2.6. Reactions of Inorganic Compounds in Aqueous Solution

Lewis acids and bases

Definitions: **Lewis acid**: electron pair acceptor
Lewis base: electron pair donator

In the formation of complex ions the ligand is the Lewis base because it is donating a pair of electrons in the dative covalent bond and the metal ion is the Lewis acid.

Metal-aqua ions

Metal aqua ions are formed in aqueous solution.

$[M(H_2O)_6]^{2+}$, limited to M = Fe (green) and Cu (blue);
$[M(H_2O)_6]^{3+}$, limited to M = Al (colourless), and Fe (violet)

In solution and Fe(III) appears yellow/brown due to hydrolysis reactions. The violet colour is only really seen in solid hydrated salts that contain these complexes.

Acidity or hydrolysis reactions

The following equilibria happen in aqueous solutions of metal ions.

$[M(H_2O)_6]^{2+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{+} + H_3O^{+}$

$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5(OH)]^{2+} + H_3O^{+}$

The equilibria lead to generation of acidic solutions with M^{3+} ions, and very weakly acidic solutions with M^{2+} ions. The 3^+ ions are noticeably more acidic.

The acidity of $[M(H_2O)_6]^{3+}$ is greater than that of $[M(H_2O)_6]^{2+}$ in terms of the greater polarising power (charge/size ratio) of the 3+ metal ion. The greater the polarising power, the more strongly it attracts the water molecule. This weakens the O-H bond so it breaks more easily.

Reaction with limited OH^- and limited NH_3

The bases OH^- and ammonia when in limited amounts form the same hydroxide precipitates. They form in **deprotonation acid base reactions**

$M(OH)_2(H_2O)_{4\,(s)}$: Cu blue ppt, Fe (II) green ppt
$M(OH)_3(H_2O)_{3\,(s)}$: Fe(III) brown ppt, Al white ppt

$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(H_2O)_4(OH)_{2\,(s)} + 2H_2O_{(l)}$

$[Al(H_2O)_6]^{3+}{}_{(aq)} + 3OH^-{}_{(aq)} \rightarrow Al(H_2O)_3(OH)_{3\,(s)} + 3H_2O_{(l)}$

$[Fe(H_2O)_6]^{2+}{}_{(aq)} + 2NH_3{}_{(aq)} \rightarrow Fe(H_2O)_4(OH)_{2\,(s)} + 2NH_4^+{}_{(aq)}$

$[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3NH_3{}_{(aq)} \rightarrow Fe(H_2O)_3(OH)_{3\,(s)} + 3NH_4^+{}_{(aq)}$

This process can happen step wise removing one proton at a time. Be able to write equations for this too.

e.g. $[Al(H_2O)_6]^{3+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow [Al(H_2O)_5(OH)]^{2+}{}_{(aq)} + H_2O_{(l)}$

$[Al(H_2O)_5(OH)]^{2+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow [Al(H_2O)_4(OH)_2]^{+}{}_{(aq)} + H_2O_{(l)}$

Here the NH_3 and OH^- ions are acting as **Bronsted-Lowry bases** accepting a proton

Reaction with excess OH^-

With excess NaOH the Al hydroxide dissolves.
Al becomes $[Al(OH)_4]^-$ (aq) colourless solution.

This hydroxides is classed as **amphoteric** because it reacts and dissolves in both acids and bases.

$Al(H_2O)_3(OH)_{3\,(s)} + OH^-{}_{(aq)} \rightarrow [Al(OH)_4]^-{}_{(aq)} + 3H_2O_{(l)}$

$Al(H_2O)_3(OH)_{3\,(s)} + 3H^+{}_{(aq)} \rightarrow [Al(H_2O)_6]^{3+}{}_{(aq)}$

Reaction with excess NH_3

With **excess NH_3 a ligand substitution** reaction occurs with Cu and its precipitate dissolve

This substitution is incomplete with Cu.

Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution

$Cu(OH)_2(H_2O)_{4(s)} + 4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 2H_2O_{(l)} + 2OH^-{}_{(aq)}$

In this reactions NH_3 is acting as a **Lewis base** donating an electron pair.

Reactions with Carbonate solution

The 2+ ions react differently to the 3+ ions with carbonate solutions.

The **2+** ions with **carbonate** solution results in **MCO_3 ppt** being formed (Cu blue/green, Fe(II) green)

$Cu^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow CuCO_{3\,(s)}$

$Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow FeCO_{3\,(s)}$

$[Cu(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CuCO_3 + 6H_2O$

$[Fe(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow FeCO_3 + 6H_2O$

These are **precipitation** reactions

The **3+** ions with **carbonate** solution form **a $M(OH)_3$ ppt and CO_2** gas is evolved.

Al forms white ppt of $Al(OH)_3\,(H_2O)_3 + CO_2$
Fe(III) forms brown ppt of $Fe(OH)_3\,(H_2O)_3 + CO_2$

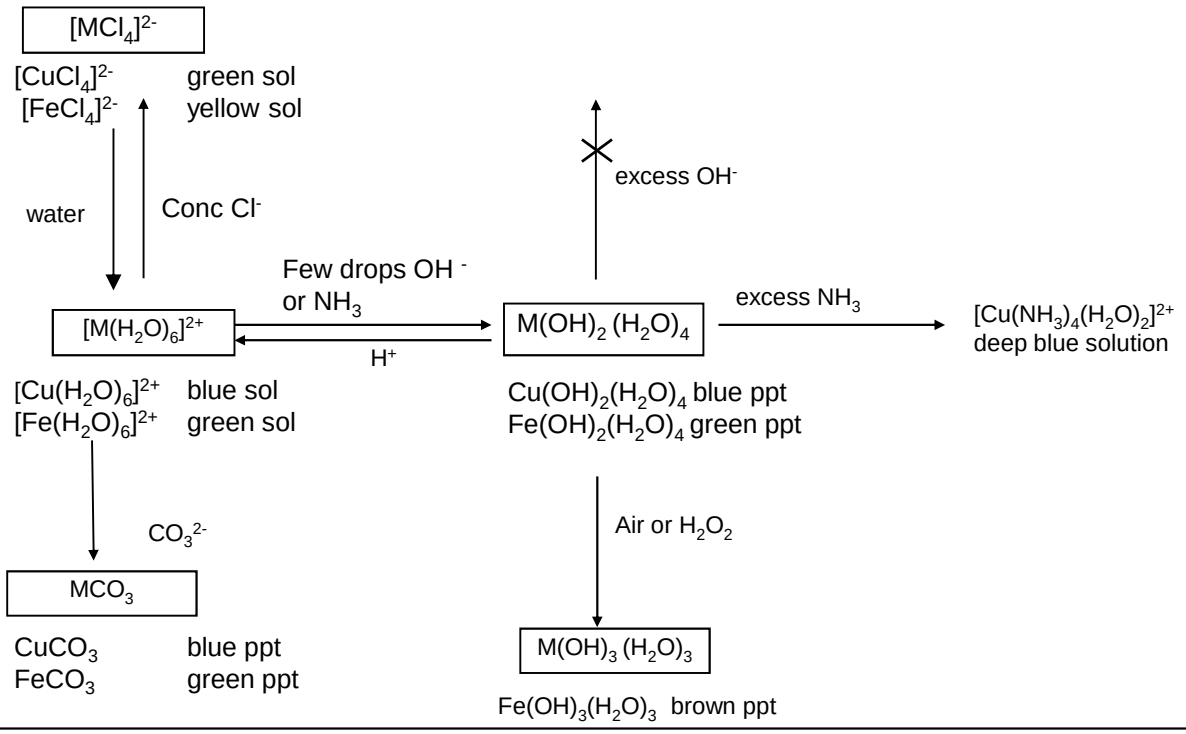
$2[Fe(H_2O)_6]^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Fe(OH)_3(H_2O)_{3(s)} + 3CO_2 + 3H_2O_{(l)}$

$2[Al(H_2O)_6]^{3+}{}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightarrow 2Al(OH)_3(H_2O)_{3(s)} + 3CO_2 + 3H_2O_{(l)}$

These are classed as **acidity reactions.**

MCO_3 is formed with 2+ ions but $M_2(CO_3)_3$ is not formed with 3+ ions. The difference is explained by the greater polarising power of the 3+ ion due to its higher charge density.

2+ Ion Summary



3+ Ion Summary