Topic 5 –Transition Elements
Revision Notes

1) Introduction

- The d-block is the ten short columns in the middle of the Periodic Table. All of the elements in the d-block have their highest energy (outermost) electron in a d sub-shell
- Transition elements have 3 characteristic properties: they form coloured ions, they have more than one oxidation state and they act as catalysts
- To be a transition metal and display these properties, there must be at least one ion that has an incomplete d sub-shell
- This definition rules out Sc (whose only ion, Sc^{3+}, is $3d^0$) and Zn (whose only ion, Zn^{2+}, is $3d^{10}$). Sc and Zn are d-block elements but not transition metals
- Ions of transition elements undergo three types of reaction:
    - Precipitation
    - Ligand substitution
    - Redox

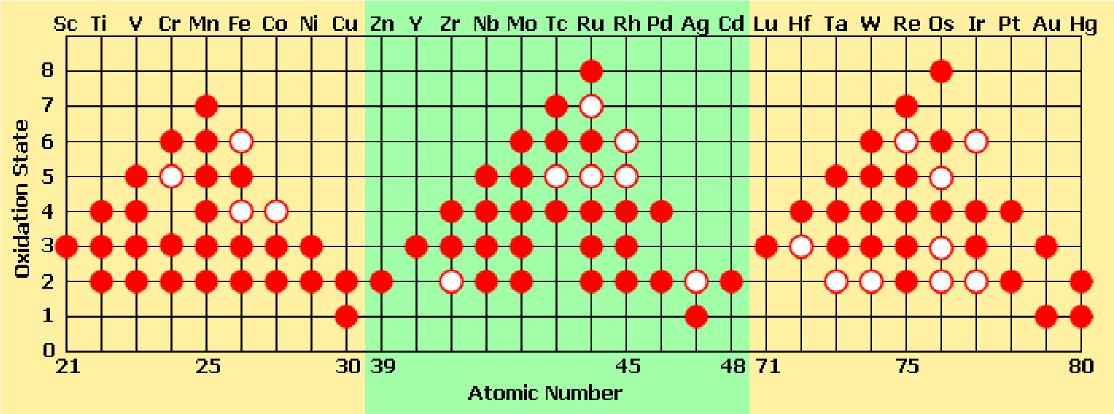
2) Electron arrangements

- The order in which electron orbitals are filled is as follows: 1s 2s 2p 3s 3p 4s 3d 4p
- There are 2 exceptions to the pattern: chromium and copper
- Cr is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$ and Cu is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
- These electronic structures are more stable than the alternative structures that follow the pattern
- When transition metals, like iron and copper, form ions they lose their 4s electrons before their 3d electrons
- Fe^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^6$ (4s⁰ is optional)
- Cu^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^9$

3) Illustration of Properties

a) Variable oxidation state

- The table below indicates the oxidation states of transition elements in compounds



Source: http://commons.wikimedia.org/wiki/File:Transition_metal_oxidation_states.png

- Ti has oxidation state +4 in TiO_2
- V has oxidation state +5 in VO_3^- and +4 in VO^{2+}
- Cr has oxidation state +6 in $K_2Cr_2O_7$ and +3 in $CrCl_3$
- Mn has oxidation state +4 in MnO_2 and is +7 in $KMnO_4$
- Fe is +2 in $FeSO_4$ and +3 in $FeCl_3$. Co and Ni follow the same pattern
- Cu is +1 in CuI and +2 in $CuSO_4$

b) Formation of coloured ions

- The dichromate(VI) ion, $Cr_2O_7^{2-}$, is orange and the chromate(VI) ion, CrO_4^-, is yellow
- The manganate(VII) ion, MnO_4^-, is purple
- Cu^{2+}(aq) is blue, Fe^{2+}(aq) is pale green, Fe^{3+}(aq) is yellow-brown, Co^{2+}(aq) is pink

c) Ability to act as catalysts

- Transition elements and their compounds can act as catalysts
- Fe is a heterogeneous catalyst in the Haber process, $N_2 + 3H_2 \qquad 2NH_3$
- Ni is the catalyst for hydrogenation of alkenes e.g. $CH_2{=}CH_2 + H_2 \qquad CH_3CH_3$
- V_2O_5 is the catalyst in the Contact Process, $2SO_2 + O_2 \qquad 2SO_3$, which is one of the steps in the manufacture of sulphuric acid

4) Ligands and complex ions

a) Definitions

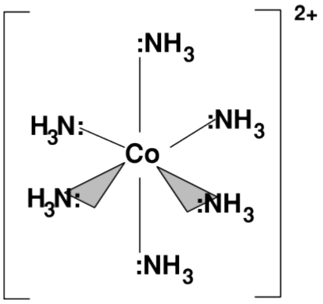
- A complex consists of a central metal ion bonded to one or more ligands e.g. $[Fe(H_2O)_6]^{2+}$, $[CuCl_4]^{2-}$
- Ligands have lone pairs of electrons e.g. H_2O, Cl^-, NH_3, SCN^-
- Ligands form co-ordinate bonds with the metal ion. The ligand is an electron pair donor and the metal ion accepts an electron pair

b) Shapes

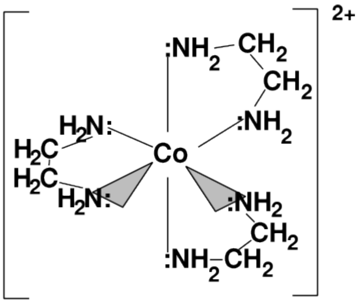
- With 6 ligands bonded to a metal ion, the complex is octahedral in shape with a bond angle of 90°
- With 4 ligands bonded to a metal ion, the complex is usually tetrahedral in shape with a bond angle of 109.5°. The exceptions are complexes of nickel and platinum which are square planar with a bond angle of 90°

c) Co-ordination number

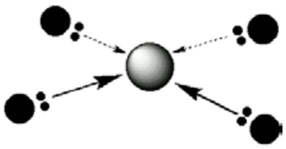
- The co-ordination number of a complex is the number of lone pairs bonded to the central ion (not the number of ligands)
- Unidentate ligands bond through one lone pair e.g. H_2O, NH_3, Cl^-, SCN^-, CN^-
- Bidentate ligands can form two bonds because they have two lone pairs e.g. 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, which bonds through the lone pairs on the nitrogen atoms



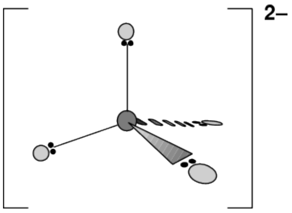
$[Co(NH_3)_6]^{2+}$
Co-ordination number 6
Octahedral shape



$[Co(H_2NCH_2CH_2NH_2)_3]^{2+}$
co-ordination number 6 (not 3)
octahedral shape



$[Pt(NH_3)_2Cl_2]$
Co-ordination number 4
Square planar shape



$[CoCl_4]^{2-}$
co-ordination number 4
tetrahedral shape

Source of these 4 diagrams: http://www.btinternet.com/~chemistry.diagrams/

d) Bond angles in ligands

- In a water molecule, there are 2 bonding pairs and 2 lone pairs on the oxygen atom. Lone pairs repel more than bonding pairs so the bond angle is 104.5°.
- When water acts as a ligand, it has 1 lone pair and 3 bonding pairs. 1 lone pair repels less than 2 lone pairs so the bond angle is 107°.
- Similarly, in an ammonia molecule, the bond angle is 107° as there are 3 bonding pairs and 1 lone pair on the N.
- When ammonia acts as a ligand, there are 4 bonding pairs so the bond angle is 109.5°.

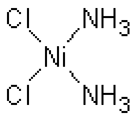
e) Naming complexes

- The name of a complex gives the number and type of ligand and the oxidation state of the transition element e.g.

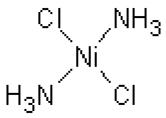
$[Cr(H_2O)_6]^{3+}$	hexaaquachromium(III)	Cr^{3+} bonded to 6 waters
$[Fe(CN)_6]^{4-}$	hexacyanoferrate(II)	Fe^{2+} bonded to 6 cyanides

f) Cis-trans isomerism in complexes

- Square planar complexes, such as $[Ni(NH_3)_2Cl_2]$, can show cis-trans isomerism

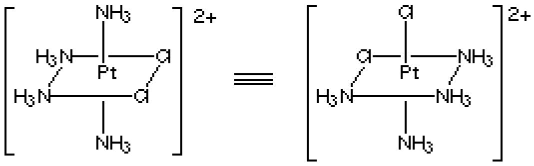


cis-isomer

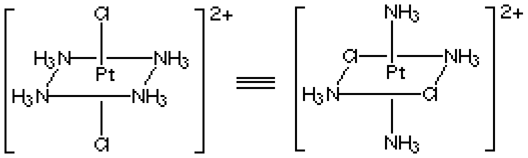


trans-isomer

- Octahedral complexes, such as $[Pt(NH_3)_4Cl_2]$, can show cis-trans isomerism because the chlorides can be at either 90° (cis) or 180° (trans)



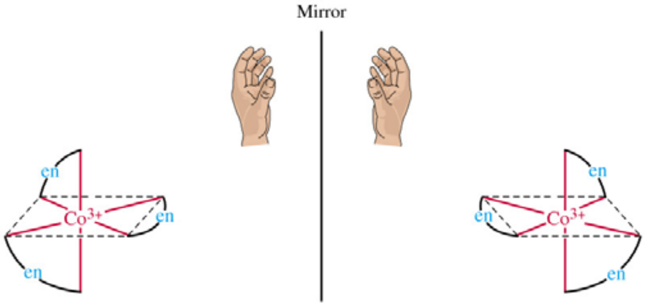
both diagrams show the cis isomer



both diagrams show the trans isomer

g) Optical isomerism in complexes

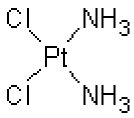
- Optical isomers are non-superimposable mirror images
- Optical isomers rotate plane-polarised light in opposite directions by the same number of degrees
- Examples include $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$ which is abbreviated to $[Co(en)_3]^{3+}$ in the following diagram



Source of this diagram: http://www.tau.ac.il/chemistry/OnlineCourses/UrbakhLectures/complexes.pdf

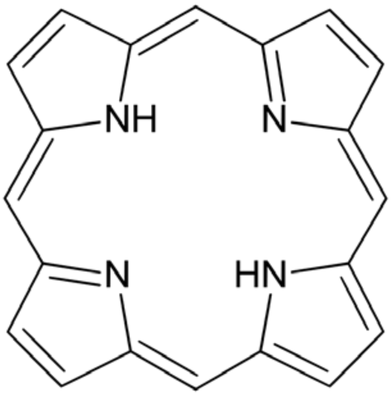
h) Cis-platin

- Cis-platin is an anti-cancer drug
- It binds to DNA and prevents it from replicating



h) Haemoglobin

- Porphyrin is a planar tetradentate ligand



Source: http://en.wikipedia.org/wiki/Porphyrin

- When porphyrin forms four co-ordinate bonds with Fe^{2+}, the resulting complex is called haem
- The iron achieves a co-ordination number of 6 by bonding to the protein globin and to either an oxygen or water molecule. If the sixth bond is to oxygen, the complex produced is oxyhaemoglobin. If the sixth bond is to water the complex is deoxyhaemoglobin.
- The oxygen bonds only weakly to the Fe^{2+}. Carbon monoxide forms a much stronger bond with Fe^{2+} and is therefore poisonous because it reduces the oxygen carrying capacity of the blood

4) Precipitation reactions

- When reacted with NaOH(aq), solutions of copper (II), cobalt (II), iron (II) and iron (III) salts produce precipitates of the metal hydroxide
- These reactions can be used as tests for Cu^{2+}(aq), Co^{2+}(aq), Fe^{2+}(aq) and Fe^{3+}(aq)

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$	blue solution → blue precipitate
$Co^{2+}(aq) + 2OH^-(aq) \rightarrow Co(OH)_2(s)$	pink solution → blue precipitate
$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$	pale green solution → green ppt
$Fe^{3+}(aq) + 3OH^-(aq) \rightarrow Fe(OH)_3(s)$	yellow solution → orange precipitate

5) Ligand substitution reactions

- In ligand substitution reactions, one ligand is displaced by a stronger ligand.

a) Copper(II) with ammonia solution

- With excess concentrated NH_3(aq) added dropwise, two reactions occur
- Firstly, a precipitation reaction because ammonia solution contains some OH^-(aq) produced by the following reaction: $NH_3(aq) + H_2O(l) \quad NH_4^+(aq) + OH^-(aq)$

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

- With more ammonia, the blue precipitate dissolves to produce a dark blue solution

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

Blue precipitate dark-blue solution

- The overall reaction between copper(II) and ammonia is shown has below. Ammonia has displaced water as a ligand

$$\mathbf{[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)}$$

Blue solution dark blue solution

b) Copper(II) and cobalt (II) with concentrated HCl or saturated NaCl(aq)

- Concentrated HCl and saturated NaCl(aq) are sources of the chloride ligand, Cl^-
- When reacted with copper(II) solutions, chloride displaces water as a ligand

$$\mathbf{[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)}$$

Blue solution yellow-green solution

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

Pink solution blue solution

c) Stability constants, K_{stab}

- Expressions for stability constants, K_{stab}, can be written for ligand substitution reactions e.g. for the reaction

$$\mathbf{[Fe(H_2O)_6]^{2+} + 6NH_3 \quad [Fe(NH_3)_6]^{2+} + 6H_2O}$$

- K_{stab} expressions exclude the solvent (usually water). Note the double square brackets for the complexes

$$K_{stab} = \frac{[[Fe(NH_3)_6]^{2+}]}{[[Fe(H_2O)_6]^{2+}]\ [NH_3]^6}$$

- A large value for K_{stab} indicates the formation of a more stable complex ion. More stable complexes contain stronger dative bonds than less stable complexes

6) Redox reactions

a) Constructing half-equations

- Because transition elements have more than one oxidation state, they undergo redox reactions.
- Redox reactions can be split into two half-equations
- Constructing simple half-equations involves two steps: balancing atoms and balancing charge by adding electrons e.g. oxidation of iodide ions, I^-, to iodine, I_2.

Write down formulae:	$\mathbf{I^- \rightarrow I_2}$
Balance atoms:	$\mathbf{2I^- \rightarrow I_2}$
Balance charge:	$\mathbf{2I^- \rightarrow I_2 + 2e^-}$

- Constructing more complicated half-equations involves 2 extra steps, namely: balancing oxygens by adding water and balancing hydrogens by adding H+ e.g. oxidation of V^{2+} to VO^{3-}

Write down formulae:	$\mathbf{V^{2+} \rightarrow VO_3^-}$
Balance atoms (vanadiums):	not needed
Balance oxygens:	$\mathbf{V^{2+} + 3H_2O \rightarrow VO_3^-}$
Balance hydrogens:	$\mathbf{V^{2+} + 3H_2O \rightarrow VO_3^- + 6H^+}$
Balance charge:	$\mathbf{V^{2+} + 3H_2O \rightarrow VO_3^- + 6H^+ + 3e^-}$

b) Constructing overall equations

- To produce the overall equation, multiply one or both half-equations until the number of electrons is the same e.g. iron(II) and manganate(VII)

$$\mathbf{Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-}$$
$$\mathbf{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)}$$

- In this case, multiply the first half-equation by 5 to get 5 electrons in both.

$$\mathbf{5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-}$$

- Now add the half-equations together, cancelling the electrons at the same time.

$$\mathbf{5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)}$$

- Any species that appears on both sides of the equation needs to be cancelled e.g. H^+

c) Redox titration calculations

- As with acid-base reactions in Module 2811, redox reactions can be used to determine unknown concentrations etc.
- The method involves three steps:

Step 1	Calculate moles using concentration x volume/1000
Step 2	Use the redox equation to calculate moles of other chemical
Step 3	Use moles from step 2 to calculate unknown concentration etc

Example – A student takes 25.0 cm^3 of aqueous hydrogen peroxide, H_2O_2, and places this in a conical flask and then adds sulphuric acid to acidify the hydrogen peroxide.

The student titrates this sample of acidified hydrogen peroxide against a solution containing 0.0200 mol dm^{-3} $MnO_4^-(aq)$ ions. For complete reaction with the acidified hydrogen peroxide, the student used 17.5 cm^3 of this solution containing $MnO_4^-(aq)$ ions.

Calculate the concentration, in mol dm^{-3}, of the aqueous hydrogen peroxide. 2 mol MnO_4^- reacts with 5 mol H_2O_2.

Step 1 moles MnO_4^- = conc x vol/1000
= 0.02 x 17.5/1000
= 3.5×10^{-4}

Step 2 moles H_2O_2 = $3.5 \times 10^{-4} \times 5/2$
= 8.75×10^{-4}

Step 3 conc H_2O_2 = moles/volume
= $8.75 \times 10^{-4}/25 \times 10^{-3}$
= 0.035 mol dm^{-3}

Source: OCR paper January 2004

d) Estimation of copper in alloys

- An alloy is a mixture of metals. Brass is an alloy of copper and zinc (about 60 to 70% copper). Bronze is an alloy of copper and tin
- The percentage of copper in brass can be estimated by reaction with iodide and titration of the iodine produced with thiosulphate, $S_2O_3^{2-}$
- Iodide ions reduce Cu^{2+} to Cu^+

$$\mathbf{Cu^{2+} + I^- \rightarrow Cu^+ + \tfrac{1}{2}I_2}$$

- Cu^+ then reacts with more iodide ions to form a precipitate of CuI

$$\mathbf{Cu^+ + I^- \rightarrow CuI}$$

- Overall:

$$\mathbf{Cu^{2+}(aq) + 2I^-(aq) \rightarrow CuI(s) + \tfrac{1}{2}I_2(aq)}$$

White (but appears brown due to I_2)

- Brass is dissolved in nitric acid producing copper (II) nitrate and zinc nitrate
- An excess of potassium iodide, KI(aq), is added. This precipitates CuI(s) and forms iodine, I_2
- The amount of iodine produced can be found by titration against sodium thiosulphate, $Na_2S_2O_3$

$$\mathbf{2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-}$$

- Near the end-point, starch solution is added which produces a blue-black colour with the remaining iodine
- The end-point is when the blue-black colour just disappears

e) Estimation of copper - example

- A solution was prepared by dissolving some copper (II) sulphate to give 250 cm^3 of aqueous solution
- 25.0 cm^3 of this solution was treated with an excess of aqueous potassium iodide, KI

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

- The iodine produced was titrated with 0.100 mol dm^{-3} sodium thiosulphate

$$\mathbf{I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)}$$

- The average titre obtained was 22.0 cm^3 of the thiosulphate solution

(a) Calculate the amount of $S_2O_3^{2-}$ ions in the titre

Moles $S_2O_3^{2-}$ = conc x vol/1000
= 0.100 x 22.0/1000
= 2.2 x 10^{-3} mol

(b) Calculate the amount of I_2 produced

Moles I_2 = moles $S_2O_3^{2-}$/2
= 1.1 x 10^{-3} mol

(c) Calculate the amount of Cu^{2+} ions in 25.0 cm^3 of solution

Moles Cu^{2+} = moles I_2 x 2
= 2.2 x 10^{-3} mol

(d) Calculate the concentration of the aqueous copper (II) sulphate solution in mol dm^{-3}

Conc Cu^{2+} = moles/vol
= 2.2 x 10^{-3}/(25.0/1000)
= 0.088 mol dm^{-3}