Reactions of Aqueous Ions

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Metal-aqua ions

Metal aqua ions are formed in aqueous solution

Most transition metals form either +2 or +3 metal aqua ions

\[ [\text{M(H}_2\text{O)}_6]^{2+}, \text{are formed by M = Fe, Co and Cu;} \]
\[ [\text{M(H}_2\text{O)}_6]^{3+}, \text{are formed by M = Al, V, Cr and Fe}. \]

Aqua ions can also be present in the solid state (e.g. FeSO\(_4\).7H\(_2\)O and Co(NO\(_3\))2.6H\(_2\)O).
Colour of aqueous ions

\[ [M(H_2O)_6]^{2+} \text{, limited to } M = \text{Fe (green)}, \text{Co (pink)} \text{ and } \text{Cu (blue)}; \]
\[ [M(H_2O)_6]^{3+} \text{, limited to } M = \text{Al (colourless)}, \text{Cr (ruby)} \text{ and } \text{Fe (violet)} \]

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

Acidity/hydrolysis reactions of metal aqua ions

Metal aqua ions form acidic solutions.

One of the water molecules acting as the ligand is split so that H\(^+\) ions come off leaving the OH\(^-\) on the complex.

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

and

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

For example,

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

The \( M^{3+} \) ions form acidic solutions and the \( M^{2+} \) ions form very weakly acidic solutions.
The acidity of \([\text{M(H}_2\text{O)}_6]^{3+}\) is greater than that of \([\text{M(H}_2\text{O)}_6]^{2+}\) because the polarising power (charge/size ratio) of the metal ion is greater on the 3+ 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.

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**Reaction of Metal aqua ions with bases**

Metal aqua ions can also do acidity type reactions with the bases (sodium hydroxide) \(\text{OH}^-\), (ammonia) \(\text{NH}_3\) and (sodium carbonate) \(\text{CO}_3^{2-}\).

**Reaction with hydroxides**

Aqueous complex ions react with sodium hydroxide to form coloured precipitates.

\[
\text{Cu(H}_2\text{O)}_6^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Cu(OH)}_4(\text{OH})_2 (\text{s}) + \text{H}_2\text{O} (\text{l})
\]

**Examples**

- \(\text{Cu(H}_2\text{O)}_4(\text{OH})_2 (\text{s})\) \text{blue ppt}
- \(\text{Co(H}_2\text{O)}_4(\text{OH})_2 (\text{s})\) \text{blue green ppt}
- \(\text{Fe(H}_2\text{O)}_4(\text{OH})_2 (\text{s})\) \text{green ppt}
- \(\text{Al(H}_2\text{O)}_3(\text{OH})_3 (\text{s})\) \text{white ppt}
- \(\text{Cr(OH)}_3(\text{H}_2\text{O)}_3 (\text{s})\) \text{green ppt.}
- \(\text{Fe(H}_2\text{O)}_3(\text{OH})_3 (\text{s})\) \text{brown ppt}
The reaction between the metal ions and sodium hydroxide occurs stepwise.

One proton is removed at each step until the hydroxide precipitate is formed.

\[
[\text{Cr(H}_2\text{O)}_6^{3+} + \text{OH}^- \rightarrow [\text{CrOH(H}_2\text{O)}_5]^{2+} + \text{H}_2\text{O}
\]

\[
[\text{CrOH(H}_2\text{O)}_5]^{2+} + \text{OH}^- \rightarrow [\text{Cr(OH)}_2(\text{H}_2\text{O})_4]^{2+} + \text{H}_2\text{O}
\]

\[
[\text{Cr(OH)}_2(\text{H}_2\text{O})_4]^{2+} + \text{OH}^- \rightarrow \text{Cr(OH)}_3(\text{H}_2\text{O})_3(\text{s}) + \text{H}_2\text{O}
\]

\[
\text{Cr(OH)}_3(\text{H}_2\text{O})_3(\text{s}) \text{ is a green ppt.}
\]

If we continue adding sodium hydroxide then further deprotonation takes place, the hydroxide precipitate dissolves and \([\text{Cr(OH)}_6]^{3-}\) is formed.

Only Cr and Al dissolve in excess NaOH. Al forms \([\text{Al(OH)}_4]^-\).

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**Reaction with limited amount of Ammonia**

If a few drops of ammonia is added to metal aqua ions the same acidity reactions occur as with sodium hydroxide and the same coloured precipitates form.

**Reaction of copper ion with NaOH.**

\[
\text{Cu(H}_2\text{O)}_6^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{Cu(H}_2\text{O)}_4(\text{OH})_2 (\text{s}) + \text{H}_2\text{O} (\text{l})
\]

**Reaction of copper ion with NH}_{3.**

\[
\text{Cu(H}_2\text{O)}_6^{2+} (\text{aq}) + 2\text{NH}_3 (\text{aq}) \rightarrow \text{Cu(H}_2\text{O)}_4(\text{OH})_2 (\text{s}) + 2\text{NH}_4^+ (\text{aq})
\]

If excess ammonia is added some of the precipitates dissolve in a different type of reaction.
**Cu²⁺ copper(II)**

\[ [\text{Cu(H}_2\text{O)}_6]^{2+} (\text{aq}) \rightarrow \text{Cu(H}_2\text{O)}_4(\text{OH})_2 (\text{s}) + 2\text{H}_2\text{O(l)} \]

\[ [\text{Cu(H}_2\text{O)}_6]^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow [\text{Cu(OH)}_2(\text{H}_2\text{O})_4] (\text{s}) + 2\text{H}_2\text{O(l)} \]

**Co²⁺ cobalt(II)**

\[ [\text{Co(H}_2\text{O)}_6]^{2+} (\text{aq}) \rightarrow \text{Co(H}_2\text{O)}_4(\text{OH})_2 (\text{s}) + 2\text{H}_2\text{O(l)} \]

\[ [\text{Co(H}_2\text{O)}_6]^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow [\text{Co(OH)}_2(\text{H}_2\text{O})_4] (\text{s}) + 2\text{H}_2\text{O(l)} \]
Fe$^{2+}$ iron(II)

$[\text{Fe(H}_2\text{O)}_6\text{]}^{2+} \text{(aq)}$ (green) → $\text{NaOH (aq)}$ or $\text{NH}_3 (aq)$ (green precipitate (turns brown in air))

$[\text{Fe(H}_2\text{O)}_6\text{]}^{2+} (\text{aq}) + 2\text{OH}^{-} (\text{aq}) \rightarrow [\text{Fe(OH)}_2(\text{H}_2\text{O})_4] (\text{s}) + 2\text{H}_2\text{O (l)}$

$[\text{Fe(H}_2\text{O)}_6\text{]}^{2+} (\text{aq}) + 2\text{NH}_3 (\text{aq}) \rightarrow [\text{Fe(OH)}_2(\text{H}_2\text{O})_4] (\text{s}) + 2\text{NH}_4^{+}(\text{aq})$

$\text{Fe(OH)}_2(\text{s}) + \text{OH}^{-}(\text{aq}) \rightarrow \text{Fe(OH)}_3(\text{s}) + \text{e}^{-}$

dirty green rusty brown

Fe$^{3+}$ iron(III)

$[\text{Fe(H}_2\text{O)}_6\text{]}^{3+} \text{(aq)}$ (violet) appears orange because of hydrolysis → $\text{NaOH (aq)}$ or $\text{NH}_3 (aq)$ (brown precipitate)

$[\text{Fe(H}_2\text{O)}_6\text{]}^{3+} (\text{aq}) + 3\text{OH}^{-} (\text{aq}) \rightarrow [\text{Fe(OH)}_3(\text{H}_2\text{O})_3] (\text{s}) + 3\text{H}_2\text{O (l)}$

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

\[\text{[Cr(H}_2\text{O)}_{6}]^{3+} \quad \rightarrow \quad \text{Cr(H}_2\text{O)}_3\text{(OH)}_3\text{(s)} \quad \rightarrow \quad \text{[Cr(OH)}_3\text{]}^{3-} \quad (\text{aq})\]

- Red-blue solution appears green because of hydrolysis
- NaOH (aq) or NH₃ (aq) precipitate excess NaOH (aq)

\[
\text{[Cr(H}_2\text{O)}_{6}]^{3+} \quad + \quad 3\text{OH}^- \quad (\text{aq}) \quad \rightarrow \quad \text{[Cr(OH)}_3\text{(H}_2\text{O)}_3\text{]} \quad (\text{s}) \quad + \quad 3\text{H}_2\text{O} \quad (\text{l})
\]

\[
\text{[Cr(H}_2\text{O)}_{6}]^{3+} \quad + \quad 3\text{NH}_3 \quad (\text{aq}) \quad \rightarrow \quad \text{[Cr(OH)}_3\text{(H}_2\text{O)}_3\text{]} \quad (\text{s}) \quad + \quad 3\text{NH}_4^+ \quad (\text{aq})
\]

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

**Al^{3+} Aluminium(III)**

\[\text{[Al(H}_2\text{O)}_{6}]^{3+} \quad \rightarrow \quad \text{Al(H}_2\text{O)}_3\text{(OH)}_3\text{(s)} \quad \rightarrow \quad \text{[Al(OH)}_4^- \quad (\text{aq})\]

- Colourless solution
- NaOH (aq) or NH₃ (aq) white precipitate excess NaOH (aq)

\[
\text{[Al(H}_2\text{O)}_{6}]^{3+} \quad + \quad 3\text{OH}^- \quad (\text{aq}) \quad \rightarrow \quad \text{[Al(OH)}_3\text{(H}_2\text{O)}_3\text{]} \quad (\text{s}) \quad + \quad 3\text{H}_2\text{O} \quad (\text{l})
\]

\[
\text{[Al(H}_2\text{O)}_{6}]^{3+} \quad + \quad 3\text{NH}_3 \quad (\text{aq}) \quad \rightarrow \quad \text{[Al(OH)}_3\text{(H}_2\text{O)}_3\text{]} \quad (\text{s}) \quad + \quad 3\text{NH}_4^+ \quad (\text{aq})
\]

\[
\text{[Al(OH)}_3\text{(H}_2\text{O)}_3\text{]} \quad + \quad \text{OH}^- \quad (\text{aq}) \quad \rightarrow \quad \text{[Al(OH)}_4^- \quad (\text{aq}) \quad + \quad 3\text{H}_2\text{O} \quad (\text{l})
\]
Amphoteric Character of some hydroxides

Some metal hydroxides show amphoteric character by dissolving in both acids and bases (e.g. hydroxides of Al$^{3+}$ and Cr$^{3+}$).

\[
\text{[Al(H}_2\text{O)}_6\text{]}^{3+} \xrightleftharpoons{\text{H}^+} \text{[Al(OH)}_3\text{(H}_2\text{O)}_3\text{]}_{\text{s}} \xrightarrow{\text{OH}^-} \text{[Al(OH)}_4\text{]}^{-}
\]

The amphoteric hydroxides dissolve in excess sodium hydroxide

\[
\text{[Cr(OH)}_3\text{(H}_2\text{O)}_3\text{]}_{\text{s}} + 3\text{OH}^-_{\text{(aq)}} \rightarrow \text{[Cr(OH)}_6\text{]}^{3+}_{\text{(aq)}} + 3\text{H}_2\text{O}_{\text{l}}
\]

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

Reactions of chromium (VI) with acid and alkali

The equilibrium reaction between chromate and dichromate is also caused by the addition of acid or alkali

\[
2\text{CrO}_4^{2-} + 2\text{H}^+ \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

Note this is not a redox reaction because the Cr does not change oxidation number.
If $H^+$ ions are added in sufficient concentrations to carbonate ions the following equilibria are pushed towards products and $CO_2$ is produced:

\[
\begin{align*}
H^+ + CO_3^{2-} & \leftrightarrow HCO_3^- \\
H^+ + HCO_3^- & \leftrightarrow H_2O + CO_2
\end{align*}
\]

The metal aqua $2^+$ ions are acidic but not sufficiently acidic to bring about the changes mentioned above:

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

So when $2^+$ metal aqua ions are added to carbonate ions they form coloured carbonate precipitates:

\[
\begin{align*}
[Cu(H_2O)_6]^{2+} + CO_3^{2-} & \rightarrow CuCO_3(s) + 6H_2O(l) & \text{blue precipitate} \\
[Co(H_2O)_6]^{2+} + CO_3^{2-} & \rightarrow CoCO_3(s) + 6H_2O(l) & \text{pink precipitate} \\
[Fe(H_2O)_6]^{2+} + CO_3^{2-} & \rightarrow FeCO_3(s) + 6H_2O(l) & \text{green precipitate}
\end{align*}
\]

These are Precipitation reactions.
The acidity of $[\text{M}][\text{H}_2\text{O}_6]^{3+}$ is greater than that of $[\text{M}][\text{H}_2\text{O}_6]^{2+}$ because the polarising power (charge/size ratio) of the metal ion is greater on the $3^+$ ion.

This acidity decomposes the $\text{CO}_3^{2-}$ ions

$$\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$$

The metal aqua reacts releasing $\text{H}^+$ ions and forms the hydroxide precipitate $\text{M(OH)}_3(\text{H}_2\text{O})_3$

The distinctive coloured hydroxide precipitate is formed in addition to the fizzing of the CO$_2$ evolved.

It is not possible to form solid $+3$ carbonates $\text{M}_2(\text{CO}_3)_3$ whereas $+2$ carbonate form easily $\text{MCO}_3$

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**Reactions of 3+ metal ions with carbonate ions**

**Chromium**

$$2[\text{Cr(H}_2\text{O}_6)]^{3+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} \rightarrow 2[\text{Cr(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{CO}_2 + 3\text{H}_2\text{O}_{(l)}$$

green precipitate and colourless bubbles of CO$_2$ (g)

**Iron III**

$$2[\text{Fe(H}_2\text{O}_6)]^{3+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} \rightarrow 2[\text{Fe(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{CO}_2 + 3\text{H}_2\text{O}_{(l)}$$

brown precipitate and colourless bubbles of CO$_2$ (g)

**Aluminium**

$$2[\text{Al(H}_2\text{O}_6)]^{3+}_{(aq)} + 3\text{CO}_3^{2-}_{(aq)} \rightarrow 2[\text{Al(OH)}_3(\text{H}_2\text{O})_3]_{(s)} + 3\text{CO}_2 + 3\text{H}_2\text{O}_{(l)}$$

white precipitate and colourless bubbles of CO$_2$ (g)

These are classed as acidity reactions
Substitution Reactions of complex ions

The metal aqua ions can also react by substituting one ligand for another

\[
[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O
\]
light blue \hspace{1cm} deep blue

\[
[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O
\]
light blue \hspace{1cm} green

Different ligands form complex ions of varying stability. One ligand can displace another in a complex ion if it can form a more stable complex.

Reaction of excess ammonia with metal aqua ions

When ammonia is added to some metal aqua ions the hydroxide precipitate first forms which then dissolves on addition of more ammonia. This second step is a ligand substitution reaction

\[
[Cr(OH)_3(H_2O)_3](s) + 6NH_3(aq) \rightarrow [Cr(NH_3)_6]^{3+}(aq) + 3H_2O(l) + 3OH^-(aq)
\]

The ligands NH_3 and H_2O are similar in size and are uncharged, and so ligand exchange occurs without change of co-ordination number (e.g. Co^{2+} and Cr^{3+}).

When excess ammonia is added to Chromium hydroxide a purple solution forms
Reaction of excess ammonia with cobalt

Similarly when excess ammonia is added to Cobalt hydroxide a pale brown solution forms

\[ \text{[Co(OH)(H}_2\text{O})_4\text{]}\text{(s)} + 6\text{NH}_3\text{(aq)} \rightarrow \text{[Co(NH}_3\text{)6]}^{2+}\text{(aq)} + 4\text{H}_2\text{O(l)} + 2\text{OH}^-\text{(aq)} \]

but ... ammonia ligands make the Co(II) state unstable. Air oxidises Co(II) to Co(III).

\[ \text{[Co(NH}_3\text{)6]}^{2+}\text{(aq)} \rightarrow \text{[Co(NH}_3\text{)6]}^{3+}\text{(aq)} + \text{e}^- \]

yellow / brown \hspace{1cm} red / brown

So it is important to keep air away from this mixture

Reaction of excess ammonia with copper

However, with copper(II) the reaction with excess ammonia gives incomplete substitution

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

royal blue solution
Substitution with Cl⁻ ligand

The Cl⁻ ligand is larger than the uncharged water and ammonia ligands. Therefore ligand exchange with Cl⁻ ions can involve a change of co-ordination number.

\[
[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O
\]

Green solution

\[
[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O
\]

Blue solution

There is therefore a change from octahedral to tetrahedral shape.

Explaining the trends in stability using entropy

In general the order of stability for a complex ion goes

unidentate- bidentate – tetradentate- hexadentate

increasing stability

\[
\text{Ni(H}_2\text{O)}_6^{2+_(aq)} + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2_{(aq)} \quad \text{Ni(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_{3}^{2+_(aq)} + 6\text{H}_2\text{O}_{(l)}
\]

The Ni complex ion has changed from having unidentate ligands to bidentate ligands.

In this reaction there is an increase in the entropy of the system because there are more moles of products than reactants (from 4 to 7), creating more disorder.
Stability constants

\[ \text{[Cu(H}_2\text{O)}_6\text{]}^{2+} + 4\text{Cl}^- \rightarrow \text{[CuCl}_4\text{]}^{2-} + 6\text{H}_2\text{O} \]

If this reaction is considered as equilibria then equilibrium expressions can be written:

\[
K = \frac{[\text{CuCl}_4^{2- \text{aq}}]}{[\text{Cu(H}_2\text{O)}_6^{2+ \text{aq}}][\text{Cl}^- \text{aq}]}^4
\]

\(\text{H}_2\text{O}\) is not included in the expression because it is concentration is assumed to be constant.

The value of \(K\) is called the stability constant for complex ions. The larger the stability constant the more stable the complex ion.

A complex ion with a small stability constant will not displace the ligand from a more stable complex ion with a large stability constant.

eg adding ammonia to a complex ion of copper and edta will not result in a colour change.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Lg K</th>
</tr>
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<tbody>
<tr>
<td>Cl(^-)</td>
<td>5.62</td>
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<tr>
<td>NH(_3)</td>
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<tr>
<td>2-hydroxybenzoate</td>
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<td>1,2-dihydroxybenzene</td>
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<td>Edta(^4-)</td>
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