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 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.

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

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

The equilibria lead to generation of acidic solutions with M³⁺ ions, and very weakly acidic solutions with M²⁺ ions. The 3⁺ ions are noticeably more acidic.

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

Reaction with limited OH- and limited NH₃

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

$$\begin{split} & [\text{Cu}(\text{H}_2\text{O})_6]^{2^+}{}_{(\text{aq})} \ + 2\text{OH}^-{}_{(\text{aq})} \rightarrow \ \text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2{}_{(\text{s})} + 2\text{H}_2\text{O}{}_{(\text{l})} \\ & [\text{Al}(\text{H}_2\text{O})_6]^{3^+}{}_{(\text{aq})} + 3\text{OH}^-{}_{(\text{aq})} \rightarrow \ \text{Al}(\text{H}_2\text{O})_3(\text{OH})_3{}_{(\text{s})} + 3\text{H}_2\text{O}{}_{(\text{l})} \end{split}$$

$$[\text{Fe}(\text{H}_2\text{O})_6]^{2^+}_{(\text{aq})} + 2\text{NH}_3_{(\text{aq})} \rightarrow \text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2_{(\text{s})} + 2\text{NH}_4^+_{(\text{aq})}$$

$$[\text{Fe}(\text{H}_2\text{O})_6]^{3^+}_{(\text{aq})} + 3\text{NH}_3_{(\text{aq})} \rightarrow \text{Fe}(\text{H}_2\text{O})_3(\text{OH})_3_{(\text{s})} + 3\text{NH}_4^+_{(\text{aq})}$$

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

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

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

Here the NH₃ and OH⁻ ions are acting as **Bronsted-Lowry bases** accepting a proton

Reaction with excess OH-

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

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

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

Reaction with excess NH₃

With excess NH₃ a ligand substitution reaction occurs with Cu and its precipitate dissolves to form a deep blue solution.

This substitution is incomplete with Cu.

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

$$\mathrm{Cu}(\mathrm{OH})_2(\mathrm{H}_2\mathrm{O})_{4(\mathrm{s})} + 4\mathrm{NH}_{3\;(\mathrm{aq})} \\ \boldsymbol{\to} [\mathrm{Cu}(\mathrm{NH}_3)_4(\mathrm{H}_2\mathrm{O})_2]^{2^+}{}_{(\mathrm{aq})} + 2\mathrm{H}_2\mathrm{O}{}_{(\mathrm{l})} + 2\mathrm{OH}^{-}{}_{(\mathrm{aq})} \\$$

In this reactions NH₃ 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 MCO₃ 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 CO₂ gas is evolved.

Al forms white ppt of Al(OH) $_3$ (H $_2$ O) $_3$ + CO $_2$ Fe(III) forms brown ppt of Fe(OH) $_3$ (H $_2$ O) $_3$ + CO $_2$

$$\begin{split} &2[\text{Fe}(\text{H}_2\text{O})_6]^{3+}_{(\text{aq})} + 3\text{CO}_3^{2-}_{(\text{aq})} \Rightarrow 2\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_{3(\text{s})} + 3\text{CO}_2 + 3\text{H}_2\text{O}_{(\text{I})} \\ &2[\text{Al}(\text{H}_2\text{O})_6]^{3+}_{(\text{aq})} + 3\text{CO}_3^{2-}_{(\text{aq})} \Rightarrow 2\text{Al}(\text{OH})_3(\text{H}_2\text{O})_{3(\text{s})} + 3\text{CO}_2 + 3\text{H}_2\text{O}_{(\text{I})} \end{split}$$

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.



