



# PHYSICAL CHEMISTRY

## Unit-8

### IONIC EQUILIBRIUM

**Brønsted-Lowry: Implications**

they are complementary: Theory

they can play both roles

acid =  $H^+$  donor

base =  $H^+$  acceptor

In a reaction we find conjugated species

In a reaction they form conjugated species

Acids & Bases can not exist without the other

Amphoteric

**Diagram illustrating Brønsted-Lowry acid-base reactions:**

Reaction 1:  $Cl-H + H_2O \rightleftharpoons Cl^- + H_3O^+$

Reaction 2:  $Cl-H + NH_3 \rightleftharpoons Cl^- + NH_4^+$

Reaction 3:  $Cl-H + H_2O \rightleftharpoons Cl^- + H_3O^+$

Reaction 4:  $Cl^- + H_3O^+ \rightleftharpoons Cl-H + H_2O$

Reaction 5:  $Cl^- + NH_4^+ \rightleftharpoons Cl-H + NH_3$

Reaction 6:  $Cl^- + H_3O^+ \rightleftharpoons Cl-H + H_2O$

Reaction 7:  $Cl^- + NH_4^+ \rightleftharpoons Cl-H + NH_3$

**FACTORS AFFECTING EQUILIBRIUM**

- CONCENTRATION CHANGES
- PRESSURE CHANGES
- TEMPERATURE CHANGES
- ADDITION OF A CATALYST

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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  $\text{BF}_3$ ,  $\text{AlCl}_3$  etc

All metal ions (or) atoms :  $\text{Fe}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$  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:  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{R-O-H}$ ,  $\text{R-O-R}$ ,  $\text{R-NH}_2$

All anions :  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CN}^-$  and Carbanion ..

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

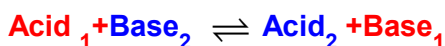
According to their concept,

**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

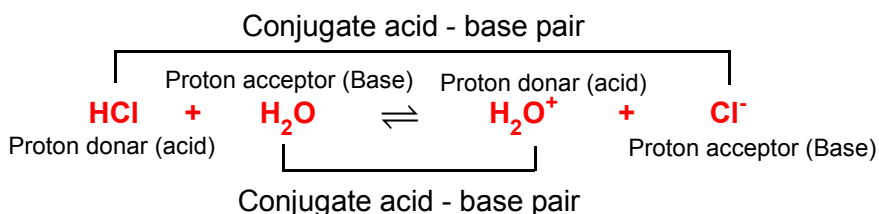


$\text{Acid}_1 \longrightarrow$  conjugate acid - (Proton donar )

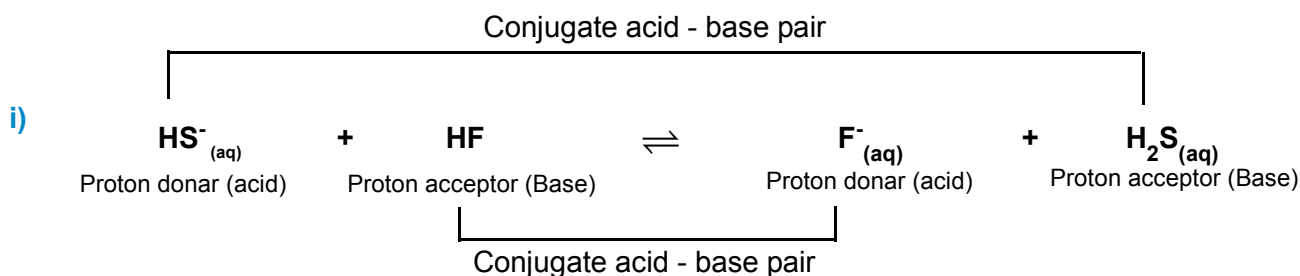
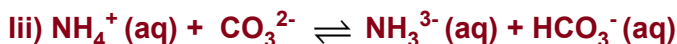
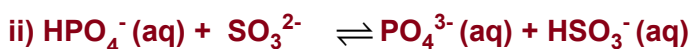
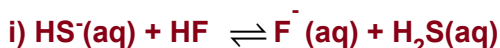
$\text{Base}_2 \longrightarrow$  conjugate base - (Proton acceptor )

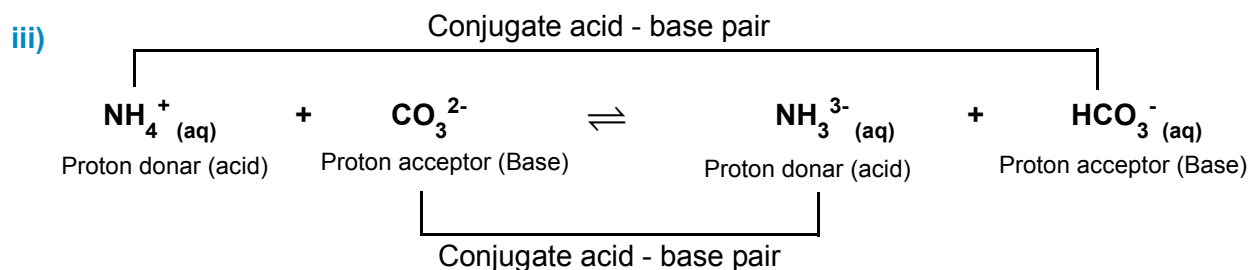
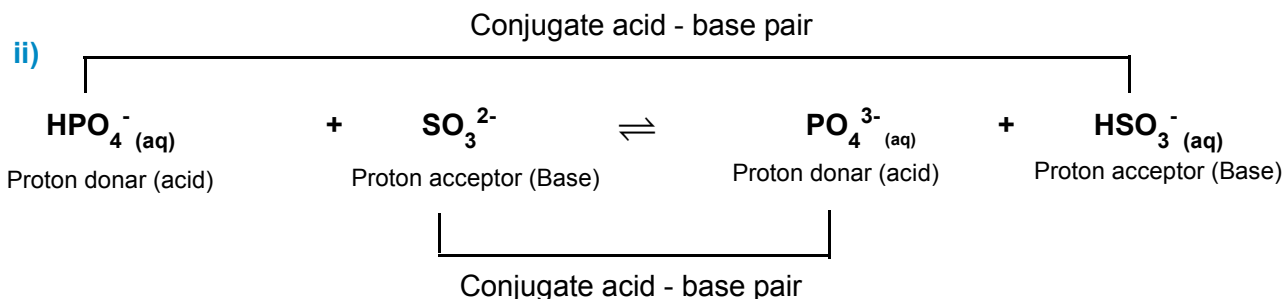
$\text{Acid}_2 \longrightarrow$  conjugate acid - (Proton donar )

$\text{Base}_1 \longrightarrow$  conjugate base - (Proton acceptor )

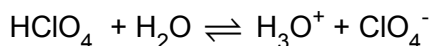


### 3. Identify the conjugate acid base pair for the following reaction in aqueous solution





4. **Account for the acidic nature of  $\text{HClO}_4$ . In terms of Bronsted – Lowry theory, identify its conjugate base.**



When an acid dissociates in water into  $\text{H}_3\text{O}^+$  ions and the anion of the acid, the anion ( $\text{ClO}_4^-$ ) is termed the conjugate base of that acid.

**In this case, the acid is perchloric acid and its conjugate base is the perchlorate ion ( $\text{ClO}_4^-$ )**

5. **When aqueous ammonia is added to  $\text{CuSO}_4$  solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex,  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+} + 4\text{NH}_3 \text{ (aq)} \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$ , among  $\text{H}_2\text{O}$  and  $\text{NH}_3$  which is stronger Lewis base**

$\text{H}_2\text{O}$  has two nonbonding electron pairs and is, therefore, a stronger Lewis base than  $\text{NH}_3$  which only has one.

$\text{H}_2\text{O}$  is a stronger Lewis base because the extra hydrogen in  $\text{NH}_3$  shields the lone pair of the central nitrogen atom.

$\text{H}_2\text{O}$  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  $2.5 \times 10^{-6} \text{ M}$ . Identify the nature of the solution**

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

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

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

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

$$\text{pOH} = -0.3979 - (-6 \times 1)$$

$$\text{pOH} = -0.3979 + 6 \times 1$$

$$\text{pOH} = 5.6021$$

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

$$\text{pH} = 14 - 5.6021 = 8.3979$$

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

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7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas 25°C to get a solution with  $[H_3O^+] = 4 \times 10^{-5} M$ . Is the solution neutral (or) acidic (or) basic.

$$[H_3O^+] = 4 \times 10^{-5} M$$

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

$$pH = -\log[4 \times 10^{-5}]$$

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

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

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

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

8. Calculate the pH of 0.04 M HNO<sub>3</sub> Solution.

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

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

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

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

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

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

$$pH = 1.398 \approx 1.40$$

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 coefficient in a balanced equilibrium equation.

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

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

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

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

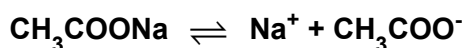
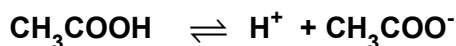
$$K_w = (1 \times 10^{-7})(1 \times 10^{-7})$$

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

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,**



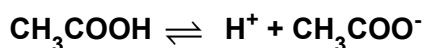
the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH<sub>3</sub>COOH and CH<sub>3</sub>COONa have the common ion, CH<sub>3</sub>COO<sup>-</sup>.

**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 ( $\alpha$ ) 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



	$\text{CH}_3\text{COOH}$	$\text{H}^+$	$\text{CH}_3\text{COO}^-$
Initial number of moles	1	-	-
Degree of dissociation	$\alpha$		
Number of moles at equilibrium	$1 - \alpha$	$\alpha$	$\alpha$
Equilibrium concentration	$C(1 - \alpha)$	$C\alpha$	$C\alpha$

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

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

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

$$K_a = C\alpha^2$$

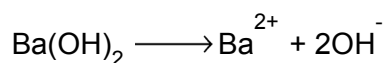
$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$[\text{H}^+] = C\alpha \quad [\text{H}^+] = C\sqrt{\frac{K_a}{C}} \quad \text{for weak acid is } [\text{H}^+] = \sqrt{K_a \cdot C}$$

**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.

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

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

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

$$\text{pOH} = -\log [2 \times 1.5 \times 10^{-3}]$$

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

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

$$\text{pOH} = -\log 3 + 3 \log 10$$

$$\text{pOH} = -\log 3 + 3 \times 1$$

$$\text{pOH} = -0.4771 + 3 = 2.53$$

$$\therefore \text{pH} = 14 - 2.53 = 11.47$$

15. 50ml of 0.05M  $\text{HNO}_3$  is added to 50ml of 0.025 M KOH. Calculate the pH of the resultant solution.

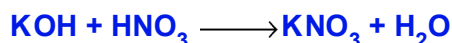
$$\text{Mole} = \text{Concentration} \times \text{Volume}$$

$$\text{mole of KOH} = 50 \text{ ml} \times 0.025 = 1.25$$

$$\text{mole of } \text{HNO}_3 = 50 \text{ ml} \times 0.05\text{M} = 2.5$$

$$\text{Total volume of solution (50+50 ml} = 100 \text{ ml)}$$

1.25 mole of KOH exactly neutralized by 1.25 mole of  $\text{HNO}_3$



that is  $2.5 - 1.25 = 1.25 \text{ HNO}_3$  mole

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

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

$$\text{pH} = -\log [\text{H}^+]$$

$$\text{pH} = -\log [0.0125]$$

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

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

$$\text{pH} = -\log 1.25 + 2 \log 10$$

$$\text{pH} = -0.0969 + 2 \times 1$$

$$\text{pH} = 1.9031$$

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

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

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

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

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

$$\text{pH} = -\log [\text{H}^+]$$

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

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

$$\text{pH} = -\log 2 + 5 \log 10$$

$$\text{pH} = -0.3010 + 5 \times 1$$

$$\text{pH} = 4.699$$

## 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 =  $0.55 \times 10^{-2}$** 

$$\text{pH} = \frac{1}{2}\text{pK}_w + \frac{1}{2}\text{pK}_a - \frac{1}{2}\text{pK}_b$$

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

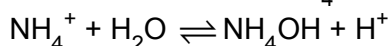
$$\frac{1}{2}\text{pK}_a = -\frac{1}{2}\log K_a = -\frac{1}{2}\log(1.8 \times 10^{-5}) = \frac{1}{2}4.7447 = 2.3723$$

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

$$\text{pH} = 7 + 2.3723 - 2.3723 = 7 + 0$$

**pH = 7**

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

Weak base -  $\text{NH}_4\text{OH}$  and strong acid -  $\text{HCl}$ **Hydrolysis constant** : Applying the Law of Mass Action

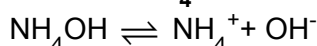
$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+][\text{H}_2\text{O}]}$$

Since  $[\text{H}_2\text{O}]$  is very large, it is taken to be constant and the hydrolysis constant expression is reduced to

$$K_h = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} \text{ ----- 1}$$

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

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

**For the dissociation of a weak base,  $\text{NH}_4\text{OH}$** 

The dissociation constant,  $K_b$ , can be expressed as

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \text{----- 3}$$

**Dividing (2) by (3)**

$$\frac{K_w}{K_b} = [\text{H}^+][\text{OH}^-] \times \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+][\text{OH}^-]} = \frac{[\text{NH}_4\text{OH}][\text{H}^+]}{[\text{NH}_4^+]} = K_h$$

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

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

$$K_h \cdot K_b = K_w$$

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

$$K_h = h^2 C \text{ and}$$

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

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

$$\text{pH} = -\log [\text{H}^+]$$

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

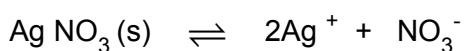
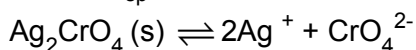
$$\text{pH} = -\frac{1}{2} \log K_w - \frac{1}{2} \log C + \frac{1}{2} \log K_b$$

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

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  $\text{Ag}_2\text{CrO}_4$  is  $1 \times 10^{-12}$ . What is the solubility of  $\text{Ag}_2\text{CrO}_4$  in 0.01M  $\text{AgNO}_3$  solution?**

$$K_{sp} = 1 \times 10^{-12}$$



$$0.01 \text{ M} \qquad \qquad 0.01 \text{ M} \qquad 0.01 \text{ M}$$

$$[\text{Ag}^+] = 2s + 0.01$$

$$\therefore 0.01 \gg 2s$$

$$\therefore [\text{Ag}^+] = 0.01 \text{ M}$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

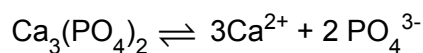
$$K_{sp} = (s)^2 (s)$$

$$1 \times 10^{-12} = (0.01)^2 (s)$$

$$[\text{CrO}_4^{2-}] = (s) = \frac{1 \times 10^{-12}}{(10^{-2})^2} = 1 \times 10^{-8}$$



20. Write the expression for the solubility product of  $\text{Ca}_3(\text{PO}_4)_2$



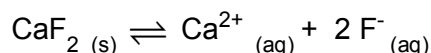
$$K_{\text{sp}} = [\text{Ca}^{2+}]^3 \cdot [\text{PO}_4^{3-}]^2$$

$$K_{\text{sp}} = (3s)^3 \cdot (2s)^2$$

$$K_{\text{sp}} = (27s^3) \cdot (4s^2)$$

$$K_{\text{sp}} = 108s^5$$

21. A saturated solution, prepared by dissolving  $\text{CaF}_2$  in water, has  $[\text{Ca}^{2+}] = 3.3 \times 10^{-4}$ . What is the  $K_{\text{sp}}$  of  $\text{CaF}_2$ ?



( breaks into 2  $\text{F}^-$  ions not  $\text{F}_2$  )

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

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

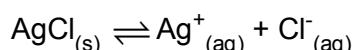
$$[2\text{F}^-] = 6.6 \times 10^{-4} \text{ M}$$

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

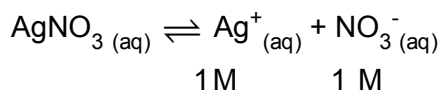
$$K_{\text{sp}} = 3.3 \times 10^{-4} \cdot (6.6 \times 10^{-4})^2$$

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

22.  $K_{\text{sp}}$  of  $\text{AgCl}$  is  $1.8 \times 10^{-10}$ . Calculate molar solubility in 1 M  $\text{AgNO}_3$ .



**x = solubility of  $\text{AgCl}$  in 1M  $\text{AgNO}_3$ .**



$$[\text{Ag}^+] = x + 1 \text{ M} \approx 1 \text{ M} \quad (\because x \ll 1)$$

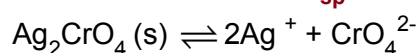
$$[\text{Cl}^-] = x$$

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

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

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

23. A particular saturated solution of silver chromate  $\text{Ag}_2\text{CrO}_4$  has  $[\text{Ag}^+] = 5 \times 10^{-5}$  and  $[\text{CrO}_4^{2-}] = 4.4 \times 10^{-4}$ . What is the value of  $K_{\text{sp}}$  for  $\text{Ag}_2\text{CrO}_4$ ?



$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

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

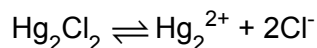
$$K_{\text{sp}} = (25 \times 10^{-10}) (4.4 \times 10^{-4})$$

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

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

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

24. Write the expression for the solubility product of  $\text{Hg}_2\text{Cl}_2$ .

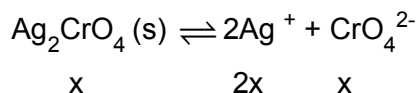


$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2$$

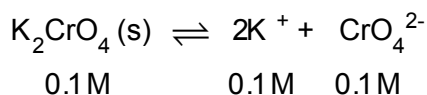
$$K_{sp} = [s] \cdot [2s]^2$$

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

25.  $K_{sp}$  of  $\text{Ag}_2\text{CrO}_4$  is  $1.1 \times 10^{-12}$ . What is solubility of  $\text{Ag}_2\text{CrO}_4$  in  $0.1\text{M K}_2\text{CrO}_4$ .



$x$  is the solubility of  $\text{Ag}_2\text{CrO}_4$  in  $0.1\text{M K}_2\text{CrO}_4$ .



$$[\text{Ag}^+] = 2x$$

$$[\text{CrO}_4^{2-}] = (x + 0.1) \approx 0.1 \quad (\because x \ll 0.1)$$

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

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

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

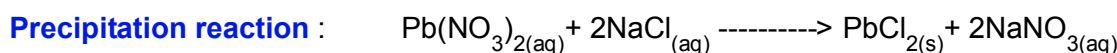
$$x^2 = \frac{1.1 \times 10^{-12}}{0.4}$$

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

$$x = \sqrt{2.75 \times 10^{-12}}$$

$$x = 1.658 \times 10^{-6}\text{M}$$

26. Will a precipitate be formed when  $0.150\text{ L}$  of  $0.1\text{M Pb}(\text{NO}_3)_2$  and  $0.100\text{L}$  of  $0.2\text{ M NaCl}$  are mixed?  $K_{sp}(\text{PbCl}_2) = 1.2 \times 10^{-5}$ .



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

**1:1 mole ratios so initial  $[\text{Pb}^{2+}] = [\text{Pb}(\text{NO}_3)_2] = 0.1\text{ M}$  ; initial  $[\text{Cl}^-] = [\text{NaCl}] = 0.2\text{ M}$**

After we combine the solution the total volume becomes  $.250\text{ L}$ ,

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

**Number of moles  $\text{Pb}^{2+}$  = molarity x Volume of the solution in lit =  $0.1 \times 0.150\text{ L}$**

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

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

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

**$Q > K_{sp}$ ,  $[3.8 \times 10^{-4} < 1.2 \times 10^{-5}]$  so  $\text{PbCl}_2$  does precipitate. Eq shifts to the left .**

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27.  $K_{sp}$  of  $\text{Al}(\text{OH})_3$  is  $1 \times 10^{-15} \text{M}$ . At what pH does  $1.0 \times 10^{-3} \text{M}$   $\text{Al}^{3+}$  precipitate on the addition of buffer of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  solution?

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

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

3. Plug into the  $K_{sp}$  expression:  $1 \times 10^{-15} \text{M} = (1.0 \times 10^{-3} \text{M}) [\text{OH}^-]^3$

4) Solve for s, which is the  $[\text{OH}^-]$  :  $[\text{OH}^-]^3 = \frac{K_{sp}}{[\text{Al}^{3+}]}$

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

$$[\text{OH}^-] = 3 \sqrt{\frac{1 \times 10^{-15}}{1 \times 10^{-3}}}$$

$$[\text{OH}^-] = 3 \sqrt{1 \times 10^{-12}}$$

$$[\text{OH}^-] = (1 \times 10^{-12})^{\frac{1}{3}}$$

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

5) Calculate the pH:

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

$$\text{pOH} = -\log(1 \times 10^{-4}) = 4$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4 = 10$$

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