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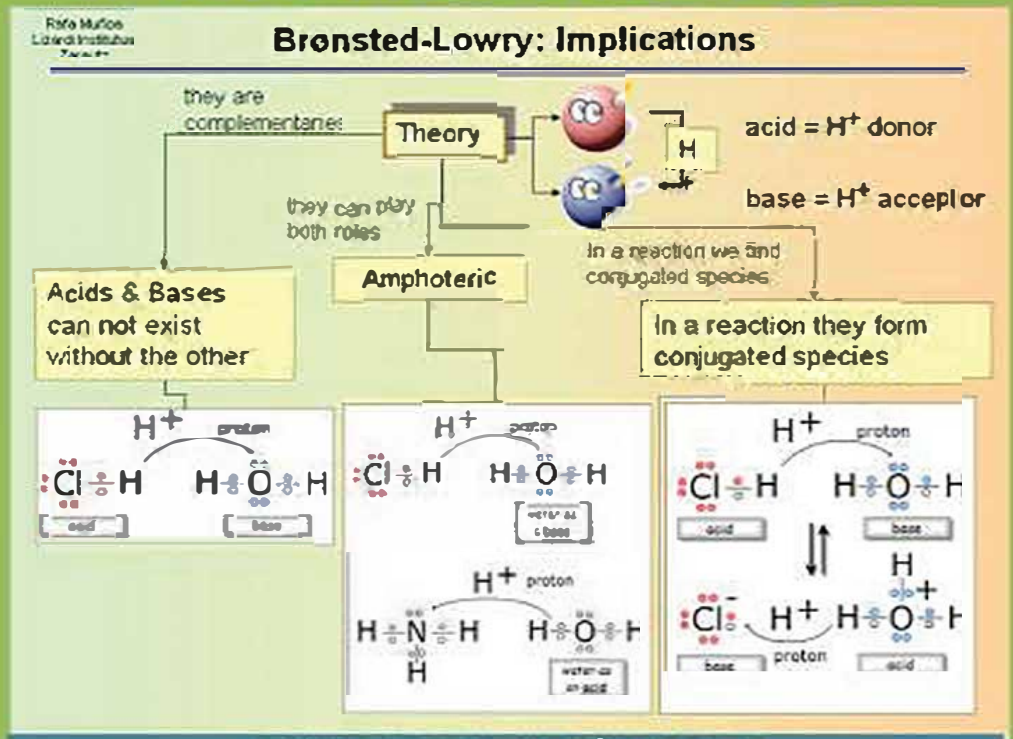
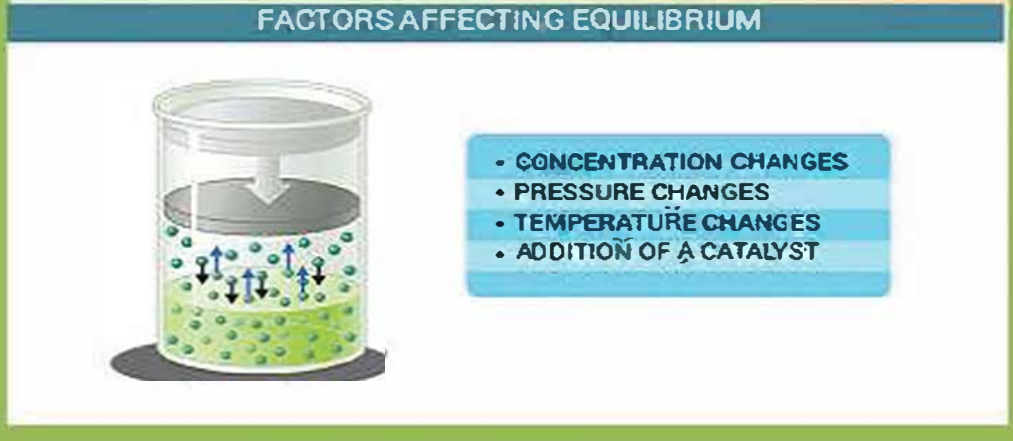
PHYSICAL CHEMISTRY

Unit-8

IONIC EQUILIBRIUM





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IONIC EQUILIBRIUM

1. What are Lewis acids and bases? Give two example for each.

i) Lewis acid is a species that accepts an electron pair and it is a positive ion (or) an electron deficient molecule

example :Electron deficient molecules BF_3 ,$AlCl_3$.etc

All metal ions (or) atoms : Fe^{2+} , Cr^{3+}, Cu^{2+} and Carbonium ion

ii) Lewis base is a species that donates an electron pair and it is a anion (or) neutral molecule with at least one lone pair of electrons.

example :more lone pairs of electrons: NH_3, H_2O, R-O-H, R-O-R, R-NH_2

All anions : F^- , Cl^-, CN^- and Carbanion ..

2. Discuss the Lowry – Bronsted concept of acids and bases.

According to their concept,

An Acid is defined as a substance that has a tendency to donate a proton to another substance

Base is a substance that has a tendency to accept a proton from other substance.

In other words, an acid is a proton donor and a base is a proton acceptor.

In general, Lowry – Bronsted (acid – base) reaction is represented as

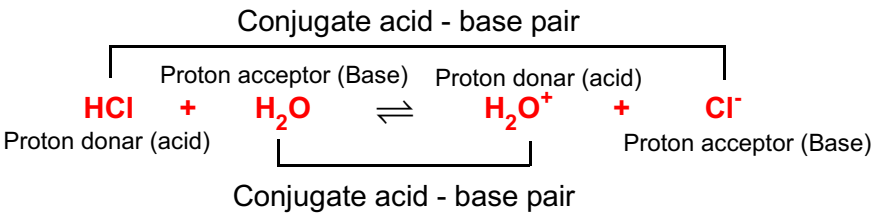
$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

$Acid_1 \longrightarrow$ conjugate acid - (Proton donar)

$Base_2 \longrightarrow$ conjugate base - (Proton acceptor)

$Acid_2 \longrightarrow$ conjugate acid - (Proton donar)

$Base_1 \longrightarrow$ conjugate base - (Proton acceptor)



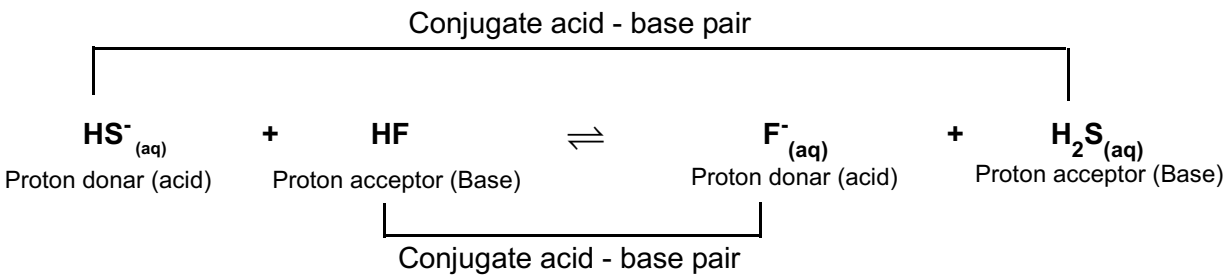
3. Indentify the conjugate acid base pair for the following reaction in aqueous solution

i) $HS^-(aq) + HF \rightleftharpoons F^-(aq) + H_2S(aq)$

ii) $HPO_4^-(aq) + SO_3^{2-} \rightleftharpoons PO_4^{3-}(aq) + HSO_3^-(aq)$

Iii) $NH_4^+(aq) + CO_3^{2-} \rightleftharpoons NH_3^{3-}(aq) + HCO_3^-(aq)$

i)



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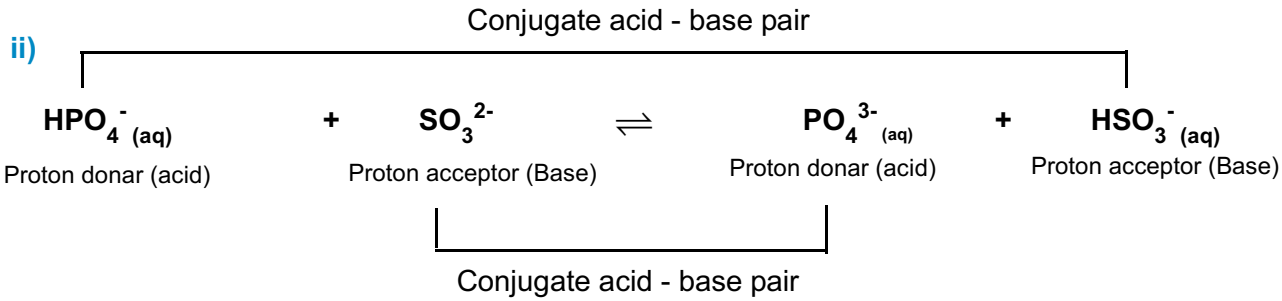

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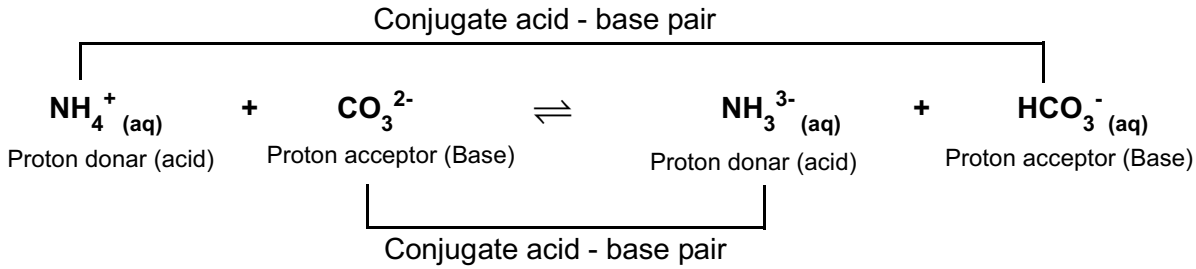

4. **Account for the acidic nature of $HClO_4$. In terms of Bronsted – Lowry theory, identify its conjugate base.**

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

When an acid dissociates in water into H_3O^+ ions and the anion of the acid, the anion (ClO_4^-) is termed the conjugate base of that acid.

In this case, the acid is perchloric acid and its conjugate base is the perchlorate ion (ClO_4^-)

5. **When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]^{2+} + 4NH_3$ (aq) $\rightleftharpoons [Cu(NH_3)_4]^{2+}$,among H_2O and NH_3 which is stronger Lewis base**

H_2O has two nonbonding electron pairs and is, therefore, a stronger Lewis base than NH_3 which only has one.

H_2O is a stronger Lewis base because the extra hydrogen in NH_3 shields the lone pair of the central nitrogen atom.

H_2O should be a stronger Lewis base because oxygen is more electronegative than nitrogen.

6. The concentration of hydroxide ion in a water sample is found to be 2.5×10^{-6}M. Identify the nature of the solution

$$[OH^-] = 2.5 \times 10^{-6} M$$

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

$$pOH = - \log [\ 2.5 \times 10^{-6}\ ]$$

$$pOH = - [\ \log 2.5 - 6 \log 10]$$

$$pOH = - 0.3979 - (- 6 \times 1)$$

$$pOH = - 0.3979 + 6 \times 1$$

$$pOH = 5.6021$$

$pOH + pH = 14$ $\qquad$ $pH = 14 - 5.6021 = 8.3979$

pH = 8.3979 pH > 7 , The nature of the solution is basic

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas 25°C to get a solution with [H_3O^+] = 4x10^{-5}M . Is the solution neutral (or) acidic (or) basic.

$$[H_3O^+] = 4x10^{-5}M$$

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

$$pH = - \log[4x10^{-5}]$$

$$pH = - [\log 4 - 5 \log 10]$$

$$pH = - \log 4 + 5 \log 10$$

$$pH = - 0.6020 + 5 \times 1 = 4.398$$

pH = 4.398 , pH < 7 , The solution is acidic nature

8. Calculate the pH of 0.04 M HNO_3 Solution.

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

$$pH = -\log [0.04]$$

$$pH = -\log [4 \times 10^{-2}]$$

$$pH = - [\log 4 - 2 \log 10]$$

$$pH = - \log 4 + 2 \log 10$$

$$pH = - 0.6020 + 2 \times 1$$

$$pH = 1.398 \simeq 1.40$$

9. Define solubility product

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

10. Define ionic product of water. Give its value at room temperature.

The product of concentrations of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water.

Therefore, the ionic product of water at 25°C is

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

$$K_w = (1x10^{-7})(1x10^{-7})$$

$$K_w = 1 \times 10^{-14} \ mol^2dm^{-6} \text{ at } 298 \ K$$

11. Explain common ion effect with an example

The dissociation of a weak acid is suppressed in the presence of a salt containing an ion common to the weak electrolyte. It is called the common ion effect.

For example,

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

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

the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the **common ion,CH_3COO^-.**

12. Derive an expression for Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c).

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

The dissociation of acetic acid can be represented as

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

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation	α		
Number of moles at equilibrium	$1-\alpha$	α	α
Equilibrium concentration	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} \quad , (1-\alpha \simeq 1)$$

$$K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$[H+] = C\alpha$ $\qquad$ $[H+] = C\sqrt{\frac{K_a}{C}}$ $\qquad$ for weak acid is $[H+] = \sqrt{K_a.C}$

13. Define pH

pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$\mathbf{pH = -\log [H_3O^+]}$$

14. Calculate the pH of 1.5×10^{-3}M solution of $Ba(OH)_2$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$$

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

$pOH = -\log [2 \times 1.5\times10^{-3}]$

$pOH = -\log [3 \times 10^{-3}]$

$pOH = -[\log 3 - 3\log 10]$

$pOH = -\log 3 + 3\log 10$

$pOH = -\log 3 + 3 \times 1$

$pOH = -0.4771 + 3 = 2.53$ $\qquad$ $\therefore$ **pH = 14 - 2.53 = 11.47**

15. 50ml of 0.05M HNO_3 is added to 50ml of 0.025 M KOH.Calculate the pH of the resultant solution.

Mole = Concentration x Volume

mole of KOH = 50 ml x 0.025 = 1.25

mole of HNO_3 = 50 ml x 0.05M = 2.5

Total volume of solution (50+50 ml = 100 ml)

1.25 mole of KOH exactly neutralized by 1.25 mole of HNO_3

$$KOH + HNO_3 \longrightarrow KNO_3 + H_2O$$

that is 2.5 -1.25 = 1.25 HNO_3mole

$$\text{Conc of } H^+ = \frac{\text{no of mole of } H^+}{\text{total volume of solution } (50 + 50 \text{ ml} = 100 \text{ ml})}$$

$$\text{Conc of } [H^+] = \frac{1.25}{100} = 0.0125$$

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

$pH = - \log [0.0125]$

$pH = - \log [1.25 \times 10^{-2}]$

$pH = - [\log 1.25 - 2 \log 10]$

$pH = - \log 1.25 + 2 \log 10$

$pH = - 0.0969 + 2 \times 1$

pH = 1.9031

16. The K_a value for HCN is 10^{-9} .What is the pH of 0.4M HCN solution?

$K_a = 10^{-9}$ C= 0.4 M

$[H^+] = \sqrt{K_a.C}$

$[H^+] = \sqrt{10^{-9} \times 0.4}$

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

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

$pH = - \log [2 \times 10^{-5}]$

$pH = - [\log 2 - 5 \log 10]$

$pH = - \log 2 + 5 \log 10$

$pH = - 0.3010 + 5 \times 1$

pH = 4.699

17. **Calculate the extent of hydrolysis and the pH of 0.1M ammonium acetate Given that $K_a = K_b = 1.8 \times 10^{-5}$**

For hydrolysis of salt of weak acid and weak base,

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

$$K_h = \frac{\alpha^2}{(1-\alpha)^2}$$

$$K_h = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

$$\frac{\alpha^2}{(1-\alpha)^2} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}$$

$$\frac{\alpha}{(1-\alpha)} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}} = \sqrt{\frac{1 \times 10^{-4}}{3.24}} = \frac{1 \times 10^{-2}}{1.8} = 0.55 \times 10^{-2}$$

hydrolysis = 0.55×10^{-2}

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

$$\frac{1}{2}pK_w = -\frac{1}{2}\log(1 \times 10^{-14}) = 7$$

$$\frac{1}{2}pK_a = -\frac{1}{2}\log K_a = -\frac{1}{2}\log(1.8 \times 10^{-5}) = \frac{1}{2}4.7447 = 2.3723$$

$$\frac{1}{2}pK_b = -\frac{1}{2}\log K_b = -\frac{1}{2}\log(1.8 \times 10^{-5}) = \frac{1}{2}4.7447 = 2.3723$$

pH = 7 + 2.3723 – 2.3723 = 7 + 0

pH = 7

18. **Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base.**

Weak base - NH_4OH and strong acid - HCl

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

Hydrolysis constant : Applying the Law of Mass Action

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+][H_2O]}$$

Since $[H_2O]$ is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \text{---------- 1}$$

Relation between K_h, K_w and K_b. We know that the ionic product of water K_w is expressed as :

$$K_w = [H^+][OH^-] \quad \text{----------2}$$

For the dissociation of a weak base, NH_4OH

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

The dissociation constant, K_b, can be expressed as

$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_4OH]} \quad \text{---------- 3}$$

Dividing (2) by (3)

$$\frac{K_w}{K_b} = [H^+][OH^-] \times \frac{[NH_4OH]}{[NH_4^+]\ [OH^-]} = \frac{[NH_4OH][H^+]}{[NH_4^+]} = K_h$$

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

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the K_h and K_b as

$$K_h . K_b = K_w$$

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration of salt

$K_h = h^2C$ and

$$[H^+] = \sqrt{K_h.C}$$

$$[H^+] = \sqrt{\frac{K_w}{K_b}.C}$$

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

$$pH = - \log \sqrt{\frac{K_w}{K_b}.C} \quad \text{(or)} \quad pH = - \log \left(\frac{K_w}{K_b}.C\right)^{\frac{1}{2}}$$

$$pH = - \frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}\log K_b$$

$$pH = 7 + \frac{1}{2} pK_b - \frac{1}{2}\log C \quad \text{(or)} \quad pH = 7 + \frac{1}{2} pK_b = \frac{1}{2}\log C$$

In this case it is evident that pH will always be less than 7. Thus, **the solution of a salt of weak base and strong acid will always be acidic.**

19. Solubility product of Ag_2CrO_4 is 1 x10^{-12}. What is the solubility of Ag_2CrO_4 in 0.01M $AgNO_3$ solution?

$K_{sp} = 1\ x10^{-12}$

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

$AgNO_3\ (s) \rightleftharpoons 2Ag^+ + NO_3^-$

0.01 M 0.01 M 0.01 M

$[Ag^+] = 2s + 0.01$

$\because 0.01 >> 2s$

$\therefore [Ag^+] = 0.01\ M$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$K_{sp} = (s)^2(s)$

$1\ x10^{-12} = (0.01)^2\ (s)$

$$[CrO_4^{2-}] = (s) = \frac{1\ x10^{-12}}{(10^{-2})^2} = 1\ x10^{-8}$$

20. Write the expression for the solubility product of $Ca_3(PO_4)_2$

$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2\ PO_4^{3-}$

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

$K_{sp} = (3s)^3.(2s)^2$

$K_{sp} = (27s^3).(4s^2)$

$K_{sp} = 108s^5$.

21. A saturated solution, prepared by dissolving $CaF_{2(s)}$ in water, has $[Ca^{2+}]= 3.3 \times 10^{-4}$ What is the K_{sp} of CaF_2?

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

(breaks into 2 F^- ions not F_2)

$[F^-]$ is double the $[Ca^{2+}]$

$[2\ F^-] = 2[Ca^{2+}] = 2 \times 3.3 \times 10^{-4}$

$[2\ F^-] = 6.6 \times 10^{-4}$ M

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

$K_{sp} = 3.3 \times 10^{-4} . (6.6 \times 10^{-4})^2$

$K_{sp} = 1.44 \times 10^{-10}$.

22. K_{sp} of AgCl is 1.8×10^{-10}.Calculate molar solubility in 1 M $AgNO_3$.

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

x = solubility of AgCl in 1M $AgNO_3$.

$AgNO_{3\ (aq)} \rightleftharpoons Ag^+{}_{(aq)} + NO_3^-{}_{(aq)}$

1 M 1 M

$[Ag^+] = x + 1\ M \simeq 1M \quad (\because x << 1)$

$[Cl^-] = x$

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

$1.8 \times 10^{-10} = (1)\ (x)$

$x = 1.8 \times 10^{-10} M$

23. A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+] = 5 \times 10^{-5}$ and $[\ CrO_4^{2-}] = 4.4 \times 10^{-4}$ What is the value of K_{sp} for Ag_2CrO_4 ?

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

$K_{sp} = [\ Ag^+]^2[\ CrO_4^{2-}]$

$K_{sp} = (5 \times 10^{-5})^2\ (\ 4.4 \times 10^{-4}\ )$

$K_{sp} = (\ 25 \times 10^{-10}\ )\ (4.4 \times 10^{-4})$

$K_{sp} = (25 \times 4.4) \times 10^{-10} \times 10^{-4}$

$K_{sp} = 110 \times 10^{-14}$

$K_{sp} = 1.10 \times 10^{-12}$

24. Write the expression for the solubility product of Hg_2Cl_2.

$$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$$

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2$$

$$K_{sp} = [s].[2s]^2$$

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

25. K_{sp} of Ag_2CrO_4 is 1.1 x 10^{-12} . What is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$$Ag_2CrO_4\,(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$x \qquad 2x \qquad x$$

x is the solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.

$$K_2CrO_4\,(s) \rightleftharpoons 2K^+ + CrO_4^{2-}$$

$$0.1\,M \qquad 0.1\,M \qquad 0.1\,M$$

$$[Ag^+] = 2x$$

$$[CrO_4^{2-}] = (x + 0.1) \simeq 0.1 \quad (\because x << 0.1)$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$1.1 \times 10^{-12} = (2x)^2 (0.1)$$

$$1.1 \times 10^{-12} = 0.4x^2$$

$$x^2 = \frac{1.1 \times 10^{-12}}{0.4} \qquad x = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}}$$

$$x = \sqrt{2.75 \times 10^{-12}} \qquad \mathbf{x = 1.658 \times 10^{-6} M}$$

26. Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100L of 0.2 M NaCl are mixed? $K_{sp}(PbCl_2) = 1.2 \times 10^{-5}$.

Precipitation reaction : $Pb(NO_3)_{2(aq)} + 2NaCl_{(aq)} \text{ ----------> } PbCl_{2(s)} + 2NaNO_{3(aq)}$

Solubility reaction : $PbCl_2(s) \text{ -----> } Pb^{2+} + 2Cl^-$

K_{sp} is given and in order to find out if a precipitate form we need to find out Q **$Q = [Pb^{2+}][Cl^-]^2$**

1:1 mole ratios so initial $[Pb^{2+}] = [Pb(NO_3)_2] = 0.1$ M ; initial $[Cl^-] = [NaCl] = 0.2$ M

After we combine the solution the total volume becomes .250 L ,

so the concentration of Pb^{2+} and Cl^- ions is :

Number of moles Pb^{2+}= molarity x Volume of the solution in lit= 0.1 × 0.150 L

$$[Pb^{2+}] = \frac{0.1\ M\ Pb^{2+} \times 0.150 L}{0.250\ L} = 0.06\ M\ Pb^{2+}$$

$$[Cl^-] = \frac{0.2\ M\ Cl^- \times 0.100 L}{0.250\ L} = 0.08\ M\ Cl^-$$

$Q = [Pb^{2+}].[Cl^-]^2$ $\qquad Q = (0.060)(0.080)^2 = 3.8 \times 10^{-4}$

$Q > K_{sp}$, [$3.8 \times 10^{-4} < 1.2 \times 10^{-5}$] so $PbCl_2$ does precipitate.Eq shifts to the left .

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27. K_{sp} of $Al(OH)_3$ is $1x10^{-15}M$. At what pH does $1.0x10^{-3}M$ Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

1) Write the dissociation equation: $Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$

2) Write the Ksp expression: $K_{sp} = [Al^{3+}][OH^-]^3$

3. Plug into the K_{sp} expression: $1x10^{-15}M = (1.0x10^{-3}M)\ [OH^-]^3$

4) Solve for s, which is the $[OH^-]$:

$$[OH^-]^3 = \frac{K_{sp}}{[Al^{3+}]}$$

$$[OH^-] = \sqrt[3]{\frac{K_{sp}}{[Al^{3+}]}}$$

$$[OH^-] = \sqrt[3]{\frac{1x10^{-15}}{1x10^{-3}}}$$

$$[OH^-] = \sqrt[3]{1x10^{-12}}$$

$$[OH^-] = \left(1x10^{-12}\right)^{\frac{1}{3}}$$

$[OH^-] = 1 \times 10^{-4}$

5) Calculate the pH:

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

$pOH = -\log(1x10^{-4}) = 4$

pH = 14 - pOH = 14 - 4 = 10

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