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 zinc not a transition metal?

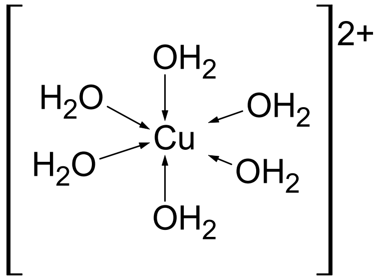
Zinc can only form a +2 ion. In this ion the Zn^{2+} has a **complete** d orbital and so does not meet the criteria of having an incomplete d orbital in atom or ion form.

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 (e.g. Co^{2+} and Cu^{2+}).

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + 6NH_{3\,(aq)} \rightarrow [Co(NH_3)_6]^{2+}{}_{(aq)} + 6H_2O_{\,(l)}$$

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

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

$$[Cu(H_2O)_6]^{2+}{}_{(aq)} + 4NH_{3\,(aq)} \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}{}_{(aq)} + 4H_2O_{\,(l)}$$

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.

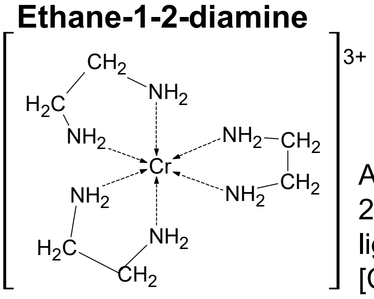
Addition of conc HCl to aqueous ions of Cu and Co leads to a change in coordination number from 6 to 4.
$[CuCl_4]^{2-}$ yellow/green solution
$[CoCl_4]^{2-}$ blue solution
These are tetrahedral in shape

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$$
$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$$
$$[Fe(H_2O)_6]^{3+} + 4Cl^- \rightarrow [FeCl_4]^- + 6H_2O$$

Bidentate ligands

Ligands can be **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.

Ethane-1-2-diamine



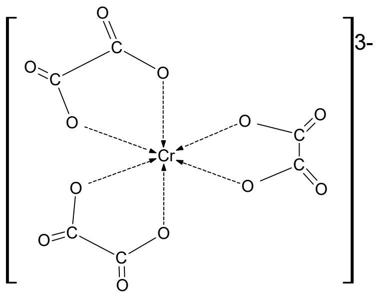
Ethane-1-2-diamine is a common bidentate ligand.

A complex with ethane-1-2-diamine bidentate ligands e.g. $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$

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

It has a coordination number of 6.

Ethanedioate $C_2O_4{}^{2-}$



A complex with bidentate ethanedioate ligands e.g. $[Cr(C_2O_4)_3]^{3-}$

Octahedral shape with 90° bond angles.

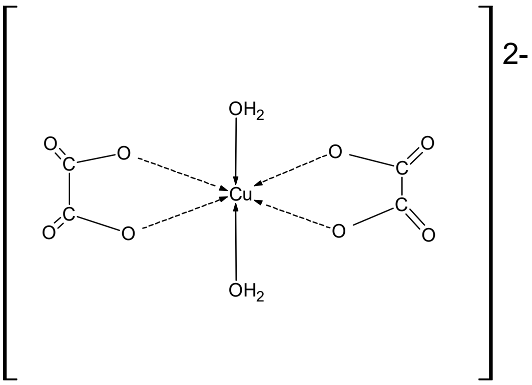
Equations to show formation of bidentate complexes:

$[Cu(H_2O)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Cu(NH_2CH_2CH_2NH_2)_3]^{2+} + 6H_2O$

$[Cu(H_2O)_6]^{2+} + 3C_2O_4{}^{2-} \rightarrow [Cu(C_2O_4)_3]^{4-} + 6H_2O$

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.

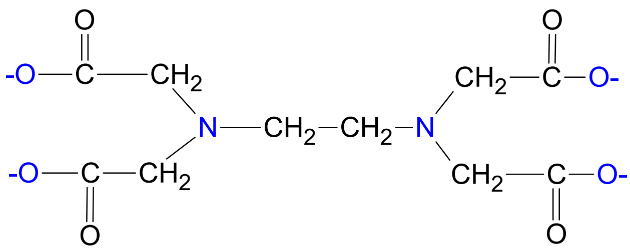
$[Cu(H_2O)_6]^{2+} + 2C_2O_4{}^{2-} \rightarrow [Cu(C_2O_4)_2(H_2O)_2]^{2-} + 4H_2O$



Multidentate ligands

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

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



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

Equations to show formation of mutidentate complexes

$[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$

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

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 because 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.

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 there are more molecules of products than reactants.

$[Cu(H_2O)_6]^{2+}{}_{(aq)} + EDTA^{4-}{}_{(aq)} \rightarrow [Cu(EDTA)]^{2-}{}_{(aq)} + 6H_2O_{(l)}$

The copper complex ion has changed from having monodentate 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 ΔG will be **negative** as **ΔS is positive** and **ΔH 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.

$[Co(NH_3)_6]^{2+} + 3NH_2CH_2CH_2NH_2 \rightarrow [Co(NH_2CH_2CH_2NH_2)_3]^{2+} + 6NH_3$

This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **ΔS is positive.**
Its enthalpy change **ΔH** 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 ΔG** 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.

$[Cu(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 6H_2O$ Always the same 1:1 ratio with any metal ion.

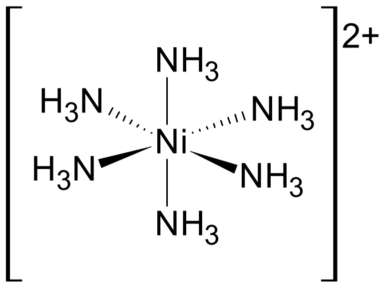
A river was polluted with copper(II) ions. 25.0 cm^3 sample of the river water was titrated with a 0.0150 mol dm^{-3} solution of $EDTA^{4-}$, 6.45 cm^3 were required for complete reaction.
Calculate the concentration, in mol dm^{-3}, of copper(II) ions in the river water.

Step1 : find moles of $EDTA^{4-}$
moles = conc x vol = 0.0150 x 6.45/1000
= 9.68 $\times 10^{-5}$ mol
Step 2 : using balanced equation find moles Cu^{2+}
1:1 ratio
= 9.68 $\times 10^{-5}$ mol
Step 3 : find conc Cu^{2+} in 25 cm^3
= 9.68 $\times 10^{-5}$ /0.025
= 0.00387 mol dm^{-3}

Shapes of complex ions

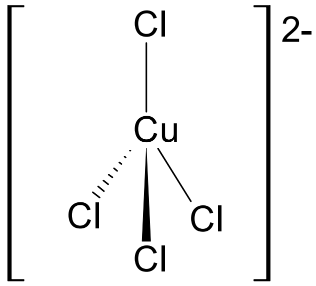
Transition metal ions commonly form **octahedral** complexes with small ligands (e.g. H_2O and NH_3).

$[Co(NH_3)_6]^2$ $[Cu(H_2O)_6]^{2+}$

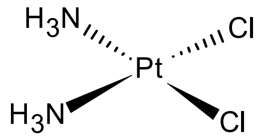


Transition metal ions can form **tetrahedral** complexes with larger ligands (e.g. Cl^-).

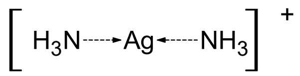
$[CoCl_4]^{2-}$



Square planar complexes are also formed, e.g. cisplatin



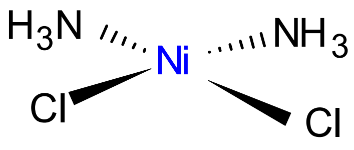
Ag^+ commonly forms **linear** complexes e.g. $[Ag(NH_3)_2]^+$ used as Tollen's reagent



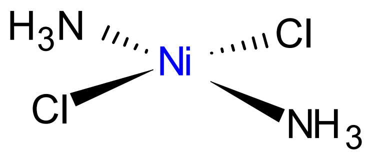
Isomerism in complex ions

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

Cis-trans isomerism in square planar complexes



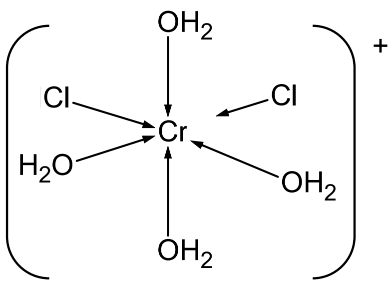
Cis-$Ni(NH_3)_2Cl_2$



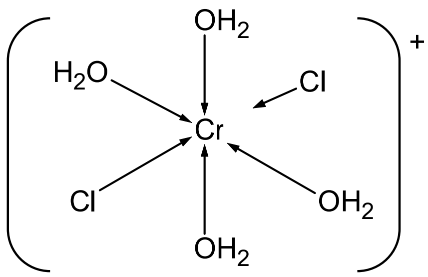
trans-$Ni(NH_3)_2Cl_2$

Cis–trans isomerism is a special case of *E–Z* isomerism

Cis-trans isomerism in octahedral complexes



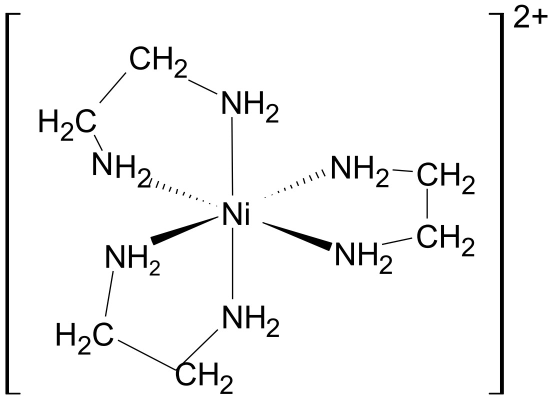
Cis-$[Cr(H_2O)_4Cl_2]^+$

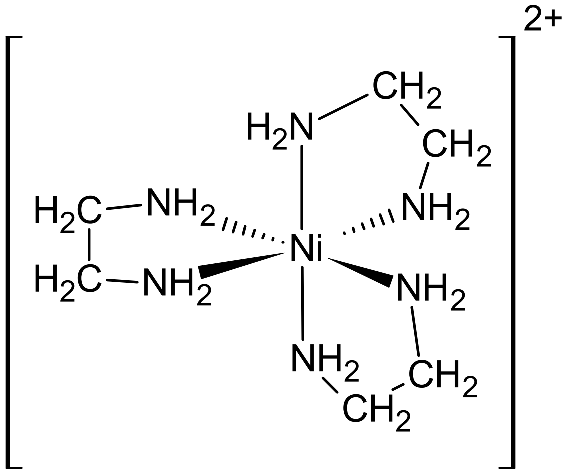


trans-$[Cr(H_2O)_4Cl_2]^+$

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
1. **oxidation state**
2. **co-ordination number**
3. **ligand**

$[Co(NH_3)_6]^{2+}(aq) \xrightarrow{O_2} [Co(NH_3)_6]^{3+}(aq) + e^-$
yellow → brown

In this equation only oxidation state is changing.

$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$
pink → blue

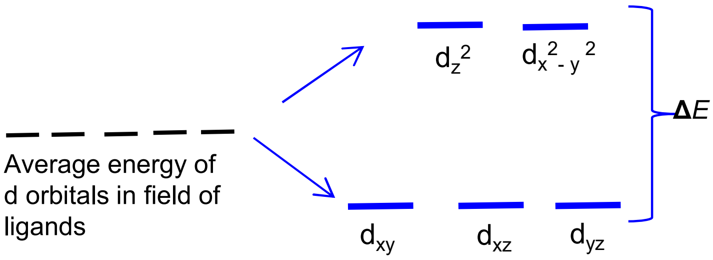
In this equation both ligand and co-ordination number are changing.

$[Co(H_2O)_6]^{2+} + 6\,NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$
Pink → yellow brown

In this equation only the ligand is changing.

How colour arises

The ligands cause the energy levels of the **d orbitals to split.** A **portion of visible light is absorbed** to **promote d electrons** from ground state to excited state. The **light that is not absorbed is transmitted** to give the substance colour.



Octahedral complex ion

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

Equations to learn
These equations link the colour, wavelength and frequency of the light absorbed with the energy difference between the split d orbitals.

$\Delta E = hv$ or $\Delta E = hc/\lambda$

v = frequency of light absorbed (unit s^{-1} or Hz)
h = Planck's constant 6.63×10^{-34} (J s)
ΔE = energy difference between split orbitals (J)
c = speed of light 3.00×10^8 ($m\,s^{-1}$)
λ = wavelength of light absorbed (m)

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

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

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

Compounds without colour

Scandium is a member of the d block. Its ion (Sc^{3+}) hasn't got any d electrons left to move around. Therefore no d-d electron transitions are possible and cannot absorb visible light.

In the case of Zn^{2+} ions and Cu^+ ions the d shell is full e.g.$3d^{10}$ so there is no space for electrons to transfer. Therefore no d-d electron transitions are possible and cannot absorb 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. MnO_4^-
•Compounds with low oxidation states are often reducing agents e.g. V^{2+} & 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

VO_2^+ Oxidation state +5 (a yellow solution)

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

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

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 VO_3^- ion, usually as NH_4VO_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 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 will successively change from yellow to blue to green to violet.

Zinc metal with acid is a strong reducing agent that can reduce most transition metal ions from a higher oxidation state to the lowest state. E.g. Fe^{3+} to Fe^{2+}

$[Ag(NH_3)_2]^+$ is used in Tollens' reagent to distinguish between aldehydes and ketones . Aldehydes reduce the silver in the Tollens' reagent to silver.

Red ½ eq: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$

Ox ½ eq: $CH_3CHO + H_2O \rightarrow CH_3CO_2H + 2H^+ + 2e^-$

Manganate redox titration
The redox titration between Fe^{2+} with MnO_4^- (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product.

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

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 → purple

Choosing correct acid for manganate titrations.
The acid is needed to supply the $8H^+$ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.
Only **use dilute sulfuric acid** for manganate titrations.

Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+}.
$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightarrow MnO_2(s) + 2H_2O$
The brown 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 ($8H^+$).

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\ominus$ $MnO_4^-/Mn^{2+} > E^\ominus Cl_2/Cl^-$
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ $E^o = +1.51V$
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ $E^o = +1.36V$
This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\ominus$ $NO_3^-/HNO_2 > E^\ominus Fe^{3+}/Fe^{2+}$
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$ $E^\ominus +0.94V$
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ $E^\ominus = +0.77 V$
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 2.41 g nail made from an alloy containing iron is dissolved in 100 cm^3 acid. The solution formed contains Fe(II) ions.
10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02 mol dm^{-3}. 9.80 cm^3 of $KMnO_4$ were needed to react with the solution containing the iron.
Calculate the percentage of iron by mass in the nail.

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

Step1 : find moles of $KMnO_4$
moles = conc x vol
0.02 × 9.8/1000
= 1.96 ×10^{-4} mol
Step 2 : using balanced equation find moles Fe^{2+} in 10 cm^3
= moles of $KMnO_4$ × 5
= 9.8 ×10^{-4} mol
Step 3 : find moles Fe^{2+} in 100 cm^3
= 9.8 ×10^{-4} mol × 10
= 9.8 ×10^{-3} mol
Step 4 : find mass of Fe in 9.8x10^{-3} mol
mass= moles x *Ar* = 9.8 x10^{-3} × 55.8 = 0.547g
Step 5 : find % mass
%mass = 0.547/2.41 x100
= 22.6%

Other useful manganate titrations
With hydrogen peroxide

Ox $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2 \rightarrow 5O_2 + 2Mn^{2+}(aq) + 8H_2O$

With ethanedioate

Ox $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
Red $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O$
Overall $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$

The reaction between MnO_4^- and $C_2O_4^{2-}$ 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^{2+} and the $C_2O_4^{2-}$ react with the MnO_4^-
1 MnO_4^- reacts with 5 Fe^{2+} and 2 MnO_4^- reacts with $5C_2O_4^{2-}$

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 4H_2O + 5Fe^{3+}$
$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-} \rightarrow 10CO_2 + 2Mn^{2+}(aq) + 8H_2O$
So overall
$\mathbf{3MnO_4^-}(aq) + 24H^+(aq) + \mathbf{5FeC_2O_4} \rightarrow 10CO_2 + 3Mn^{2+}(aq) + 5Fe^{3+} + 12H_2O$

So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4

A 1.412 g sample of impure $FeC_2O_4.2H_2O$ was dissolved in an excess of dilute sulfuric acid and made up to 250 cm^3 of solution. 25.0 cm^3 of this solution decolourised 23.45 cm^3 of a 0.0189 mol dm^{-3} solution of potassium manganate(VII).
Calculate the percentage by mass of $FeC_2O_4.2H_2O$ in the original sample.

Step1 : find moles of $KMnO_4$
moles = conc x vol
0.0189 x 23.45/1000
= 4.43x10^{-4} mol
Step 2 : using balanced equation find moles $FeC_2O_4.2H_2O$ in 25cm^3
= moles of $KMnO_4$ x 5/3 (see above for ratio)
= 7.39x10^{-4} mol
Step 3 : find moles $FeC_2O_4.2H_2O$ in 250 cm^3
= 7.39x10^{-4} mol x 10
= 7.39x10^{-3} mol
Step 4 : find mass of $FeC_2O_4.2H_2O$ in 7.39x10^{-3} mol
mass= moles x *Mr* = 7.39x10^{-3} x 179.8 = 1.33g
Step 5 : find % mass
%mass = 1.33/1.412 x100
= 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.

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 leading to a higher collision frequency.

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.

Transition metals can use the 3d and 4s electrons 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 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 sulfur 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**.

$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ E^o+2.01V

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ E^o+0.77V

$I_2 + 2e^- \rightarrow 2I^-$ E^o+0.54V

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants. It will first reduce the reactant with the more positive electrode potential and then in the second step oxidise the reactant with the more negative electrode potential.

Catalysed alternative route

stage 1 $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$

stage2 $2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2$

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^-

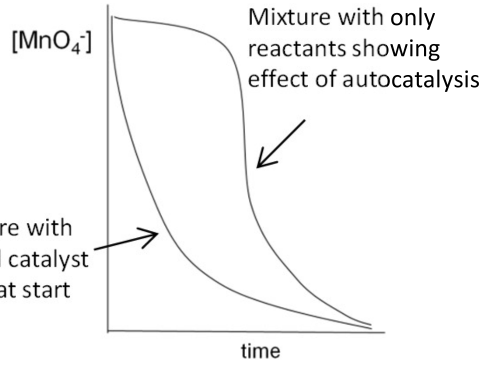
overall $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Catalysed alternative route

Step 1 $4Mn^{2+} + MnO_4^- + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O$

Step 2 $2Mn^{3+} + C_2O_4^{2-} \rightarrow 2Mn^{2+} + 2CO_2$

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



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.**

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 Co^{2+} ions in an acidic solution. $SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$.
Write a mechanism for the catalysed reaction by writing two equations involving Co^{2+} and Co^{3+} ions.

Split the full equation into its two half equations.

$SO_3^{2-} + ½ O_2 \rightarrow SO_4^{2-}$

$½ O_2 + 2H^+ + 2e^- \rightarrow H_2O$

$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

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.

$Co^{2+} \rightarrow Co^{3+} + e^-$

$½ O_2 + 2H^+ + 2Co^{2+} \rightarrow H_2O + 2Co^{3+}$

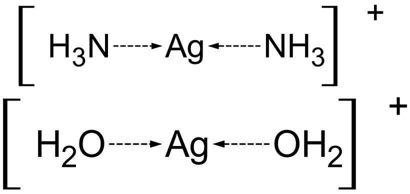
$Co^{3+} + e^- \rightarrow Co^{2+}$

$2Co^{3+} + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2Co^{2+}$

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

Silver Chemistry

Ag^+ commonly forms **linear** complexes
e.g. $[Ag(H_2O)_2]^+$ $[Ag(NH_3)_2]^+$,
$[Ag(S_2O_3)_2]^{3-}$ and $[Ag(CN)_2]^-$
All are colourless solutions.



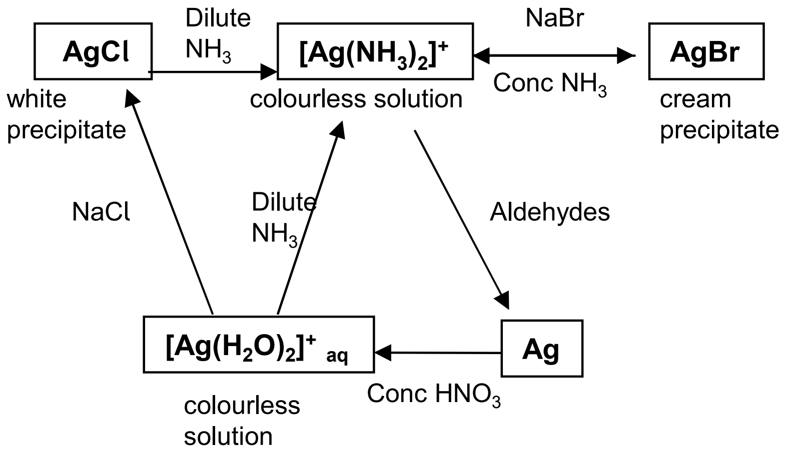
Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples).

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 ($4d^{10}$). As it is $4d^{10}$ 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
$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
Bromides produce a cream precipitate
$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
Iodides produce a pale yellow precipitate
$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

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.
$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$
Colourless solution
Silver bromide dissolves in **concentrated ammonia** to form a complex ion.
$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$
Colourless solution
Silver iodide does not react with ammonia – it is too insoluble.

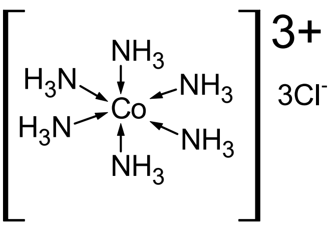
$[Ag(NH_3)_2]^+$ is used in Tollens' reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollens' reagent to silver.

Red ½ eq: $[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$
Ox ½ eq: $CH_3CHO + H_2O \rightarrow CH_3CO_2H + 2H^+ + 2e^-$

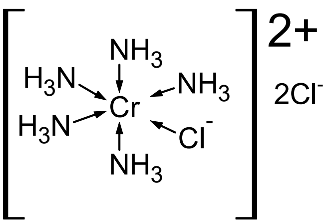
Using silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl^- ions acting as ligands inside the complex and Cl^- 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. $Co(NH_3)_6Cl_3$ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl^- ions. So all 3 Cl^- ions are outside the complex.



e.g. $Cr(NH_3)_5Cl_3$ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl^- ions. So 1 Cl^- is a ligand and 2 are outside the complex.



e.g. $Cr(NH_3)_4Cl_3$ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl^- ion. So 2 Cl's are ligands and 1 is outside the complex.