underset{S_1\text{ mol L}^{-1}}{Hg_2Cl_2} \rightleftharpoons \underset{S_1}{Hg_2^{2+}} + \underset{2S_1}{2Cl^-}$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (S_1)(2S_1)^2$$
$$= S_1 \cdot 4S_1^2 = 4S_1^3$$
$$\therefore \text{ Solubility, } S_1 = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

(ii) $\underset{S_2\text{ mol L}^{-1}}{Cr_2(SO_4)_3} \rightleftharpoons \underset{2S_2}{2Cr^{3+}} + \underset{3S_2}{3SO_4^{2-}}$

$$K_{sp} = [Cr^{3+}]^2[SO_4^{2-}]^3$$
$$= (2S_2)^2(3S_2)^3$$
$$= 4S_2^2 \times 27S_2^3 = 108\,S_2^5$$
$$\therefore \text{ Solubility, } S_2 = \left(\frac{K_{sp}}{108}\right)^{1/5}$$

(iii) $\underset{S_3\text{ mol L}^{-1}}{BaSO_4} \rightleftharpoons \underset{S_3}{Ba^{2+}} + \underset{S_3}{SO_4^{2-}}$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (S_3)^2$$
$$\therefore \text{ Solubility, } S_3 = (K_{sp})^{1/2}$$

(iv) $\underset{S_4\text{ mol L}^{-1}}{CrCl_3} \rightleftharpoons \underset{S_4}{Cr^{3+}} + \underset{3S_4}{3Cl^-}$

$$K_{sp} = [Cr^{3+}][Cl^-]^3$$
$$= (S_4)(3S_4)^3 = 27S_4^4$$
$$\therefore \text{ Solubility, } S_4 = \left(\frac{K_{sp}}{27}\right)^{1/4}$$

32 $NaBrO_3 \rightleftharpoons Na^+ + BrO_3^-$

$$AgBrO_3 \rightleftharpoons Ag^+ + BrO_3^-$$

Due to common ion effect (BrO_3^-), the solubility of $AgBrO_3$ in an aqueous solution of $NaBrO_3$ is suppressed.

33 Solubility is decreased due to common ion effect.

$$AgI \rightleftharpoons Ag^+ + I^-, \quad NaI \rightleftharpoons Na^+ + I^-$$

34 In group III of analysis, addition of NH_4Cl increases NH_4^+ ion and decreases OH^- ion concentration produced from NH_4OH due to common ion effect.

35 CH_3NH_2 (base) on reaction with HCl (acid) give a salt of weak base and strong acid as $CH_3NH_3^+Cl^-$.

$$\begin{array}{llll} & CH_3NH_2 & +\ HCl \longrightarrow & CH_3NH_3^+\,Cl^- \\ \text{At } t = 0 & 0.1\text{ mol} & 0.08\text{ mol} & 0 \\ \text{After reaction} & (0.1 - 0.08) & 0 & 0.08\text{ mol} \\ & = 0.02\text{ mol} & & \end{array}$$

So, it acts as basic buffer solution due to the presence of weak base and its salt in solution of one litre.

$$\text{pOH} = -\log K_b \times \log \frac{[\text{salt}]}{[\text{base}]}$$
$$\text{pOH} = -\log K_b \times \log \frac{[CH_3NH_3^+Cl^-]}{[CH_3NH_2]}$$
$$= -\log(5 \times 10^{-4}) + \log \frac{[0.08]}{[0.02]}$$
$$= -\log 5 + 4\log 10 + \log 4$$
$$= -0.699 + 4 + 0.602 = 3.903$$

$$\text{pH} = 14 - \text{pOH} = 14 - 3.903$$
$$= 10.097 = -\log\,[\text{H}^+]$$
$$[\text{H}^+] = 8.0 \times 10^{-11}$$

36 When the concentration of NH_4OH (weak base) is higher than the strong acid (HCl), a mixture of weak base and its conjugate acid is obtained, which acts as basic buffer.

$$\begin{array}{lcccc} & NH_4OH + HCl & \longrightarrow & NH_4Cl & + H_2O \\ \text{Initially} & 0.1\text{M} & 0.05\text{M} & 0 & \\ \text{After reaction} & 0.05\text{M} & 0 & 0.05\text{M} & \end{array}$$

37 Concentration $= \dfrac{\text{mass}}{\text{molar mass} \times V\,(\text{mL})}$

$$\therefore\quad [CH_3COOH] = \frac{5 \times 1000}{60 \times 500} = 0.166\text{ M}$$

$$\text{Similarly, } [CH_3COONa] = \frac{7.5 \times 1000}{82 \times 500}$$
$$= 0.183\text{ M}$$

For the buffer solution ,
$CH_3COOH + NaOH \rightleftharpoons$
$$CH_3CO\overset{-}{O}\overset{+}{Na} + H_2O$$

$$\text{pH} = \text{p}K_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$
$$= 4.76 + \log\left[\frac{0.183}{0.166}\right]$$
$$= 4.76 + \log\,(1.10)$$
$$= 4.76 + 0.042 = 4.80$$
$$\therefore\quad 4.76 < \text{pH} < 5.0$$

38 From the aqueous buffered solution of *HA*, 50% *HA* is ionised.

$$[HA] = [A^-]$$

Buffer solution of weak acid
$HA \longrightarrow$ acidic buffer

$$\text{pH} = \text{p}K_a + \log\frac{[A^-]}{[HA]}$$
$$= \text{p}K_a + \log 1$$
$$\text{pH} = \text{p}K_a = 4.5$$
$$\text{pOH} = \text{p}K_w - \text{pH}$$
$$\text{pOH} = 14 - 4.5 = 9.5$$

39 NaCl is the salt of strong acid and strong base. It is not a buffer as aqueous solution of NaCl is itself an exact neutral solution.

40 The ionisation of NaCl is suppressed due to the common ion effect of Cl^- which results in the precipitation of NaCl.

41 The value of solubility product of AgCl is greater than that of AgBr. Since, compounds with lower value of solubility product is precipitated first, therefore AgBr precipitates out more easily than AgCl.

42 HCl gives the common H^+ ions and hence, ionisation equilibrium $H_2S \rightleftharpoons 2H^+ + S^{2-}$ is suppressed.

43 HgI_2 combines with KI to form the soluble complex K_2HgI_4 and thus the solubility of $Hg\,I_2$ is expected to be less in KI due to common ion effect.

44 A solution containing a mixture of acetic acid and the sodium acetate acts as a buffer solution as it maintains a constant value of pH (= 4.75) and its pH is not affected on addition of small amounts of acid or alkali.

SESSION 2

1 Strong acids have low pH value while strong bases have high pH value. Hence, the order of pH is

$$\underset{\text{Strong acid}}{HCl} < \underset{\text{Weak acid}}{CH_3COOH} < \underset{\text{Salt of weak base and strong acid}}{NH_4Cl} < \underset{\text{Salt of weak acid and strong base}}{CH_3CO\overset{-}{O}\overset{+}{Na}}$$

2 In 1×10^{-8} M HCl solution, H_2O is also present and undergoes self ionisation.

$$H_2O \rightleftharpoons H^+ + OH^-$$
$$[H^+] = 10^{-7}\text{ M at } 25°\text{C}$$

H^+ from HCl decreases self ionisation which decreases $[H^+]$ concentration, hence net concentration must be smaller than 10^{-7} M.

Thus, the pH of 1×10^{-8} M HCl is less than 8.

3 Given that, $K_a = 1.74 \times 10^{-5}$

Concentration of CH_3COOH
$$= 0.01\text{ mol dm}^{-3}$$
$$[H^+] = \alpha C$$

According to Ostwald dilution law,

$$K_a = \alpha^2 C$$
$$\alpha = \sqrt{\frac{K_a}{C}}$$
$$\therefore\qquad H^+ = \sqrt{\frac{K_a}{C}} \times C$$
$$[H^+] = \sqrt{K_a \cdot C}$$
$$= \sqrt{1.74 \times 10^{-5} \times 0.01}$$
$$= 4.17 \times 10^{-4}$$
$$\text{pH} = -\log\,[H^+]$$
$$= -\log\,(4.17 \times 10^{-4}) = 3.4$$

4 $HA \rightleftharpoons H^+ + A^-$

$$K_a = C\alpha^2 = 1 \times \left(\frac{4}{100}\right)^2 = 1.6 \times 10^{-3}$$
$$K_a = \frac{[H^+][A^-]}{[HA]},\ [H^+] = C\alpha = 1 \times 0.01$$
$$= 0.01\text{ M}$$
$$\therefore\ 1.6 \times 10^{-3} = \frac{0.01\,[A^-]}{1};\quad [A^-] = 0.16\text{ M}$$

5 Its given that the final volume is 500 mL and this final volume was arrived when 50 mL of 1 M Na_2SO_4 was added to unknown Ba^{2+} solution. So, we can interpret the volume of unknown Ba^{2+} solution as 450 mL i.e.

$$\underset{Ba^{2+}\text{ solution}}{450\text{mL}} + \underset{Na_2SO_4\text{ solution}}{50\text{mL}} \longrightarrow \underset{BaSO_4\text{ solution}}{500\text{mL}}$$

From this we can calculate the concentration of SO_4^{2-} ion in the solution *via*

$$M_1V_1 = M_2V_2$$
$$1 \times 50 = M_2 \times 500$$

(as 1M Na_2SO_4 is taken into consideration)

$$M_2 = \frac{1}{10} = 0.1\text{ M}$$

Now for just precipitation,
Ionic product = Solubility product (K_{sp})
i.e. $[Ba^{2+}][SO_4^{2-}] = K_{sp}$ of $BaSO_4$

Given, K_{sp} of $BaSO_4 = 1 \times 10^{-10}$

So, $[Ba^{2+}][0.1] = 1 \times 10^{-10}$

or $[Ba^{2+}] = 1 \times 10^{-9}$ M

This is the concentration of Ba^{2+} ions in final solution. Hence, for calculating the $[Ba^{2+}]$ in original solution we have to use

$$M_1V_1 = M_2V_2$$

as $M_1 \times 450 = 10^{-9} \times 500$

so, $M_1 = 1.1 \times 10^{-9}$M

6 CH_3COO^- acts as buffer

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$
$$\therefore\qquad OH^- = Cx = C\sqrt{\frac{K_b}{C}} = \sqrt{C\,K_b}$$
$$\text{But}\qquad K_a \cdot K_b = K_w$$
$$\therefore\qquad K_b = \frac{K_w}{K_a}$$
$$\therefore\qquad OH^- = \sqrt{\frac{CK_w}{K_a}}$$

7 $[Ag^+] = 0.1$ mg

$$= (0.1 \times 10^{-3}\text{ g}) \text{ in } 500 \text{ mL } H_2O$$

$$= \frac{0.1 \times 10^{-3}}{108} \text{ mol in } 500 \text{ mL } H_2O$$

$$= \frac{0.1 \times 10^{-3} \times 2}{108} \text{ mol in } 1 \text{ L } H_2O$$

$$= 1.85 \times 10^{-6} \text{ M}$$

$$[Ag^+]\,[Cl^-] = 1.0 \times 10^{-10}$$

$$\therefore \quad [Cl^-] = \frac{1.0 \times 10^{-10}}{1.85 \times 10^{-6}} = 5.4 \times 10^{-5} \text{ M}$$

8 $\alpha_1 = 0.005 = \sqrt{K_a}$ $(\because C_1 = 1 \text{ mol L}^{-1})$

Molarity of the diluted solution,

$$C_2 = \frac{2}{32} = \frac{1}{16} \text{mol L}^{-1}$$

According to Ostwald dilution law,

$$\alpha_2 = \sqrt{\frac{K_a}{C_2}} = 0.005\sqrt{16} = 0.02$$

$$[H_3O^+] = C_2\alpha_2$$

$$= \frac{1 \times 0.02}{16} = 1.25 \times 10^{-3}\text{M}$$

9 For precipitation,

Ionic product > solubility product (K_{sp})

For Ag_2CrO_4, ionic product

$$= [Ag^+]^2[CrO_4^-]$$

$$= (10^{-4})^2(10^{-5}) = 10^{-13}$$

K_{sp} of $Ag_2CrO_4 = 4 \times 10^{-12}$

Here, K_{sp} > Ionic product

Thus, no precipitate is obtained.

For AgCl, ionic product

$$= [Ag^+][Cl^-] = (10^{-4})(10^{-5})$$

$$= 10^{-9}$$

K_{sp} (AgCl) $= 1 \times 10^{-10}$

Here, Ionic product > K_{sp}

So, precipitate will form. Thus, silver chloride gets precipitated first.

10 $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq)$

$$K_{sp} = [Ag^+][IO_3^-]$$

$$1.0 \times 10^{-8} = (S)(S)$$

$$1.0 \times 10^{-8} = S^2$$

$$S = \sqrt{1.0 \times 10^{-8}}$$

$$= 1.0 \times 10^{-4} \text{ mol/L}$$

In 1000 mL, moles of $AgIO_3$ dissolved

$$= 1 \times 10^{-4} \text{ mol}$$

In 100 mL, moles of $AgIO_3$ dissolved

$$= 1 \times 10^{-5} \text{ mol}$$

Mass of $AgIO_3$ in 100 mL

$$= 1 \times 10^{-5} \times 283 = 2.83 \times 10^{-3} \text{ g}$$

11

$$\underset{C}{HA} + H_2O \longrightarrow \underset{0}{H_3^+O} + \underset{0}{A^-}$$

$$C(1-\alpha) \qquad C\alpha \qquad C\alpha$$

$$K_a = \frac{[H_3^+O][A^-]}{[HA]} = \frac{C^2\alpha^2}{C(1-\alpha)}$$

With in an error of 10%,

$$C(1-\alpha) \text{ or } C - C\alpha = 0.90\,C$$

or $\quad C\alpha = 0.10\,C$

$$\because \quad K_a = \frac{(0.10\,C)^2}{0.90\,C} = \frac{C}{90}$$

or $\quad C = 90K_a$

12 $Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$

	Na_2CO_3	HCl	NaCl	$NaHCO_3$
Meq. before reaction	$\frac{30}{106} \times 1000$ $= 283$	150×1 $= 150$	0	0
Meq after reaction	133	0	150	150

The solution contains Na_2CO_3 and HCO_3^- and thus, acts as buffer.

$$\therefore \text{pH} = -\log K_a + \log\frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$\text{pH} = -\log K_a + \log(133/150)$$

$$\text{pH} = -\log(5.63 \times 10^{-11}) + \log(133/150)$$

$$= 10.249 - 0.052$$

$$\text{pH} = 10.197$$

13 $\underset{\text{(Base)}}{N_1V_1} = \underset{\text{(Acid)}}{N_2V_2}$

$$2.5 \times \frac{2}{5} = \frac{2}{15} \times V_2 \qquad \text{or}$$

$$V_2 = \frac{15}{2} = 7.5 \text{ mL}$$

$$BOH + HCl \longrightarrow BCl + H_2O$$

2.5 mL of $\frac{2}{5}$ M base contains, base

$$= 2.5 \times \frac{2}{5} = 1 \text{ mmol}$$

$\therefore$ Salt BCl formed = 1m mol

Volume of solution = 2.5 mL + 7.5 mL = 10 mL

$\therefore$ Concentration of salt [BCl] in the solution $= \frac{1}{10}$ M = 0.1 M

For salt of weak base and strong acid

$$[H^+] = \sqrt{\frac{K_wC}{K_b}} = \sqrt{\frac{10^{-14} \times 0.1}{10^{-12}}}$$

$$= 3.2 \times 10^{-2} \text{ M}$$

14 pH = 9.26 indicates $[NH_4OH] > [HCl]$ and thus mixture is a basic buffer since, HCl will react with equivalent amount of NH_4OH forming NH_4Cl.

Let $\quad HCl = x$ mL $= x$ millimol

$NH_4OH = (300 - x)$ mL

$= (300 - x)$ millimol

NH_4Cl formed $= x$ millimol

NH_4OH unreacted

$= 300 - x - x = (300 - 2x)$ millimol

$$\text{pOH} = 14 - 9.26 = 4.74$$

$$\text{p}K_b = 14 - 9.26 = 4.74$$

$$\text{pOH} = \text{p}K_b + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$\text{or} \quad 4.74 = 4.74 + \log\frac{x}{300 - 2x}$$

$$\Rightarrow \frac{x}{300 - 2x} = 1$$

$x = 100$ mL = volume of HCl

$(300 - x) = 200$ mL = volume of NH_4OH

Hence, volume ratio of NH_4OH and HCl = 2 : 1.