<u>Topic 14 – Metal Ions in Solution</u> <u>Revision Notes</u>

1) <u>Metal-aqua ions</u>

- When metal compounds dissolve in water, metal-aqua ions are formed
- 2+ metal-aqua ions include: $[Fe(H_2O)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$ and $[Cu(H_2O)_6]^{2+}$
- 3+ metal-aqua ions include: $[AI(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$
- The metal ions are behaving as Lewis acids because they are electron pair acceptors
- The water molecules are behaving as Lewis bases because they are electron pair donors

2) Acidity of metal-aqua ions

• M²⁺ solutions are very weakly acidic (pH about 6) due to the following equilibrium:

 $[\mathsf{M}(\mathsf{H}_2\mathsf{O})_6]^{2+} + \mathsf{H}_2\mathsf{O} \leftrightarrows [\mathsf{M}(\mathsf{H}_2\mathsf{O})_5\mathsf{OH}]^+ + \mathsf{H}_3\mathsf{O}^+$

• M³⁺ solutions are acidic (pH about 3) due to the following equilibrium:

$$[M(H_2O)_6]^{3+} + H_2O \rightleftharpoons [M(H_2O)_5OH]^{2+} + H_3O^+$$

- The acidity is caused by an O-H bond breaking in one of the ligands. This is an example of hydrolysis.
- M³⁺ solutions are more acidic than M²⁺ solutions because, in M³⁺, the metal ion has a greater charge/size ratio which means it has more ability to weaken bonds in the water molecules

3) <u>Reactions with bases</u>

a) NaOH

• With OH⁻ ions, a precipitation reaction occurs. The OH⁻ acts as a Bronsted-Lowry base

[Cu(H ₂ O) ₆] ²⁺ (aq) + 2OH ⁻ (aq) ≒	[Cu(H ₂ O) ₄ (OH) ₂](s) + 2H ₂ O(I)
Blue solution	blue precipitate
[Fe(H₂O)₀] ²⁺ (aq) + 2OH ⁻ (aq) ⇔	[Fe(H ₂ O) ₄ (OH) ₂](s) + 2H ₂ O(I)
Pale green solution	green precipitate
[Co(H₂O) 6] ²⁺ (aq) + 2OH ⁻ (aq) ≒	[Co(H ₂ O) ₄ (OH) ₂](s) + 2H ₂ O(I)
Pink solution	blue-green precipitate
[Fe(H₂O)₀] ³⁺ (aq) + 3OH ⁻ (aq) ≒	[Fe(H ₂ O) ₃ (OH) ₃](s) + 3H ₂ O(l)
Pale violet solution (appears yellow)	brown precipitate
[Cr(H₂O)₀] ³⁺ (aq) + 3OH ⁻ (aq) ⇒	[Cr(H ₂ O) ₃ (OH) ₃](s) + 3H ₂ O(l)
Red-violet solution	green precipitate
[AI(H₂O)₀] ³⁺ (aq) + 3OH ⁻ (aq) ⇒	[AI(H ₂ O) ₃ (OH) ₃](s) + 3H ₂ O(I)
Colourless solution	white precipitate

- [Fe(H₂O)₄(OH)₂](s) is a green precipitate that turns to a brown solid on standing as it is oxidised by air to [Fe(H₂O)₃(OH)₃](s)
- The precipitation reactions are reversible. If acid is added to [Cu(H₂O)₄(OH)₂](s), for example, the precipitate will dissolve to give a blue solution containing [Cu(H₂O)₆]²⁺(aq)
- The precipitates of aluminium hydroxide and chromium hydroxide dissolve in excess NaOH

 $[AI(H_2O)_3(OH)_3](s) + OH^{-}(aq) \rightarrow [AI(H_2O)_2(OH)_4]^{-}(aq) + H_2O(I)$ Colourless solution

 $[Cr(H_2O)_3(OH)_3](s) + 3OH^{-}(aq) \rightarrow [Cr(OH)_6]^{3-}(aq) + 3H_2O(I)$

Green solution

• Because the precipitates of aluminium hydroxide and chromium hydroxide dissolve in both acids and bases they are described as amphoteric

b) NH₃(aq)

• The same precipitates are obtained with ammonia solution, NH₃(aq). The ammonia acts as a Bronsted-Lowry base

 $[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \approx [Cu(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$ $[Fe(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \approx [Fe(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$ $[Co(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \approx [Co(H_2O)_4(OH)_2](s) + 2NH_4^+(aq)$ $[Fe(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \approx [Fe(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$ $[Cr(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \approx [Cr(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$ $[Al(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \approx [Al(H_2O)_3(OH)_3](s) + 3NH_4^+(aq)$

c) Carbonates

• With M²⁺, the metal carbonate is precipitated e.g.

 $Cu^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CuCO_3(s)$ Blue solution blue-green precipitate

- CoCO₃ is a mauve precipitate and FeCO₃ is a green precipitate
- With the more acidic M³⁺, effervescence and a coloured precipitate are seen e.g.

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

3) Ligand substitution reactions

• In ligand substitution, the incoming ligand acts as a Lewis base (lone pair donor)

a) With ammonia solution

- Ammonia and water are similar in size and uncharged. Ligand exchange occurs without change of co-ordination number
- Firstly, a precipitation reaction occurs (see above). In some cases, with excess ammonia, the precipitate dissolves.
- With copper(II) the overall effect is to replace 4 water ligands by ammonias
- With cobalt(II) and chromium(III), the overall effect is to replace all 6 waters by ammonias

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow$	$[Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$
Blue solution	dark blue solution
[Co(H₂O)₀] ²⁺ (aq) + 6NH₃(aq) →	[Co(NH ₃) ₆] ²⁺ (aq) + 6H ₂ O(I)
Pink solution	straw coloured solution
$[Cr(H_2O)_6]^{3+}(aq) + 6NH_3(aq) \rightarrow$	[Cr(NH ₃) ₆] ³⁺ (aq) + 6H ₂ O(I)
Red-blue solution	purple solution

[Co(NH₃)₆]²⁺(aq) is rapidly oxidised by air to [Co(NH₃)₆]³⁺(aq) and the solution goes darker in colour

b) With concentrated HCI or saturated NaCI(aq)

- Chloride is larger than ammonia and water. When Cl⁻ replaces water the coordination number is reduced from 6 to 4
- Concentrated HCI and saturated NaCI(aq) are sources of the chloride ligand, CI⁻

 $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \rightarrow$ Blue solution

 $[Co(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \rightarrow$ Pink solution $[CoCl_4]^{2-}(aq) + 6H_2O(l)$

 $[CuCl_4]^{2-}(aq) + 6H_2O(l)$

yellow-green solution

blue solution

c) Entropy effects

- Substitution of a unidentate ligand by a bidentate or multidentate ligand leads to a more stable complex
- These reactions have small enthalpy changes because one co-ordinate bond is formed for each co-ordinate bond that is broken
- However, the reactions have positive entropy changes because the number of particles increases from left to right so disorder increases
- As ΔH is small and ΔS is positive, ΔG is negative

 $[Cu(H_2O)_6]^{2+}(aq) + EDTA^{4-}(aq) \rightarrow [CuEDTA]^{2-}(aq) + 6H_2O(l)$ 2 particles 7 particles

4) <u>Variable oxidation state</u>

a) <u>Chromium</u>

- The main oxidation states of chromium are +6, +3 and +2
- The +6 state occurs in chromate(VI), CrO₄²⁻, and dichromate(VI), Cr₂O₇²⁻
- Chromium(VI) species can be interconverted using H⁺ and OH⁻ (applying Le Chatelier's principle). Note that there is no change of oxidation state in this reaction

 $\begin{array}{c} 2CrO_4^{2-} + 2H^+ \leftrightarrows Cr_2O_7^{2-} + H_2O \\ \text{Yellow} \qquad \text{orange} \end{array}$

• Chromium can be reduced from its +6 oxidation state to the +3 state using zinc in acid solution:

- In the absence of air, the reduction with zinc can continue to give blue $Cr^{2+}(aq)$
- Chromium(III) can be oxidised to chromium(VI) using hydrogen peroxide in alkaline solution (H₂O₂/NaOH):

$$2Cr^{3+} + 3O_2^{2-} + 4OH^{-} \rightleftharpoons 2CrO_4^{2-} + 2H_2O$$

b) <u>Cobalt</u>

 Cobalt(II) can be oxidised to cobalt(III) using hydrogen peroxide in alkaline solution (H₂O₂/NaOH):

 $\begin{array}{ll} 2[Co(NH_3)_6]^{2+} + H_2O_2 \rightarrow 2[Co(NH_3)_6]^{3+} + 2OH^-\\ \text{Pale yellow solution} & \text{brown solution} \end{array}$

• Cobalt(II) can be oxidised to cobalt(III) by air in ammoniacal solution:

$$4[Co(NH_3)_6]^{2+} + 4H^+ + O_2 \rightarrow 4[Co(NH_3)_6]^{3+} + 2H_2O$$