Chem Factsheet

January 2003 Number 46

Transition Metals 2 - Compounds and Reactions

To succeed in this topic you need to:
- Understand the principle of oxidation numbers.
- Understand types of bonding and molecular shapes.
- Understand the basics of Transition Metals (covered in Factsheet 38)

After working through this Factsheet you will:
- Have more experience of transition metal compounds;
- Recall the reactions of transition metal ions with hydroxides and ammonia;
- Recall the oxidation states of vanadium, and how they can be interconverted.

The following simple test tube reactions illustrate the behaviour of transition metal ions.

Addition of aqueous alkali to transition metal ions

Practical 1 – Addition of sodium hydroxide solution
Dilute sodium hydroxide solution is added dropwise to aqueous transition metal ions. Initially a precipitate is looked for, then the sodium hydroxide is added to excess to find out if the precipitate will eventually re-dissolve.

Ion	Addition of NaOH (aq)	Excess NaOH (aq)
Cr^{3+}	Green ppt	Green solution
Mn^{2+}	Buff ppt, darkens in air	Precipitate does not dissolve
Fe^{2+}	Pale green ppt, browns on surface	Precipitate does not dissolve
Fe^{3+}	Red brown ppt	Precipitate does not dissolve
Co^{2+}	Blue ppt, turns brown in air	Precipitate does not dissolve
Ni^{2+}	Pale green	Precipitate does not dissolve
Cu^{2+}	Pale blue ppt	Precipitate does not dissolve
Zn^{2+}	White ppt	Colourless solution

The equations for these reactions are similar; each of the transition metal ions should be written as the hexa-aqua ion, except for zinc which forms a tetra-aqua ion. In each case the precipitates formed are the simple hydroxide compounds.

For example:

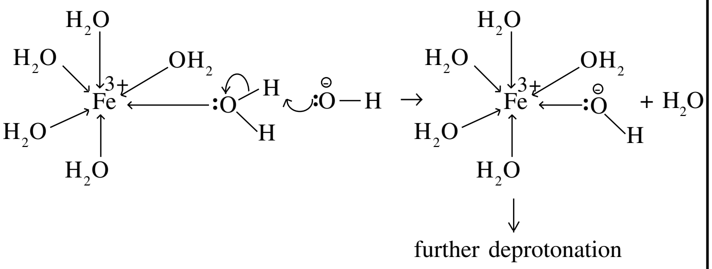
$$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow Mn(OH)_2(s) + 6H_2O(l)$$

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

and for zinc,

$$[Zn(H_2O)_4]^{2+}(aq) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 4H_2O(l)$$

The reaction mechanism for this process is important and often examined. When aquatic transition metal ion react with hydroxide ions the reaction mechanism is **deprotonation**.



Notice how a H^+ ion (a proton) is removed from the aqua ligand leaving a hydroxide ion. Note that this is **not** a ligand exchange.

As can be seen from the results, few transition metal ions react in excess sodium hydroxide.

Most metal hydroxides are basic, so the metal hydroxide precipitates formed in these reactions do not react in excess sodium hydroxide, itself a strong base.

However, some metal hydroxides (e.g. $Cr(OH)_3$) are **amphoteric**, so **will** react with NaOH.

$$Cr(OH)_3(s) + 3OH^-(aq) \rightarrow \underset{\text{Deep green solution}}{[Cr(OH)_6]^{3-}(aq)}$$

Practical 2 – Addition of ammonia solution
Dilute ammonia solution is added dropwise to aquatic transition metal ions. Initially a precipitate is looked for, then the ammonia solution is added to excess to find out if the precipitate will eventually re-dissolve.

Ion	Addition of NH_3 (aq)	Addition of excess NH_3 (aq)
Cr^{3+}	Green ppt	Precipitate does not dissolve
Mn^{2+}	Buff ppt, darkens in air	Precipitate does not dissolve
Fe^{2+}	Pale green ppt, browns on surface	Precipitate does not dissolve
Fe^{3+}	Red brown ppt	Precipitate does not dissolve
Co^{2+}	Blue ppt, turns brown in air	Precipitate does not dissolve
Ni^{2+}	Pale green	Blue sloution
Cu^{2+}	Pale blue ppt	Deep blue solution
Zn^{2+}	White ppt	Colourless solution

On adding aqueous ammonia solution, it is hydroxide (OH^-) ions, which are again introduced and react with the transition metal ions.

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$

The precipitates which form are therefore the metal hydroxides again, just as when sodium hydroxide was the aqueous alkali added.

It is when the ammonia solution is added to excess that the reactions vary when comparing results to practical 1.

Ammonia is a **weak** base, too weak to react with the amphoteric metal hydroxides (e.g. $Cr(OH)_3$).

However, some transition metals will form complexes with ammonia as a ligand when it is added to excess.

For example: Copper

Stage 1 – NH_3 (aq) added dropwise

$$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow \underset{\text{pale blue precipitate}}{Cu(OH)_2(s)} + 2NH_4^+(aq) + 4H_2O(l)$$

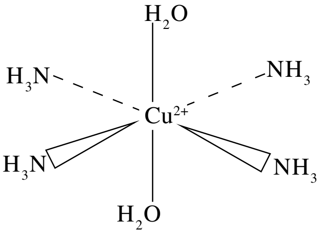
A **deprotonation** reaction

Stage 2 - NH_3 (aq) added to excess

$$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow \underset{\text{Deep blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 2OH^-(aq)$$

A **ligand exchange** reaction

The resulting solution is an **ammine complex**, where the NH_3 ligand has taken the place of the H_2O ligands (or at least some of them).



The Chemistry of Vanadium

Vanadium compounds exist in 4 oxidation states.

Oxidation state	Common ion	Colour
V(+5)	VO_2^+	Yellow
V(+4)	VO^{2+}	Blue
V(+3)	V^{3+}	Green
V(+2)	V^{2+}	Lavender

Reduction by zinc

If zinc is added to a solution of sodium vanadate (VO_2^+ ions) in dilute hydrochloric acid the +5 oxidation state is steadily reduced to the +2 oxidation state, and the colour changes can be observed.

$$\underset{\text{yellow}}{VO_2^+} \longrightarrow \underset{\text{blue}}{VO^{2+}} \longrightarrow \underset{\text{green}}{V^{3+}} \longrightarrow \underset{\text{lavender}}{V^{2+}}$$

Oxidation by potassium manganate (VII)

V^{2+} ions can be oxidised all the way to yellow VO_2^+ ions by the steady addition of potassium manganate (VII), a strong oxidising agent. Again the associated colour changes can be observed with careful addition.

$$\underset{\text{lavender}}{V^{2+}} \longrightarrow \underset{\text{green}}{V^{3+}} \longrightarrow \underset{\text{blue}}{VO^{2+}} \longrightarrow \underset{\text{yellow}}{VO_2^+}$$

More redox reactions of vanadium

Depending on the oxidising or reducing strengths of the vanadium species and the reagents reacting with them, the four oxidation states can be interconverted.

In an exam situation candidates would be expected to deduce different conversions between oxidation states given their $E^\ominus$ values and those of the reagents. See Factsheet 47 for the data and explanation required for these questions, plus examples.

Questions

1. Copper (II) nitrate crystals are dissolved in water and the solution is split between two test tubes, A and B.
   2M sodium hydroxide solution is added to test tube A dropwise and then to excess.
   2M ammonia solution is added to test tube B dropwise and then to excess.

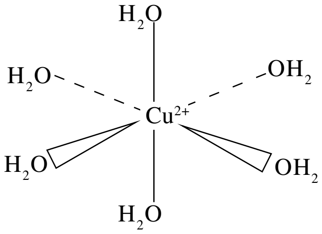
   (a) Draw and name the aqua complex of copper formed when copper (II) nitrate crystals are dissolved in water.

   (b) Describe the expected observations in:
      (i) Test tube A.
      (ii) Test tube B.

   (c) Give equations for the chemical changes, and name the reaction mechanisms, caused by the addition of the different alkalis in:
      (i) Test tube A (1 equation).
      (ii) Test tube B (2 equations).

Answers

1. (a)



Hexaaquacopper (II) ions

(b) (i) Pale blue precipitate formed on addition of NaOH (aq). Precipitate does not dissolve on further addition of alkali.

(ii) Pale blue precipitate formed on addition of ammonia solution. Precipitate dissolves to give deep blue solution on addition of ammonia solution to excess.

(c) (i)

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{pale blue precipitate}}{Cu(OH)_2(s)} + 6H_2O(l)$$

This is a deprotonation reaction.

(ii)

$$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightarrow \underset{\text{pale blue precipitate}}{Cu(OH)_2(s)} + 2NH_4^+(aq) + 4H_2O(l)$$

This is a depronoration reaction

$$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow \underset{\text{Deep blue solution}}{[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)} + 2OH(aq)$$

This is a ligand exchange reaction.

Acknowledgements:
This Factsheet was researched and written by Kieron Heath
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