# 2.6 Reactions of ions in aqueous solution

**Hydration of metal ions**

- These are **complex ions** where the ligand is water.
- Often referred to as the **metal – aqua complex ion**

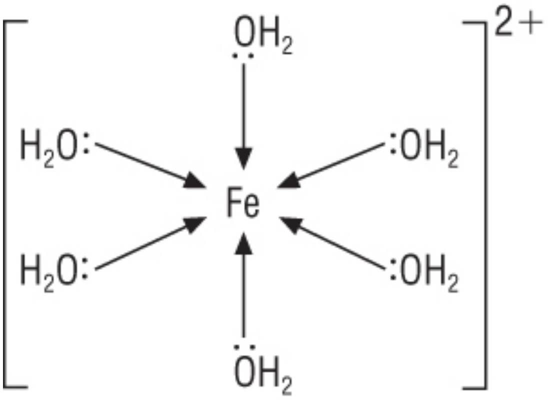
**Recap:**

| |
|---|
| **Complex ion:**<br>***A central metal ion surrounded by ligands*** |

| |
|---|
| **Ligand:**<br>***A molecule or ion that forms a dative covalent bond with a central metal ion by donating a pair of electrons*** |

| |
|---|
| **Dative covalent bond (co-ordinate bond)**<br>***A covalent bond where the pair of electrons have been donated by the same atom / molecule*** |

| |
|---|
| **Co-ordination number:**<br>***Is the number of dative (co-ordinate) bonds to the central metal ion*** |




$[Fe(H_2O)_6]^{2+}$

- **Fe $^{2+}$** is the **Transition metal ion**.
- **Ligands** are the **water** molecules.
- **Coordination number** is the number of coordinate bonds to the central metal ion **= 6**.
- **Square brackets** group the species and the **overall charge** is written outside the brackets.
- **Overall charge** is the sum of the charges of the metal ion and the ligands (if the ligands have a charge)

**Coloured solutions:**

- Most transition metal solutions exist as hexa-aqua complex ions.
- With an incomplete d sub shell they will form coloured solutions.
- This is because specific frequencies (wavelengths) of light are absorbed.
- This happens as electrons move from the **ground state** to an **exited state.**
- The remaining frequencies (and therefore colours) are transmitted:

| Metal ion | Formula of hexa-aqua ion | Colour |
|---|---|---|
| $Fe^{2+}$ | $[Fe(H_2O)_6]^{2+}$ | Green |
| $Cu^{2+}$ | $[Cu(H_2O)_6]^{2+}$ | Blue |
| $Fe^{3+}$ | $[Fe(H_2O)_6]^{3+}$ | Purple (may look yellow – brown) |
| $Al^{3+}$ | $[Al(H_2O)_6]^{3+}$ | Colourless |

**The acidic nature of metal aqua ions (recap from Period 3):**

**Bronsted – Lowry acid:**

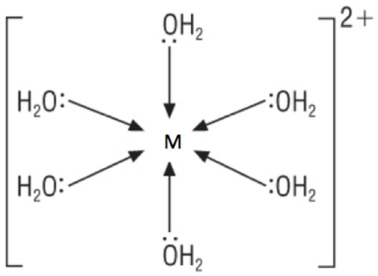
***Acids are proton donors***

**Hydrolysis:**

***Breaking of a bond with water***

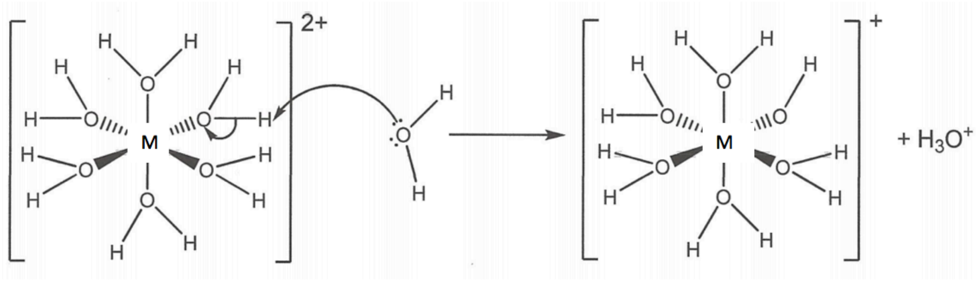
- Consider a dissolved 2+ ion:

$M^{2+}_{(aq)}$ →

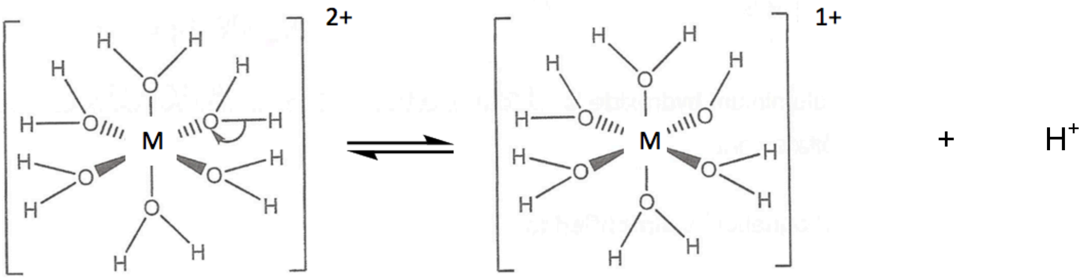



→ $[M(H_2O)_6]^{2+}$

**Proton donor:**



- $M^{2+}$ is a **small highly charged ion**, $M^{2+}$ therefore has a **high charge density.**
- This **high charge density** will **polarise** the water molecule.
- This **weakens the O – H bond**.
- The O – H bond breaks **releasing $H^+$ ions**, a **proton donor**, making **the complex ion acidic:**



- This reaction is often referred to as **hydrolysis** or **acidity** reaction as there is a reaction with water producing an acidic solution

**Acidity of the metal aqua 2+ and 3+ ions:**
**Example of a 2+ ion:**

$[Fe(H_2O)_6]^{2+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$ pKa = 5.89

Can be written as:

$[Fe(H_2O)_6]^{2+}{}_{(aq)} \rightleftharpoons [Fe(H_2O)_5(OH)]^{+}{}_{(aq)} + H^{+}{}_{(aq)}$

**Example of a 3+ ion:**

$[Al(H_2O)_6]^{3+}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}{}_{(aq)} + H_3O^{+}{}_{(aq)}$ pKa = 2.46

Can be written as:

$[Al(H_2O)_6]^{3+}{}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}{}_{(aq)} + H^{+}{}_{(aq)}$

- 3+ ions are smaller and more highly charged ion.
- Polarises water ligand more.
- More protons donated.
- Dissociates more.
- Larger Ka.
- Smaller pKa

**Acid base reactions:**

**1) Reactions with hydroxides, $OH^-$**

**$M^{3+}$ ion:** Consider the dissolved metal 3+ ion:

$$[M(H_2O)_6]^{3+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [M(H_2O)_5(OH)]^{2+}_{(aq)} + H_2O_{(l)}$$

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

$$[M(H_2O)_4(OH)_2]^{+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{[M(H_2O)_3(OH)_3]_{(s)}} + H_2O_{(l)}$$

- Adding more $OH^-$ shifts the equilibrium to the right
- The product has neutral charge and therefore precipitates out of solution.

**Simplifying to:**

$$[M(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{[M(H_2O)_3(OH)_3]_{(s)}} + 3H_2O_{(l)}$$

$$M^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{M(OH)_{3(s)}}$$

**Examples:**

$$\underset{\text{Yellow – brown solution}}{[Fe(H_2O)_6]^{3+}_{(aq)}} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{Brown precipitate}}{[Fe(H_2O)_3(OH)_3]_{(s)}} + 3H_2O_{(l)}$$

$$\underset{\text{Yellow – brown solution}}{Fe^{3+}_{(aq)}} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{Brown precipitate}}{Fe(OH)_{3(s)}}$$

$$[Al(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{White precipitate}}{[Al(H_2O)_3(OH)_3]_{(s)}} + 3H_2O_{(l)}$$

$$Al^{3+}_{(aq)} + 3OH^-_{(aq)} \rightleftharpoons \underset{\text{White precipitate}}{Al(OH)_{3(s)}}$$

- Adding acid will reverse these reactions.

**The amphoteric nature of aluminium hydroxide, $Al(OH)_3$:**

**Amphoteric:**

***A species that can behave as an acid or a base***

- Remember, aluminium hydroxide can be written as:

$$Al(OH)_3 \quad \text{or} \quad [Al(H_2O)_3(OH)_3]$$

**With an acid:**

$$\underset{\text{White precipitate}}{[Al(H_2O)_3(OH)_3]} + 3H^+ \rightarrow \underset{\text{colourless solution}}{[Al(H_2O)_6]^{3+}}$$

Can be simplified to:

$$\underset{\text{White precipitate}}{Al(OH)_3} + 3H^+ \rightarrow \underset{\text{colourless solution}}{Al^{3+}} + 3H_2O$$

- White precipitate dissolves to give a clear colourless solution

**With a base:**

$$\underset{\text{White precipitate}}{[Al(H_2O)_3(OH)_3]} + OH^- \rightarrow \underset{\text{colourless solution}}{[Al(H_2O)_2(OH)_4]^-} + H_2O$$

Can be simplified to:

$$\underset{\text{White precipitate}}{Al(OH)_3} + OH^- \rightarrow \underset{\text{colourless solution}}{Al(OH)_4^-} + H_2O$$

- White precipitate dissolves to give a clear colourless solution

**$M^{2+}$ ion:** Consider the dissolved metal 2+ ion:

$$[M(H_2O)_6]^{2+}_{(aq)} + OH^-_{(aq)} \rightleftharpoons [M(H_2O)_5(OH)]^+_{(aq)} + H_2O_{(l)}$$

$$[M(H_2O)_5(OH)]^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{[M(H_2O)_4(OH)_2]_{(s)}} + H_2O_{(l)}$$

- The product has neutral charge and therefore precipitates out of solution.

**Simplifying to:**

$$[M(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{[M(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

$$M^{2+}_{(aq)} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{M(OH)_{2(s)}}$$

**Examples:**

$$\underset{\text{Blue solution}}{[Cu(H_2O)_6]^{2+}_{(aq)}} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Pale blue precipitate}}{[Cu(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

$$\underset{\text{Blue solution}}{Cu^{2+}_{(aq)}} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Pale blue precipitate}}{Cu(OH)_{2(s)}}$$

$$\underset{\text{Green solution}}{[Fe(H_2O)_6]^{2+}_{(aq)}} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Green precipitate}}{[Fe(H_2O)_4(OH)_2]_{(s)}} + 2H_2O_{(l)}$$

$$\underset{\text{Green solution}}{Fe^{2+}_{(aq)}} + 2OH^-_{(aq)} \rightleftharpoons \underset{\text{Green precipitate}}{Fe(OH)_{2(s)}}$$

- The green precipitate goes brown in air as it is oxidised by the air

$$\underset{\text{Green precipitate}}{[Fe(H_2O)_4(OH)_2]_{(s)}} \rightleftharpoons \underset{\text{Brown precipitate}}{[Fe(H_2O)_3(OH)_3]_{(s)}} + H^+_{(aq)} + e^-$$

- Adding acid will reverse these reactions.

## 2) Reactions with ammonia, $NH_3$:

**$M^{3+}$ ion:**

- Reacts with ammonia in the same way as the hydroxide:
- Each $NH_3$ accepts a proton from the waters in the complex ion until a neutral salt is made:

$$[M(H_2O)_6]^{3+}{}_{(aq)} + 3NH_{3(aq)} \rightleftharpoons [M(H_2O)_3(OH)_3]_{(s)} + 3NH_4{}^+{}_{(aq)}$$

Precipitate

- The product has neutral charge and therefore precipitates out of solution.

**Examples:**

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

Yellow – brown solution → Brown precipitate

$$[Al(H_2O)_6]^{3+}{}_{(aq)} + 3NH_{3(aq)} \rightleftharpoons [Al(H_2O)_3(OH)_3]_{(s)} + 3NH_4{}^+{}_{(aq)}$$

Clear colourless solution → White precipitate

**$M^{2+}$ ion:**

$$[M(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [M(H_2O)_4(OH)_2]_{(s)} + 2NH_4{}^+{}_{(aq)}$$

Precipitate

- The product has neutral charge and therefore precipitates out of solution.

**Examples:**

$$[Fe(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Fe(H_2O)_4(OH)_2]_{(s)} + 2NH_4{}^+{}_{(aq)}$$

Green solution → Green precipitate

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_4(OH)_2]_{(s)} + 2NH_4{}^+{}_{(aq)}$$

Blue solution → Pale blue precipitate

With excess $NH_3$, Ligand substitution follows:

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

Pale blue precipitate → Dark blue solution

Overall:

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(H_2O)_2(NH_3)_4]^{2+}{}_{(aq)} + 4H_2O_{(l)}$$

Blue solution → Dark blue solution

### 3) Reactions with carbonates, $CO_3^{2-}$:

**$M^{3+}$ ion:**

- Reacts in the same way as the hydroxide but, as it is more acidic, it reacts with the carbonate forming $CO_2$ and $H_2O$.
- Each $CO_3^{2-}$ accepts a proton from the waters forming $CO_2$ and $H_2O$. The complex ion forms the neutral salt:

$$2[M(H_2O)_6]^{3+}_{(aq)} + 3CO_3^{2-}{}_{(aq)} \rightleftharpoons \underset{\text{Precipitate}}{2[M(H_2O)_3(OH)_3]_{(s)}} + 3CO_{2(g)} + 3H_2O_{(l)}$$

- The product has neutral charge and therefore precipitates out of solution.
- $CO_2$ gas is made so you will also see fizzing.

**Examples:**

$$\underset{\text{Yellow – brown solution}}{2[Fe(H_2O)_6]^{3+}_{(aq)}} + 3CO_3^{2-}{}_{(aq)} \rightarrow \underset{\text{Brown precipitate}}{2[Fe(H_2O)_3(OH)_3]_{(s)}} + 3CO_{2(g)} + 3H_2O_{(l)}$$

$$\underset{\text{Clear colourless solution}}{2[Al(H_2O)_6]^{3+}_{(aq)}} + 3CO_3^{2-}{}_{(aq)} \rightarrow \underset{\text{White precipitate}}{2[Al(H_2O)_3(OH)_3]_{(s)}} + 3CO_{2(g)} + 3H_2O_{(l)}$$

**$M^{2+}$ ion:**

- The $M^{2+}$ is not acidic enough to produce $CO_2$ with the carbonates.
- They react to from the insoluble metal carbonate:

$$[M(H_2O)_6]^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightarrow \underset{\text{Precipitate}}{MCO_{3(s)}} + 6H_2O_{(l)}$$

- The product has neutral charge and therefore precipitates out of solution.

**Examples:**

$$\underset{\text{Green solution}}{[Fe(H_2O)_6]^{2+}_{(aq)}} + CO_3^{2-}{}_{(aq)} \rightarrow \underset{\text{Green precipitate}}{FeCO_{3(s)}} + 6H_2O_{(l)}$$

$$\underset{\text{Blue solution}}{[Cu(H_2O)_6]^{2+}_{(aq)}} + CO_3^{2-}{}_{(aq)} \rightarrow \underset{\text{Blue - green precipitate}}{CuCO_{3(s)}} + 6H_2O_{(l)}$$

- ***Generally: Transition metal carbonates with an oxidation state of 3+ do not exist***

**Summary – Required practical 11: Carry out test tube reactions to identify metal ions in solution:**

| Metal | Aqueous ion | Addition of NaOH | Addition of excess NaOH | Addition of $NH_3(aq)$ | Addition of excess $NH_3$ (aq) | Addition of $Na_2CO_3$ (aq) |
|---|---|---|---|---|---|---|
| Fe(II) | | | | | | |
| Cu(II) | | | | | | |
| Fe(III) | | | | | | |
| A*l*(III) | | | | | | |