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.

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

\[ [\text{Co(H_2O)_6}]^{2+} + 6\text{NH}_3 \rightarrow [\text{Co(NH}_3)_6]^{2+} + 6\text{H}_2\text{O} \]

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

\[ [\text{Cu(H_2O)_6}]^{2+} + 4\text{NH}_3 \rightarrow [\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 4\text{H}_2\text{O} \]

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

\[ [\text{Cu(H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CuCl}_4]^{2-} + 6\text{H}_2\text{O} \]
\[ [\text{Co(H}_2\text{O})_6]^{2+} + 4\text{Cl}^- \rightarrow [\text{CoCl}_4]^{2-} + 6\text{H}_2\text{O} \]
\[ [\text{Fe(H}_2\text{O})_6]^{3+} + 4\text{Cl}^- \rightarrow [\text{FeCl}_4]^{3-} + 6\text{H}_2\text{O} \]
Ligands can be bidentate (e.g. NH$_2$CH$_2$CH$_2$NH$_2$ and ethanedioate ion C$_2$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](image)

Ethane-1-2-diamine is a common bidentate ligand. A complex with ethane-1-2-diamine bidentate ligands e.g. [Cr(NH$_2$CH$_2$CH$_2$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**

![Ethanedioate](image)

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

Octahedral shape with 90° bond angles.

Equations to show formation of bidentate complexes

\[
{[\text{Cu(H}_2\text{O)}_6]^{2+} + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2} \rightarrow {[\text{Cu(NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+} + 6\text{H}_2\text{O}}
\]

\[
{[\text{Cu(H}_2\text{O)}_6]^{2+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow [\text{Cu(C}_2\text{O}_4)_3]^{4+} + 6\text{H}_2\text{O}}
\]

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.

\[
{[\text{Cu(H}_2\text{O)}_6]^{2+} + 2\text{C}_2\text{O}_4^{2-} \rightarrow [\text{Cu(C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-} + 4\text{H}_2\text{O}}
\]

**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**

![The EDTA$^{4-}$ anion](image)

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 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.

Equations to show formation of multidentate complexes

\[
{[\text{Cu(H}_2\text{O)}_6]^{2+} + \text{EDTA}^{4-} \rightarrow [\text{Cu(EDTA)}]^{2-} + 6\text{H}_2\text{O}}
\]

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 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 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** \( \Delta G \) will be negative as \( \Delta S \) is positive and \( \Delta H \) 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.

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

This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. \( S \) is positive.
Its enthalpy change \( \Delta H \) 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** \( \Delta G \) 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.

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

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.

**Step 1**: find moles of EDTA\(^{4-}\):
\[
\text{moles} = \text{conc} \times \text{vol} = 0.0150 \times 6.45/1000 = 9.68 \times 10^{-5} \text{ mol}
\]

**Step 2**: using balanced equation find moles Cu\(^{2+}\):
\[
\text{1:1 ratio} = 9.68 \times 10^{-5} \text{ mol}
\]

**Step 3**: find conc Cu\(^{2+}\) in 25 cm\(^3\):
\[
= 9.68 \times 10^{-5} / 0.025 = 0.00387 \text{ moldm}^{-3}
\]
Shapes of complex ions

Transition metal ions commonly form **octahedral** complexes with small ligands (e.g. $\text{H}_2\text{O}$ and $\text{NH}_3$). $[\text{Co(NH}_3)_6]^{2+}$ $[\text{Cu(H}_2\text{O})_6]^{2+}$

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

$\text{Ag}^+$ commonly forms **linear** complexes e.g. $[\text{Ag(NH}_3)_2]^+$ 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($\text{NH}_3$)$_2$Cl$_2$  

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

**Cis-trans isomerism in octahedral complexes**

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

trans-[Cr($\text{H}_2\text{O}$)$_4$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
1. oxidation state,
2. co-ordination number
3. ligand.

 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.

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 (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 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 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.

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$^{2+}$

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

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)

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.

The ion with the V at oxidation state +5 exists as a solid compound in the form of a VO$_2^+$ ion, usually as NH$_4$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 VO$_2^+$ ion.

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$^{2+}$

Manganese 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) → Mn$^{2+}$ (aq) + 4H$_2$O (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) + 8H$^+$ (aq) + 5e$^-$ → Mn$^{2+}$ (aq) + 4H$_2$O (l) + 5Fe$^{3+}$ (aq)

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$^o$ MnO$_4^-/Mn^{2+}$ > E$^o$ Cl$_2$/Cl$^-$

MnO$_4^-$ (aq) + 8H$^+$ (aq) + 5e$^-$ → Mn$^{2+}$ (aq) + 4H$_2$O (l) E$^o$ = +1.51V

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$^o$ NO$_3^-/HNO_2$ > E$^o$ Fe$^{3+}$/Fe$^{2+}$

NO$_3^-$ (aq) + 3H$^+$ (aq) + 2e$^-$ → HNO$_2$(aq) + H$_2$O (l) E$^o$ = +0.94V

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

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Manganese 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. 10 cm$^3$ portions of this solution are titrated with potassium manganate (VII) solution of 0.02 M. 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.

\[
\text{MnO}_4^- (aq) + 8H^+ (aq) + 5Fe^{2+} \rightarrow Mn^{2+} (aq) + 4H_2O + 5Fe^{3+}
\]

Other useful manganate titrations

With hydrogen peroxide

\[
\text{Ox} \quad \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2H^+ + 2e^- \\
\text{Red} \quad \text{MnO}_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + 4H_2O \\
\text{Overall} \quad 2\text{MnO}_4^- (aq) + 6H^+ (aq) + 5\text{H}_2\text{O} \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}
\]

With ethanedioate

\[
\text{Ox} \quad \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^- \\
\text{Red} \quad \text{MnO}_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + 4\text{H}_2\text{O} \\
\text{Overall} \quad 2\text{MnO}_4^- (aq) + 16H^+ (aq) + 5\text{C}_2\text{O}_4^{2-} (aq) \rightarrow 10\text{CO}_2(g) + 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}(l)
\]

With iron (II) ethanedioate both the Fe$^{2+}$ and the C$_2$O$_4^{2-}$ react with the MnO$_4^-$

1 MnO$_4^-$ reacts with 5 Fe$^{2+}$ and 2 MnO$_4^-$ reacts with 5 C$_2$O$_4^{2-}$

\[
\text{MnO}_4^- (aq) + 8H^+ (aq) + 5Fe^{2+} \rightarrow Mn^{2+} (aq) + 4\text{H}_2\text{O} + 5\text{Fe}^{3+} \\
2\text{MnO}_4^- (aq) + 16H^+ (aq) + 5\text{C}_2\text{O}_4^{2-} (aq) \rightarrow 10\text{CO}_2(g) + 2\text{Mn}^{2+} (aq) + 8\text{H}_2\text{O}
\]

So overall

\[
3\text{MnO}_4^- (aq) + 24H^+ (aq) + 5\text{FeC}_2\text{O}_4 \rightarrow 10\text{CO}_2 + 3\text{Mn}^{2+} (aq) + 5\text{Fe}^{3+} + 12\text{H}_2\text{O}
\]

So overall the ratio is 3 MnO$_4^-$ to 5 FeC$_2$O$_4$

A 1.412 g sample of impure FeC$_2$O$_4$.2H$_2$O 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$_2$O$_4$.2H$_2$O in the original sample.

Step 1 : find moles of KMnO$_4$
\[
\text{moles} = \text{conc} \times \text{vol} \\
= 0.0189 \times 23.45/1000 \\
= 0.443 \times 10^{-4} \text{ mol}
\]

Step 2 : using balanced equation find moles FeC$_2$O$_4$.2H$_2$O in 25cm$^3$
\[
= \text{moles of KMnO}_4 \times 5/3 \text{ (see above for ratio)} \\
= 7.39 \times 10^{-3} \text{ mol}
\]

Step 3 : find moles FeC$_2$O$_4$.2H$_2$O in 250 cm$^3$
\[
= 7.39 \times 10^{-3} \times 10 \\
= 7.39 \times 10^{-3} \text{ mol}
\]

Step 4 : find mass of FeC$_2$O$_4$.2H$_2$O in 7.39x10$^{-3}$ mol
\[
\text{mass} = \text{moles} \times M_r = 7.39 \times 10^{-3} \times 179.8 = 1.33 \text{ g}
\]

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.

**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 the surface of the catalyst. This can result in a decrease of 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.

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

### 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.

### 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

- **V₂O₅** is used as a catalyst in the Contact Process.
  - Overall equation: \(2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3\)
  - **Step 1**: \(\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4\)
  - **Step 2**: \(2\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5\)

- **Cr₂O₃** catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen.
  - \(\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}\)

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

- **Fe** is used as a catalyst in the Haber process.
  - \(\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3\)

### Learn the equations

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.

### Poisonsing Catalysts

Poisoning Catalysts have 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.

Poisoning Catalysts 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.

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.

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

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

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 $Mn^{2+}$ 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\textsuperscript{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 Co\textsuperscript{2+} and Co\textsuperscript{3+} ions.

Split the full equation into its two half equations

\[
\begin{align*}
\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 & \rightarrow \text{SO}_4^{2-} \\
\text{SO}_3^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- \\
\end{align*}
\]

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

\[
\begin{align*}
\text{Co}^{2+} & \rightarrow \text{Co}^{3+} + \text{e}^- \\
\text{Co}^{3+} + \text{e}^- & \rightarrow \text{Co}^{2+} \\
\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{Co}^{2+} & \rightarrow \text{H}_2\text{O} + 2\text{Co}^{3+} \\
2\text{Co}^{3+} + \text{SO}_3^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{Co}^{2+} \\
\end{align*}
\]

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

Ag⁺ commonly forms linear complexes
e.g. [Ag(H₂O)₂]⁺ [Ag(NH₃)₂]⁺,
[Ag(S₂O₃)₂]⁻ 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 (4d¹⁰). As it is 4d¹⁰ 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

<table>
<thead>
<tr>
<th>Halide</th>
<th>Reagent</th>
<th>Precipitate</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>Dilute NH₃</td>
<td>White precipitate</td>
<td>Colourless</td>
</tr>
<tr>
<td>AgCl</td>
<td>Conc NH₃</td>
<td>Cream precipitate</td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td>Dilute NH₃</td>
<td>Colourless solution</td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td>Conc HNO₃</td>
<td>Conc NH₃</td>
<td></td>
</tr>
</tbody>
</table>

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) + 2NH₃(aq) → [Ag(NH₃)₂]⁺ + Cl⁻ (aq)
Colourless solution

**Silver bromide** dissolves in concentrated ammonia to form a complex ion.
AgBr(s) + 2NH₃(aq) → [Ag(NH₃)₂]⁺ + Br⁻ (aq)
Colourless solution

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

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(NH₃)₆Cl₃ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl⁻ ions. So all 3 Cl⁻ are outside the complex.

\[
\begin{align*}
\text{Co(NH}_3\text{)}_6\text{Cl}_3 & \quad \text{3+} \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
3\text{Cl}^- & \\
\end{align*}
\]

- e.g. Cr(NH₃)₃Cl 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.

\[
\begin{align*}
\text{Cr(NH}_3\text{)}_3\text{Cl} & \quad \text{2+} \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
2\text{Cl}^- & \\
\end{align*}
\]

- e.g. Cr(NH₃)Cl reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl⁻ ion. So 2 Cl⁻ are ligands and 1 is outside the complex.

\[
\begin{align*}
\text{Cr(NH}_3\text{)}\text{Cl} & \quad \text{1+} \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{Cl}^- & \\
\end{align*}
\]