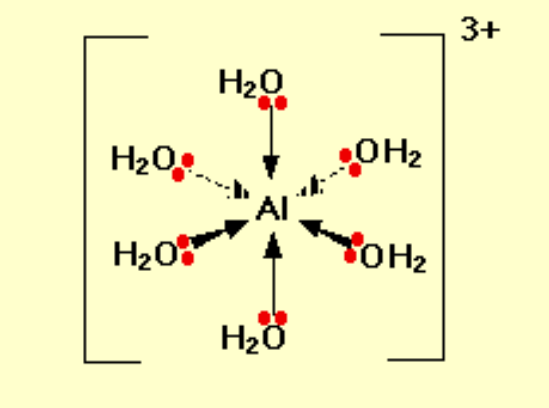
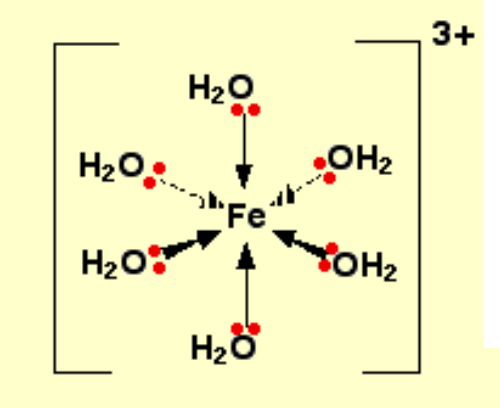
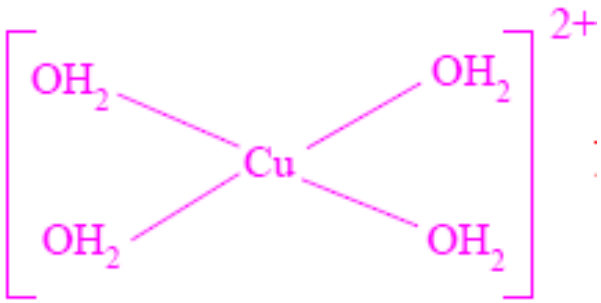
METAL SOLUBILITY and COMPLEX FORMATION

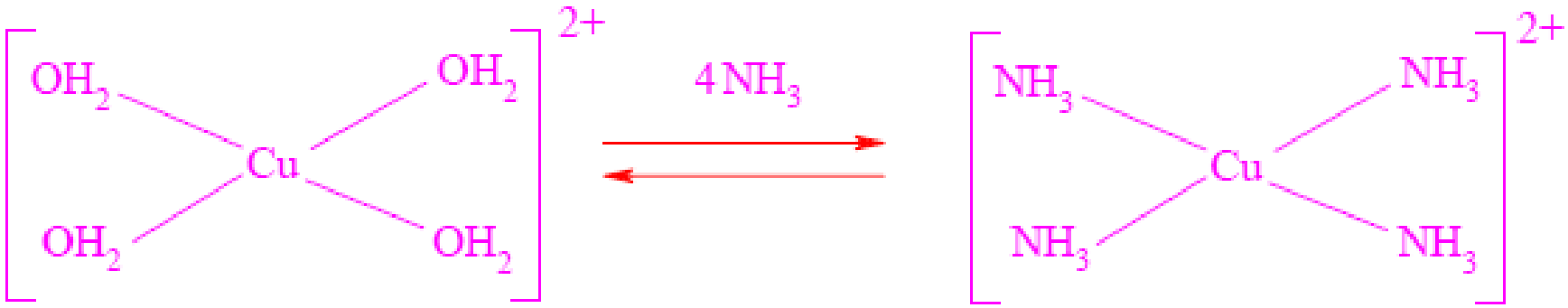
Metal ions in solution are always solvated, which means a definite number of solvent molecules (usually 2, 4 or 6) are firmly bound to the metal ion.





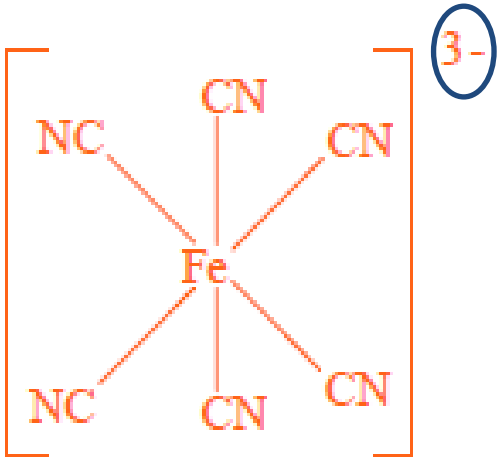


However, these bound solvent molecules are replaced by other solvent molecules or ions during the formation of a ***metal complex.***



The molecules or ions which displace the solvent molecules are called ***Ligands***.

Ligands or ***complexing agents*** or ***chelating agents*** can be any electron donating entity, which has the ability to bind to the metal ion and produce a complex ion.



Assume we have ammonia (NH_3) in wastewater.

The formation of complex Cu $(NH_3)_4^{2+}$ proceeds in the following steps:

Step 1 $Cu(H_2O)_4^{2+} + NH_3 \leftrightarrow Cu(H_2O)_3NH_3^{2+} + H_2O$

Step 2 $Cu(H_2O)_3\,NH_3^{2+} + NH_3 \leftrightarrow Cu(H_2O)_2\,(NH_3)_2^{2+} + H_2O$

Step 3 $Cu(H_2O)_2\,(NH_3)_2^{2+} + NH_3 \leftrightarrow Cu(H_2O)\,(NH_3)_3^{2+} + H_2O$

Step 4 $Cu(H_2O)\,(NH_3)_3^{2+} + NH_3 \leftrightarrow Cu\,(NH_3)_4^{2+} + H_2O$

To simplify writing chemical equations, we do not show the solvent molecules bound to the metal ion.

Step 1 $Cu^{2+} + NH_3 \leftrightarrow Cu(NH_3)^{2+}$

Step 2 $Cu(NH_3)^{2+} + NH_3 \leftrightarrow Cu(NH_3)_2^{2+}$

Step 3 $Cu(NH_3)_2^{2+} + NH_3 \leftrightarrow Cu(NH_3)_3^{2+}$

Step 4 $Cu(NH_3)_3^{2+} + NH_3 \leftrightarrow Cu\,(NH_3)_4^{2+}$

Finally, the overall reaction is

$$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+}$$

How Does Complex Formation Affect of the Solubility of Metals?

- Complex formation inceases the solubity.

For example, zinc is removed from wastewaters by adding base to increase the pH to form the insoluble $Zn(OH)_2$. However, if excess base is added, zinc will form soluble complexes with OH^- and will return to solution.

Precipitation reaction

$$Zn(OH)_2(s) \leftrightarrow Zn^{2+} + 2OH^- \qquad K_{sp} = 8x10^{-18}$$

Comlex formation reactions

$$Zn^{2+} + OH^- \leftrightarrow ZnOH^+ \qquad K_1 = 1{,}4x10^4$$

$$ZnOH^+ + OH^- \leftrightarrow Zn(OH)_2(aq) \qquad K_2 = 1x10^6$$

$$Zn(OH)_2(aq) + OH^- \leftrightarrow Zn(OH)_3^- \qquad K_3 = 1{,}3x10^4$$

$$Zn(OH)_3^- + OH^- \leftrightarrow Zn(OH)_4^{2-} \qquad K_4 = 1{,}8x10^1$$

for the precipitation reaction

$\log[Zn^{2+}] \alpha pH$

$Ksp = [Zn^{2+}].[OH^-]^2$

$\log(8x10^{-18}) = \log[Zn^{2+}] + 2\log[OH^-]$

$Kw = [H^+].[OH^-]$

$\log Kw = \log[H^+] + \log[OH^-]$

$-14 = \log[H^+] + \log[OH^-]$

$\log[OH^-] = -14 - \log[H^+]$

$\log[OH^-] = pH - 14$

$\log[OH^-] = pH-14$

$\log(8x10^{-8}) = \log[Zn^{2+}] + 2\log[OH^-]$

$-17.1 = \log[Zn^{2+}] + 2[\ pH-14]$

$-17.1 + 28 = \log[Zn^{2+}] + 2pH$

$\log[Zn^{2+}] = 10.9 - 2pH$

$y = b - 2x$

When pH = 10, $\log[Zn^{2+}] = -9.1$

When pH = 6, $\log[Zn^{2+}] = -1.1$

for $ZnOH^+$ formation

$\log[ZnOH^+] \ \alpha \ pH$

$$K = 1{,}4 \times 10^4 = \frac{[ZnOH^+]}{[Zn^{2+}].[OH^-]}$$

$$\log 1{,}4 \times 10^4 = \log[ZnOH^+] - (\log[Zn^{2+}] + \log[OH^-])$$

$$4{,}15 = \log[ZnOH^+] - (10{,}9 - 2pH + pH - 14)$$

$$\log[ZnOH^+] = 1.05 - pH$$

When pH = 10, $\log[Zn^{2+}] = -8.95$

When pH = 6, $\log[Zn^{2+}] = -4.95$

for $Zn(OH)_2](aq)$ formation

$$1x10^6 = \frac{[Zn(OH)_2](aq)}{[ZnOH^+].[OH^-]}$$

$$\log 1x10^6 = \log[Zn(OH)_2] - (\log[ZnOH^+] + \log[OH^-])$$

$$\log 1x10^6 = \log[Zn(OH)_2] - (1{,}05 - pH + pH - 14)$$

$$\log[Zn(OH)_2] = -6{,}95$$

All the dissolved zinc species :

Zn^{2+} , $ZnOH^{+}$,$Zn(OH)_{2(aq)}$, $ZnOH)_3^{-}$, $ZnOH)_4^{2-}$

$C_{T,zn} = [Zn^{2+}] + [ZnOH^{+}] + [Zn(OH)_2] + [ZnOH)_3^{-}] + [ZnOH)_4^{2-}]$

<u>At pH = 6</u>

$C_{T,zn} = 3{,}2x10^{-2}$ M+ 10^{-5} M+ 10^{-7} M+ negligible + negligible

$C_{T,zn} = 3{,}2x10^{-2}$M

<u>At pH = 12</u>

$C_{T,zn}$ = negligible + negligible + 10^{-7}M + 10^{-5} M+ $5x10^{-6}$M

$C_{T,zn} = 1{,}5x10^{-5}$M

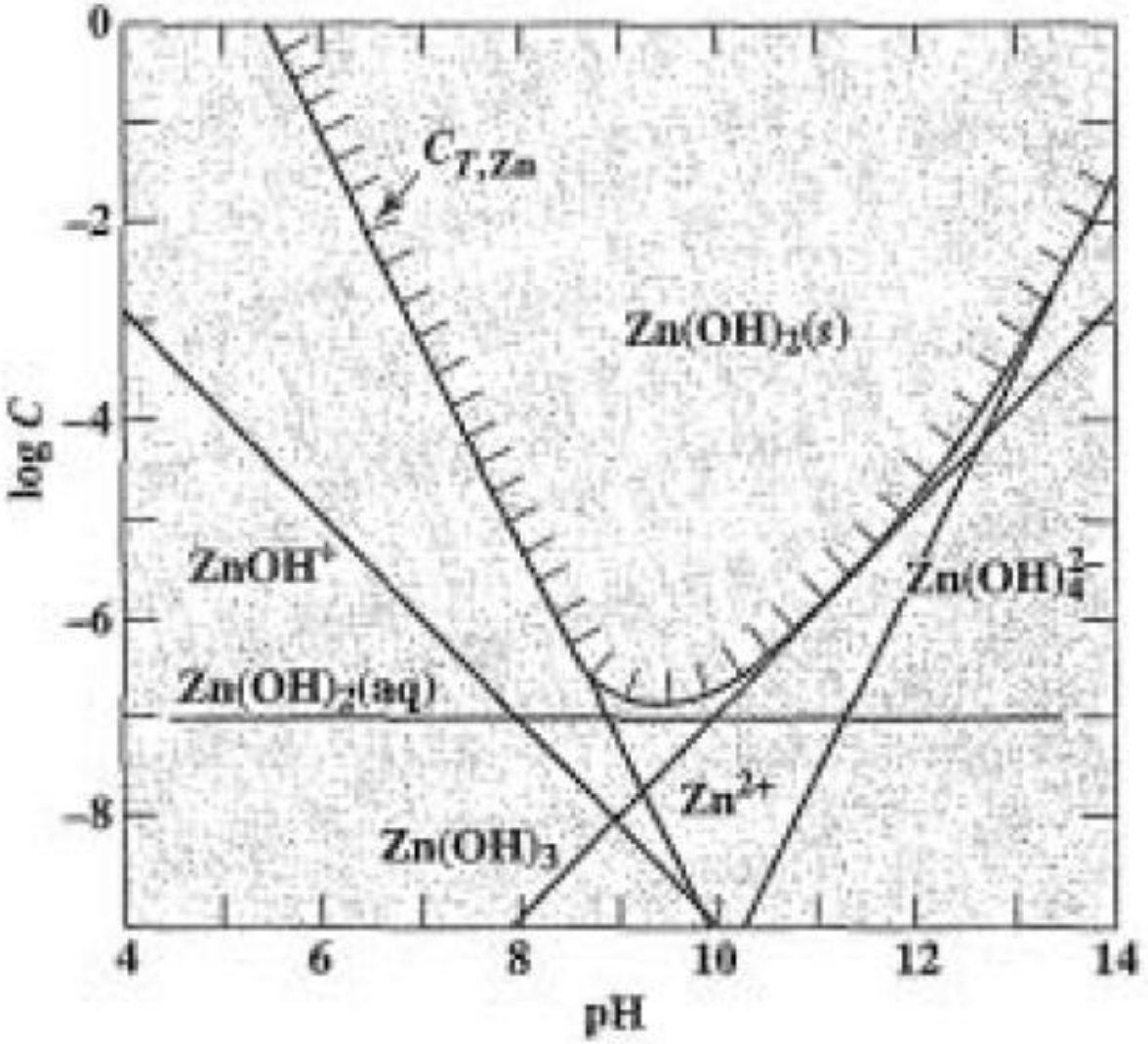


Figure 4.16 Solubility of $Zn(OH)_2(s)$ as a function of pH.

Ex : What is the pH of minimum Zn solubility ?

Answer

Minimum solubility occurs at pH = 9.4

Total equilibrium zinc solution concentration = $10^{-6.8}$M

Ex : A plating waste has a zinc conc. of 10^{-3}M. At what pH will zinc precipitate? What minimum pH should be used to decrease the zinc conc. below 10^{-5}M.

Answer

From Figure 4.16

At pH above 7 zinc will start to precipitate.

pH should be 7.9.