

## 2.5 Transition Metals

### General properties of transition metals

transition metal characteristics of elements Sc → Cu arise from an **incomplete d sub-level** in atoms or ions

these characteristics include

- **complex formation,**
- **formation of coloured ions,**
- **variable oxidation state**
- **catalytic activity.**

Sc  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$   
 Ti  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$   
 V  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$   
 Cr  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$   
 Mn  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$   
 Fe  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$   
 Co  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$   
 Ni  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$   
 Cu  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$   
 Zn  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

→  
 When forming ions lose 4s before 3d

Sc  $3^+ [Ar] 4s^0 3d^0$   
 Ti  $3^+ [Ar] 4s^0 3d^1$   
 V  $3^+ [Ar] 4s^0 3d^2$   
 Cr  $3^+ [Ar] 4s^0 3d^3$   
 Mn  $2^+ [Ar] 4s^0 3d^5$   
 Fe  $3^+ [Ar] 4s^0 3d^5$   
 Co  $2^+ [Ar] 4s^0 3d^7$   
 Ni  $2^+ [Ar] 4s^0 3d^8$   
 Cu  $2^+ [Ar] 4s^0 3d^9$   
 Zn  $2^+ [Ar] 4s^0 3d^{10}$

### Why is Zn not a transition metal?

Zn can only form a +2 ion. In this ion the  $Zn^{2+}$  has a **complete** d orbital and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

### Complex formation

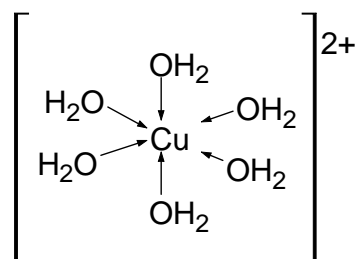
**complex**: is a central metal ion surrounded by ligands.

**ligand**.: An atom, ion or molecule which can donate a **lone electron pair**.

Co-ordinate bonding is involved in complex formation.

Co-ordinate bonding is when **the shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**.

**Co-ordination number**: The number of co-ordinate bonds formed to a central metal ion.



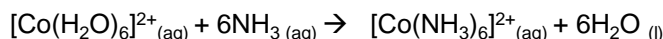
Ligands can be **monodentate** (e.g.  $H_2O$ ,  $NH_3$  and  $Cl^-$ ) which can form one coordinate bond per ligand or **bidentate** (e.g.  $NH_2CH_2CH_2NH_2$  and ethanedioate ion  $C_2O_4^{2-}$ ) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g.  $EDTA^{4-}$  which can form six coordinate bonds per ligand).

### Substitution Reactions

$H_2O$ ,  $NH_3$  and  $Cl^-$  can act as monodentate ligands.

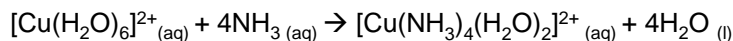
The ligands  $NH_3$  and  $H_2O$  are **similar in size** and are **uncharged**.

Exchange of the ligands  $NH_3$  and  $H_2O$  occurs without change of co-ordination number (eg  $Co^{2+}$  and  $Cu^{2+}$ ).



This substitution may, however, be incomplete as in the case with Cu.

Cu becomes  $[Cu(NH_3)_4(H_2O)_2]^{2+}$  deep blue solution



### Reactions with Chloride Ions

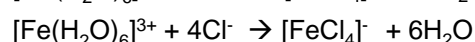
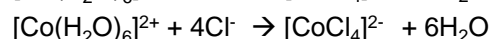
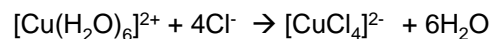
Addition of a high concentration of chloride ions (from conc HCl or saturated NaCl) to an aqueous ion leads to a **ligand substitution** reaction.

The  $Cl^-$  ligand is larger than the uncharged  $H_2O$  and  $NH_3$  ligands so therefore ligand exchange can involve a change of co-ordination number.

**Be careful**: If solid copper chloride (or any other metal) is **dissolved in water** it forms the **aqueous**  $[Cu(H_2O)_6]^{2+}$  complex and **not** the chloride  $[CuCl_4]^{2-}$  complex.

Addition of conc HCl to aqueous ions of Cu and Co lead to a change in coordination number from 6 to 4.

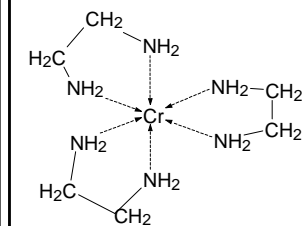
$[CuCl_4]^{2-}$  yellow/green solution      These are tetrahedral in shape  
 $[CoCl_4]^{2-}$  blue solution



## Bidentate Ligands

Ligands can be **bidentate** (e.g.  $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$  and ethanedioate ion  $\text{C}_2\text{O}_4^{2-}$ ) which have two atoms with lone pairs and can form two coordinate bonds per ligand

### Ethane-1-2-diamine



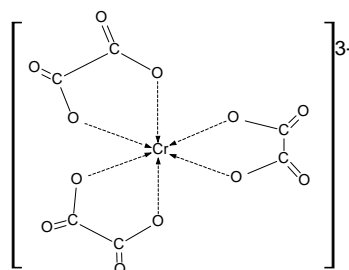
Ethane-1-2-diamine is a common bidentate ligand.

A complex with Ethane-1-2-diamine bidentate ligands e.g.  $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$

There are 3 bidentate ligands in this complex each bonding in twice to the metal ion.

It has a coordination number of 6

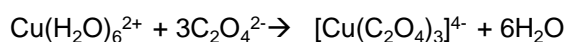
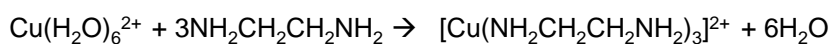
### Ethanedioate $\text{C}_2\text{O}_4^{2-}$



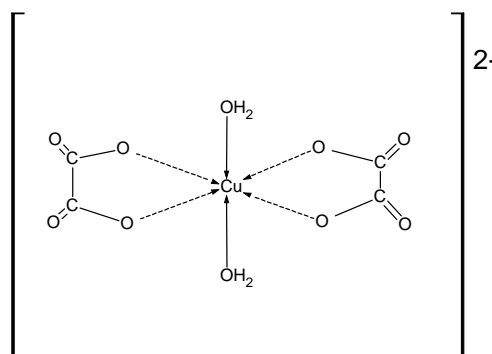
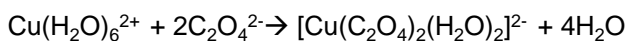
A complex with bidentate ethanedioate ligands e.g.  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Octahedral shape with  $90^\circ$  bond angles

Equations to show formation of bidentate complexes



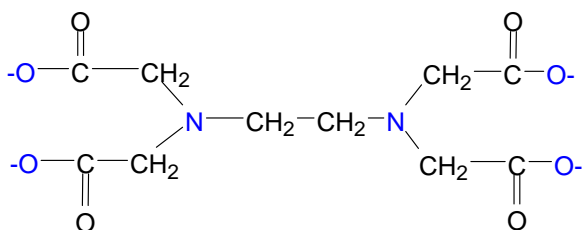
Partial substitution of ethanedioate ions may occur when a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions. In this reaction four water molecules are replaced and a new complex is formed.



## Multidentate Ligands

Ligands can be **multidentate** (e.g.  $\text{EDTA}^{4-}$  which can form six coordinate bonds per ligand).

The  $\text{EDTA}^{4-}$  anion has the formula



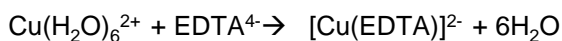
with six donor sites (4O and 2N) and forms a 1:1 complex with metal(II) ions

Haem is an iron(II) complex with a multidentate ligand.

Oxygen forms a co-ordinate bond to Fe(II) in haemoglobin, enabling oxygen to be transported in the blood.

CO is toxic to humans as CO can form a strong coordinate bond with haemoglobin. This is a stronger bond than that made with oxygen and so it replaces the oxygen attaching to the haemoglobin.

Equations to show formation of multidentate complexes

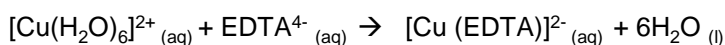


Learn the two bidentate ligands mentioned above but it is not necessary to remember the structure of EDTA.

## Stability of complexes

The substitution of monodentate ligand with a bidentate or a multidentate ligand leads to a more stable complex. This is called the chelate effect

This chelate effect can be explained in terms of a positive entropy change in these reactions as more molecules of products than reactants

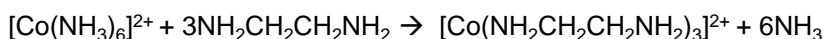


The copper complex ion has changed from having unidentate ligands to a multidentate ligand. In this reaction there is **an increase** in the **entropy** because there are **more moles of products** than reactants (from 2 to 7), creating more disorder.

The enthalpy change is small as there are similar numbers of bonds in both complexes.

**Free energy G** will be **negative** as **S is positive** and **H is small**.

The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.



This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **S is positive**.

Its enthalpy change **H** is close to zero as **the number** of dative covalent and **type** (N to metal coordinate bond) **are the same** so the energy required to break and make bonds will be the same. Therefore **Free energy G** will be **negative** and the complex formed is stable.

## EDTA titrations

The formation of the stable EDTA complex with metal ions can with the choice of suitable indicator be done in a quantitative titration.



A river was polluted with copper(II) ions. 25.0 cm<sup>3</sup> sample of the river water was titrated with a 0.0150 mol dm<sup>-3</sup> solution of EDTA<sup>4-</sup>, 6.45 cm<sup>3</sup> were required for complete reaction.

Calculate the concentration, in mol dm<sup>-3</sup>, of copper(II) ions in the river water.

Step 1 : find moles of EDTA<sup>4-</sup>

$$\begin{aligned} \text{moles} &= \text{conc} \times \text{vol} = 0.0150 \times 6.45/1000 \\ &= 9.68 \times 10^{-5} \text{ mol} \end{aligned}$$

Step 2 : using balanced equation find moles Cu<sup>2+</sup>  
1:1 ratio

$$= 9.68 \times 10^{-5} \text{ mol}$$

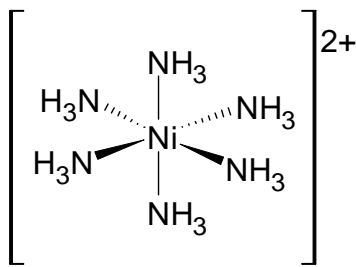
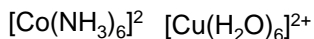
Step 3 : find conc Cu<sup>2+</sup> in 25cm<sup>3</sup>

$$= 9.68 \times 10^{-5} / 0.025$$

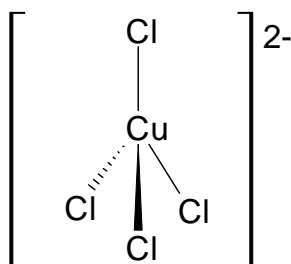
$$= 0.00387 \text{ mol dm}^{-3}$$

## Shapes of complex ions

transition metal ions commonly form **octahedral** complexes with small ligands (e.g.  $\text{H}_2\text{O}$  and  $\text{NH}_3$ ).

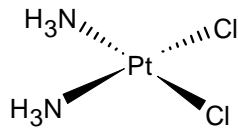


transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g.  $\text{Cl}^-$ ).  $[\text{CoCl}_4]^{2-}$

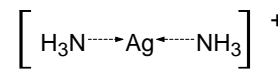


### square planar

complexes are also formed, e.g. cisplatin



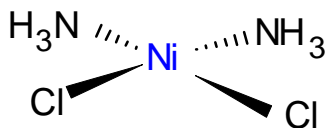
$\text{Ag}^+$  commonly forms **linear** complexes e.g.  $[\text{Ag}(\text{NH}_3)_2]^+$  used as Tollen's Reagent



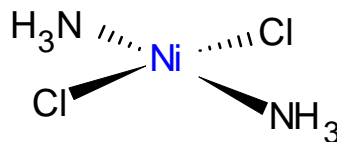
## Isomerism in complex ions

Complexes can show two types of stereoisomerism: cis-trans isomerism and optical isomerism

### Cis-trans isomerism in square planar complexes



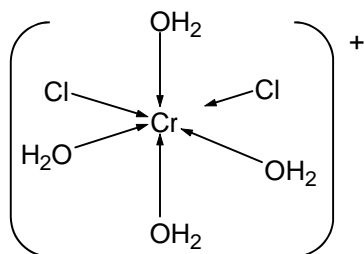
Cis- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$



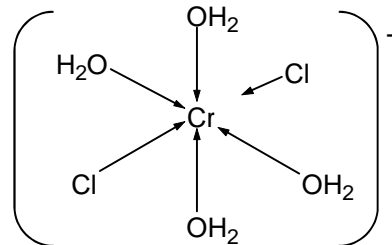
trans- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$

*cis-trans* isomerism is a special case of *E-Z* isomerism

### Cis-trans isomerism in octahedral complexes



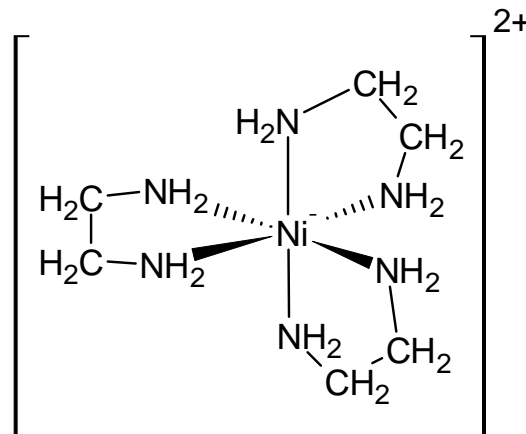
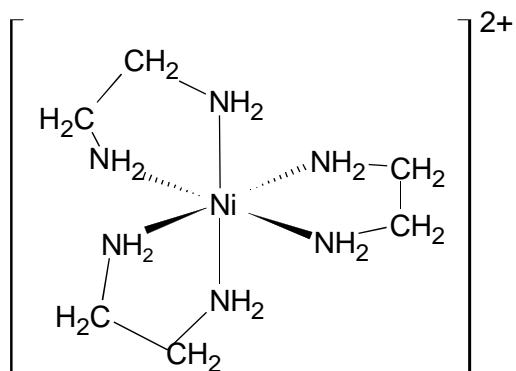
Cis- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$



trans- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

### Optical isomerism in octahedral complexes

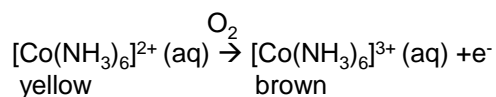
Complexes with 3 bidentate ligands can form two optical isomers (non-superimposable mirror images).



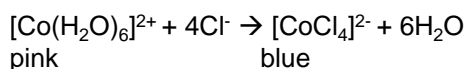
## Formation of coloured ions

**Colour** changes arise from changes in

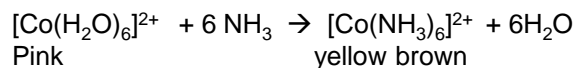
- oxidation state,**
- co-ordination number**
- ligand.**



In this equation only oxidation state is changing.



In this equation both ligand and co-ordination number are changing.

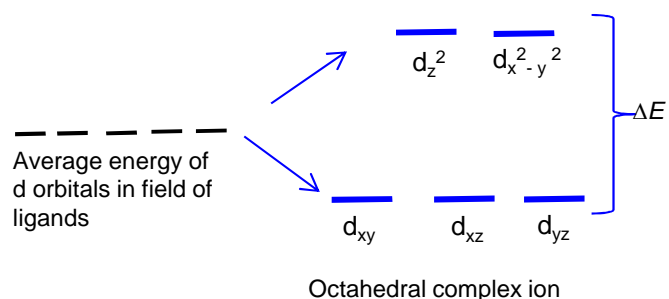


In this equation only the ligand is changing.

## How colour arises

Colour arises from **electronic transitions** from the **ground state to excited states**: between different d orbitals.

A **portion of visible light is absorbed** to promote d electrons to higher energy levels. The **light that is not absorbed is transmitted** to give the substance colour.



### Equation to learn!

This equation links the colour and frequency of the light absorbed with the energy difference between the split d orbitals.

$$U E = h \nu$$

$\nu$  = frequency of light absorbed (unit  $\text{s}^{-1}$  or Hz)

$h$  = Planck's constant  $6.63 \times 10^{-34}$  (J s)

$\Delta E$  = energy difference between split orbitals (J)

Ligands cause the 5 d orbitals to split into two energy levels.

A solution will appear blue if it absorbs orange light. The energy split in the d orbitals  $U E$  will be equal to the frequency of orange light ( $5 \times 10^{14} \text{ s}^{-1}$ )  $\times$  Planck's constant

$$U E \text{ in a blue solution} = h \nu$$

$$= 6.63 \times 10^{-34} \times 5 \times 10^{14}$$
$$= 3.32 \times 10^{-19} \text{ J}$$

## Changing colour

**Changing a ligand or changing the coordination number will alter the energy split between the d-orbitals, changing  $\Delta E$  and hence change the frequency of light absorbed.**

## Compounds without colour

Scandium is a member of the d block. Its ion ( $\text{Sc}^{3+}$ ) hasn't got any d electrons left to move around. So there is not an energy transfer equal to that of visible light.

In the case of  $\text{Zn}^{2+}$  ions and  $\text{Cu}^+$  ions the d shell is full e.g.  $3d^{10}$  so there is no space for electrons to transfer. Therefore there is not an energy transfer equal to that of visible light.

## Spectrophotometry

If visible light of increasing frequency is passed through a sample of a coloured complex ion, some of the light is absorbed.

The amount of light absorbed is proportional to the concentration of the absorbing species (and to the distance travelled through the solution).

Some complexes have only pale colours and do not absorb light strongly. In these cases a suitable ligand is added to intensify the colour.

Absorption of visible light is used in spectrometry to determine the concentration of coloured ions.

### method

- Add an appropriate ligand to **intensify** colour
- Make up solutions of known concentration
- Measure absorption or transmission
- Plot graph of absorption vs concentration
- Measure absorption of unknown and compare

Spectrometers contain a coloured filter. The colour of the filter is chosen to allow the wavelengths of light through that would be most strongly absorbed by the coloured solution.

## Variable oxidation states

Transition elements show variable oxidation states.

When transition metals form ions they lose the 4s electrons before the 3d.

### General trends

- Relative stability of +2 state with respect to +3 state increases across the period
- Compounds with high oxidation states tend to be oxidising agents e.g  $\text{MnO}_4^-$
- Compounds with low oxidation states are often reducing agents e.g  $\text{V}^{2+}$  &  $\text{Fe}^{2+}$

The redox potential for a transition metal ion changing from a higher to a lower oxidation state is influenced by pH and by the ligand.

### Vanadium

Vanadium has four main oxidation states

$\text{VO}_2^+$  Oxidation state +5 ( a yellow solution)

$\text{VO}^{2+}$  Oxidation state + 4 (a blue solution)

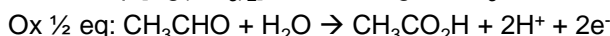
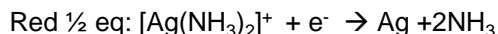
$\text{V}^{3+}$  Oxidation state + 3 (a green solution)

$\text{V}^{2+}$  Oxidation state + 2 (a violet solution)

The ion with the V at oxidation state +5 exists as a solid compound in the form of a  $\text{VO}_3^-$  ion, usually as  $\text{NH}_4\text{VO}_3$  (ammonium vanadate (V)). It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the  $\text{VO}_2^+$  ion.

Addition of **zinc** to the vanadium (V) in acidic solution will reduce the vanadium down through each successive oxidation state, and the colour would successively change from yellow to blue to green to violet

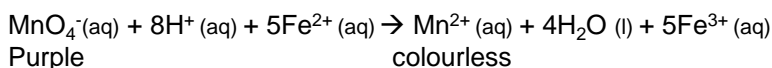
$[\text{Ag}(\text{NH}_3)_2]^+$  is used in Tollen's reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollen's reagent to silver.



### Manganate Redox Titration

The redox titration between  $\text{Fe}^{2+}$  with  $\text{MnO}_4^-$  (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product.

The purple colour of manganate can make it difficult to see the bottom of meniscus in the burette.



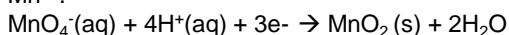
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.  
Colourless  $\rightarrow$  purple

### Choosing correct acid for manganate titrations.

The acid is needed to supply the  $8\text{H}^+$  ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulphuric acid** for manganate titrations.

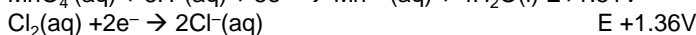
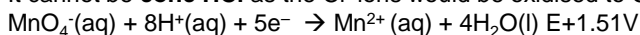
Insufficient volumes of sulphuric acid will mean the solution is not acidic enough and  $\text{MnO}_2$  will be produced instead of  $\text{Mn}^{2+}$ .



The brown  $\text{MnO}_2$  will mask the colour change and lead to a greater (inaccurate) volume of Manganate being used in the titration.

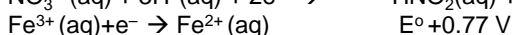
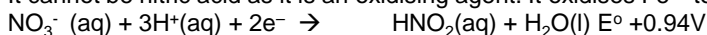
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed ( $8\text{H}^+$ ).

It cannot be **conc HCl** as the  $\text{Cl}^-$  ions would be oxidised to  $\text{Cl}_2$  by  $\text{MnO}_4^-$  as the  $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous  $\text{Cl}_2$  being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  as  $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$



This would lead to a smaller volume of manganate being used.

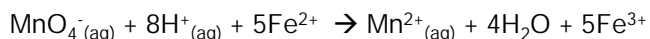
Be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.

### Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm<sup>3</sup> acid. The solution formed contains Fe(II) ions.

10cm<sup>3</sup> portions of this solution are titrated with potassium manganate (VII) solution of 0.02M. 9.80cm<sup>3</sup> of KMnO<sub>4</sub> were needed to react with the solution containing the iron.

What is the percentage of Iron by mass in the nail?



Step1 : find moles of KMnO<sub>4</sub>

moles = conc x vol

$$0.02 \times 9.8/1000$$

$$= 1.96 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles Fe<sup>2+</sup> in 10cm<sup>3</sup>

$$= \text{moles of KMnO}_4 \times 5$$

$$= 9.8 \times 10^{-4} \text{ mol}$$

Step 3 : find moles Fe<sup>2+</sup> in 100cm<sup>3</sup>

$$= 9.8 \times 10^{-4} \text{ mol} \times 10$$

$$= 9.8 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of Fe in 9.8x10<sup>-3</sup> mol

$$\text{mass} = \text{moles} \times \text{RAM} = 9.8 \times 10^{-3} \times 55.8 = 0.547\text{g}$$

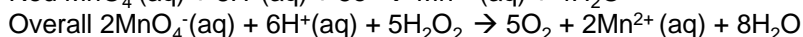
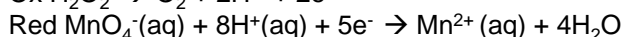
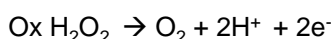
Step 5 : find % mass

$$\% \text{mass} = 0.547/2.41 \times 100$$

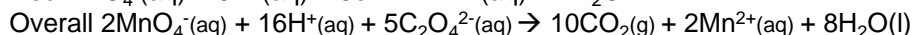
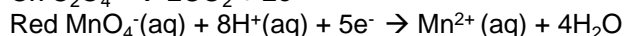
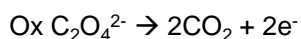
$$= 22.6\%$$

### Other useful manganate titrations

With hydrogen peroxide

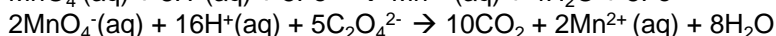
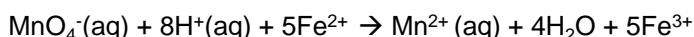


With ethanedioate

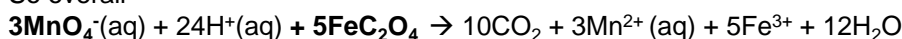


The reaction between MnO<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to 60° C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe<sup>2+</sup> and the C<sub>2</sub>O<sub>4</sub><sup>2-</sup> react with the MnO<sub>4</sub><sup>-</sup>  
1MnO<sub>4</sub><sup>-</sup> reacts with 5Fe<sup>2+</sup> and 2 MnO<sub>4</sub><sup>-</sup> reacts with 5C<sub>2</sub>O<sub>4</sub><sup>2-</sup>



So overall



So overall the ratio is 3 MnO<sub>4</sub><sup>-</sup> to 5 FeC<sub>2</sub>O<sub>4</sub>

A 1.412 g sample of impure FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O was dissolved in an excess of dilute sulphuric acid and made up to 250 cm<sup>3</sup> of solution. 25.0 cm<sup>3</sup> of this solution decolourised 23.45 cm<sup>3</sup> of a 0.0189 mol dm<sup>-3</sup> solution of potassium manganate(VII).

What is the percentage by mass of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in the original sample?

Step1 : find moles of KMnO<sub>4</sub>

moles = conc x vol

$$0.0189 \times 23.45/1000$$

$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in 25cm<sup>3</sup>

$$= \text{moles of KMnO}_4 \times 5/3 \text{ (see above for ratio)}$$

$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in 250 cm<sup>3</sup>

$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$

$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in 7.39x10<sup>-3</sup> mol

$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33\text{g}$$

Step 5 ; find % mass

$$\% \text{mass} = 1.33/1.412 \times 100$$

$$= 94.1\%$$

## Catalysis

Catalysts increase reaction rates without getting used up. They do this by **providing an alternative route** with a **lower activation energy**.

Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

### Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

#### Strength of adsorption

The strength of adsorption helps to determine the effectiveness of the catalytic activity.

Some metals e.g. **W** have **too strong** adsorption and so the products cannot be released.

Some metals e.g. **Ag** have **too weak** adsorption, and the reactants do not adsorb in high enough concentration.

Ni and Pt have about the right strength and are most useful as catalysts.

**Adsorption of reactants at active sites on the surface may lead to catalytic action.** The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface so leading to a higher collision frequency.

Transition Metals can use the 3d and 4s e- of atoms on the metal surface to form weak bonds to the reactants.

#### Steps in Heterogeneous Catalysis

1. Reactants form bonds with atoms at **active sites** on the surface of the catalyst (adsorbed onto the surface)
2. As a result bonds in the reactants are weakened and break
3. New bonds form between the reactants held close together on catalyst surface.
4. This in turn weakens bonds between product and catalyst and product leaves (desorbs).

#### Surface area:

Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

### Examples of heterogeneous catalysts

$V_2O_5$  is used as a catalyst in the Contact Process.

**Overall equation** :  $2SO_2 + O_2 \rightarrow 2SO_3$

**step 1**  $SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$

**step 2**  $2V_2O_4 + O_2 \rightarrow 2V_2O_5$

**Learn the equations** for this mechanism. Note the oxidation number of the vanadium changes and then changes back. It is still classed as a catalyst as it returns to its original form.

$Cr_2O_3$  catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen.  
 $CO + 2H_2 \rightarrow CH_3OH$

Fe is used as a catalyst in the Haber Process  
 $N_2 + 3H_2 \rightarrow 2NH_3$

#### Poisoning Catalysts

Catalysts can become poisoned by impurities and consequently have reduced efficiency.

Poisoning has a cost implication e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced.

It is important to ensure the purity of the reactants if poisoning can occur.

Leaded petrol cannot be used in cars fitted with a catalytic converter since lead strongly adsorbs onto the surface of the catalyst.



## Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species.

The intermediate will often have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis.

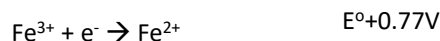
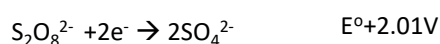
Transition metals can act as homogeneous catalysts because they can form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons.

### Examples of homogeneous catalysts

Learn these 2 examples and equations carefully

#### Reaction between iodide and persulfate ions

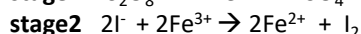
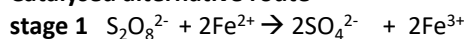
The reaction between  $I^-$  and  $S_2O_8^{2-}$  catalysed by  $Fe^{2+}$   
**overall**  $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$



The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential

#### Catalysed alternative route



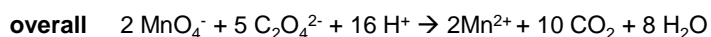
Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

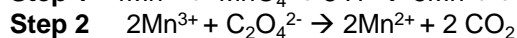
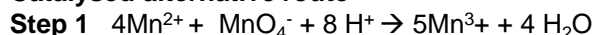
$Fe^{3+}$  ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

#### Autocatalytic Reaction between Ethanedioate and Manganate ions

The autocatalysis by  $Mn^{2+}$  in titrations of  $C_2O_4^{2-}$  with  $MnO_4^-$



#### Catalysed alternative route

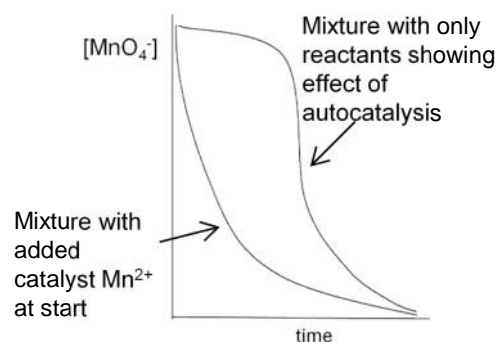


The initial uncatalysed reaction is **slow** because the reaction is a collision between **two negative ions** which **repel each other** leading to a **high activation energy**.

The  $Mn^{2+}$  ions produced act as an **autocatalyst** and therefore the reaction starts to speed up because they bring about the alternative reaction route with lower activation energy.

The reaction eventually slows as the  $MnO_4^-$  concentration drops.

This is an example of **autocatalysis** where one of the products of the reaction can catalyse the reaction.



#### Following the reaction rate

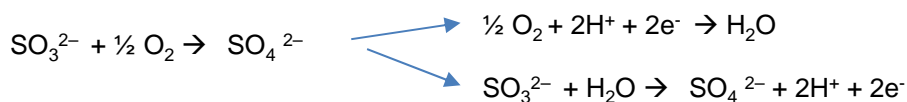
This can be done by removing samples at set times and titrating to work out the concentration of  $MnO_4^-$ . It could also be done by use of a spectrometer measuring the intensity of the purple colour. This method has the advantage that it **does not disrupt the reaction mixture**, using up the reactants and it leads to a much **quicker determination of concentration**.

## Constructing a catalysed mechanism for a reaction

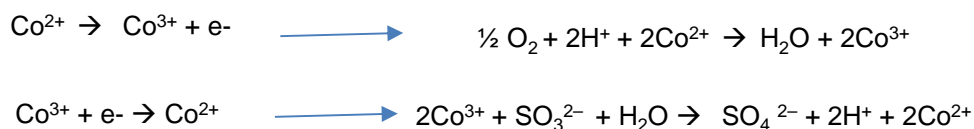
### Example

The following reaction is catalysed by  $\text{Co}^{2+}$  ions in an acidic solution.  $\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}$ .  
Write a mechanism for the catalysed reaction by writing two equations involving  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  ions.

Split the full equation into its two half equations



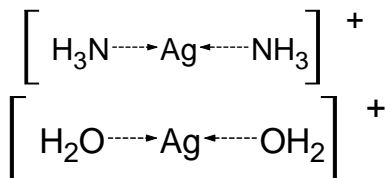
Add in cobalt to make two new redox equations. Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa



Check your two mechanism equations add up to the original full non-catalysed equation.

## Silver Chemistry

Ag<sup>+</sup> commonly forms **linear** complexes  
 e.g. [Ag(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>,  
 [Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]<sup>3-</sup> and [Ag(CN)<sub>2</sub>]<sup>-</sup>  
 All are colourless solutions.



Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples).

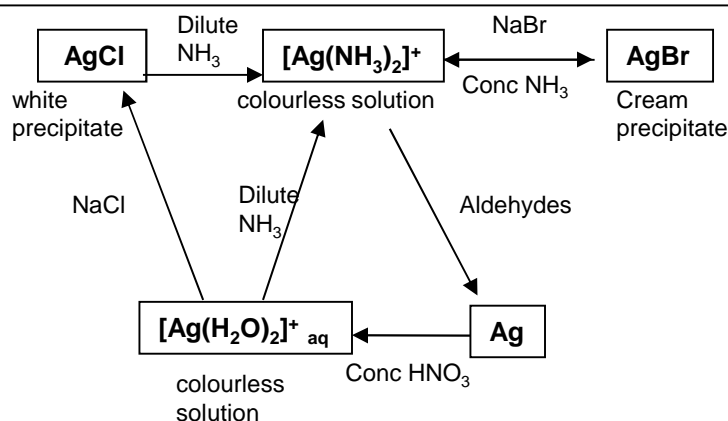
Silver is unlike the transition metals in that it does not form coloured compounds and does not have variable oxidation states.

Silver complexes all have a +1 oxidation state with a full 4d subshell (4d<sup>10</sup>). As it is 4d<sup>10</sup> in both its atom and ion, it does not have a partially filled d subshell and so is not a transition metal by definition. It is not therefore able to do electron transitions between d orbitals that enable coloured compounds to occur.

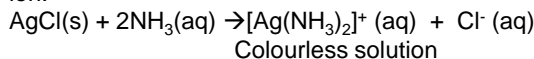
### Reactions of Halides with Silver nitrate

Fluorides produce no precipitate  
 Chlorides produce a white precipitate  
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$   
 Bromides produce a cream precipitate  
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$   
 Iodides produce a pale yellow precipitate  
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

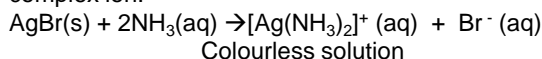
The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:



**Silver chloride** dissolves in **dilute ammonia** to form a complex ion.

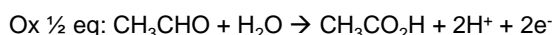
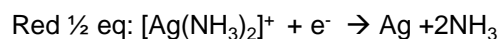


**Silver bromide** dissolves in **concentrated ammonia** to form a complex ion.



**Silver iodide** does not react with ammonia – it is too insoluble.

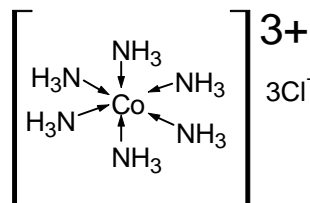
[Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> is used in Tollen's reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollen's reagent to silver.



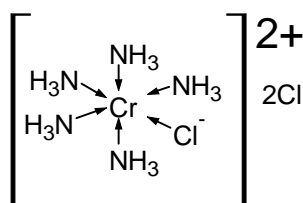
### Using Silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl<sup>-</sup> ions acting as ligands inside the complex and Cl<sup>-</sup> ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

e.g. Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl<sup>-</sup> ions. So all 3 Cls are outside the complex.



e.g. Cr(NH<sub>3</sub>)<sub>5</sub>Cl<sub>3</sub> reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl<sup>-</sup> ions. So 1 Cl is a ligand and 2 are outside the complex.



e.g. Cr(NH<sub>3</sub>)<sub>4</sub>Cl<sub>3</sub> reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl<sup>-</sup> ion. So 2 Cl<sup>-</sup>s are ligands and 1 is outside the complex.

