B. Sc. (Semester-I)
General Chemistry-I (US01CCHE21)
Unit: III Ionic Equilibria in Aqueous Solutions

Sparingly soluble salts:

Equilibrium concentration of a slightly soluble salt can be obtained using principles of chemical equilibrium.

Consider the dissolution of solid silver chloride in water,

$$AgCl_{(s)} \rightarrow AgCl_{(aq)} \rightleftharpoons Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \quad …….. \quad …….. \quad …… (1)$$

At equilibrium only 1.67 x 10^{-5} mole of AgCl is dissolved in one litre of water at 25°C. This concentration is very small, but it is very important in many laboratory situations. Now, we are going to derive expressions giving the solubilities of sparingly soluble salts.

Equilibrium constant for equation (1)

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

$$\therefore \quad K \cdot [AgCl] = K_{sp} = [Ag^+]\,[Cl^-]$$

K_{SP} is known as ion product constant or solubility product. It is an equilibrium constant for sparingly soluble salt where product of concentrations of respective ions produced due to ionization considering their stoichiometric coefficients as exponents.

Equilibrium constant can be applied to the solubility of sparingly soluble salts only. This is because concentrated solutions are not ideal and equilibrium constant expression can not be applied to non-ideal solutions. Solubilities of sparingly soluble salts can not be measured directly. It can be calculated from K_{sp}. K_{sp} is obtained from voltage measurements.

For example,

$$AgCl_{(aq)} \rightleftharpoons Ag^+{}_{(aq)} + Cl^-{}_{(aq)}$$

$K_{sp} = [Ag^+]\,[Cl^-] =$ 2.8 x 10-10

From stoichiometry, $[Ag^+] = [Cl^-]$

$[Ag^+]\,[Cl^-] = [Ag^+]^2 = 2.8 \times 10^{-10}$

$[Ag^+] = 1.7 \times 10^{-5}$ M

From stoichiometry it is clear that this is the maximum number of moles of silver chloride that dissolve in one litre of water. Thus, the solubility of AgCl in pure water at 25°C is 1.7 x 10^{-5} M.

Similarly, we can calculate solubility of CaF_2.

$$CaF_{2(aq)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-}_{(aq)}$$

$K_{sp} = [Ca^{+2}] [F^{-}]^2 = 1.7 \times 10^{-10}$

From stoichiometry $[F^-] = 2[Ca^{+2}]$

$[Ca^{+2}] (2[Ca^{+2}])^2 = 1.7 \times 10^{-10}$
$4 [Ca^{+2}]^3 = 1.7 \times 10^{-10}$
$[Ca^{+2}] = 3.5 \times 10^{-4}$ M

From stoichiometry, it is clear that one mole CaF_2 will give one mole Ca^{+2}, Thus, the solubility of CaF_2 in pure water is 3.5×10^{-4} M at 25 ^{0}C.

Common ion effect: The suppression of the dissociation of the weak electrolyte on the addition of its own ions is called common ion effect.

To understand the use of solubility product of a salt, let us calculate the solubility of AgCl in 0.1 M $AgNO_3$ solution. Add $AgNO_3$ in a saturated solution of AgCl to reach the concentration of 0.1 M. The addition of $AgNO_3$ will disturb the equilibrium. Now, according to Le Chatelier's principle that is: “When a stress is applied on a system in equilibrium, the system tends to adjust itself so as to reduce the stress”, the position of the equilibrium will be shifted. Thus, as we add AgNO, in a saturated solution of AgCl, AgCl must tend to precipitate. Thus, we can say that the solubility of AgCl in a solution of 0.1 M Ag^+ is less than the solubility of AgCl in pure water.

This can be verified quantitatively. For this we have to calculate chloride ion concentration in this solution.

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

$$\therefore \quad [Cl^-] = \frac{K_{sp}}{[Ag^+]}$$

Now, Ag^+ in the solution is from AgCl as well as $AgNO_3$.

$[Ag^+] = [Ag^+]$ (from $AgNO_3$) + $[Ag^+]$ (from AgCl). Ag^+ from AgCl is less than 1.7×10^{-5} M, and from $AgNO_3$ is 0.1 M. Thus, second term is very very less than the first term, so can be neglected.

$$\therefore \quad [Ag^+] \cong 0.1 \text{ M}$$

$$\therefore \quad [Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9}$$

This is the solubility of AgCl in 0.1 M Ag^+ solution. It is clear that this solubility is less than that of in pure water.

Example: Let us calculate the solubility of CaF_2 in (i) a solution of 0.1 M $Ca(NO_3)_2$ and (ii) a solution of 0.1 M NaF.

(i) Solubility of CaF_2 in a solution of 0.1 M $Ca(NO_3)_2$

We can not say that the solubility of CaF_2 is equal to the equilibrium concentration of Ca^{+2}, because Ca^{+2} comes from $Ca(NO_3)_2$ also. One mole of CaF_2 gives two moles of F^-. Thus, the solubility of CaF_2 is:

$$\text{Solubility} = \frac{1}{2}\,[F^-]$$

Thus, if we calculate fluoride ion concentration, we can get the solubility of CaF_2.

$K_{sp} = [Ca^{+2}]\,[F^-]^2$

$$\therefore \quad [F^-] = \left(\frac{K_{sp}}{[Ca^{+2}]}\right)^{\frac{1}{2}}$$

$[Ca^{+2}] = [Ca^{+2}]$ (from $Ca(NO_3)_2$ + $[Ca^{+2}]$ (from CaF_2). Calcium ion concentration from CaF_2 in pure water is 3.5×10^{-4} M. In 0.1 M $Ca(NO_3)_2$, it is less than 3.5×10^{-4} M. Therefore, concentration of calcium ion from CaF_2 can be neglected compared with 0.1 M from $Ca(NO_3)_2$.

$$\therefore \quad [Ca^{+2}] \cong 0.1\ M$$

$$[F^-] = \left(\frac{K_{sp}}{[Ca^{+2}]}\right)^{\frac{1}{2}} \cong \left(\frac{1.7 \times 10^{-10}}{0.1}\right)^{\frac{1}{2}} = 4.1 \times 10^{-5}\ M$$

Solubility of CaF_2 = ½$[F^-]$ = 2.05×10^{-5} M. Thus, the solubility of CaF_2 is lowered by the presence of an excess of one of its ions. It is clear that calcium ion coming from CaF_2 is only 2.05×10^{-5} M, so neglect of this quantity is justified.

(ii) Now, we calculate the solubility of CaF_2 in 0.1 M NaF.
In this situation we can take the solubility of CaF_2 equal to the concentration of calcium ion at equilibrium.

Solubility of CaF_2 = $[Ca^{+2}]$

$[F^-]$= $[F^-]$ (from NaF) + $[F^-]$ (from CaF_2). $[F^-]$ from NaF is 0.1 M and $[F^-]$ from

CaF_2 is less than 7×10^{-4} M, the concentration of F^- in a pure saturated solution of CaF_2. Thus, second term can be neglected.

$$\therefore \quad [F^-] \cong 0.1\ M$$

$$K_{sp} = [Ca^{+2}]\,[F^-]^2$$

$$\therefore \quad [Ca^{+2}] = \frac{K_{sp}}{[F^-]^2} \cong \frac{1.7 \times 10^{-10}}{(0.1)^2}$$

$$\therefore \quad [Ca^{+2}] = 1.7 \times 10^{-8}\ M$$

Therefore, the solubility of CaF_2 is 1.7×10^{-8} M. Thus, our decision to neglect $[F^-]$ contributed by CaF_2 in comparison with 0.1 M is justified.

Selective Precipitation:
In both the quantitative and qualitative analysis, we can take the advantage of the difference in solubility of salt to remove only one salt from several salts in solution. Calculations using solubility products can tell us when a separation of this type is possible.

Consider a solution that contains 0.1 M Cl^- and 0.01 M CrO_4^{-2}. By adding a solution of $AgNO_3$, first chloride ion will be precipitated as AgCl and chromate ion will remain in solution.
$K_{sp} = [Ag^+] [Cl^-] = 2.8 \text{ x } 10^{-10}$
$K_{sp} = [Ag^+]^2 [CrO_4^{-2}] = 1.9 \text{ x } 10^{-12}$

AgCl and Ag_2CrO_4 are slightly soluble salts. Solubility product is a number which

the product of ion concentrations can never exceed at equilibrium. For example, if the product $[Ag^+] [CI^-]$ is greater than $2.8 \text{ x } 10^{-10}$, the system is not at equilibrium and precipitation of AgCl must occur. On the other hand, the product $[Ag^+] [CI^-]$ can be less than K_{sp}. Therefore, upon adding Ag^+ to a solution of Cl^-, no precipitation of AgCl will occur until the Ag^+ concentration becomes high enough so that $[Ag^+] [CI^-] = K_{sp}$. In this case we are considering, no precipitation of AgCl will occur until the concentration of Ag^+ is

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ M}$$

Similarly, no precipitation of Ag_2CrO_4 will occur until the concentration of Ag^+ is

$$[Ag^+]^2 = \frac{K_{sp}}{\left[CrO_4^{-2}\right]} = \frac{1.9 \times 10^{-12}}{0.01} = 1.9 \times 10^{-10}$$

$$\therefore \quad [Ag^+] = 1.4 \times 10^{-5} \text{ M.}$$

Now, it is interesting to know the concentration of CI^- at the time when Ag_2CrO_4 first begins to precipitate.

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{1.4 \times 10^{-5}} = 2.0 \times 10^{-5}$$

Only very small amount of chloride ion is left in the solution. Thus, we can say that precipitation of chloride ion is almost completed.

In the titration of chloride ion by silver ion, CrO_4^{-2} is used as end point indicator. The chromate ion is bright yellow in aqueous solution, but a precipitate of silver chromate is dark red. As we have seen, the precipitate of Ag_2CrO_4 appears only after complete precipitation of chloride ions. Thus, the formation of Ag_2CrO_4 indicates the end point of the precipitation titration of the chloride ion.

Consider another example of the use of selective precipitation in chemical analysis. Separation of Zn^{+2} and Fe^{+2} by controlled precipitation of their sulphides is possible.

The solubility products of ZnS and FeS are

$K_{sp} = [Zn^{+2}] [S^{-2}] = 4.5\text{x } 10\text{-}24$
$K_{sp} = [Fe^{+2}] [S^{-2}] = 1 \text{ x } 10\text{-}19$

From these values it is clear that ZnS is less soluble than FeS. Thus, if take 0.1 M Zn^{+2} and 0.1 M Fe^{+2}, it is possible to precipitate only ZnS leaving all the Fe^{+2} in the solution.

From the K_{sp} value of FeS, we can calculate sulphide ion concentration.

$$[S^{-2}] = \frac{K_{sp}}{[Fe^{+2}]} = \frac{1 \times 10^{-19}}{0.1} = 10^{-18} \text{ M}$$

Thus, the concentration of sulphide ion must be less than 10^{-18} M in order to avoid precipitation of FeS.

For better separation maximum sulphide ion concentration is taken equal to 10^{-19} M.
At a sulphide ion concentration of 10^{-19} M, the concentration of Zn^{+2} remaining in the solution is

$$[Zn^{+2}] = \frac{K_{sp}}{[S^{-2}]} = \frac{4.5 \times 10^{-24}}{1 \times 10^{-19}} = 4.5 \times 10^{-5} \text{ M}$$

This concentration of zinc ion left in solution is very small. Thus, it is possible to carry out a quantitative separation.

Acids and Bases:

Equilibria involving acids and bases are very important. Acid-base reaction includes number of chemical changes.

Arrhenius theory of acids and bases:

According to this theory an acid is a substance that dissociates to give H^+ when dissolved in water and base is a substance which dissociates into hydroxyl ion (OH^-) when dissolved in water.

Initially, classification of substances as acids was done by their sour taste and bases were taken as those substances that could reverse or neutralize the action of acids. Acid must have oxygen element. But, in 1810 Davy demonstrated that HCl contains only hydrogen and chlorine. Thereafter it was believed that all acids having hydrogen as an essential element.

Arrhenius ionic dissociation theory gives explanation of why acids have different strengths.

$HCl = H^+ + Cl^-$; $CH_3COOH = CH_3COO^- + H^+$

Degree of dissociation of different acids is different, so different acids have different strengths.
Similar scheme can be applied to the behaviour of bases.

$NaOH = Na^+ + OH^-$; $Mg(OH)_2 = Mg^{+2} + 2OH^-$

Thus, the proton is responsible for acidic properties and hydroxyl ion is responsible for basic properties.

This theory has certain limitations. First is concerned with the nature of the proton in aqueous solution and second is substances which do not contain OH^- also act as bases.

Water is excellent solvent for ionic compounds. Ions in aqueous solution are stabilized by their strong attraction to the water molecules. This is because of the asymmetry of charge distribution in the water molecule. Each ion in aqueous solution is strongly attached to a number of water molecules. Proton is unique as it has no electrons. Radius of H^+ is just the nuclear radius, 10^{-13} cm. Approximate radius of other ions is 10^{-8} cm. Therefore, the proton can approach and incorporate itself in the electronic system of a solvent molecule to a greater extent.

Thus, we can not say "free" protons are produced upon dissociation of acid.

There is considerable experimental evidence that the hydrated proton H_3O^+ (hydronium ion) is stable. H_3O^+ exist as a distinct species in several crystals. For example, $HClO_4 \cdot H_2O$ really consists of H_3O^+ and ClO_4^-. Thus, true form of H^+ in aqueous solution can be taken as H_3O^+.

Thus, dissociation is represented as transfer of proton:

$$HCl + H_2O = H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Thus, an acid is a molecule capable of transferring or donating a proton to another molecule.

Another limitation of Arrhenius theory is that it suggests that all basic properties are the hydroxide ion. There are substances that do not contain hydroxide ion even though they neutralize acids. For example,

$$HCl + NH_3 = NH_4^+ + Cl^-$$

Similarly, when sodium carbonate (Na_2CO_3) is dissolved in water it can neutralize acids. Thus, a broader view of acids and bases is necessary.

The Lowry-Bronsted Concept:

According to Lowry-Bronsted an acid is a species having a tendency to lose or to donate a proton, and a base is a species having the tendency to accept a proton.

$$\underset{\text{acid}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O} = H_3O^+_{(aq)} + Cl^-_{(aq)}$$

This reaction is reversible. Cl^- may accept a proton from H_3O^+ and become HCl. Thus, the chloride ion is a base and H_3O^+ is acid. Since HCl and Cl^- differ only by a proton, they are known as a conjugate acid-base pair. Similarly, H_3O^+ and H_2O are such pair.

$$\underset{\text{acid 1}}{HCl} + \underset{\text{base 2}}{H_2O} = \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-}$$

The behaviour of carbonate ion as a base can be represented by

$$\underset{\text{base 1}}{CO_3^{-2}} + \underset{\text{acid 2}}{H_2O} = \underset{\text{acid 1}}{HCO_3^-} + \underset{\text{base 2}}{OH^-}$$

Thus, Lowry-Bronsted definitions include substances which do not contain OH^- as base.

Strength of acids and bases:

The Lowry-Bronsted definition suggests that a strong acid has a large tendency to transfer a proton to another molecule, and a strong base has a large tendency to accept a proton. Thus, acid strength can be measured quantitatively by the extent to which reactants are converted to products in a reaction.

$HSO_4^- \quad + \quad H_2O \quad = \quad H_3O^+ \quad + \quad SO_4^{-2}$
acid 1 base 2 acid 2 base 1

The extent of this reaction depends on tendency of acid 1 to lose a proton as well as on the tendency of base 2 to accept that proton.
For comparison of strengths of different acids, same base must be taken. Acid dissociation constant is a quantitative measure of acid strength.
There is a relation between the strength of an acid and its conjugate base, HCl has a large tendency to lose a proton, so it is a strong acid. Its conjugate base chloride ion has a less tendency to accept a proton, so it is a weak base. In general, if an acid is a strong its conjugate base is a weak and vice versa.

The Lewis Concept:
According to Lewis, an acid is any substance that can accept electrons and a base is a substance that can donate electrons.
For example,
$BF_3 \quad + \quad F^- \quad = \quad BF_4^-$
acid base

$Ag^+ \quad + \quad 2CN^- \quad = \quad Ag(CN)_2^-$
acid base

This concept is also useful for reactions in which protons are not involved.
Lowry-Bronsted bases react by donating electrons to a proton, So Lowry-Bronsted base is also a Lewis base. However, a Lowry-Bronsted acid must have a proton to donate, however this is not required by the Lewis definition. So, Lewis acid may not be Lowry-Bronsted acid.

The pH Scale:
In dilute solutions hydrogen ion concentration is very small. If concentration is in moles per litre, it is expressed as negative powers of 10. For example, the hydrogen ion concentration in a saturated solution of CO_2 is 1.3×10^{-4} M. It is convenient to give these concentrations as negative logarithm.

Thus, pH is defined as,

$pH = -\log [H_3O^+]$

For saturated solution of CO_2 ,

$pH = -\log [H_3O^+] = -\log (1.3 \times 10^{-4}) = 3.89$

Similarly, $[H_3O^+]$ can be calculated if pH is known. A solution having a pH of 4.5 must have $[H_3O^+] = 3.2 \times 10^{-5}$.

$4.5 = -\log [H_3O^+]$
$-4.5 = \log [H_3O^+]$
$[H_3O^+] = 3.2 \times 10^{-5}$

Negative logarithms can be used for other ions also. For example, pOH is the negative logarithm of the hydroxide ion concentration and pAg is the negative logarithm of Silver ion. Equilibrium constant can also be expressed as pK.

Self-ionization of water:
Water can act as either an acid or a base, so the reaction

H_2O + H_2O = H_3O^+ + OH^-
acid 1 base 2 acid 2 base 1

proceeds to a small extent in pure water

$K = [H_3O^+]\,[OH^-]$

The quantity K_w is known as the ion product constant for water. The value of K_w is 10^{-14} at 25 ^{0}C when concentrations are expressed in moles per litre.
A solution that is neither acidic nor basic has equal concentrations of H_3O^+ and OH^-.
Thus, $[H_3O^+] = [OH^-] = 10^{-7}$ M in a neutral solution at 25 °C. We can say that pH = pOH = 7.

pH + pOH = pK_w = 14 at 25 °C. pH can be obtained by subtracting pOH from 14.
The self-ionization of water gives hydrogen ion and hydroxide ion. This factor doesn't affect much in calculating the hydrogen ion concentration in solutions of acids and bases. For example, take 0.1 M HCl solution. HCl is strong acid so it will completely be dissociated into its ions. H_3O^+ concentration of the solution is slightly different because of the self-ionization of water. In pure water, H_3O^+ concentration is 10^{-7} M. If H_3O^+ in the form of HCl is added to pure water, self-ionization of water must diminish. H_3O^+ contributed by the self-ionization of water become less than 10^{-7} M. This very small quantity can be neglected.

In a 0.1 M HCl solution, H_3O^+ concentration can be taken as 0.1 M.

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

$$[OH^-] = \frac{10^{-14}}{[H_3O^+]} = \frac{10^{-14}}{0.1} = 10^{-13}\ \text{M}$$

Thus, in an acidic solution the H_3O^+ concentration is greater and OH^- concentration is less than in pure water. Only source of OH^- in this solution is self-ionization of wate. From stoichiometry, it is clear that H_3O^+ due to self-ionization of water is 10^{-13} M. This value is very less as compared to 0.1 M H_3O^+ produced due to dissociation of HCl. Thus, our assumption, H_3O^+ contributed by self-ionization of water, is justified.

Similarly, in a 0.01 M NaOH, the contribution of self-ionization of water to OH^- concentration is negligible.

Hydrolysis

A weak acid and its anion are a conjugate acid-base pair. If an acid is weak, its conjugate base is strong. For example, acetic acid is a weak acid, so acetate ion is a strong base.

CH_3COO^- + H_2O = CH_3COOH + OH^- ……. ……. …….. (1)

This reaction is the hydrolysis of the acetate ion.

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} \qquad \dots \quad \dots \quad \dots \ (2)$$

K_h is known as hydrolysis constant. It can be evaluated from the ionization constant of the corresponding acid.
Upon multiplying equation (2) by $[H_3O^+]/\ [H_3O^+]$,

$$K_h = \frac{[CH_3COOH]\,[OH^-]\,[H_3O^+]}{[CH_3COO^-]\,[H_3O^+]}$$

$$[OH^-]\ [H_3O^+] = K_w \text{ and } K_a = \frac{[H_3O^+]\,[CH_3COO^-]}{[CH_3COOH]}$$

$$\therefore \quad K_h = \frac{K_w}{K_a}$$

Now, K_a for acetic acid is 1.85×10^{-5}, So K_h of its conjugate base, acetate ion is

$$K_h = \frac{K_w}{K_a} = \frac{10^{-14}}{1.85 \times 10^{-5}} = 5.4 \times 10^{-10}$$

It is clear that weaker the acid, smaller the K_a value and the corresponding anion will be hydrolysed strongly.
In other words, it is a quantitative demonstration that weaker the acid, stronger is its conjugate base, and vice versa.

Now, let us calculate the hydroxide ion concentration in 1 M sodium acetate solution.

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

Our first assumption is-contribution of self-ionization of water to OH concentration can be neglected.

$$[OH^-] \cong [CH_3COOH]$$

Acetate ion is a weak base, so most of acetate ion remains as such in the solution. This is our second assumption.

$$[CH_3COO^-] \cong 1.0 \text{ M}$$

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}$$

$$5.4 \times 10^{-10} \cong \frac{[OH^-]^2}{1.0}$$

$$[OH^-] \cong 2.3 \times 10^{-5} \text{ M.}$$

This value is greater than OH^- contribution from self-ionization of water, so our first assumption is justified. This value is much less than 1 M, so our second assumption is also justified.

The salts of weak bases are weak acids. For example, ammonia is a weak base.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Salt NH_4Cl is a weak acid and hydrolysed as

$$NH_4^+ + H_2O = NH_3 + H_3O^+$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Upon multiplying equation (2) by $\frac{[OH^-]}{[OH^-]}$

$$K_h = \frac{[NH_3][H_3O^+][OH^-]}{[NH_4^+][OH^-]}$$

$$[H_3O^+][OH^-] = K_w \text{ and } K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\therefore \quad K_h = \frac{K_w}{K_b}$$

This equation relates the ionization constant of a weak base to the hydrolysis constant of its salt. It is clear from this equation that weaker the base, smaller the K, value and the corresponding cation will be hydrolysed strongly.

In other words, it is a quantitative demonstration that weaker the base, stronger 1s its conjugate acid and vice versa.

Now, let us calculate H_3O^+ concentration in 0.1 M NH_4Cl solution.

$$NH_4^+ \quad + \quad H_2O \quad = \quad NH_3 \quad + \quad H_3O^+$$

Our first assumption is contribution of self-ionization of water to H_3O^+ concentration can be neglected.

$$[H_3O^+] \cong [NH_3]$$

NH_4^+ is a weak acid, so most of NH_4^+ remains as such in the solution. This is our second assumption.

$$[NH_4^+] \cong 0.1 \text{ M}$$

$$K_h = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$5.6 \times 10^{-10} \cong \frac{[H_3O^+]^2}{0.1}$$

$$\therefore \qquad [H_3O^+] \cong 7.5 \times 10^{-6} \text{ M}$$

This value is greater than H_3O^+ contribution from self-ionization of water, so our first assumption is justified. This value is much less than 0.1 M, so our second assumption is also justified.

Buffer Solutions:

We have discussed solutions of a pure weak acid and a pure weak base.

Now, let us calculate the equilibrium concentrations for solutions containing a mixture of a weak acid and its salt, or a weak base and its salt.

Let us calculate H_3O^+ concentration in a solution prepared by mixing 0.70 mole of acetic acid and 0.6 mole of sodium acetate.

The ionization constant of acetic acid,

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.85 \times 10^{-5}$$

$$[H_3O^+] = \frac{[CH_3COOH]}{[CH_3COO^-]} \times 1.85 \times 10^{-5}$$

To calculate $[H_3O^+]$, we must know acetic acid and acetate ion concentrations.

Out of 0.7 mole of acetic acid, some amount is lost by dissociation into ions. However, acetic acid is a weak acid so most of it remains as such in the solution. In addition to this the solution contains acetate ion. Therefore, dissociation of acid will be repressed. Thus, loss of acetic acid due to dissociation can be neglected.

So we can take $[CH_3COOH] = 0.70$ M.

Due to hydrolysis of the excess acetate ion acetic acid is produced.

$CH_3COO + H_2O = CH_3COOH + OH^-$

In a solution containing acetic acid, the hydrolysis will be repressed. So, its contribution to the acetic acid concentration can be neglected. Amount lost by dissociation or gained by hydrolysis are very small. So, we can take $[CH_3COOH] = 0.7$ M.

Sodium acetate is totally dissociated into ions, so acetate ion concentration is appreciable. The loss of acetate ion by hydrolysis is small even in a pure solution of sodium acetate and is smaller in a solution containing acetic acid. The gain of acetate ion from the dissociation of acetic acid is also very small. Thus,

$$[CH_3COO^-] = 0.60\ M$$

$$[H_3O^+] = \frac{[CH_3COOH]}{[CH_3COO^-]} \times 1.85 \times 10^{-5}$$

$$= \frac{0.70}{0.60} \times 1.85 \times 10^{-5}$$

$$= 2.2 \times 10^{-5}\ M.$$

The approximations that we have used require that both - the acid and its anion must have more concentrations. The absolute concentration of the acid is numerically much greater than its dissociation constant.
A solution that contains appreciable amounts of both a weak acid and its salt is called a buffer solution.

Buffer solution has remarkable and useful properties. Buffer solutions can be diluted without changing H_3O^+ concentration.

The general expression for $[H_3O^+]$ is:

$$[H_3O^+] = \frac{[acid]}{[anion]} \cdot K_a$$

H_3O^+ concentration depends on K_a and the ratio of the concentrations of acid and anion. When the buffer solution is diluted, concentrations of acid and anion changes, but their ratio remains the same. Thus, concentration of H_3O^+ will not change.

Upon addition of small amounts of strong acid or strong base into the buffer solution, H_3O^+ concentration remains constant.

Let us calculate the change in H_3O^+ concentration upon addition of 1 ml 1 M HCl into (i) pure water and (ii) the buffer solution made up of acetic acid and acetate ion.

Case (i): We add 1 ml 1 M HCl to 1 litre pure water. 1 ml = 0.001 litre. 1 ml 1 M HCl means 0.001 litre x 1 mole litre^{-1} = 0.001 mole. We can say that 0.001 mole of H_3O^+ is added to one litre of pure water. Concentration of H_3O^+ in 1 litre pure water at 25 ^{0}C is 10^{-7} M. Upon addition of 1 ml 1 M HCl to this water, the concentration of H_3O^+ becomes 10^{-3} M. H_3O^+ concentration is changed by 10^4 times.

Now ***case (ii):***

We add 0.001 mole of H_3O^+ to the buffer solution made up of acetate ion and acetic acid. The following chemical reaction occurs.

$CH_3COO^- + H_3O^+ = CH_3COOH + H_2O$

For this reaction

$$K = \frac{[CH_3COOH]}{[CH_3COO^-][H_3O^+]} = \frac{1}{K_a} = \frac{1}{1.85 \times 10^{-5}}$$

$$= 5.4 \times 10^4$$

The value of K is large means all the added acid reacts with the acetate ion giving acetic acid.

$$[CH_3COOH] = 0.70 + 0.001 = 0.701 \text{ M.}$$

0.001 mole of acetate ion is used to produce acetic acid.

$$[CH_3COO^-] = 0.60 - 0.001 = 0.599 \text{ M}$$

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

$$= \frac{0.701}{0.599} \times 1.85 \times 10^{-5}$$

$$= 2.2 \times 10^{-5}$$

Thus, the concentration of H_3O^+ remains unchanged upon addition of small amount of strong acid to buffer solution.

Similarly, addition of small amount of strong base, H_3O^+ concentration remains unchanged. Buffer solutions have tendency to resist the change in H_3O^+ concentration. By storing excess protons as the weak acid, and excess base as the anion, they are able to modify the effect of any added acid or base.

Buffer solutions can also be prepared by mixing appreciable amounts of a weak base and its salt.

Ammonia is a weak base and in aqueous solution produces OH^-.

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$\therefore \quad [OH^-] = \frac{[NH_3]}{[NH_4^+]} K_b$$

Concentration of OH^- depends on the ratio of the concentration of ammonia to that of ammonium ion. Consequently $[OH^-]$ remains unchanged by any dilution of the solution. Excess base is stored in the solution as NH_3 and excess acid as NH_4^+. Therefore, any strong acids or bases added to the solution will be neutralized and OH^- concentration remains unchanged.

To understand the use of buffer solutions consider the separation of 0.1 M Zn^{+2} and 0.1 M Fe^{+2}. For better separation sulphide ion concentration should be 10^{-19}M. This can be maintained by using a saturated solution of H_2S and an appropriate buffer.

In aqueous solution, H_2S dissociates very slightly into sulphide ions by the reaction,

$H_2S(aq) + 2H_2O = 2H_3O^+ + S^{-2}$

$$K = \frac{[H_3O^+]^2 [S^{-2}]}{[H_2S]} = 1.1 \times 10^{-21}$$

In a saturated solution of H_2S, $[H_2S] = 0.1$ M. In this solution, sulphide ion concentration can be controlled by setting the concentration of H_3O^{+}.

$$[H_3O^+]^2 = \frac{[H_2S]}{[S^{-2}]} \times 1.1 \times 10^{-21}$$

$$[S^{-2}] = 10^{-19} \text{ M and } [H_2S] = 0.1 \text{ M}$$

$$[H_3O^+]^2 = \frac{0.1}{10^{-19}} \times 1.1 \times 10^{-21} = 1.1 \times 10^{-3}$$

$$[H_3O^+] = 3.3 \times 10^{-2} \text{ M}$$

Thus, if we maintain H_3O^+ concentration at about 0.03 M, the separation can be made. Now let us select an appropriate buffer solution.

$$[H_3O^+] = \frac{[\text{acid}]}{[\text{salt}]} K_a$$

In order to have a good buffer solution, H_3O^+concentration should be almost equal to K_a.

The bisulphate ion, HSO_4^- is a weak acid.

$$HSO_4^- + H_2O = SO_4^{-2} + H_3O^+$$

$$\therefore \quad K_a = \frac{[H_3O^+][SO_4^{-2}]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

$$\therefore \quad [H_3O^+] = \frac{[HSO_4^-]}{[SO_4^{-2}]} \times 1.2 \times 10^{-2}$$

To maintain H_3O^+ concentration at about 0.03 M, $NaHSO_4$ and Na_2SO_4 should be taken in the ratio of 2.5: 1.

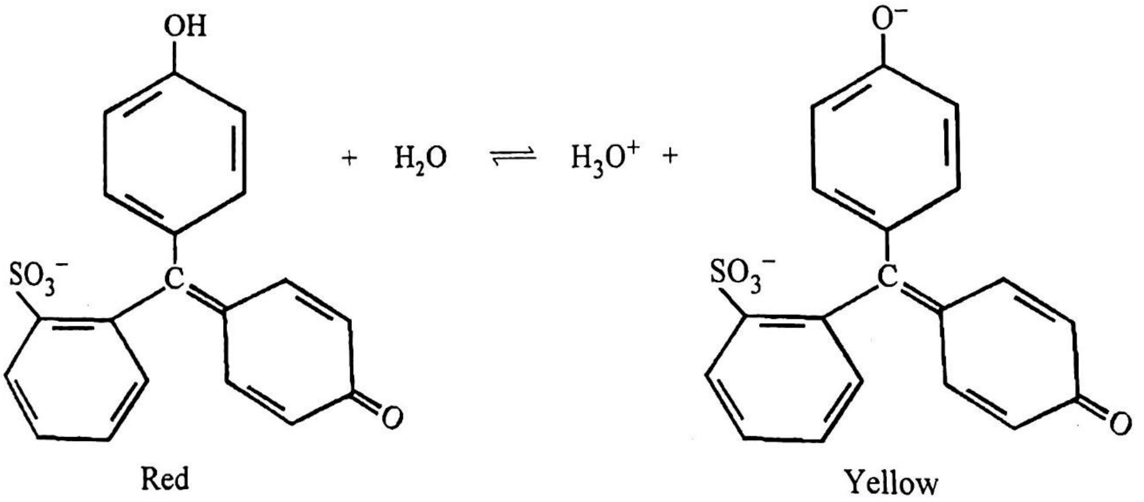
When ZnS is precipitated, H_3O^+ produces.

$$H_2S + Zn^{+2} + 2H_2O = ZnS + H_3O^+$$

Even though H_3O^+ concentration remains constant.

Indicators:
Dye molecules whose colour depends upon the concentration of H_3O^+can be used to estimate the pH of a solution and known as indicators. Indicators are weak acids or weak bases. Conjugate acid base forms of indicator have different colours.

For example, Phenol red.



We can write using abbreviations,

$$H\,I_n + H_2O = H_3O^+ + In^-$$

$$K_I = \frac{[H_3O^+]\,[In^-]}{[H\,In]}$$

As the amount of indicator used is very less, H_3O^+produced due to dissociation of indicator doesn't affect H_3O^+ concentration. H_3O^+ concentration in the solution determines the ratio of $[In^-]$ to $[H\,In^-]$ by the equation,

$$\frac{[In^-]}{[H\,In]} = \frac{K_1}{[H_3O^+]}$$

If the concentration of H_3O^+ is large, $[H\,In] >> [In^-]$ and the solution becomes red.
If $[H_3O^+]$ is small, $[In^-] >> [H\,In]$, and the solution becomes yellow.

There is a natural limitation on the range of pH values. The eye can detect change in colour only when the ratio or the concentrations of two-coloured forms falls in the range

0.1 to 10. In case of Phenol red, $[In^-] / [H In] = 0.1$, the solution is red, if it is 1, solution is orange and if it is 10, the solution is yellow.

Because of three ratios corresponds to $[H_3O^+]$ equal to 10 K_I, K_I and 0.1 K_I, the indicator is sensitive to change of pH only in a 100 fold range of H_3O^+ concentration. In order to measure pH in the range of 6 to 8, we must use an indicator having ionization constant about 10^{-7}, similarly for other pH ranges.

Example-1: For the following reaction $K_{sp} = 2.8 \times 10^{-10}$ moles $litre^{-1}$. What is the solubility of AgCl in pure water? $AgCl_{(aq)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$.

Solution:

Let the solubility of AgCl is 'S' moles $litre^{-1}$.

$$\therefore \quad [Ag^+] = [Cl^-] = \text{'S' M}$$

$$K_{sp} = [Ag^+][Cl^-] = 2.8 \times 10^{-10}$$

$$[Ag^+]^2 = 2.8 \times 10^{-10}$$

$$\therefore \quad [Ag^+] = 1.7 \times 10^{-5} \text{ M}$$

From stoichiometry, it is clear that this is the maximum number of moles of AgCl that dissolve in one litre of water. Thus, the solubility of AgCl in pure water is 1.7×10^{-5} M.

Example-2: What is the solubility of CaF_2 in pure water? $K_{sp} = 1.7 \times 10^{-10}$ M.

Solution:

$$CaF_{2\,(aq)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^-_{(aq)}$$

The only source of Ca^{+2} and F^- in pure water is the salt itself. From stoichiometry it is clear that upon dissociation of one mole of CaF_2, one mole of Ca^{+2} and two moles of F^- are produced.

$$\therefore \quad [F^-] = 2[Ca^{+2}].$$

Let the solubility of CaF_2 is 'S' M.

$$[Ca^{+2}] = \text{'S' M}, \; [F^-] = 2S \text{ M}$$

$$K_{sp} = [Ca^{+2}][F^-]^2 = S\,(2S)^2 = 4S^3 = 1.7 \times 10^{-10}$$

$$\therefore \quad S = 3.5 \times 10^{-4} \text{ M}$$

Example-3: The solubility product of Ag_2CrO_4 is 1.9 10^{-12} M. Calculate the solubility of Ag_2CrO_4.

Solution:

$$Ag_2CrO_{4(aq)} \rightleftharpoons 2Ag^{+}_{(aq)} + CrO^{-2}_{4\,(aq)}$$

$$K_{sp} = [Ag^+]^2\,[CrO_4{}^{-2}] = 1.9 \times 10^{-12}\ \text{M}$$

Let the solubility of the salt is 'S' M.

$$[Ag^+] = 2\ S,\ [CrO_4{}^{-2}] = S$$

$$K_{sp} = (2S)^2\,(S) = 4S^3 = 1.9 \times 10^{-12}$$

$$\therefore \quad S = 0.78 \times 10^{-4}\ \text{M}$$

Example 4: Calculate the solubility of AgCl in a solution of 0.1 M $AgNO_3$. K_{sp} of AgCl is 2.8 x 10^{-10} M.

Solution:

$$AgCl_{(aq)} \rightleftharpoons Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}.$$

Ag^+ in the solution is from AgCl as well as $AgNO_3$, so from Ag^+ concentration we can not say about solubility. Cl^- comes only from AgCl. From Cl^- concentration solubility can be known, so we have to calculate $[Cl^-]$.

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

$$\therefore \quad [Cl^-] = \frac{K_{sp}}{[Ag^+]}$$

$$[Ag^+] = [Ag^+]\ (\text{from } AgNO_3) + [Ag^+]\ (\text{from AgCl}).$$

Second term is very very less than the first term, so can be neglected.

$$[Ag^+] \cong 0.1\ \text{M}$$

$$[Cl^-] = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9}\ \text{M}$$

From stoichiometry, this is the solubility of AgCl in 0.1 M $AgNO_3$.

Example 5: The solubility product of lead sulphate is 1.8 x 10^{-8}, Calculate the solubility of lead sulphate in (i) pure water (ii) 0.10 M $Pb(NO_3)_2$ solution and (iii) 1.0 x 10^{-3} M Na_2SO_4 solution.

Solution:

$$PbSO_{4(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + SO^{-2}_{4\,(aq)}$$

Let the solubility of $PbSO_4$ is 'S' M.

(i) in pure water :

$$K_{sp} = [Pb^{+2}]\,[SO_4^{-2}] = 1.8 \times 10^{-8}\ M$$

$$S \cdot S = 1.8 \times 10^{-8}$$

$$\therefore\ S = 1.3 \times 10^{-4}\ M$$

Solubility of $PbSO_4$ in pure water is 1.3×10^{-4} M.

(ii) in 0.1 M $Pb(NO_3)_2$ solution:

Pb^{+2} in the solution is from $PbSO_4$ as well as $Pb(NO_3)_2$, so from Pb^{+2} concentration we can not say about the solubility. SO_4^{-2} comes only from $PbSO_4$.
From SO_4^{-2} concentration solubility can be known, so we have to calculate SO_4^{-2} concentration.

$$Ksp = [Pb^{+2}]\,[SO_4^{-2}]$$

$$[SO_4^{-2}] = \frac{K_{sp}}{[Pb^{+2}]}$$

$$[Pb^{+2}] = [Pb^{+2}]\ (\text{from Pb }(NO_3)_2] + [Pb^{+2}]\ (\text{from } PbSO_4)$$

$$= (0.1) + (1.3 \times 10^{-4})$$

Second term is very very less than the first term, so can be neglected

$$\therefore\quad [Pb^{+2}] \cong 0.1$$

$$[SO_4^{-2}] = \frac{1.8 \times 10^{-8}}{0.1} = 1.8 \times 10^{-7}\ M$$

From stoichiometry, this is the solubility of $PbSO_4$ in 0.1 M $Pb(NO_3)_2$ solution.

(iii) in 1 x 10^{-3} M Na_2SO_4 solution:

SO_4^{-2} in the solution is from $PbSO_4$ as well as Na_2SO_4, so from SO_4^{-2} concentration we can not say about the solubility. Pb^{+2} comes only from $PbSO_4$. From Pb^{+2} concentration solubility can be known, so we have to calculate Pb^{+2} concentration.

$$K_{sp} = [Pb^{+2}]\,[SO_4^{-2}]$$

$$[Pb^{+2}] = \frac{K_{sp}}{[SO_4^{-2}]}$$

$$[SO_4^{-2}] = [SO_4^{-2}] \text{ (from } Na_2SO_4) + [SO_4^{-2}] \text{ (from } PbSO_4)$$
$$= (1 \times 10^{-3}) + (1.3 \times 10^{-4}) = 1.13 \times 10^{-3}$$

$$\therefore \quad [Pb^{+2}] = \frac{1.8 \times 10^{-8}}{1.13 \times 10^{-3}} = 1.59 \times 10^{-5} \text{ M}$$

This is the solubility of $PbSO_4$ in 1 x 10^{-3} M Na_2SO_4 solution.

Example-6: The solubility product of $Mg(OH)_2$ is 1.8 x 10^{-11} M. What is the solubility of $Mg(OH)_2$ in pure water ? What is the concentration of OH^- in the saturated solution? What is the pH of the solution?

Solution:

$$Mg(OH)_{2(aq)} \rightleftharpoons Mg^{+2}_{(aq)} + 2\,OH^-_{(aq)}$$

Let the solubility of $MgOH)_2$ is 'S' M.
In pure water, the only source of Mg^{+2} and OH^- is the salt itself. From stoichiometry, it is clear that upon dissociation of one mole of $Mg(OH)_2$, one mole of Mg^{+2} and two moles of OH^- are produced.

$$\therefore \quad [OH^-] = 2[Mg^{+2}]$$
$$K_{sp} = [Mg^{+2}]\,[OH^-]^2 = S \cdot (2S)^2 = 1.8 \times 10^{-11} \text{ M}$$
$$4S^3 = 1.8 \times 10^{-11} \quad \therefore \quad S = 1.65 \times 10^{-4} \text{ M}$$

Solubility of $Mg(OH)_2$ is 1.65×10^{-4} M

$$[OH^-] = 2[Mg^{+2}] = 2 \times 1.65 \times 10^{-4} = 3.3 \times 10^{-4} \text{ M}$$

Now, $[H_3O^+]\,[OH^-] = K_w = 1 \times 10^{-14}$

$$\therefore \quad [H_3O^+] = \frac{1.0 \times 10^{-14}}{3.3 \times 10^{-4}} = 3.03 \times 10^{-11} \text{ M}$$

$$pH = -\log\,[H_3O^+] = -\log\,(3.03 \times 10^{-11}) = 10.518$$

Example-7: A saturated solution of lead iodate in a pure water has a concentration of iodate ion equal to 8.0 x 10^{-5} moles litre^{-1} at 25 °C. What is the concentration of Pb^{+2} ? Calculate the solubility product of $Pb(IO_3)_2$ at 25°C.

Solution:

$$Pb(IO_3)_{2(aq)} \rightleftharpoons Pb^{+2}_{(aq)} + 2\,IO^-_{3(aq)}$$

$$[IO_3^-] = 8.0 \times 10^{-5} \text{ moleslitre}^{-1}$$

From stoichiometry it is clear that

$$[Pb^{+2}] = \frac{1}{2}\left[IO_3^-\right] = \frac{1}{2}\ (8.0 \times 10^{-5}) = 4.0 \times 10^{-5}$$

$$K_{sp} = [Pb^{+2}]\ [IO_3^-]^2 = (4.0 \times 10^{-5})\ (8.0 \times 10^{-5})^2$$

$$\therefore \quad K_{sp} = 2.56 \times 10^{-13}$$

Example 8: To a solution of 0.1 M Cl^- and 0.1 M CrO_4^{-2}, $AgNO_3$ solution is added slowly. K_{sp} of Ag_2CrO_4 is 1.9×10^{-12} and that of AgCl is 2.8×10^{-10}. (a) Which solid will precipitate out first? (b) What is the concentration of Ag^+ when first solid precipitates? (c) What is the concentration of Ag^+ when second solid precipitates? (d) What is the concentration of Cl^- when second solid precipitates?

Solution:

Using K_{sp} values first find out which substance is less soluble.

$$Ag_2CrO_{4(aq)} \rightleftharpoons 2\,Ag^+_{(aq)} + CrO^{-2}_{4\,(aq)}$$

Suppose the solubility is 'S' M

$$K_{sp} = [Ag^+]^2 \left[CrO_4^{-2}\right] = 1.9 \times 10^{-12}$$

$$(2S)^2\ (S) = 1.9 \times 10^{-12}$$

$$4S^3 = 1.9 \times 10^{-12}$$

$$S = 0.77 \times 10^{-4} \text{ M}$$

The solubility of Ag_2CrO_4 is 0.77×10^{-4} M

$$AgCl_{(aq)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

$$K_{sp} = [Ag^+]\ [Cl^-] = 2.8 \times 10^{-10}$$

$$S \cdot S = 2.8 \times 10^{-10}$$

$$S = 1.7 \times 10^{-5} \text{ M}$$

The solubility of AgCl is 1.7×10^{-5} M

Solubility of AgCl is less, so AgCl will precipitate out first on addition of $AgNO_3$ solution. AgCl will precipitate out first,

$$K_{sp} = [Ag^+]\ [Cl^-] = 2.8 \times 10^{-10}$$

$$[Ag^+] = \frac{2.8 \times 10^{-10}}{[Cl^-]} = \frac{2.8 \times 10^{-10}}{0.1} = 2.8 \times 10^{-9} \text{ M}$$

The concentration of Ag^+ is 2.8 x 10^{-9} M, when first solid precipitates.

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

$$K_{sp} = [Ag^+]^2\,[CrO_4^{-2}] = 1.9 \times 10^{-12}$$

$$[Ag^+]^2 = \frac{1.9 \times 10^{-12}}{[CrO_4^{-2}]} = \frac{1.9 \times 10^{-12}}{0.1} = 1.9 \times 10^{-11}$$

$$[Ag^+] = 4.36 \times 10^{-6}\ M$$

Thus, the concentration of Ag^+ is 4.36 x 10^{-6} M when second solid precipitates. When [Ag] = 4.36 x 10^{-6} M, second solid starts to precipitate. At that time concentration of Cl^- is

$$K_{sp} = [Ag^+]\,[Cl^-] = 2.8 \times 10^{-10}$$

$$[Cl^-] = \frac{2.8 \times 10^{-10}}{4.36 \times 10^{-6}} = 6.42 \times 10^{-5}\ M$$

Example 9: To a solution that contains 0.1 M Ca^{+2} and 0.1 M Ba^{+2}, sodium sulphate is added slowly. K_{sp} of calcium sulphate is 2.4 X 10^{-5} M and that of barium sulphate is 1.1 x 10^{-10} M. (a) What is the sulphate ion concentration at the instant the first solid precipitates? (b) What is that solid? (C) Neglect dilution and calculate the barium ion concentration present when the precipitation of $CaSO_4$ starts. (d) Do you think it should be possible to separate Ca^{+2} and Ba^{+2} by selective precipitation of sulphates?

Solution:

$$CaSO_{4\,(aq)} \rightleftharpoons Ca^{+2}_{(aq)} + SO^{-2}_{4(aq)} : K_{sp} = 2.4 \times 10^{-5}\ M$$

$$BaSO_{4(aq)} \rightleftharpoons Ba^{+2}_{(aq)} + SO^{-2}_{4\,(aq)} : K_{sp} = 1.1 \times 10^{-10}\ M$$

K_{sp} of $BaSO_4$ is smaller than that of $CaSO_4$. Therefore, the solubility of $BaSO_4$ is less than $CaSO_4$ and thus $BasO_4$ will precipitate first.

$$K_{sp} = [Ba^{+2}]\,[SO_4^{-2}] = 1.1 \times 10^{-10}$$

$$[SO_4^{-2}] = \frac{K_{sp}}{[Ba^{+2}]} = \frac{1.1 \times 10^{-10}}{0.1} = 1.1 \times 10^{-9}\ M$$

The concentration of sulphate ion is 1.1 x 10^{-9} M, when first solid precipitates.

$$K_{sp} = [Ca^{+2}]\,[SO_4^{-2}] = 2.4 \times 10^{-5}$$

$$[SO_4^{-2}] = \frac{K_{sp}}{[Ca^{+2}]} = \frac{2.4 \times 10^{-5}}{0.1} = 2.4 \times 10^{-4}\ M$$

Thus, when $CaSO_4$ start to precipitate, SO_4^{-2} concentration is 2.4 x 10^{-4} M and at that time Ba^{+2} concentration is

$$[Ba^{+2}] = \frac{K_{sp}}{[SO_4^{-2}]} = \frac{1.1 \times 10^{-10}}{2.4 \times 10^{-4}} = 4.6 \times 10^{-7}\ M$$

Concentration of Ba^{+2} which was 0.1 M initially is reduced to 4.6×10^{-7} M. This shows that most of the Ba^{+2} is precipitated as $BaSO_4$ when the precipitation of Ca^{+2} begins. Thus, we can say that Ca^{+2} and Ba^{+2} can be separated by selective precipitation method as the difference between K_{sp} of $BaSO_4$ and $CaSO_4$ is very large.

Example 10: Calculate pH of a buffer solution containing 0.1 M CH_3COONa in 0.1 M CH_3COOH. ($K_a = 1.76 \times 10^{-5}$ M)

Solution:

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

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

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

let $[H_3O^+] = x$, then $[CH_3COO^-] = 0.1 + x$ and $[CH_3COOH] = 0.1 - x$

$$K_a = \frac{x\,(0.1 + x)}{(0.1 - x)} = 1.76 \times 10^{-5}$$

x is very small compare to 0.1 so it can be neglected.

$$\frac{0.1\,x}{0.1} = x = 1.76 \times 10^{-5}$$

$$pH = -\log\,[H_3O^+] = -\log\,(1.76 \times 10^{-5})$$

$$\therefore \quad pH = 4.76$$

Example 11: Calculate the solubility of FeS in a saturated solution of H_2S. In this $[H_2S] = 0.1$ M and $[H_3O^+] = 1.0 \times 10\text{-}3$ M. The equilibrium constant for the dissociation of H_2S by the reaction $H_2S + 2H_2O = 2H_3O^+ + S^{-2}$ is 1.1×10^{-21}. $K_{sp} = 1 \times 10^{-19}$ for FeS.

Solution:

$$H_2S + 2H_2O \rightleftharpoons 2H_3O^+ + S^{-2}$$

$$K_a = \frac{[H_3O^+]^2\,[S^{-2}]}{[H_2S]} = 1.1 \times 10^{-21}$$

$$\therefore \quad [S^{-2}] = \frac{Ka\,[H_2S]}{[H_3O^+]^2} = \frac{0.1 \times 1.1 \times 10^{-21}}{(1.0 \times 10^{-3})^2}$$

$[S^{-2}] = 1.1 \times 10^{-16}$ M

$$FeS_{(aq)} \rightleftharpoons Fe^{+2}_{(aq)} + S^{-2}_{(aq)}$$

$$K_{sp} = [Fe^{+2}]\,[S^{-2}]$$

$$\therefore \quad [Fe^{+2}] = \frac{K_{sp}}{[S^{-2}]} = \frac{1 \times 10^{-19}}{1.1 \times 10^{-16}}$$

$[Fe^{+2}] = 0.9 \times 10^{-3}$ M

Fe^{+2} in the solution is only due to FeS, so from stoichiometry the solubility of FeS is 0.9×10^{-3} M.

Example 12: Calculate the percentage dissociation of a 0.10 M HCN (hydrocyanic acid) solution. $K_a = 4.93 \times 10^{-10}$

Solution:

$$HCN + H_2O \rightleftharpoons CN^- + H_3O^+$$

$$K_a = \frac{[H_3O^+]\,[CN^-]}{[HCN]}$$

Let $x = [H_3O^+]\,[CN^-]$

Assume that $[HCN] \cong 0.1$ M at equilibrium.

$$\therefore \quad 4.93 \times 10^{-10} = \frac{x^2}{0.1}$$

$$\therefore \quad x = 7.0 \times 10^{-6} \text{ mol litre}^{-1}$$

$$\text{Percentage dissociation} = \frac{\text{moles of HCN dissociated}}{\text{total moles of HCN}} \times 100$$

$$= \frac{7.0 \times 10^{-6}}{0.10} \times 100 = 0.0070\ \%$$

Example 13 : What is the pH of a 0.2 M HCOOH (formic acid) solution ?

$(K_a = 1.77 \times 10^{-4})$

Solution :

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

$$K_a = \frac{[H_3O^+]\,[HCOO^-]}{[HCOOH]} = 1.77 \times 10^{-4}$$

Let $x = [H_3O^+]\,[HCOO^-]$

Assume that $[HCOOH] \cong 0.2$ M at equilibrium

$$1.77 \times 10^{-4} = \frac{x^2}{0.2}$$

$[H_3O^+] = x = 5.95 \times 10^{-3}$ mollitre^{-1}

$pH = -\log\,[H_3O^+] = -\log\,(5.95 \times 10^{-3})$

$\therefore\ pH = 2.23$

Example 14: Calculate the pH of a buffer solution containing 0.1 M of sodium acetate in a 0.1 M acetic acid (K_a = 1.76 x 105).

Solution:

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

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

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

Let $x = [H_3O^+]$, then

$[CH_3COO^-] = 0.1 + x$ and $[CH_3COOH] = 0.1 - x$

$$\therefore\ K_a = \frac{x(0.1 + x)}{0.1 - x} = 1.76 \times 10^{-5}$$

'x' is very small, compare to 0.1 so it can be neglected.

$$K_a = \frac{0.1\,x}{0.1} = x = 1.76 \times 10^{-5} = [H_3O^+]$$

$pH = -\log\,[H_3O^+] = -\log\,(1.76 \times 10^{-5})$

$pH = 4.76$

Example 15: A saturated solution of $La(IO_3)_3$ in pure water has iodate ion concentration 2.07 x 10-3 M at 25°C. What is the concentration of La^{+3} ion? Calculate the solubility product of $La(IO_3)_3$?

Solution:

$$La(IO_3)_{3(aq)} \rightleftharpoons La^{+3}_{(aq)} + 3\,IO^-_{3(aq)}$$

$$K_{sp} = [La^{+3}]\ [IO_3^-]^3$$

$$[IO_3^-] = 3[La^{+3}]$$

$$[La^{+3}] = \frac{1}{3}\left[IO_3^-\right] = \frac{1}{3}\,(2.07 \times 10^{-3}) = 6.9 \times 10^{-4}\ M$$

$$K_{sp} = [La^{+3}]\ [IO_3^-]^3$$

$$K_{sp} = (6.9 \times 10^{-4})\ (2.07 \times 10^{-3})^3 = 6.12 \times 10^{-12}$$

Example 16: **Lead iodate is a sparingly soluble salt with K_{sp} 2.6 x 10^{-13}, To 35 ml 0.15 M $Pb(NO_3)_2$ solution, 15 ml 0.8 M KIO_3 solution is added. What are the concentrations of Pb^{+2} and IO_3^- left in the solution after precipitation of $Pb(IO_3)_2$?**

Solution:

$$\text{Moles of } Pb^{+2} \text{ in 35 ml 0.15 M } Pb(NO_3)_2 \text{ solution} = \frac{35 \times 0.15}{1000} = 5.25 \times 10^{-3}$$

$$\text{Moles of } IO_3^- \text{ in 15 ml 0.8 M } KIO_3 \text{ solution} = \frac{15 \times 0.8}{1000} = 12 \times 10^{-3}$$

$Pb(IO_3)_2$ is formed by the reaction

$$Pb^{+2}_{(aq)} + 2\,IO^-_{3(aq)} \rightleftharpoons Pb(IO_3)_{2\,(aq)}$$

From stoichiometry, $2[Pb^{+2}] = [IO_3^-]$

In the solution, moles of Pb^{+2} present is 5.25×10^{-3}.

Moles of IO_3^- used will be $2 \times (5.25 \times 10^{-3}) = 10.5 \times 10^{-3}$.

In the solution, 12 x 10^{-3} moles of IO_3^- is there, so (12 x 10^{-3}) - (10.5 x 10^{-3}) = 1.5 x 10^{-3} moles of IO_3^- will be left after precipitation.

50 ml solution contains 1.5×10^{-3} moles of IO_3^- ,

1000 ml solution contains (?)

$$\frac{1000 \times 1.5 \times 10^{-3}}{50} = 3 \times 10^{-2}$$

So $[IO_3^-] = 3 \times 10^{-2}$ M

$$K_{sp} = [Pb^{+2}]\ [IO_3^-]^2$$

$$[Pb^{+2}] = \frac{K_{sp}}{[IO_3^-]^2} = \frac{2.6 \times 10^{-13}}{(3 \times 10^{-2})^2} = 2.9 \times 10^{-10}\ M$$

Example 17: The solubility of AgCl in water at 25°C is 0.00179 gm litre^{-1}. Calculate K$_{sp}$ of AgCl (Atomic weight: Ag = 108 gm mole^{-1} and Cl = 35.5 gm mole^{-1}).

Solution:

Solubility of AgCl is given in gm litre^{-1}. It should be in mole litre^{-1}. Molecular weight of AgCl = 108 + 35.5 = 143.5 gm mole^{-1}.

$$\frac{0.00179}{143.5}\ \frac{\text{gm}}{\text{litre}}\ \frac{\text{mole}}{\text{gm}} = 1.25 \times 10^{-5}\ \text{molelitre}^{-1}$$

$$AgCl_{(aq)} \rightleftharpoons Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Let the solubility is 'S'

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

$$K_{sp} = (1.25 \times 10^{-5})^2$$

$$\therefore \quad K_{sp} = 1.56 \times 10^{-10}$$

Example 18: The solubility product of Mg(OH)$_2$ is 1.4 x 10^{-11} at 25°C. What is the solubility of Mg(OH)$_2$ in gm litre^{-1}. Molecular weight of Mg(OH)$_2$ is 58 gm mole^{-1}.

Solution:

$$Mg(OH)_{2(aq)} \rightleftharpoons Mg^{+2}_{(aq)} + 2OH^{-}_{(aq)}$$

Let the solubility is 'S' M

$$K_{sp} = [Mg^{+2}]\ [OH^{-}]^2 \text{ and } 2\ [Mg^{+2}] = [OH^{-}]$$

$$K_{sp} = S\ (2\ S)^2 = 4\ S^3$$

$$\therefore \quad S = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$$

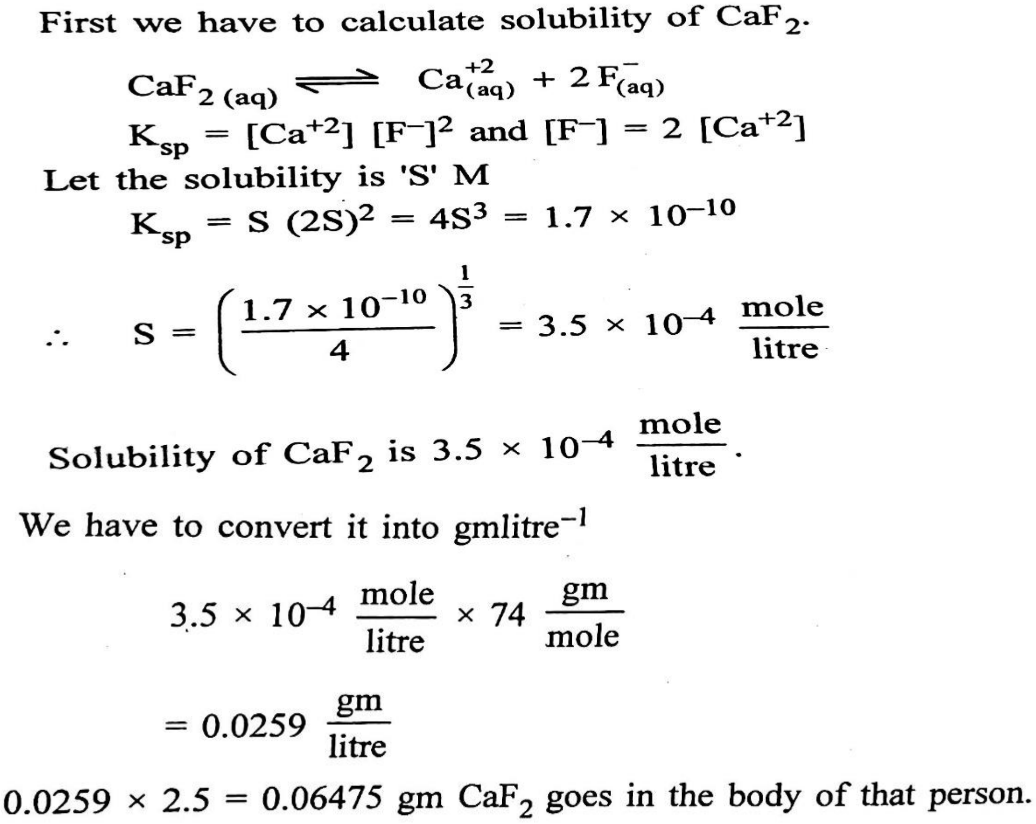
$$\therefore \quad S = \left(\frac{1.4 \times 10^{-11}}{4}\right)^{\frac{1}{3}}$$

$$\therefore \quad S = 1.5 \times 10^{-4}\ M$$

$$S = 1.5 \times 10^{-4}\ \frac{\text{mole}}{\text{litre}} \times 58\ \frac{\text{gm}}{\text{mole}}$$

$$\therefore \quad S = 0.0087\ \text{gmlitre}^{-1}$$

Example 19: A person drinks 2.5 litre of water saturated with CaF_2 every day. How much CaF_2 goes in the body of that person every day? K_{sp} of CaF_2 is 1.7×10^{-10} and molecular weight of CaF_2 is 74 gm $mole^{-1}$.
Solution:



First we have to calculate solubility of CaF_2.

$$CaF_{2\,(aq)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-}_{(aq)}$$

$$K_{sp} = [Ca^{+2}]\,[F^{-}]^2 \text{ and } [F^{-}] = 2\,[Ca^{+2}]$$

Let the solubility is 'S' M

$$K_{sp} = S\,(2S)^2 = 4S^3 = 1.7 \times 10^{-10}$$

$$\therefore \quad S = \left(\frac{1.7 \times 10^{-10}}{4}\right)^{\frac{1}{3}} = 3.5 \times 10^{-4}\ \frac{\text{mole}}{\text{litre}}$$

Solubility of CaF_2 is $3.5 \times 10^{-4}\ \frac{\text{mole}}{\text{litre}}$.

We have to convert it into gmlitre^{-1}

$$3.5 \times 10^{-4}\ \frac{\text{mole}}{\text{litre}} \times 74\ \frac{\text{gm}}{\text{mole}}$$

$$= 0.0259\ \frac{\text{gm}}{\text{litre}}$$

$0.0259 \times 2.5 = 0.06475$ gm CaF_2 goes in the body of that person.

Question Bank

Multiple Choice Questions:

(1) According to Lowry-Bronsted concept, base is a substance which is
(a) proton donor (b)proton acceptor
(c) electrons acceptor (d) electrons donor

(2) Which of the following is a base according to Lowry-Bronsted concept ?
(a) I^- (b) H_3O^+ (c)HCl (d) NH_4^+

(3) According to Lowry-Bronsted concept, which one of the following is considered as an acid ?
(a) H_3O^+ (b) BF_3 (c) OH^- (d) Cl^-

(4) A conjugate acid differs from its conjugate base by
(a) electron pair **(b) proton** (c) electron (d) neutron

(5) The conjugate acid of NH_2^- is
(a) NH_4^+ **(b) NH_3** (c) N_2H_4 (d) NH_2OH

(6) pH of buffer solution depends upon concentration of
(a) acid (b) conjugate base (c) salt **(d) both (a) and (b)**

(7) pH can be kept constant with the help of
(a) saturated solution (b) unsaturated solution
(c) buffer solution (d) super saturated solution

(8) K_{sp} is known as
(a) solubility product (b) solubility reactant
(c) dynamic equilibrium (d) solubility equilibrium

(9) Reduction in solubility of dissolved salt is gained by addition of solution of compound, which has an ion common with that of dissolved salt it is
(a) common ion effect (b) ion reaction
(c) reduction of ion (d) compound reduction

(10) Scientific definition of pH is negative logarithm to base 10 of
(a) H_3O^+ ion concentration (b) OH ion concentration
(c) power of hydroxyl group (d) power of hydrogen

(11) When two solutions are mixed solubility product helps in determining whether there will be formation of
(a) salts (b) oxides **(c) precipitates** (d) all of them

(12) Value of K_a can be calculated by determining
(a) concentration of acid (b) pH of solution
(c) concentration of water molecules **(d) both (a) and (b)**

(13) If a solution on addition of small amounts of acid or base doesn't change significantly and maintains its pH, this type of solution is called
(a) saturated solution (b) unsaturated solution
(c) buffer solution (d) super saturated solution

(14) Water may act as
(a) acid (b) base (c) alkali **(d) both (a) and (b)**

(15) Solubility product is only applicable for
(a) soluble salts (b) insoluble salts
(c) sparingly soluble salts (d) sparingly insoluble salts

(16) K_a is called
(a) acid dissociation constant (b) base dissociation constant
(c) Avogadro constant (d) salt dissociation constant

(17) Excessive addition of acid or alkalis cannot be handled by
(a) saturated solution (b) unsaturated solution
(c) buffer solution (d) super saturated solution

(18) Water has very low extent of
(a) ionization (b) bonding (C) temperature (d) all of these

(19) Dye which changes colour over a specific pH range is

(a) acid-base indicator (b) reactant (c) catalyst (d) product

(20) On self-ionization, water molecules produce

(a) H_3O^+ (b) OH^- ion **(c) both (a) and (b)** (d) oxygen

(21) In the reaction, $HNO_3 + H_2O = NO_3^- + H_3O^+$ the conjugate base of HNO_3 is

(a) H_2O (b) H_3O^+ **(c) NO_3^-** (d) unpredictable

(22) Which of the following is a Lewis acid ?

(a) H_2O **(b) $SnCl_4$** (c) C_2H_5OH (d) Cl^-

(23) The sum of pH and pOH in aqueous solution at 25 ^{0}C is equal to

(a) 7 (b) 0 (c) 1 **(d) pK_w**

(24) On passing H_2S, which of the following metal sulphides will be precipitated first from a solution having almost equal concentration of metal ion ?

(a) FeS (K_{sp} = 11 x 10^{-20}) **(b) HgS (K_{sp} = 3.2 x 10^{-55})**

(c) ZnS (K_{sp} =1.1 x 10^{-22}) (d) CdS (K_{sp}= 3.6 x 10^{-31})

(25) A buffer solution is one whose pH value on keeping in the air

(a) increases rapidly (b) decreases rapidly

(c) may increase or decreases **(d) does not change**

(26) On diluting a buffer solution, its pH

(a) increases (b) decreases

(c) remains the same (d) may increase or decrease depending upon type of buffer

(27) When NH_4Cl is added to a solution of NH_4OH

(a) only he concentration of OH^- ions increases

(b) only the concentration of OH^- ions decreases

(c) the concentration of NH_4^+ ions decreases

(d) the concentration of NH_4^+ as well as OH^- ions increases

(28) 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

(29) The pH of blood doesn't change appreciably by a small addition of an acid or base because blood

(a) contains serum protein which acts as buffer

(b) contains iron as a part of the molecule

(c) can be easily coagulated

(d) is body fluid

(30) The conjugate acid of HPO_4^{2-} is

(a) H_3PO_4 (b) PO_4^{3-} **(c) $H_2PO_4^-$** (d) H_3O^+

(31) The conjugate base of HCO_3^- is
(a) H_2CO_3 **(b) CO_3^{2-}** (c) CO_2 (d) H_2O

(32) Which of the following can act both as Lowry-Bronsted acid and base ?
(a) HCl (b) H_3PO_4 **(c) HCO_3^-** (d) O_2^-

(33) In which of the following reactions NH_3 acts as acid ?
(a) $NH_3 + HCI \rightarrow NH_4Cl$ (b) $NH_3 + H^+ = NH_4^+$
(c) $NH_3 + Na \rightarrow NaNH_2 + 1/2\ H_2$ (d) NH3 cannot act as acid

(34) Ammonia gas dissolves in water to give NH_4OH. In this reaction water acts
(a) an acid (b) a salt (c) a base (d) a conjugate base

(35) According to Lowry-Bronsted concept, the acids in the following reaction
$NH_3 + H_2O = NH_4^+ + OH^-$ are
(a) NH_3 and NH_4^+ (b) H_2O and OH^-
(c) H_2O and NH_4^+ (d) NH_3 and OH^-

(36) According to Lowry-Bronsted concept, water is:
(a) acid (b) base (c) salt **(d) both an acid and a base**

(37) Consider the following reactions:
(i) $CO_3^{2-} + H_2O = HCO_3^- + OH^-$ (ii) $CO_2 + H_2O = H_2CO_3$
(iii) $NH_3 + H_2O = NH_4OH$ (iv) $HCl + H_2O = Cl^- + H_3O^+$
Which of the pairs of reactions prove that water can act both as Lowry-Bronsted acid and base?
(a) (i) and (ii) (b) (ii) and (iii) **(c) (iii) and (iv)** (d) (i) and (iii)

(38) One of the 1ollowing is Lowry-Bronsted acid but not a Lowry-Bronsted base
(a) H_2S (b) H_2O (c) HCO_3^- (d) NH_3

(39) In the reaction, $HNO_3 + H_2O = H_3O^+ + NO_3^-$ the conjugate base of HNO_3 is
(a) H_2O (b) H_3O^+ **(c) NO_3^-** (d) unpredictable

(40) The conjugate bases in the following reaction:
$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$ are
(a) H_2O, H_3O^+ **(b) H_2O, HSO_4^-** (c) H_2SO_4, H_3O^+ (d) H_2SO_4, HSO_4^-

(41) Which of the following represents the conjugate pair of NH_3?
(a) NH_2^- (b) NH_4^+ (c) **both (a) and (b)** (d) N_3^-

(42) Conjugate base of a strong acid is
(a) a weak base (b) a strong base (c) neutral (d) a weak acid

(43) The Lowry-Bronsted acid which has the weakest conjugate base is
(a) HCl (b) HF (c) H_2S (d) H_2O

(44) CH_3OO^- ion is a
(a) weak conjugate base **(b) strong conjugate base**
(c)weak conjugate acid (d) strong conjugate acid

(45) Which of the following is strongest conjugate base?
(a) ClO_4^- (b) HCO_3^- (c) F^- (d) HSO_4^-

(46) BF_3 acts as acid according to the concept of
(a) Lowry-Bronsted (b) Arrhenius **(c) Lewis** (d) all of these

(47) Which of the following acids is the strongest ?
(a) HCN ($K_a = 4 \times 10^{-10}$) (b) HS^- ($K_a = 1 \times 10^{-14}$)
(c) HCO_4^- ($K_a = 4.8 \times 10^{-10}$) (d) $HAsO_4^{-2}$ ($K_a = 3 \times 10^{-13}$)

(48) Which of the following is the weakest ?
(a) C_6H_5 NH_2 ($K_b = 3.8 \times 10^{-10}$) (b) NH_4OH ($K_b = 1.6 \times 10^{-5}$)
(c) $C_2H_5NH_2$ (K_b = 5.6 x 10) (d) C_9H_7N (K_b = 6.3 x 10-10)

(49) Which equilibrium can be described as an acid-base reaction using the Lewis definition but not using Lowry-Bronsted concept ?
(a) $NH_3 + CH_3COOH = CH_3COO^- NH_4^+$
(b) $H_2O + CH_3COOH = CH_3COO^- + H_3O^+$
(c) $4NH_3 + Cu^{2+} = [Cu(NH_3)4]^{2+}$
(d) $HCl + CH_3COOH = CH_3COO^- H_2 + Cl^-$

(50) Which of the following species can act as Lewis base ?
(a) Cu^{2+} (b) $AlCl_3$ **(c) NH_3** (d) BF_3

(51) Which of the following species can act as Lewis acid ?
(a) NH_4Cl (b) $MgCl_2$ **(c) CO_2** (d) H_2O

(52) Which of the following species can act as Lewis acid?
(a) H_2O **(b) $SnCl_4$** (c) C_2H_5OH (d) Cl^-

(53) Which of the following species can act as Lewis acid?
(a) Cl^- (b) H_3O^+ **(c) BF_3** (d) C_2H_5OH

(54) Among the following species which is not a Lewis acid ?
(a) $SnCl_2$ (b) $AlCl_3$ **(c) CCl_4** (d) $SiCl_4$

(55) Ionic product of water is 1.0×10^{-14} at 25 °C. This is so
(a) only for water (b) only for acidic solution
(c) only for basic solution **(d) for all the three above**

(56) On adding ammonia to water,
(a) ionic product will increase (b) ionic product will decrease
(c) $[H_3O^+]$ will increase **(d) $[H_3O^+]$ will decrease**

(57) On adding a few drops of H_2SO_4 to water,
(a) ionic product will increase (b) ionic product will decrease
(c) $[OH^-]$ will increase **(d) $[OH^-]$ will decrease**

(58) The pH of a solution is equal to
(a) $\log [H_3O^+]$ (b) $-\log \{1/[H_3O^+]\}$
(c) $1/[H_3O^+]$ **(d) $-\log [H_3O^+]$**

(59) When a solution contains equal concentration of H_3O^+ and OH^- ions at 25 °C, its pH would be around

(a) 14 (b) 0 **(c) 7** (d) 1

(60) The addition of solid sodium carbonate to pure water causes

(a) increase in$[H_3O^+]$ (b) decrease in pH

(c) increase in pH (d) no change in pH

(61) For a solution at 298 K, the sum of pH and pOH will be equal to

(a) zero **(b) fourteen** (c) a negative number (d) infinity

(62) The value of pk_w at 25 ^{0}C is

(a) 1×10^{-14} (b) 7 **(c) 14** (d) 0

(63) Which is the correct representation for the solubility product constant of Ag_2CrO_4?

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

(64) The solubility product of Hg_2I_2 is equal to

(a) $[Hg_2^{++}] [I^-]$ (b) $[Hg^{++}] [I^-]$ **(c) $[Hg_2^{++}] [I^-]^2$** (c) $[Hg^{++}] [I^-]^2$

(65) If concentration is expressed in mol/liter then, the units of solubility product of Ag_2SO_4 will be

(a) mol / liter (b) mol^2 /$liter^{-2}$ **(c) mol^3 / $liter^{-3}$** (d) none these

(66) Precipitation takes place when the ionic product

(a) equals their solubility product **(b) exceeds their solubility product**

(c) is less than their solubility product (d) is almost zero

(67) The ionic product of an electrolyte

(a) is always equal to its solubility product (K_{sp})

(b) can be equal to or less than K_{sp}

(c) is always less than K_{sp}

(d) can be less than, equal to or greater than K_{sp}

(68) When HCl gas is passed through a saturated solution of common salt, pure NaCl is precipitated because

(a) the impurities dissolved in HCl

(b) HCl is highly soluble in water

(c) the ionic product of $[Na^+][Cl^-]$ exceeds the solubility product of NaCl

(d) The solubility product of NaCl is lowered by Cl^- from aqueous HCl

(69) If the solubility of Ag_2CrO_4 is 'S' mol / liter , its solubility product is

(a) S^2 (b) S^3 **(c) $4 S^3$** (d) $2 S^3$

(70) For the sulphides below the solubility products are shown within brackets, the least soluble sulphide is

(a) CoS ($K_{sp} = 3.0 \times 10^{-25}$) (b) MnS ($K_{sp} = 1.5 \times 10^{-10}$)

(c) ZnS ($K_{sp} = 1.2 \times 10^{-28}$) (d) NiS ($K_{sp} = 1.5 \times 10^{-24}$)

(71) The solubility of Al(OH)3 and Zn(OH), are 8.5 x 102 M and 1.8 x 10-14 M respectively. If a solution contains equal concentrations of Al and Zn, on adding $NH_4Cl + NH_4OH$

(a) $Al(OH)_3$ is precipitated first (b) $Zn(OH)_2$ is precipitated first
(c)both are precipitated together (d) neither of them is precipitated

(72) About buffer solution which is correct ?
(a) it contains a weak acid and its conjugate base
(b) it contains a weak base and its conjugate acid
(c) it shows little change in pH on adding small amount of acid or base
(d) none of these

(73) Which of the following is a buffer ?
(a) HCl and NaCl (b) NaOH and $NaNO_3$
(c) KOH and KCl **(d) NH_4OH and NH_4Cl**

(74) Which of the following solution acts as a buffer ?
(a) HCl + NaCl (b) NaOH+ NaCl
(c) $CH_3COOH + CH_3COONa$ (d) HCOOH + $HCOONH_4$

(75) 100 ml of solution contains 0.1 M NH_4OH and 0.1 M NH_4Cl. The pH of the solution will not change on adding
(a) 20 ml of 0.1 M NH_4OH solution (b) 20 ml of 0.1 M NH_4Cl solution
(c) 10 ml of 0.1 M NaOH solution **(d) 10 ml distilled water**

(76) Which of the following substances on dissolving in water will give a basic solution?
(a) Na_2CO_3 (b) $Al_2(SO_4)_3$ (c) NH_4Cl (d) KNO_3
(77) Which of the following will suppress the ionization of acetic acid in aqueous solution ?
(a) NaCl **(b) HCl** (c) KCl (d) unpredictable
(78) The origin of the word acid relates to acids' taste, which is best described as
(a) bitter **(b) sour** (c) sweet (d) salty

(79) A mixture of a weak acid and its salt with a strong base is a buffer solution. Which other pair of substances from the following may have a similar properties ?
(a) HCl and NaCl (b) NaOH and $NaNO_3$
(c) KOH and KCl **(d) NH_4OH and NH_4Cl**

(80) Which of the following is most soluble ?
(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-17}$) **(b) MnS ($K_{sp} = 7 \times 10^{-16}$)**
(c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)

(81) Buffer solution can be obtained by mixing aqueous solutions of
(a) CH_3COONa and excess HCl **(b) CH_3COONa and CH_3COOH**
(c) NaOH + NaCl (d) CH_3COONa and excess NaOH

(82) When HCl gas is passed through a saturated solution of NaCl, the solubility of NaCl
(a) increases **(b) decreases** (c) NaCl is decomposed (d) doesn't change

(83) In the reaction, $NH_3 + H_2O = NH_2^- + H_3O^+$ the conjugate base of NH_3 is
(a) H_2O (b) H_3O^+ **(d) NH_2^-** (d) none of these

(84) Substances get precipitated in aqueous solution when

(a) ionic product of water exceeds 10^{-14} at 25 ^{0}C

(b) ionic product of water exceeds solubility product

(c) solubility product exceeds ionic product of the substance

(d) ionic product of the substance exceeds its solubility product

(85) The conjugate base of a weak acid is

(a) a strong base (b) a weak base

(c) a neutral species (d) may be weak or strong base

(86) In the following reaction

$HC_2O_4^- + PO_4^{-3} = HPO_4^{-2} + C_2O_4^{-2}$ which are the two Lowry-Bronsted bases ?

(a) $HC_2O_4^-$ and PO_4^{-3} (b) HPO_4^{-2} and $C_2O_4^{-2}$

(c) $HC_2O_4^-$ and HPO_4^{-2} **(d) PO_4^{-3} and $C_2O_4^{-2}$**

(87) The following equilibrium is established when hydrogen chloride is dissolved in acetic acid $HCl + CH_3COOH = Cl^- + CH_3COOH_2^+$

The set of conjugate acid- base pairs is

(a) (HCl, CH_3COOH) and ($CH_3COOH_2^+$, Cl^-)

(b) (HCl, $CH_3COOH_2^+$) and (CH_3COOH, Cl^-)

(c) ($CH_3COOH_2^+$, HCl) and (Cl^-, CH,COOH)

(d) (HCl, Cl^-) and ($CH_3COOH_2^+$, CH_3COOH)

(88) Aqueous solution of acetic acid contains

(a) CH_3COO^- and H^+ **(b) CH_3COO^-, H_3O^+ and CH_3COOH**

(c) CH_3COO^-, H_3O^+ and H^+ (d) CH_3COOH, CH_3COO^- and H^+

(89) Which of the following is not a Lewis base ?

(a) Ag^+ (b) H_2O (c) CN^- (d) C_2H_5OH

(90) The concept that acid is proton donor and base is proton acceptor was given by

(a) Arrhenius **(b) Lowry-Bronsted** (c) Lewis (d) Faraday

(91) According to Lowry-Bronsted system, the chloride ion (Cl^-) in aqueous solution is a

(a) weak base (b) strong base (c) weak acid (d) strong acid

(92) According Lewis concept, acid is

(a) proton donor (b) electrons donor **(c) electrons acceptor** (d) proton acceptor

(93) The conjugate base of H_2SO_4 in the following reaction is

$H_2SO_4 + H_2O = H_3O^+ + HSO_4^-$

(a) H_2O (b) H_3O^+ **(c) HSO_4^-** (d) SO_4^{-2}

(94) 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 than that of NaI

(d) the temperature of the solution decreases.

(95) In the reaction : $I_2 + I^- \rightarrow I_3^-$, the Lewis base is
(a) I_2 **(b) I^-** (c) I_3^- (d) none of these

(96) BF3 is acid according to
(a) Lewis (b) Arrhenius (c) Lowry- Bronsted (d) Madam Curie

(97) Which of the following is not Lewis acid ?
(a) BF_3 (b) $AlCl_3$ (c) $FeCl_3$ **(d) PH_3**

(98) Which is the value of K_{sp} for $PbCl_2$?
(a) $[Pb^{+2}]\ [2Cl^-]^2$ (b) $[Pb^+]\ [2Cl^-]^2$
(c) $[Pb^{+2}]\ [Cl^-]^2$ (d) $[Pb^{+2}]\ /\ [Cl^-]^2$

(99) Which of the following is Lowry-Bronsted as well as Lewis base?
(a) NH_4^+ (b) NH_3 (c) BF_3 (d) CO_2

(100) Which concept classifies acids and bases on the basis of proton transfer ?
(a) Lewis (b) Arrhenius **(c) Lowry-Bronsted** (d) none of these

(101) For neutral solution, the value of pH is
(a) 1 (b) 14 **(c) 7** (d) 0

(102) …………. .is sparingly soluble salt.
(a) KCl **(b) AgCl** (c) NaCl (d) all of these

Q.2 Short questions: (2 marks each)

(1) The buffer solution can be diluted without change in H_3O^+ concentration. Explain
(2) Name the Lewis acids and bases in the following reactions.
(a) $BF_3 + F = BF_4^-$ (b) $Ag^+ + 2CN^- = Ag(CN^-)_2$
(3) What are acid-base indicators ? Explain the useful pH range of an indicator.
(4) The pH of an acidic solution is 2.7. Calculate OH^- concentration present in it.
(5) Explain : H^+ ion exists in the form of H_3O^+ in aqueous medium.
(6) AgCl is less soluble in silver nitrate than in pure water. Explain.
(7) “An anion of a salt of a weak acid hydrolysed more extensively.” Justify this statement,
(8) What is common-ion effect?
(9) Complete the following equations and give labels to conjugate acid-base pair.
(a) $CH_3COOH + H_2O =$
(b) $H_2SO_4 + H_2O =$
(10) Define solubility product with a suitable example.
(11) Explain. “The solubility of a sparingly soluble salt is less in the aqueous solution containing one of its common ion.”
(12) Explain. “A mixture of sodium acetate and acetic acid resists changes in its pH values on adding acid or base.”
(13) Give a brief account of acid-base indicator.
(14) Identify and name Lewis acids and bases in the following reactions giving their definitions.
(a) $AlCl_3 + Cl = AlCl_4^-$
(b) $RNH_2 + BF_3 = F_3B\text{-}NH_2R$

Q.3 Long questions:

1. Derive an equation for calculating H_3O^+ concentration in a buffer solution. Also explain that the pH of a buffer solution remains constant upon addition of small amount of strong acid or base in the solution.

2. What is hydrolysis? Derive an equation correlating K_h and K_w for a sodium acetate salt in water.
3. Giving suitable example, explain the use of selective precipitation.
4. Discuss the Arrhenius acid-base theory with its limitations.
5. Explain self-ionization of water. Prove that pH + pOH = 14 for any aqueous system at 25 °C.
6. Discuss the Lewis acid-base theory.
7. Write a note on selective precipitation with suitable example.
8. Define hydrolysis and derive the equation for the hydrolysis constant of a weak acid and a strong base.
9. What is an indicator? Discuss the role of indicator to determine the equivalent point in an acid-base titration.
10. A buffer solution was obtained by mixing 0.80 mole of acetic acid and 0.70 mole of sodium acetate. The buffer is diluted to one liter. Calculate the hydrogen ion concentration of the solution. What will be the change in hydrogen ion concentration when one ml of 1 M HCl is added to one liter of this buffer solution?
11. Deduce an equation for calculating H_3O^+ concentration in a buffer solution. Also explain that, pH of a buffer solution remains constant even upon dilution of the solution.
12. Discuss the Lowry- Bronsted theory to the acids and bases with suitable examples.
13. Write a note on buffer solutions.
14. Derive the equation for the hydrolysis for the following reaction:
    $NH_3 + H_2O = NH_4^+ + OH^-$
15. Explain the term acid-base indicator. Why do we observe colour change in acid-base titration? What is the useful pH range? Write equation showing relation of dissociation constant of indicator with H_3O^+ concentration.
16. What is buffer solution? How it can be prepared? Why there is no appreciable change in pH on addition of little amount of acid or base or dilution with water ?
17. How do the knowledge of K_{sp} be useful for selective precipitation? Explain giving suitable example.
18. Define acid and base according to Lowry- Bronsted theory. Identify Lowry-Bronsted acids and bases in the following reactions.
    (i) $H_2SO_4 + H_2O = HSO_4^- + H_3O^+$
    (ii) $H_2PO_4^- + H_2O = HPO_4^{-2} + H_3O^+$
    (iii) $HC_2O_4^- + PO_4^{-3} = HPO_4^{-2} + C_2O_4^{-2}$
    (iv) $HNO_3 + H_2O = H_3O^+ + NO_3^-$
19. Write a short note on Lowry-Bronsted concept. Give its limitations. Explain conjugate acid-base pair.
20. Calculate the H_3O^+ concentration which is to be controlled to separate 0.1 M Zn^{+2} from 0.1 M Fe^{+2} in the same solution using 0.1 M aqueous solution of H_2S. (K_{sp} values: ZnS = 4.5×10^{-24}, FeS = 1×10^{-19}, H_2S = 1.1×10^{-21})

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