

FACTFILE: GCE CHEMISTRY

5.5 TRANSITION METALS



Transition metals

Learning Outcomes

- 5.5.1 recall that transition metals or their ions have an incomplete d-shell, variable oxidation states, catalytic activity, and form coloured complexes; and
- 5.5.2 deduce the electronic configuration of transition metals and their ions and explain their stabilities based on the filling of the sub-shells.
- 5.5.3 demonstrate understanding that complexes consist of a central metal atom or ion surrounded by a number of ligands, defined as anions or molecules possessing lone pairs of electrons;
- 5.5.4 explain that ligands are molecules or atoms that contain a lone pair which can be donated to a transition metal atom or ion;
- 5.5.5 explain the meaning of and deduce coordination numbers in complexes;
- 5.5.6 deduce the oxidation number of transition metals in complexes and use them to explain redox and disproportionation reactions;
- 5.5.7 demonstrate understanding of the distinction between monodentate, for example Cl^- , H_2O and NH_3 and bidentate, for example $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (represented by en) and polydentate ligands (edta);
- 5.5.8 explain the relative strengths of ligands in terms of the availability of lone pairs;
- 5.5.9 understand the ligand replacement reactions of hexaaquacopper(II) ions with concentrated hydrochloric acid and ammonia solution to include colours and shapes of the complexes;
- 5.5.10 explain ligand replacement in terms of positive entropy changes, for example a bidentate ligand displacing two monodentate ligands;
- 5.5.11 recall the colours of the aqueous complexes of Cr^{3+} , Cr(VI) , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , V^{2+} , V^{3+} , V(IV) , V(V) ; and
- 5.5.12 use as qualitative detection tests the formation of precipitates of the hydroxides of Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} with NaOH(aq) and $\text{NH}_3\text{(aq)}$ and, where appropriate, their subsequent dissolution.
- 5.5.13 recall the reduction of VO^{2+} (acidified ammonium metavanadate), by zinc to form VO^{2+} , V^{3+} and V^{2+} ;
- 5.5.14 deduce, given appropriate E° values, reagents for the interconversion of vanadium between its oxidation states and to combine half-cells to give an overall equation for a reaction;

A transition metal is an element which forms at least one ion with a partially filled d-subshell.

Scandium and zinc are d block elements but are not transition metals

It is the incomplete d sub-level that gives transition metals the properties listed below

- They form coloured complexes.
- They have variable oxidation states.
- The metals and their compounds act as catalysts e.g. nickel in the addition of hydrogen to alkenes.

Electronic configuration

When writing electronic configurations of the transition metals, remember that

- the 4s subshell fills before the 3d.
- when forming ions the 4s electrons are lost first
- copper has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ due to the extra stability of a filled 3d
- chromium has electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ due to the extra stability of a half filled 3d

Complexes

A complex is a central metal atom or ion with ligands bonded by coordinate bonds.

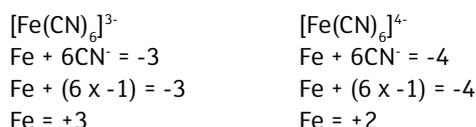
A ligand is an ion or molecule with a lone pair of electrons which forms a coordinate bond with a central metal atom or ion in a complex.

Common ligands include neutral molecules such as water (named aqua) and ammonia (named ammine) and anions such as chloro (Cl⁻), and cyano (CN⁻).

Coordination number is the number of coordinate bonds to a central metal atom or ion in a complex.

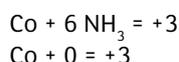
An example of a complex is $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ where the central metal ion is Cu^{2+} , the ligand is water and the coordination number is six.

It is possible to work out the oxidation state of the central metal atom. For example:-



The coordination number in each of these complexes is 6.

When the ligands in a complex are neutral then the charge on the complex is the same as the oxidation state on the metal atom or ion. For example in the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ the ligand is ammonia which is neutral so the oxidation state on the cobalt is +3.



Transition metal compounds may dissolve in water to form complex ions such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. These are called hexaaqua cations as they have six water ligands coordinately bonded to the metal ion.

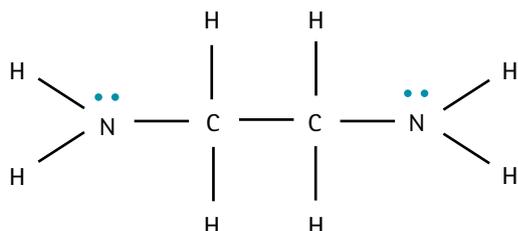
Dissolving solid copper(II) sulfate in water would produce a blue solution containing the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ion. The sulfate ion would also be present in the solution.

The table below shows the colours of some aqueous complexes.

Complex ion	Colour
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	green
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	pink
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	green
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	yellow/orange
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	pink
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	green
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	blue

Types of ligand

A monodentate ligand is a ligand which uses only one pair of electrons to form a coordinate bond with a central metal atom or ion in a complex. e.g. ammonia, water, chloride, hydroxide
 A bidentate ligand is a ligand which uses two lone pairs of electrons to form two coordinate bonds with a central metal atom or ion in a complex eg $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (1,2 diaminoethane represented by en)

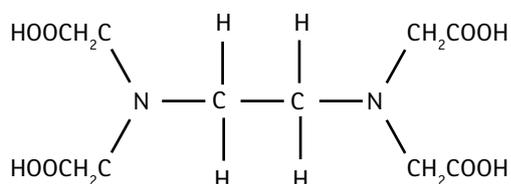


1,2 diaminoethane, showing the 2 lone pairs

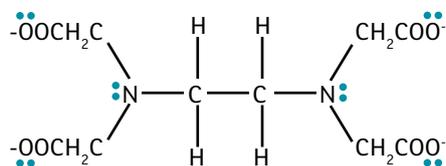
The coordinate bonds must form in a certain orientation hence for a bidentate ligand the lone pairs of ligands must be on different atoms. (water has two lone pairs but cannot be a bidentate ligand)

A polydentate ligand is one which uses many lone pairs of electrons to form more than two coordinate bonds with a central metal atom or ion in a complex.

Edta is **ethylenediaminetetraacetic acid**.



In alkaline buffered solution edta is in the anion form edta^{4-} , as the COOH groups dissociate.



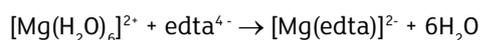
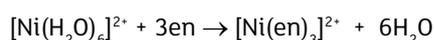
Six lone pairs are shown on the diagram and so edta^{4-} can form 6 coordinate bonds with a central metal atom or ion. It is polydentate, and more specifically hexadentate.

Nickel(II) ions and edta solution form a complex. One edta^{4-} ion bonds to one nickel(II) ion using 6 coordinate bonds. The coordination number is 6. The complex is $[\text{Ni}(\text{edta})]^{2-}$

Ligand replacement reactions

A ligand replacement reaction is one in which one ligand in a complex is replaced by a different one. A bidentate ligand will displace two monodentate ligands forming a more stable complex. The principal reason for this is due to a positive entropy change in the reaction.

Entropy is most easily thought of as a measure of disorder. Any change which increases the disorder increases the tendency of a reaction to happen - if the number of species on the right is greater, there is more disorder - reactions tend to happen in the direction from order to disorder e.g. If 1,2-diaminoethane is added to a solution of nickel ions each bidentate ligand replaces two monodentate ligands - there is an increase in the disorder of the system (an increase in its entropy). There are only 4 species on the left-hand side of the equation, but 7 on the right, hence an increase in entropy from left to right.



One edta^{4-} ion replaces 6 water molecules and this increases the entropy making the complex more stable. There are 2 species on the left and 7 on the right so entropy increases from left to right. Reversing this change is far more difficult in entropy terms. This would involve moving from a highly disordered state to a much more ordered one. That is not likely to happen, and so the magnesium-EDTA complex is very stable. Other ligand reactions will occur due to the relative strengths of ligands in terms of the availability of lone pairs. Ligands have lone pairs and are able to donate them, in some ligands the lone pair is more easily donated than in others. Some ligands may form stronger bonds to the metal than other ligands; the stronger ligand will displace the poorer one.

Water is quite a weak ligand. If a stronger ligand is added to the aqueous solution a ligand replacement will occur.

The order of the strength of some ligands is shown below.

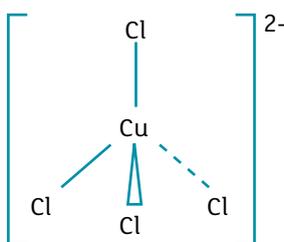
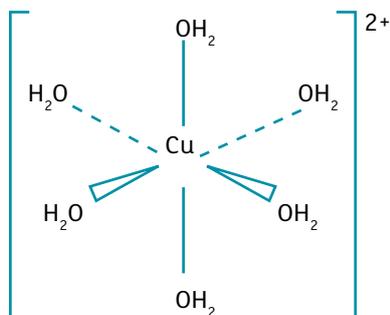


← decreasing ligand strength

Going down the halogen group, the halide ions become weaker ligands because the ions get larger and the coordinate bond would be weaker.

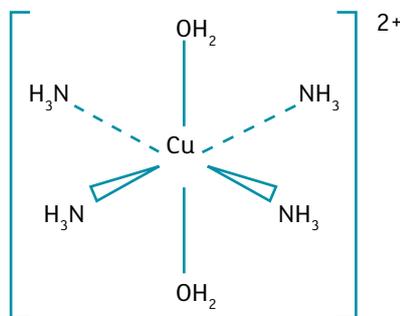
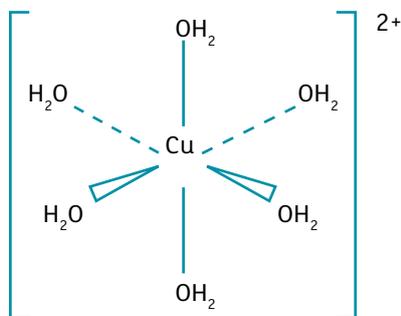
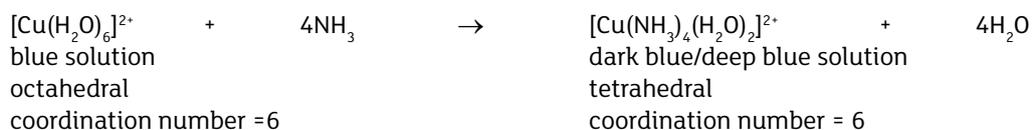
A ligand replacement reaction occurs when hexaaquacopper(II) ions are treated

(i) with concentrated hydrochloric acid



If there are 6 ligands around the complex, there are 6 bonded pairs of electrons, which repel each other equally to be as far apart as possible and so the shape is octahedral. Four ligands around the central metal ion result in a tetrahedral shape.

(ii) with ammonia solution

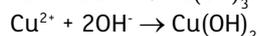
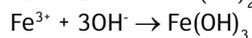
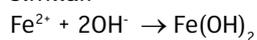


Detection tests

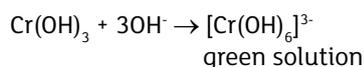
Aqueous solutions of transition metal ions can be identified by adding either sodium hydroxide solution or ammonia solution. The reagent is added until a ppt forms, the colour is recorded, and then excess reagent added; some of the precipitates are soluble in the excess of the solution added.

Metal ion in solution	Colour of ppt on adding NaOH/NH ₃ (aq)	Effect of excess NaOH(aq)	Effect of excess NH ₃ (aq)
Cr ³⁺	green-blue ppt	ppt is soluble in excess [Cr(OH) ₆] ³⁻	ppt is insoluble
Mn ²⁺	white ppt slowly turns brown/black on standing	insoluble	ppt is insoluble
Fe ²⁺	green ppt	insoluble	ppt is insoluble
Fe ³⁺	brown ppt	insoluble	ppt is insoluble
Co ²⁺	blue ppt	insoluble	ppt is soluble in excess to give a yellow solution [Co(NH ₃) ₆] ²⁺ which changes to brown on standing.
Ni ²⁺	green ppt	insoluble	ppt is soluble in excess to give a blue solution [Ni(NH ₃) ₆] ²⁺
Cu ²⁺	blue ppt	insoluble	ppt is soluble in excess to give a deep/dark blue solution [Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺

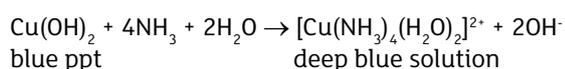
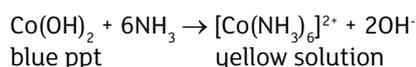
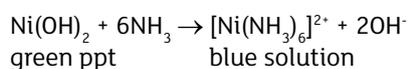
The equations for the reaction of the aqueous metal ion with sodium hydroxide or ammonia solution are similar.



Chromium(III) hydroxide is amphoteric and so will react with excess NaOH



Nickel, cobalt(II) and copper(II) hydroxides react with excess ammonia because a ligand replacement occurs



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Metal hydroxides formed by the addition of sodium hydroxide (NaOH) to solutions of metal ions. From left the precipitates are $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Cu}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$.

Chromium compounds

$\text{Cr}^{3+}(\text{aq})$	green solution
$\text{Cr}(\text{OH})_3(\text{s})$	green-blue ppt
$\text{Cr}_2\text{O}_7^{2-}(\text{aq})$	orange solution
$\text{CrO}_4^{2-}(\text{aq})$	yellow solution

Reduction of acidified ammonium vanadate(V)

Vanadium has four common oxidation states which can be observed when a solution of acidified vanadate(V) ions containing vanadium in the +5 oxidation state (VO_2^+) is reduced using zinc. The colour changes observed as vanadium is reduced from oxidation state +5 to +2 are shown in the table.

Oxidation state	complex	colour
+2	$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	violet
+3	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	green
+4	VO^{2+}	blue
+5	VO_2^+	yellow



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Test tubes containing solutions of dissolved vanadium (V) compounds in different oxidation states.

It is possible to deduce, given appropriate E^\ominus values, different reagents for the interconversion of vanadium between its oxidation states and to combine half-cells to give an overall equation for a reaction. To understand how to do this look at the fact file on electrode potentials.



Revision Questions

1 Vanadium is a typical transition metal.

a) Explain, in terms of electronic configuration, what is meant by a **transition metal**.

.....
 [1]

b) Vanadium has a variety of oxidation states.

i) What is the electronic configuration of the V^{2+} ion?

..... [1]

ii) Complete the table below giving the formula, oxidation state and colour in solution of some vanadium ions.

ion	oxidation state	colour
$V^{2+}(aq)$		
		yellow
$VO^{2+}(aq)$		
$V^{3+}(aq)$		

[4]

2 The hexaaquachromium(III) ions, $[Cr(H_2O)_6]^{3+}$, readily react with $edta^{4-}$ ions in a ligand replacement reaction.

i) What term is given to ligands such as edta?

..... [1]

ii) Write an equation for the reaction taking place between Hexaaquachromium(III) ions and $edta^{4-}$ ions.

..... [2]

iii) Explain, in terms of entropy, why the reaction takes place.

.....

 [2]



Revision Questions

- 3 Complete the table below to give the colours of the metal ions.

metal ion	colour of aqueous complex
$\text{Cu}^{2+}(\text{aq})$	
$\text{Cr}^{3+}(\text{aq})$	
$\text{Co}^{2+}(\text{aq})$	
$\text{Fe}^{3+}(\text{aq})$	

[4]

- 4 Which one of the following applies to the ligand substitution reaction shown?
 $[\text{Ni}(\text{H}_2\text{O})_6]^{2+} + 3\text{en} \rightarrow [\text{Ni}(\text{en})_3]^{2+} + 6\text{H}_2\text{O}$

	Change in Coordination Number	ΔS^\ominus
A	6 to 3	negative
B	6 to 3	positive
C	none	negative
D	none	positive

[1]

- 5 Which one of the following gives the ground state electronic configuration for the copper atom and the copper(II) ion?

	copper atom	copper(II) ion
A	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$
B	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
C	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^1$
D	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$

[1]

- 6 1,2-diaminoethane (en) is a bidentate ligand forming stable complex ions with transition metal ions.
 i) Explain the term **bidentate**.

.....
 [2]

- ii) Hexaaquanickel(II) ions react with en in solution. Write the equation for this reaction in which all the water ligands are replaced.

..... [2]

6 iii) Explain why this ligand replacement takes place.

.....
.....
..... [2]

