Chem Factsheet

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The Chemistry of Copper

To succeed in this topic you need to understand:
- the basics of transition metals (covered in Factsheet 28);
- the reactions of transition metal ions with hydroxides and ammonia (covered in Factsheet 46);
- the principles of oxidation and reduction (covered in Factsheet 11).

After working through this Factsheet you will:
- know that copper will not liberate hydrogen from dilute acids but is attacked by oxidising acids;
- know that the oxidation states of copper are +1 and +2;
- understand the action of water on copper(I) salts;
- understand the relationships between the principal compounds of copper;
- understand the chemistry of both copper(I) oxide and copper(II) oxide;
- understand the aqueous chemistry of $Cu^{2+}(aq)$;
- know the preparation of copper(I) chloride and its reaction with concentrated hydrochloric acid.

The element

Copper (atomic number = 29) is the last member of the first series of d-block transition elements.(Remember that zinc is not a transition element.)

Its electronic configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^1$. This arrangement, in which all five 3d orbitals are fully occupied, is more stable than the alternative $[Ar]\ 3d^9, 4s^2$.

Copper is a brownish red metal with a high density (8.92 g cm^{-3}). It has a high thermal conductivity (hence its use in saucepans) and a high electrical conductivity (hence its use in electrical wiring).

***Exam Hint** - Do not say that copper is used for electricity cables, because this implies that it is used for overhead power lines. It is too heavy and expensive for this purpose. Aluminium is used instead.*

Copper is a relatively unreactive metal but is attacked by oxidising acids, notably nitric acid and concentrated sulphuric acid.

Practical 1 - The action of nitric acid on copper

Heat a piece of copper foil in a boiling tube with dilute nitric acid. The copper dissolves to give a blue solution of copper(II) nitrate and brown fumes of nitrogen dioxide. **Caution!** These fumes are toxic.
Copper atoms are oxidised to Cu^{2+} ions: at the same time, NO_3^- ions are reduced to molecules of NO which, with O_2 from the air, become oxidised to molecules of NO_2.

Practical 2 - The action of hydrochloric acid on copper

Heat a piece of copper foil in a boiling tube with dilute hydrochloric acid. Notice that there is no apparent reaction.

Copper lies below hydrogen in the electrochemical series and will not liberate hydrogen from dilute acids.

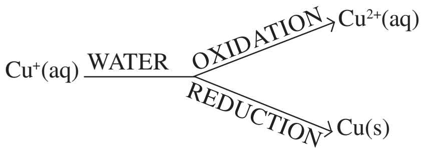
Oxidation states

The oxidation states of copper are +1 and +2.

Principal compounds and ions are as follows.
- **Cu^I** The copper(I) ion, Cu^+, copper(I) oxide, Cu_2O, copper(I) chloride, CuCl, and various complex ions such as $[CuCl_2]^-$. There is no hydroxide.
- The electronic configuration of the Cu^+ ion is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$.
- **Cu^{II}** Copper(II) oxide, CuO, copper(II) hydroxide, $Cu(OH)_2$, the copper(II) ion, Cu^{2+}, and various complex ions such as the hydrated copper(II) ion, $[Cu(H_2O)_6]^{2+}$.
- The electronic configuration of the Cu^{2+} ion is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^9$.

Stability of oxidation states

Although Cu^I and Cu^{II} are of comparable stability, the Cu^+ ion disproportionates in aqueous solution.



Copper(I) sulphate, for example, an off-white solid, dissolves in water to give a blue solution of copper(II) sulphate and a reddish brown precipitate of copper.

***Exam Hint** - Disproportionation should be defined as the simultaneous oxidation and reduction of a single species or a single substance.*

The copper(I) state is particularly stable in three circumstances.
- At high temperatures. Some copper(II) compounds decompose on heating into the corresponding copper(I) compounds, e.g.

  $$2CuCl_2(s) \rightarrow 2CuCl(s) + Cl_2(g)$$

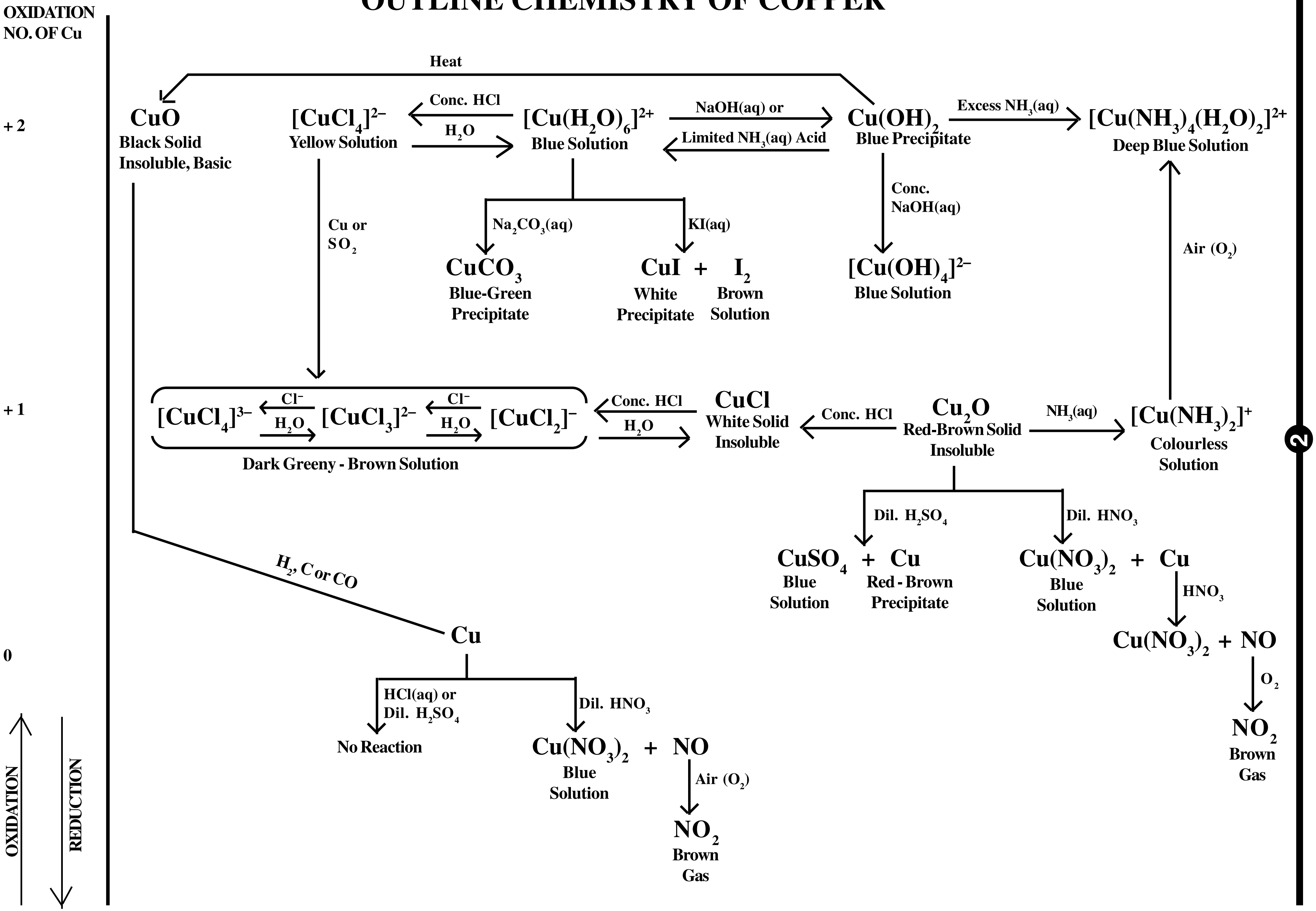
- In insoluble compounds, e.g. Cu_2O and CuCl.
- In complex ions, e.g. $[CuCl_2]^-$ and $[Cu(NH_3)_2]^+$.

Redox chart

On the redox chart of copper (p 2), the principal compounds and ions have been arranged in order of oxidation number.

- Any movement up the chart represents an oxidation process, for which an oxidising agent is required.
- Movement down the chart corresponds to reduction. For this, a reducing agent is needed.
- Movement across the chart is neither oxidation nor reduction, and is achieved with reagents such as dilute acids, NaOH(aq), $NH_3(aq)$ or $Na_2CO_3(aq)$.

OUTLINE CHEMISTRY OF COPPER



Oxides

Copper forms two oxides, both of which are basic.

Copper(I) oxide, Cu_2O
This compound is prepared by reducing copper(II) salts in alkaline solution.

Practical 3 - Preparation of copper(I) oxide
Pour into a boiling tube roughly equal volumes of Fehling's solution A (copper(II) sulphate) and Fehling's solution B (an alkaline solution of potassium sodium tartrate) and mix. Then add a few drops of ethanal and boil cautiously. The dark blue colour of the solution fades to give a reddish brown precipitate of copper(I) oxide.
A redox reaction occurs in which ethanal is oxidised to a salt of ethanoic acid while Cu^{II}, in the form of a complex tartrate, is reduced to Cu^{I} which appears as Cu_2O.

Remember - *This reaction is used in organic chemistry to distinguish between aldehydes and ketones. Ketones will not reduce Fehling's solution because, unlike aldehydes, they are resistant to oxidation.*

Copper(I) oxide is a reddish brown solid which is insoluble in water but soluble in acids.

Copper(I) oxide reacts with dilute sulphuric acid, dilute nitric acid and concentrated hydrochloric acid, but the products are ***not*** *copper(I) sulphate, copper(I) nitrate and copper(I) chloride. Copper(I) sulphate and copper(I) nitrate disproportionate in water (see above), while copper(I) chloride dissolves in conc. HCl(aq) to give complex ions.*

Practical 4 - Cu_2O with dilute H_2SO_4
Add Cu_2O to dilute sulphuric acid in a test tube and warm gently. A blue solution of copper(II) sulphate is formed. The reddish brown solid *appears* to remain unaltered, but in fact changes from Cu_2O to Cu.

Practical 5 - Cu_2O with dilute HNO_3
Add Cu_2O to dilute nitric acid in a test tube. On warming, the Cu_2O dissolves to give a clear blue solution of $CuSO_4$ plus brown fumes of NO_2. **Caution!** These fumes are toxic. From Practical 4, a red-brown deposit of Cu might be anticipated, but Practical 1 shows that Cu dissolves in dil. HNO_3.

Practical 6 - Cu_2O with concentrated HCl(aq)
Add conc. HCl(aq) to a little Cu_2O and heat to obtain a dark greenish brown solution containing various chloro-complex ions of copper(I) (p 4).

Copper(I) oxide is also attacked by concentrated aqueous ammonia because the NH_3 molecule is a ligand and can coordinate to the Cu^+ ion.

Practical 7 - Cu_2O with concentrated NH_3(aq)
Add conc. NH_3(aq) to a little Cu_2O in a test tube, warm *gently*, shake *carefully*, and allow to stand. The solution above the unreacted Cu_2O will be blue. The diamminecopper(I) ion, $[Cu(NH_3)_2]^+$, is formed, but O_2 from the air oxidises this to the dark blue copper(II) complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

Copper(II) oxide, CuO
Copper(II) oxide is a black solid that can be prepared by heating $Cu(OH)_2$, $CuCO_3$ or $Cu(NO_3)_2$. It is insoluble in water but dissolves in dilute acids to give solutions of Cu^{II} salts.

Practical 8 - Preparation of $CuSO_4.5H_2O$
Pour dil. H_2SO_4 into a beaker, heat it, and add CuO with stirring until no more will dissolve. Filter off the excess CuO. Transfer the filtrate to an evaporating basin, place it on a tripod and gauze, and boil the solution until crystals show signs of forming. Turn out the heat and allow the solution to cool and crystallise. Filter off the crystals, wash them with a little deionised water, and dry.

Exam Hint - *'Crystallisation' is different from 'evaporation to dryness'. The latter is not recommended because:*
- *it gives poorly formed crystals;*
- *there may not be enough water left to act as water of crystallisation, resulting in the formation of anhydrous copper(II) sulphate;*
- *impurities leave solution with the $CuSO_4.5H_2O$ contaminating it.*

Aqueous chemistry of copper(II)

$[Cu(H_2O)_6]^{2+}$(aq) takes part in acid-base reactions (deprotonation) with OH^-(aq) and NH_3(aq), ligand substitution with Cl^-(aq), precipitation with CO_3^{2-}(aq), and oxidation-reduction with I^-(aq).

Practical 9 - Cu^{II} salts with OH^-(aq)
Add dilute NaOH(aq) dropwise, with shaking, to a solution of a copper(II) salt. A gelatinous pale blue precipitate of hydrated copper(II) hydroxide is formed. Two protons are transferred from molecules of coordinated water to hydroxide ions:

$$\underset{-2H^+}{\overset{+2H^+}{[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \rightarrow [Cu(OH)_2(H_2O)_4](s) + 2H_2O(l)}}$$

Exam Hint - *Do not show this as a precipitation reaction. All transition metal ions, and Al^{3+}, react with OH^-(aq) and NH_3(aq) in acid-base (deprotonation) reactions.*

Divide the precipitate of copper(II) hydroxide into two portions. To one portion add *concentrated* NaOH(aq) and notice that it dissolves to give a blue solution containing the tetrahydroxocuprate(II) ion:

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

Remember - Although CuO is basic, $Cu(OH)_2$ is amphoteric.

Heat the other portion of $Cu(OH)_2$ and see how the colour changes from blue to black as the hydroxide decomposes into the oxide:

$$[Cu(OH)_2(H_2O)_4](s) \rightarrow CuO(s) + 5H_2O(l)$$

Remember - *Nearly all metal hydroxides decompose into the corresponding oxides on heating. The only ones which are stable to heat are those of the alkali metals.*

Practical 10 - Cu^{II} salts with $NH_3(aq)$

Add dilute $NH_3(aq)$ dropwise, with shaking, to a solution of a copper(II) salt. A gelatinous blue precipitate of hydrated copper(II) hydroxide is formed at first in an acid-base reaction:

$$[Cu(H_2O)_6]^{2+}(aq) \ + \ 2NH_3(aq) \ \rightarrow \ [Cu(OH)_2(H_2O)_4](s) \ + \ 2NH_4^+(aq)$$

Now add excess dil. $NH_3(aq)$. The precipitate dissolves in a ligand substitution reaction to give a deep blue solution containing the tetraamminediaquacopper(II) ion:

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

Add ethanol to this solution to obtain a deposit of tiny crystals of $[Cu(NH_3)_4]SO_4.H_2O$ which can be filtered off and dried at room temperature.

> ***Exam Hint*** *- The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion has a distorted octahedral shape. NH_3 molecules surround the Cu^{2+} ion in a square planar arrangement, with H_2O molecules above and below this plane but relatively far from Cu^{2+}. Never describe this ion as 'square planar' because this description ignores the H_2O molecules.*

Practical 11 - Cu^{II} salts with $Cl^-(aq)$

Add concentrated HCl(aq) dropwise, with shaking, to a solution of a copper(II) salt. The solution changes colour from blue to green and then to yellow as a ligand substitution reaction occurs to form the tetrachlorocuprate(II) ion:

$$\underset{\text{Blue}}{[Cu(H_2O)_6]^{2+}(aq)} \ + \ 4Cl^-(aq) \ \rightleftharpoons \ \underset{\text{Yellow}}{[CuCl_4]^{2-}(aq)} \ + \ 6H_2O(l)$$

The reaction is reversible. Add water to the $[CuCl_4]^{2-}$ solution and notice that the colour changes back to green and then to blue.

Practical 12 - Cu^{II} salts with $CO_3^{2-}(aq)$

Add $Na_2CO_3(aq)$ dropwise, with shaking, to a solution of a copper(II) salt until the reagent is eventually present in excess. Blue-green copper(II) carbonate, which does not dissolve in excess $Na_2CO_3(aq)$, is formed in a precipitation reaction:

$$Cu^{2+}(aq) \ + \ CO_3^{2-}(aq) \ \rightarrow \ CuCO_3(s)$$

> ***Remember***
> - *With $Na_2CO_3(aq)$, all $M^{2+}(aq)$ ions give a precipitate of the metal carbonate, MCO_3. $M^{3+}(aq)$ ions, in contrast, give a precipitate of the metal hydroxide, $M(OH)_3$, plus effervescence due to $CO_2(g)$.*
> - *Precipitates formed with $Na_2CO_3(aq)$ never dissolve in excess reagent.*

Practical 13 - Cu^{II} salts with $I^-(aq)$

Add KI(aq) to a solution of a copper(II) salt, shake and allow to stand. A white precipitate of copper(I) iodide settles underneath a brown solution of iodine. A redox reaction occurs in which Cu^{2+} oxidises I^- to I_2, and is itself reduced to Cu^+:

$$2Cu^{2+}(aq) \ + \ 4I^-(aq) \ \rightarrow \ 2CuI(s) \ + \ I_2(aq)$$

> ***Remember***
> - *The product is copper(I) iodide; not copper(II) iodide.*
> - *Copper(II) iodide does not exist. If it did, it would decompose into copper(I) iodide and iodine by electron transfer from anion to cation:*
>
> $$\overset{\curvearrowleft}{Cu^{++} \ \ I^- \, I^{\ominus}} \ \rightarrow \ Cu^+ I^- \ + \ I \qquad (2I \rightarrow I_2)$$
>
> - *The same applies to any other salt (e.g. iron(III) iodide) consisting of a cation that is easily reduced and an anion that is easily oxidised.*

Copper(I) chloride, CuCl

> - *Copper(I) chloride is prepared by reducing $[CuCl_4]^{2-}$ with Cu or SO_2.*
> - *It dissolves in conc. HCl(aq) to give a series of chloro-complexes.*

Practical 14 - Preparation of copper(I) chloride

To $CuSO_4(aq)$ in a boiling tube, add conc. HCl(aq) until the solution turns yellow. This produces $[CuCl_4]^{2-}$. Add a few pieces of copper foil and boil for a few minutes until the solution changes colour to a dark greenish brown. $[CuCl_4]^{2-}$ becomes reduced to chloro-complexes of copper(I), e.g.

$$[CuCl_4]^{2-}(aq) \ + \ Cu(s) \ \rightarrow \ 2[CuCl_2]^-(aq)$$

Now pour the contents of the tube into cold water in a beaker. This decomposes the chloro-complexes (see below) to give a white precipitate of CuCl that can be filtered off, washed and dried.

Practical 15 - CuCl with conc. HCl(aq)

Add conc. HCl(aq) to CuCl and shake. The white solid dissolves to give a dark greenish brown solution containing three complex ions of copper(I) in equilibrium with one another.

$$CuCl \ \xrightleftharpoons[H_2O]{Cl^-} \ [CuCl_2]^- \ \xrightleftharpoons[H_2O]{Cl^-} \ [CuCl_3]^{2-} \ \xrightleftharpoons[H_2O]{Cl^-} \ [CuCl_4]^{3-}$$

At high concentrations of Cl^- the dominant ion is $[CuCl_4]^{3-}$.
At low concentrations of Cl^- equilibrium is disturbed to the left hand side. Add water to the dark brown solution and see the reprecipitation of CuCl.

> ***Exam Hint - Do not confuse the tetrachloro-complexes of copper(I) and copper(II). They have different charges and different colours.***
>
> ***Cu^I: $[CuCl_4]^{3-}$ Dark greenish brown***
> ***Cu^{II}: $[CuCl_4]^{2-}$ Yellow***

Questions

1 Devise a simple test, not requiring laboratory reagents, for distinguishing between solutions containing $[CuCl_4]^{2-}$ and $[CuCl_4]^{3-}$ ions. State what you would observe in each case.

2 This question concerns the following ions: $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$

A **B**

(a) Name **A** and **B**.

(b) State the colours of **A** and **B**.

(c) State the shapes of **A** and **B**.

(d) Explain the difference in coordination numbers.

3 **U**, **V** and **W** are three dark coloured solids, insoluble in water. They all dissolve in dilute nitric acid to give a blue solution of compound **X**. At the same time **U** and **W** evolve brown fumes but **V** does not do so. With concentrated hydrochloric acid, **U** does not dissolve, but **V** dissolves to give a green solution **Y** and **W** dissolves to to give a greenish brown solution **Z**.

(a) Identify **U**, **V** and **W**.

(b) *Name* the blue compound **X**.

(c) Write a balanced equation, with state symbols, for **V** dissolving in dilute nitric acid.

(d) Write down the formulae of *all* copper containing ions in solutions **Y** and **Z**.

4 Suggest why, when copper(I) chloride is shaken with water, the aqueous extract is green.

5 Explain why copper(II) sulphate-5-water is coloured, although copper(I) sulphate and anhydrous copper(II) sulphate are both colourless.

Answers

1 Add water. Solution of $[CuCl_4]^{2-}$ changes colour to green and then blue. Solution of $[CuCl_4]^{3-}$ gives a white precipitate.

2 (a) **A** = hexaaquacopper(II) **B** = tetrachlorocuprate(II)
(b) **A** is blue. **B** is yellow.
(c) **A** is octahedral/distorted octahedral. **B** is tetrahedral.
(d) The Cl^- ion is a larger ligand than the H_2O molecule and fewer of them can be packed around the small Cu^{2+} cation.

3 (a) **U** = Cu **V** = CuO **W** = Cu_2O
(b) Copper(II) nitrate
(c) $CuO(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + H_2O(l)$
(d) **Y** contains $[Cu(H_2O)_6]^{2+}$ and $[CuCl_4]^{2-}$. **Z** contains $[CuCl_2]^-$, $[CuCl_3]^{2-}$ and $[CuCl_4]^{2-}$.

4 CuCl dissolves slightly to give a solution containing Cu^+ and Cl^-. Cu^+ disproportionates giving $[Cu(H_2O)_6]^{2+}$ (blue) which, with Cl^-, gives some $[CuCl_4]^{2-}$ (yellow). O_2 from the air assists the oxidation of Cu^I to Cu^{II}.

5 3d electrons are split by ligands into two sets of d-orbitals. There are three orbitals in the lower energy set and two in the upper set. Certain frequencies of white light can be absorbed in promoting electrons from the lower to the upper set. Transmitted light is deficient in these frequencies and therefore appears coloured. $[Cu(H_2O)_4]^{2+}$ in $CuSO_4.5H_2O$ absorbs the red and yellow frequencies but transmits blue and green.
Anhydrous $CuSO_4$ contains simple Cu^{2+} ions (no ligands), so there is no splitting of the d-orbitals. The Cu^+ ion in Cu_2SO_4 has all its 3d orbitals fully occupied. If there are no vacancies in the upper set, promotion cannot occur.

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