(iii) *The expression to compute pH of sodium acetate solution at 25°C is :*

(A) $pH = 7 + \frac{1}{2} pK_b\ (CH_3COOH) - \frac{1}{2} log[salt]$

(B) $pH = 7 + \frac{1}{2} pK_a\ (CH_3COOH) - \frac{1}{2} log[salt]$

(C) $pH = 7 + \frac{1}{2} pK_b\ (CH_3COOH) + \frac{1}{2} log[salt]$

(D) $pH = 7 + \frac{1}{2} pK_a\ (CH_3COOH) + \frac{1}{2} log[salt]$

(iv) *The correct order of increasing* $[H_3O^+]$ *in the following aqueous solution is :*

(A) $0.01\ M\ H_2S < 0.01\ M\ H_2SO_4 < 0.01\ M\ NaCl < 0.01\ M\ NaNO_3$

(B) $0.01\ M\ NaCl = 0.01\ M\ NaNO_3 < 0.01\ M\ H_2S < 0.01\ M\ H_2SO_4$

(C) $0.01\ M\ H_2S < 0.01\ M\ NaNO_3 = 0.01\ M\ NaCl < 0.01\ M\ H_2SO_4$

(D) $0.01\ M\ H_2S < 0.01\ M\ NaNO_3 < 0.01\ M\ NaCl < 0.01\ M\ H_2SO_4$

(v) *pH of water is 7. When a substance Y is dissolved in water, the pH becomes 11. The substances Y is a salt of :*

(A) *weak acid and weak base* **(B)** *strong acid and strong base*

(C) *strong acid and weak base* **(D)** *weak acid and strong base*

SOLUBILITY PRODUCT (K_{sp}) AND PRECIPITATION OF SALTS Section - 5

Here, we will study those salts which are generally considered as insoluble in water. (e.g. AgCl, $BaSO_4$, Ag_2S, PbS etc) Actually no insoluble salt is actually completely insoluble, they have a very small solubility. Consider a vessel containing water with a sufficient amount of AgCl being put into it. A very small amount of it dissolves in water (*because generally salts are composed of ions or contain polarised atoms*). The small amount which is soluble is almost 100% ionised.

The situation achieved at this stage is *Dynamic* in nature; with some of ions (soluble) being solidifying and some solid always dissolving. Thus a state of equilibrium exists (like in earlier cases). This means at a given temperature, the concentration of Ag^+ ions and Cl^- ions in aqueous solution remains constant. The following equilibrium exists. In this equilibrium, the equilibrium state is known as *Saturated state*.

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^- \qquad [\text{insoluble} \rightleftharpoons \text{soluble (ions)}]$$

The equilibrium constant for this reaction is known as *solubility product* (K_{sp}) and is written as :

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

K_{sp} is expressed in concentration units. The reaction coefficient, Q in such system is known as ionic product (I.P)

Note :
- The solubility of a salt in water depends upon other substances (ions) present is water (at that time) and the solubility product is a constant value (at a given temperature) and is independent of presence of any other ion present. Like other equilibrium constants such as : K_p, K_c, K_a and K_b , it is also constant at a certain temperature and can change only when temperature changes.
- The salts like AgCl are regarded as sparingly soluble salts. Some of them are : Ag_2SO_4, Ag_2CO_3, $PbCl_2$, $PbCrO_4$, PbS, ZnS, $Al(OH)_3$, $Ca_3(PO_4)_2$, $BaSO_4$, $CaSO_4$, MnS etc.

K_{sp} for Ag_2SO_4 : $\quad Ag_2SO_4(s) + aq. \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$

$$K_{sp} = [Ag^+]^2[SO_4^{2-}]$$

K_{sp} for $Ca_3(PO_4)_2$: $\quad Ca_3(PO_4)_2(s) + aq. \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

Note : In the solubilities of sparingly soluble salts, we will deal with mainly two types of problems : one to find out the solubility in water if K_{sp} of a salt is given and vice-versa. Second, to find out solubility of a salt in presence of other (common) ions in water.

Illustration - 13 *If K_{sp} of calcium iodate $Ca(IO_3)_2 = 6.3 \times 10^{-7}$ at 18°C, find the solubility of salt in* (i) *gm/L* (ii) *mol/L in water at* 18°C.

SOLUTION :

In questions, solubility is sometime asked (or given) to be expressed in gm/L.

Now the following equilibrium is established :

$$Ca(IO_3)_2 \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$

Let x mole/L be solubility of $Ca(IO_3)_2$ in water

$\Rightarrow \quad [Ca^{2+}] = x\,M$ and $[IO_3^-] = 2x\,M$

Now, $\quad K_{sp} = [Ca^{2+}][IO_3^-]^2$

$\Rightarrow \quad 6.3 \times 10^{-7} = (x)(2x)^2$

$\Rightarrow \quad 4x^3 = 6.3 \times 10^{-7} \Rightarrow x = 5.4 \times 10^{-3}$ M.

Now answer is to expressed in gm/L

$\Rightarrow \quad \text{solubility} = x \times M_0$

$$= (5.4 \times 10^{-3}) \times 390 = 2.106 \text{ g/L}$$

Illustration - 14 *The K_{sp} of AgCl at 25°C is 1.5×10^{-10}. Find the solubility of AgCl (in gm/L) in an aqueous solution containing* 0.01 *M* $AgNO_3$.

SOLUTION :

Now this is quite similar to finding the degree of dissociation of a weak acid or weak base in presence of its common ion (Le Chatelier's principle).

Here 0.01 M $AgNO_3$ will give 0.01 M Ag^+ ions in solution before the addition of AgCl. ($AgNO_3$ is 100% soluble in water).

Let the solubility be c mol/L in $AgNO_3$.

$$\underset{}{AgCl} \rightleftharpoons \underset{c}{Ag^+} + \underset{c}{Cl^-}$$

$$AgNO_3 \longrightarrow \underset{0.01M}{Ag^+} + NO_3^-$$

In solution :

$[Ag^+] = c + 0.01$ and $[Cl^-] = c$

Now K_{sp} is a constant and is independent of presence of any ion in water.

$\Rightarrow \quad K_{sp} = [Ag^+][Cl^-] = (0.01 + c)(c) = 1.50 \times 10^{-10}$

(Now assuming $0.01 + c \sim 0.01$ as $c << 1$ for sparingly soluble salt)

$\Rightarrow \quad c = \dfrac{K_{sp}}{0.01} = 1.5 \times 10^{-8}$ M

[Check that $c + 0.01 \approx 0.01$ M]

or $\quad \text{solubility} = (1.5 \times 10^{-8}) \times 143.5$

$$= 2.15 \times 10^{-6} \text{g/L}$$

Note : The solubility of AgCl in water containing Ag^+ (a common ion) is much less than in pure water.

Illustration - 15 *The solubility of* $BaSO_4$ *in water is* 2.33×10^{-4} *gm/100 mL. Calculate the % age loss in weight when* 0.2 *gm of* $BaSO_4$ *is washed with* **(a)** 1 *L of water* **(b)** 1 *L of* 0.01 *N* H_2SO_4. $\left[M_{0\ BaSO_4} = 233\ gm/mol\right]$

SOLUTION :

(a) Solubility is in general expressed in gm/L, so solubility of $BaSO_4 = 2.33 \times 10^{-3}$ g/L

Loss in weight of $BaSO_4$ = amount of $BaSO_4$ soluble.

$$\Rightarrow \quad \%\ \text{loss} = \frac{2.33 \times 10^{-3}}{0.2} \times 100 = 1.16\ \%$$

(b) $0.01\ N\ H_2SO_4 \equiv 0.01\ N\ SO_4^{2-}$ ions

$\equiv 0.005\ M\ SO_4^{2-}$ ions

Now presence of SO_4^{2-} prior to washing $BaSO_4$ will suppress the solubility of $BaSO_4$ (*due to common ion effect*). The suppression will be governed by K_{sp} value of $BaSO_4$. So first calculate K_{sp} of $BaSO_4$.

Solubility of $BaSO_4$ in fresh water = 2.33×10^{-3} g/L

$$\equiv \frac{2.33 \times 10^{-3}}{233}\ \text{mol/L} = 10^{-5}\ \text{M}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = (10^{-5})^2 = 10^{-10}$$

Now let x be solubility in mol/L in H_2SO_4

$\Rightarrow \quad [Ba^{2+}]$ in solution $= x$ mol/L

and $\quad [SO_4^{2-}]$ in solution $= (x + 0.005)$ mol/L

Ionic product $= [Ba^{2+}][SO_4^{2-}] = (x)(x + 0.005)$

K_{sp} = Ionic Product at equilibrium (saturation)

$$\Rightarrow \quad 1.0 \times 10^{-10} = (x)(x + 0.005)$$

Assuming x to be a small number $x + 0.005 \sim 0.005$

$$\Rightarrow \quad x = \frac{10^{-10}}{0.005} = 2 \times 10^{-8}\ \text{mol/L}$$

$$= 2 \times 10^{-8} \times 233\ \text{g/L} = 4.66 \times 10^{-6}\ \text{g/L}$$

$\Rightarrow \quad 4.66 \times 10^{-6}$ gm of $BaSO_4$ are washed away.

$$\Rightarrow \quad \%\ \text{loss} = \frac{4.66 \times 10^{-6} \times 100}{0.2} = 2.33 \times 10^{-3}\%$$

Note : Third type of problems are related to the precipitation of salts (sparingly soluble). To understand and solve such problems, let us read following article carefully.

Precipitation of salts

Now we will study (application of K_{sp}) how to determine whether or not a precipitate will form when we mix known concentrations of ions which combine to give a sparingly soluble salt. To understand and solve such problems, let us analyse the expression of solubility product.

For a salt (sparingly soluble) when dissolved in water : $\quad BA \rightleftharpoons B^+(aq) + A^-(aq)$

At equilibrium (saturation) : $\quad K_{sp} = [B^+][A^-]$

When we mix ions or if there be two or more ions in water, we define reaction coefficient (Q) called as *ionic-product* (*I.P.*), giving the products of ions in water (ions of soluble salts and other common ions).

I.P. is product of ionic concentration due to ions already present in water or from a salt. It may be and may not be equal to K_{sp}. To illustrate it more clearly, consider a case when 500 ml of 0.005 M solution of $AgNO_3$ is added to 500 ml of 0.001 M solution of KCl. Now in solution (mixture), there are Ag^+, NO_3^-, K^+ and Cl^- ions. The concentration of $[Ag^+] = [NO_3^-] = 0.005/2 = 0.0025$ M (*equal volumes are mixed*)

and $\quad [K^+] = [Cl^-] = \dfrac{0.001}{2} = 0.0005$ M as equal volumes of two solutions are mixed.

Now, we know that Ag^+ will react with Cl^- ions to form AgCl since :

$AgCl \rightleftharpoons Ag^+ + Cl^-$ is a reversible reaction with a high tendency towards left (solidifying or precipitating).

Now, question is, whether AgCl will be formed or not (precipitation of Ag^+ and Cl^- as AgCl) and if it formed, how much of it will be formed ? For this we define some rules.

1. If Ionic Product (IP) > K_{sp} ; precipitation takes place till I.P. equals K_{sp}.
2. If Ionic Product < K_{sp} ; a precipitate will not be formed and the solution will be *unsaturated*.
3. If Ionic Product = K_{sp} ; a precipitate just begin to form and the solution is saturated in that salt.
   (*or we can say that solution is at a critical stage, when precipitation just begins, but actually has not occurred*)

In present case, $I.P. = [Ag^+][Cl^-] = (0.0025)(0.0005) = 1.25 \times 10^{-7}$

(Only for the salt which is sparingly soluble, not for KNO_3)

Ionic product > K_{sp} in this case (K_{sp} AgCl $= 1.56 \times 10^{-10}$) which mean precipitation takes place.

Illustration - 16 *When 15mL of 0.05 M $AgNO_3$ is mixed with 45.0 mL of 0.03 M K_2CrO_4, predict whether precipitation of Ag_2CrO_4 occurs or not ? K_{sp} of Ag_2CrO_4 = 1.9×10^{-12}.*

SOLUTION :

First find the concentrations of Ag^+ and CrO_4^{2-} ions in the resulting mixture.

$$[Ag^+] = \frac{15 \times 0.05}{15+45} = 1.25 \times 10^{-2}\,M$$

$$[CrO_4^{2-}] = \frac{45 \times 0.03}{15+45} = 2.25 \times 10^{-2}\,M$$

The ionic product for Ag_2CrO_4 is given as follows.

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

Ionic product (I.P.) $= [Ag^+]^2[CrO_4^{2-}]$

$= (1.25 \times 10^{-2})^2 (2.25 \times 10^{-2})$

$= 3.51 \times 10^{-6} > K_{sp}$

Hence precipitation occurs.

Illustration - 17 *The concentration of Ni^{2+} ions in a given NiS solution is 2.0×10^{-6} moles/L. Find the minimum S^{2-} ions necessary to cause precipitation of NiS. The solubility product, K_{sp} of NiS = 1.4×10^{-14}.*

SOLUTION :

Note : Solubility product, K_{sp} gives an idea of maximum possible concentration of an ion which can be retained in solution.

K_{sp} = ionic product (I.P.) for saturated solution

For NiS $\rightleftharpoons Ni^{2+} + S^{2-}$

Now, $K_{sp} = [Ni^{2+}][S^{2-}] \Rightarrow [S^{2-}] = \dfrac{K_{sp}}{[Ni^{2+}]}$

It is the maximum permissible concentration of S^{2-} ion in solution.

- For $[S^{2-}] = \dfrac{K_{sp}}{[Ni^{2+}]}$, NiS will just start to precipitate
- If $[S^{2-}] > \dfrac{K_{sp}}{[Ni^{2+}]}$, NiS will precipitate.

This means $\dfrac{K_{sp}}{[Ni^{2+}]}$ is minimum concentration of S^{2-} ion above which precipitation occurs.

$$\Rightarrow \quad [S^{2-}]_{min} = \frac{1.4 \times 10^{-14}}{2 \times 10^{-6}} = 7 \times 10^{-9}\,M$$

Illustration - 18 *A solution contains 0.01 M each of $CaCl_2$ and $SrCl_2$. A 0.005 M solution of SO_4^{2-} is slowly added to the given solution.*

(a) *Which substance begins to precipitate first ?*

(b) *If H_2SO_4 is continuously added, determine when will other salt be precipitated ?*

(c) *When second salt starts to precipitate, find the concentration of cation of first salt.*

Assume that $CaCl_2$ and $SrCl_2$ are 100% ionised and volume of the solution remains constant.

K_{sp} *of* $CaSO_4 = 1.3 \times 10^{-4}$ *and* K_{sp} *of* $SrSO_4 = 3.2 \times 10^{-7}$.

SOLUTION :

The solution contains 0.01 M Ca^{2+} ion and 0.01 M Sr^{2+} ions (100% ionization). Now SO_4^{2-} ions are added gradually and slowly……………..

(a) First calculate the minimum $[SO_4^{2-}]$ required to start precipitation of $CaSO_4$ and $SrSO_4$

$$\left[SO_4^{2-}\right]_{\text{Min. for } CaSO_4} = \frac{K_{sp}[CaSO_4]}{[Ca^{2+}]}$$

$$= \frac{1.3\times10^{-4}}{0.01} = 1.3\times10^{-2}\ M$$

$$\left[SO_4^{2-}\right]_{\text{Min. for } SrSO_4} = \frac{K_{sp}[SrSO_4]}{[Sr^{2+}]}$$

$$= \frac{3.2\times10^{-7}}{0.01} = 3.2\times10^{-5}\ M$$

Since $[SO_4^{2-}]$ for $SrSO_4$ is much lower that required for $CaSO_4$, so $SrSO_4$ will precipitate FIRST.

(b) Now, if SO_4^{2-} ions are continuously added, at some instant, its concentration will become equal to that minimum required for precipitating out Ca^{2+} ions.

Hence $CaSO_4$ will start precipitating if

$[SO_4^{2-}] = 1.3 \times 10^{-2}$ M.

(c) Now, find the concentration of Sr^{2+} ions when $[SO_4^{2-}] = 1.3 \times 10^{-2}$ M in the solution.

$$\left[Sr^{2+}\right] = \frac{K_{sp\ SrSO_4}}{[SO_4^{2-}]} = \frac{3.2\times10^{-7}}{1.3\times10^{-2}} = 2.46\times10^{-5}\ M$$

$$\left[2.46\times10^{-5} M <<< 0.01 M\right]$$

Can you observe that when $CaSO_4$ starts to precipitate, $SrSO_4$ is almost precipitated out as the value of Sr^{2+} is very very low ?

Note : The above illustration represents a case of selective precipitation (or separation of metals cations) by adding a common anion. Observe that there is a vast difference in the K_{sp} values of two sulphates, and hence in the minimum values of sulphate ion for precipitating out the two metals ions.

Illustration - 19 *How much the concentration of Ag^+ ions in a saturated solution of AgCl diminish if such an amount of HCl is added to it that the concentration of Cl^- ions in the solution becomes equal to 0.03 M ? Also find the amount of AgCl precipitated at the given concentration. K_{sp} of AgCl = 1.8×10^{-10}.*

SOLUTION :

HCl is added to a solution containing Ag^+ ions in saturated solution. First find the concentration of Ag^+ ion in this solution.

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$\Rightarrow$ $K_{sp} = [Ag^+][Cl^-] = x^2$ where x is solubility of AgCl in mol/L

$\Rightarrow$ $[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.8\times10^{-10}} = 1.34\times10^{-5}$M

When HCl is added, the ionic product of AgCl approaches the K_{sp} value of AgCl, the precipitation of Ag^+ ions will occur. As ionic product increases (i.e. becomes greater than K_{sp} value), an appreciable amount of AgCl precipitates out, and precipitation continues till ionic product (I.P.) equals solubility product (K_{sp}).

$$\text{I.P.} = [Ag^+][Cl^-] = K_{sp}$$

$$\Rightarrow \quad [Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8\times10^{-10}}{(0.03)} = 6.0\times10^{-9}\ M$$

Now this is the amount of Ag^+ ions left un-precipitated.

$\Rightarrow$ $[Ag^+]$ diminishes in the solution by

$$\frac{6.0\times10^{-9}}{1.34\times10^{-5}} = \left(\frac{1}{2233}\right)\text{times}$$

The concentration of AgCl precipitated out of the solution

$$= [Ag^+]_{initial} - [Ag^+]_{left}$$

$$= 1.34\times10^{-5} - 6.0\times10^{-8}\,M$$

It means almost whole of AgCl is precipitated out of the solution at $[Cl^-] = 0.03$ M.

Precipitation through H_2S

The most typical technique used in precipitating the metals ions or selectively precipitating (separation) the two metal ions, is passing H_2S gas in a solution of metal ion (s) whose acidity is externally controlled (or preset by adding HCl). First consider the ionisation (equilibrium) of H_2S gas in an aqueous solution and then in an acidic solution.

➤ Passing $H_2S(g)$ in an aqueous solution :

H_2S is a dibasic acid. We have to visualize two stage ionisation for it as follows:

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq)\ ; \quad K_1 \qquad \ldots(i)$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq)\ ; \quad K_2 \qquad \ldots(ii)$$

K_1 and K_2 are Ist and IInd ionisation constants respectively for H_2S (aq). Since $K_2 << K_1$ (due to common ion effect), we usually neglect the concentration of H^+ ions from second equilibrium.

$$\Rightarrow \quad [H^+]_{in\ Solution} = [H^+]_{from\ H_2S} + [H^+]_{from\ HS^-} \approx [H^+]_{from\ H_2S}$$

Now, $\quad K_1 = \dfrac{[H^+][HS^-]}{[H_2S]} \quad$ and $\quad K_2 = \dfrac{[H^+][S^{2-}]}{[HS^-]}$

From (i), $[H^+]=[HS^-]$ and neglecting $[H^+]$ from (ii), we have from second ionisation constant :

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} \approx [S^{2-}] \quad \text{or} \quad [S^{2-}] \approx K_2$$

So if we pass H_2S in an aqueous solution, sulphide ion concentration is simply equal to the value of second ionisation constant. We can determine whether precipitation of metal sulphide will occur or not by comparing ionic product (I.P.) with solubility constant (K_{sp}).

➤ Passing $H_2S(g)$ in an acidic solution :

Now if we pass H_2S in an acidic solution of a metal ion till saturation, we simply neglect the concentration of H^+ ion from H_2S (both from first and second ionisations) totally as the concentration of H^+ from acid (strong acid added externally) is very high. In that case we can simply add two equilibriums (i) and (ii) to get :

$$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)\ ;\ K_a\,(H_2S)$$

$$K_a = K_1 \times K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Note that in a saturated solution of H_2S at 25°C, $[H_2S]$ is constant at 0.1 M.

$$\Rightarrow \quad K_a \times (0.1\text{ M}) = [H^+]^2\,[S^{2-}]$$

$$([H^+]^2\,[S^{2-}] = K_{sp} \text{ of } H_2S)$$

$$\Rightarrow \quad [S^{2-}] = \frac{K_a \times (0.1\text{ M})}{[H^+]^2} = \frac{K_1 \times K_2 \times (0.1\text{ M})}{[H^+]^2}$$

In this way, we now know the concentration of sulphide ion in an acidic solution, so accordingly we can plan precipitation of metal ions. The important aspect of this method is that we can always increase or decrease the concentration of sulphide ion by controlling the amount of acid.

Illustration - 20 *Calculate the maximum possible concentration of Mn^{2+} in water that is saturated with H_2S (which is 0.1 M at 300K) and maintained at pH = 3 with HCl. The equilibrium constant(s) for dissociation of H_2S are :*

$$H_2S \rightleftharpoons H^+ + HS^-\ ; \qquad K_1 = 9 \times 10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-}; \qquad K_2 = 1 \times 10^{-12} \text{ and } K_{sp} \text{ of } MnS = 3 \times 10^{-22}.$$

SOLUTION :

Note that solution contains S^{2-} ions (from H_2S).

So Mn^{2+} will react with S^{2-} ions to give a precipitate of MnS (being sparingly soluble salt). Hence the concentration of S^{2-} at saturation will determine the maximum possible concentration of Mn^{2+} ions in solution that will not be precipitating. So first calculate $[S^{2-}]$ at saturation.

Calculate K_a for dissociation of H_2S.

$$K_a \text{ of } H_2S = K_1 \times K_2 = 9 \times 10^{-20}$$

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

$$\Rightarrow \quad K_a = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \quad \Rightarrow \quad [S^{2-}] = \frac{K_a\,[H_2S]}{[H^+]^2}$$

Note that pH of solution is maintained at 3 (externally).

$$\Rightarrow \quad [H^+] = 10^{-3}\text{ M}$$

$$\Rightarrow \quad [S^{2-}] = \frac{9 \times 10^{-20} \times 0.1}{(10^{-3})^2} = 9 \times 10^{-15}$$

In a saturated solution, ionic product = K_{sp}

Now ionic product = $[Mn^{2+}]\,[S^{2-}]$

$$= [Mn^{2+}]\,(9 \times 10^{-15})$$

$$\Rightarrow \quad [Mn^{2+}]\,(9 \times 10^{-15}) = 3 \times 10^{-22}$$

$$\Rightarrow \quad [Mn^{2+}] = 3.33 \times 10^{-8}\text{ M}$$

IN-CHAPTER EXERCISE - D

1. *The K_{sp} of AgCl at 25°C is 1.56×10^{-10}, find the solubility of salt in gm/L when it is dissolved in water.*

2. *If solubility of calcium iodate $Ca(IO_3)_2$ in water at 18°C is 2.1 gm/L, calculate the value of K_{sp}. Given : $M_{Ca(IO_3)_2} = 390$*

3. *Find the solubility of $Ca(IO_3)_2$ (in mol/L) in a solution containing 0.1 M $Ca(NO_3)_2$ at 18°C. $K_{sp}\,(Ca(IO_3)_2] = 6.3 \times 10^{-7}$ at 18°C.*

4. *The solubility product of $BaSO_4$ is 1.5×10^{-9}. Find the solubility of $BaSO_4$ in*

(i) *pure water* **(ii)** 0.1*M $BaCl_2$*

5. *A solution contains* 2.3×10^{-3} *M* $AgNO_3$. *What concentration of NaCl will be required to initiate the precipitation of AgCl. The solubility product of AgCl is* 2.8×10^{-10} ?

6. *The concentration of* Ag^+ *ions in a saturated solution of* $Ag_2C_2O_4$ *is* 2.2×10^{-4} *M. Calculate the solubility of* $Ag_2C_2O_4$ *in a solution which is* 0.1 *M in* $Na_2C_2O_4$.

7. *The solubility product of lead bromide is* 4×10^{-6}. *Find the solubility of the salt.*

8. *Should precipitation occur when* 50 *mL of* 5.0×10^{-4} *M* $Ca(NO_3)_2$ *is mixed with* 50 *mL of* 2.0×10^{-4} *M NaF ? The* K_{sp} *of* CaF_2 *is* 1.7×10^{-10}. *Assume that the volumes are additive.*

9. *A solution contains* Zn^{2+} *ions and* Cu^{2+} *ions each at* 0.02 *M. The* K_{sp} *of ZnS is* 1×10^{-22} *and that of CuS is* 8×10^{-37}. *If the solution is made* 1 *M in* H^+ *ions and* H_2S *is passed until the solution is saturated, should a precipitate be form? In saturated solution,* $K_{a(H_2S)} = 10^{-21}$. *Concentration of* H_2S *in a saturated solution* = 0.1 *M.*

10. *A* 500 *mL hard water containing* 0.005 *moles of* Ca^{2+} *ions is treated with two* H_2SO_4 *samples each* 500 *mL separately, one containing* 0.001 *mole and other* 0.02 *mole per litre. Which one or both or none can be used to precipitate out calcium ions ? The* K_{sp} *of* $CaSO_4$ *is* 2.4×10^{-4}.

11. **Choose the correct alternative. Only one choice is correct.**

(i) *The solubility of* A_2X_3 *is y mole* dm^{-3}. *Its solubility product is :*

(A) $6y^4$ **(B)** $64\,y^4$ **(C)** $36\,y^5$ **(D)** $108\,y^5$

(ii) *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) $10^{-5}\,M\,Ca^{2+} + 10^{-3}\,M\,F^-$ **(D)** $10^{-3}\,M\,Ca^{2+} + 10^{-5}\,M\,F^-$

(iii) *If* s_0, s_1, s_2, *and* s_3 *are the solubilities of AgCl in water,* 0.01 *M* $CaCl_2$, 0.01 *M NaCl and* 0.05 *M* $AgNO_3$ *solutions respectively, then :*

(A) $s_0 > s_1 > s_2 > s_3$ **(B)** $s_0 > s_2 > s_1 > s_3$ **(C)** $s_0 > s_2 > s_3 > s_1$ **(D)** $s_0 > s_1 = s_2 > s_3$

(iv) *The pH of Mg* $(OH)_2$ *is* 10.5 *at* 25°C. *The solubility product of magnesium hydroxide would be :*

(A) $2.24 \times 10^{-11}\,M^3$ **(B)** $3.36 \times 10^{-11}\,M^3$ **(C)** $1.58 \times 10^{-11}\,M^3$ **(D)** $5.60\ 10^{-12}\,M^3$

(v) *A solution is saturated with respect to* $SrCO_3$ *and* SrF_2. *The* $[CO_3^{2}]$ *was found to be* 1.2×10^{-3} *M. The concentration of* F^- *in the solution would be :*

(A) $1.3 \times 10^{-3}\,M$ **(B)** $2.6 \times 10^{-2}\,M$ **(C)** $3.7 \times 10^{-2}\,M$ **(D)** $5.8 \times 10^{-7}\,M$

(*Given :* $K_{sp}\,(SrCO_3) = 7.0 \times 10^{-10}\,M^2$, $K_{sp}\,(SrF_2) = 7.9 \times 10^{-10}\,M^3$).

(vi) *The number of* S^{2-} *ions present in* 1 *L of* 0.1 *M* H_2S $[K_{a\,H_2S} = 10^{-21}]$ *solution having* $[H^+] = 0.1$ *M is :*

(A) 6.023×10^3 **(B)** 6.023×10^4 **(C)** 6.023×10^5 **(D)** 6.023×10^6

(vii) *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*

(viii) *Which one of the following is true for any diprotic acid,* H_2X ?

(A) $K_{a_2} > K_{a_1}$ **(B)** $K_{a_1} > K_{a_2}$ **(C)** $K_{a_2} = \frac{1}{K_{a_1}}$ **(D)** $K_{a_2} = K_{a_1}$

(ix) K_{sp} *of* $Mg(OH)_2$ *is* 1×10^{-12}. 0.01 *M* $MgCl_2$ *will be precipitating at the limiting pH* :

(A) 8 **(B)** 9 **(C)** 10 **(D)** 12

(x) *The solubility products of MA, MB, MC and MD are* 1.8×10^{-10}, 4×10^{-3}, 4×10^{-8} *and* 6×10^{-5} *respectively. If a* 0.01 *M solution of MX is added dropwise to a mixture containing* A^-, B^-, C^- *and* D^- *ions then the one to be precipitated first will be*:

(A) *MA* **(B)** *MB* **(C)** *MC* **(D)** *MD*

(xi) *For a sparingly soluble salt* $A_p B_q$, *the relationship of its solubility product* (L_S) *with its solubility* (S) *is* :

(A) $L_S = S^{p+q} \cdot p^p \cdot q^q$ **(B)** $L_S = S^{p+q} \cdot p^q \cdot q^p$

(C) $L_S = S^{pq} \cdot p^p \cdot q^q$ **(D)** $L_S = S^{pq} \; (pq)^{p+q}$

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

(A) 10^{-4} *M* (Ag^+) *and* 10^{-4} *M* (Cl^-) **(B)** 10^{-5} *M* (Ag^+) *and* 10^{-5} *M* (Cl^-)

(C) 10^{-6} *M* (Ag^+) *and* 10^{-6} *M* (Cl^-) **(D)** 10^{-10} *M* (Ag^+) *and* 10^{-10} *M* (Cl^-)

ACID BASE TITRATIONS Section - 6

pH of Mixtures of Acids and Bases

Let us take *x* millimoles of acid (HA) and *y* millimoles of base (BOH). Note that acid is monobasic and base is monoacidic.

(a) Strong acid and strong base

- If $x = y$, then complete neutralization takes place and we get x (= y). Millimoles of salt (BA) of strong acid and strong base which means no hydrolysis takes place and pH of solution = 7.
- If $x > y$, then there is an excess of strong acid and resulting solution is acidic with millimoles of acid left in excess $= x - y$. Now if V (in cc) be the volume of mixture, then :

$$\Rightarrow \quad \text{M} = \frac{x-y}{\text{V}}$$. Now calculate pH using the equation $\text{pH} = -\log_{10} [\text{H}^+]$

- If $x < y$, then there is an excess of strong base and resulting solution is basic with millimoles of base left in excess $= y - x$. Now if V (in cc) be the volume of mixture, then :

$$\Rightarrow \quad \text{M} = \frac{y-x}{\text{V}}$$. Now calculate pH using the equation $\text{pH} = 14 - \log_{10} [\text{OH}^-]$