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.

- $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, limited to $\text{M} = \text{Fe}$ (green) and $\text{Cu}$ (blue);
- $[\text{M}(\text{H}_2\text{O})_6]^{3+}$, limited to $\text{M} = \text{Al}$ (colourless), and Fe (violet)

In solution and Fe(III) appears yellow/brown due to hydrolysis reactions. The violet color 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.

- $[\text{M}(\text{H}_2\text{O})_6]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{M}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^+$
- $[\text{M}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{M}(\text{H}_2\text{O})_5\text{OH}]^{3+} + \text{H}_3\text{O}^+$

The acidity of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ is greater than that of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ 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\textsuperscript{-} and limited NH\textsubscript{3}

The bases OH\textsuperscript{-} and ammonia when in limited amounts form the same hydroxide precipitates. They form in deprotonation

- $[\text{Cu}(\text{H}_2\text{O})_6]^{3+} + 2\text{OH}^- \rightarrow [\text{Cu}(\text{H}_2\text{O})_4\text{OH}]^{2+} + 2\text{H}_2\text{O}$
- $[\text{Al}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightarrow [\text{Al}(\text{H}_2\text{O})_2\text{OH}]^{3+} + 3\text{H}_2\text{O}$

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

- $[\text{Al}(\text{H}_2\text{O})_2\text{OH}]^{3+} + \text{OH}^- \rightarrow [\text{Al}(\text{H}_2\text{O})_4\text{OH}]^{2+} + \text{H}_2\text{O}$

Here the NH\textsubscript{3} and OH\textsuperscript{-} ions are acting as Bronsted-Lowry bases accepting a proton

Reaction with excess OH\textsuperscript{-}

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

$[\text{Al(\text{H}_2\text{O})}_3\text{OH}]^{3+} + \text{OH}^- \rightarrow [\text{Al(\text{OH})}_4]^{-} + 3\text{H}_2\text{O}$

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

Reaction with excess NH\textsubscript{3}

With excess NH\textsubscript{3} a ligand substitution reaction occurs with Cu and its precipitate dissolve

- $[\text{Cu(\text{OH})}_2\text{H}_2\text{O}]^{4+} + 4\text{NH}_3 \rightarrow \text{[Cu(NH}_3)_4\text{H}_2\text{O}]^{2+} + 2\text{H}_2\text{O} + 2\text{OH}^-$

In this reactions NH\textsubscript{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)

\[
\begin{align*}
\text{Cu}^{2+} (aq) + \text{CO}_3^{2-} (aq) & \rightarrow \text{CuCO}_3 (s) \\
\text{Fe}^{2+} (aq) + \text{CO}_3^{2-} (aq) & \rightarrow \text{FeCO}_3 (s)
\end{align*}
\]

These are precipitation reactions

The 3+ ions with carbonate solution form a M(OH)$_3$ ppt and CO$_2$ gas is evolved.

\[
\begin{align*}
\text{Al} & \text{ forms white ppt of Al(OH)$_3$ (H$_2$O)$_3$ + CO}_2 \\
\text{Fe(III)} & \text{ forms brown ppt of Fe(OH)$_3$ (H$_2$O)$_3$ + CO}_2
\end{align*}
\]

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.

\[
\begin{align*}
2[\text{Fe(H}_2\text{O)}_6]^{3+} (aq) + 3\text{CO}_3^{2-} (aq) & \rightarrow 2\text{Fe(OH)}_3(\text{H}_2\text{O})_3(s) + 3\text{CO}_2 + 3\text{H}_2\text{O(l)} \\
2[\text{Al (H}_2\text{O)}_6]^{3+} (aq) + 3\text{CO}_3^{2-} (aq) & \rightarrow 2\text{Al(OH)}_3(\text{H}_2\text{O})_3(s) + 3\text{CO}_2 + 3\text{H}_2\text{O(l)}
\end{align*}
\]

These are classed as acidity reactions.
2+ Ion Summary

\[ [\text{M}(\text{H}_2\text{O})_6]^{2+} \]
- green sol
- water

\[ [\text{Cu}(\text{H}_2\text{O})_6]^{2+}, [\text{Fe}(\text{H}_2\text{O})_6]^{2+} \]
- blue sol
- green sol

Conc Cl-

Few drops OH\textsuperscript{-} or NH\textsubscript{3}

\[ \text{H}^+ \]

\[ [\text{Cu}(\text{OH})_2(\text{H}_2\text{O})_4]^{2+}, [\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^{2+} \]
- blue ppt
- green ppt

\[ [\text{Cu}([\text{NH}_3]_4(\text{H}_2\text{O})_3)]^{2+} \]
- deep blue solution

\[ \text{H}^+ + \text{excess OH}^- \]

\[ [\text{Al}(\text{OH})_4]^- \]
- colourless sol

\[ [\text{Al}(\text{H}_2\text{O})_6]^{3+}, [\text{Fe}(\text{H}_2\text{O})_6]^{3+} \]
- colourless sol
- yellow sol

Few drops OH\textsuperscript{-} or NH\textsubscript{3}

\[ \text{H}^+ \]

\[ [\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3] \]
- white ppt

\[ [\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3] \]
- brown ppt

3+ Ion Summary

\[ [\text{Al}(\text{OH})_4]^- \]
- colourless sol

\[ \text{H}^+ + \text{excess OH}^- \]

\[ [\text{Al}(\text{H}_2\text{O})_6]^{3+}, [\text{Fe}(\text{H}_2\text{O})_6]^{3+} \]
- colourless sol
- yellow sol

\[ \text{CO}_3^{2-} \]

\[ [\text{Al}(\text{OH})_3(\text{H}_2\text{O})_3] + \text{CO}_2 \]
- white ppt + bubbles of \text{CO}_2

\[ [\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3] \]
- brown ppt + bubbles of \text{CO}_2

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