UNIT 2

Transition elements – electron configurations

Key words

- transition element
- d-block
- electron configuration

Transition elements are metals. You will be concerned only with the first row of transition elements, from titanium to copper. They are located in the **d-block** of the Periodic Table because the outermost electrons are in the d sub-shell.

There are many different things to learn about transition elements. Here is a checklist. Make sure you cover them all:

- definition of a transition element
- electron configurations of the elements and their ions
- oxidation states
- catalytic behaviour
- hydroxides
- complex ions
- ligand substitution
- redox reactions and titration calculations.

Examiner tip

Remember that *partly filled d-orbital* means d^1 to d^9.

Learn this definition of a transition element.

Definition of a transition element

✔ *Quick check 1*

A transition element has at least one ion with an incomplete d sub-shell.

Electron configuration of the d-block elements

Examiner tip

[Ar] is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Scandium	Sc	[Ar] $3d^1\ 4s^2$
Titanium	Ti	[Ar] $3d^2\ 4s^2$
Vanadium	V	[Ar] $3d^3\ 4s^2$
Chromium	Cr	[Ar] $3d^5\ 4s^1$
Manganese	Mn	[Ar] $3d^5\ 4s^2$
Iron	Fe	[Ar] $3d^6\ 4s^2$
Cobalt	Co	[Ar] $3d^7\ 4s^2$
Nickel	Ni	[Ar] $3d^8\ 4s^2$
Copper	Cu	[Ar] $3d^{10}\ 4s^1$
Zinc	Zn	[Ar] $3d^{10}\ 4s^2$

Examiner tip

Scandium and zinc are d-block elements but *are excluded from the list of transition elements*. See below for explanation.

The 3d sub-shell is filled after the 4s sub-shell, so most of the elements have a full 4s sub-shell, $4s^2$. *But note that chromium and copper have $4s^1$ electron configurations, not $4s^2$*. This is to allow either a half-filled or a filled d sub-shell to be made – Cr has $3d^5\ 4s^1$ and Cu has $3d^{10}\ 4s^1$. A half-filled or completely filled sub-shell is more stable, so it makes sense in energy terms for chromium and copper to have these electron configurations.

✔ *Quick check 2*

Examiner tip

$3d^5$ and $3d^{10}$ are stable because the charge on the electrons is distributed symmetrically around the nucleus.

Zinc and scandium are not included in lists of transition metals although they are in the first row of the d-block. This is because:

- Zinc forms one ion, Zn^{2+}, with an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$. This means that its only ion has a full, not a partially full, d sub-shell – so zinc is not a transition element.

- Scandium forms one ion, Sc^{3+}, with an electron configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. This is the main ion, and it has only empty d orbitals, and so scandium is excluded from the list of transition metals.
- We commonly say that scandium and zinc are not transition elements, but they are d-block elements.

✓Quick check 4

Examiner tip

If a d-block element has a white compound, in that oxidation state it will probably have a completely full or empty d sub-shell. *Colour* is associated with *partly filled d-orbitals*.

Electron configurations of the ions

The transition elements form positive ions, as they are metals. This means that when an ion is formed, electrons are removed from the atom.

You must remember that the 4s electrons are removed first.

■ WORKED EXAMPLE 1

Give the electron configuration of Cu^{2+}.

STEP 1 Write down the electron configuration of the atom, Cu.

[Ar] $3d^{10}\ 4s^1$

STEP 2 The ion has a 2+ charge so two electrons are removed. One is taken from the 4s sub-shell, the other from the 3d sub-shell.

So the electron configuration of Cu^{2+} is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$.

■ WORKED EXAMPLE 2

Give the electron configuration of Fe^{3+}.

STEP 1 write down the electron configuration of the atom, Fe.

[Ar] $3d^6\ 4s^2$

STEP 2 The ion has a 3+ charge so three electrons are removed. Two are taken from the 4s sub-shell, the other from the 3d sub-shell.

So the electron configuration of Fe^{3+} is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$.

✓Quick check 3 and 4

QUICK CHECK QUESTIONS

1 Explain what is meant by the term *transition element*.

2 Give the electron configurations of manganese, Mn, and chromium, Cr.

3 Give the electron configurations of Mn^{2+} and Cr^{3+}.

4 Explain why you would not expect compounds of Cu^+ ions to be coloured whilst those of Cu^{2+} are different colours.

UNIT 2

Transition elements – oxidation states, catalytic behaviour and the hydroxides

Key words

- oxidation state
- catalysts

Oxidation states

One characteristic of the transition elements is that they form compounds and ions with different **oxidation states**. In forming ions the two electrons in the 4s orbital are lost first. The 3d and 4s energy levels are close in energy and therefore the 3d electrons can also be lost in forming ions.

You have to learn the different oxidation states of iron and copper.

- **Iron** can have +2, +3, +4, +5 and +6 oxidation states. The +2 and +3 oxidation states are the most common.
- **Copper** can have +1, +2 and +3 oxidation states. The +1 and +2 oxidation states are the most common.

Examiner tip

Learn these common oxidation states: for Fe, +2, +3, for Cu, +1, +2.

✔ *Quick check 1*

Catalytic behaviour

Transition metals and their compounds are very good **catalysts**. There are two reasons for this:

- They can have different oxidation states, so they can gain and lose electrons in moving between these oxidation states, thus facilitating and speeding up redox reactions.
- They provide sites at which reactions can take place, because they bond to a wide range of ions and molecules in solution and as solids.

Examiner tip

Fe and V_2O_5 are heterogeneous catalysts that lower the activation energy of the reaction by adsorbing the gas molecules onto their surface using their d-orbitals.

Examples of industrial catalysts are:

finely divided **Fe** or **Fe_2O_3** in the production of ammonia

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

solid **V_2O_5** in the production of sulfur trioxide, used to make sulfuric acid

$$2SO_2(g) + O_2 \rightleftharpoons 2SO_3(g)$$

finely divided **Ni** in the hydrogenation of alkenes

$$CH_2{=}CH_2(g) + H_2 \rightarrow CH_3CH_3(g)$$

✔ *Quick check 2*

Transition metal hydroxides

Transition metal ions react with the hydroxide ion in aqueous solution to give a solid.

OH^- (aq) + transition metal ion(aq) → metal hydroxide(s)

Example:

The reaction between aqueous copper sulfate and aqueous sodium hydroxide is

$CuSO_4(aq) + 2NaOH(aq) \rightarrow Cu(OH)_2(s) + Na_2SO_4(aq)$

The colour of the metal hydroxide can be used to identify the metal.

You need to know the colours of copper (II) hydroxide, iron(II) and iron(III) hydroxides, and cobalt(II) hydroxide. The list below shows the equations for the reactions and the colours of the aqueous solutions and precipitates obtained.

Cu^{2+} (aq) blue **+ $2OH^-$(aq) → $Cu(OH)_2$(s)** blue

Fe^{2+}(aq) pale green **+ $2OH^-$(aq) → $Fe(OH)_2$(s)** green

Fe^{3+}(aq) yellow/orange **+ $3OH^-$(aq) → $Fe(OH)_3$(s)** red-brown/rust

Co^{2+}(aq) pink **+ $2OH^-$(aq) → $Co(OH)_2$(s)** blue-green and then pink

Although these reactions are the only ones you must know, make sure you can predict the reaction between any transition metal ion and aqueous sodium hydroxide.

Examiner tip

The NaOH(aq) supplies the OH^- ions.

■ WORKED EXAMPLE

Predict the formula of the precipitate formed when aqueous sodium hydroxide is added to an aqueous solution of $CrCl_3$(aq).

STEP 1 Work out the formula of the transition metal ion:

In $CrCl_3$ the chromium ion must be Cr^{3+}.

STEP 2 The charge on the metal ion is balanced by the number of hydroxide ions in the precipitate:

The charge is 3+ so three OH^- ions are needed.

STEP 3 Write the ionic equation:

$Cr^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s)$

✔ *Quick check 3*

Module 3

QUICK CHECK QUESTIONS

1 Explain what is meant by the term *transition element*.

2 Suggest why *finely divided* iron is used as a catalyst in the production of ammonia.

3 **(a)** A transition metal ion in aqueous solution (X) was added to aqueous sodium hydroxide. A brown precipitate appeared. Identify the transition metal ion and write an ionic equation for the reaction.

(b) (i) What is the colour of the aqueous solution of the transition metal ion, X?

(ii) If sulfur dioxide gas is passed through the aqueous solution of X, the solution changes in colour to pale green. What is the ion formed in this reaction?

(iii) What would you see if sodium hydroxide was added to this green solution?

UNIT 2

Complex ions

Key words

- complex ions
- ligands
- coordination numbers
- stereoisomerism

✔ *Quick check 1*

Examiner tip

Octahedral and tetrahedral are the commonest shapes but square planar complexes are common for platinum and nickel.

A **complex ion** is a transition metal atom or ion + ligands.

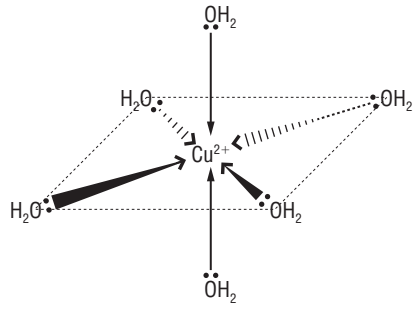
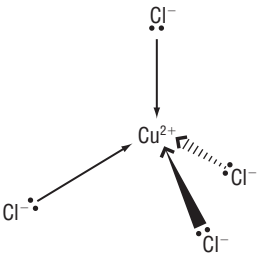
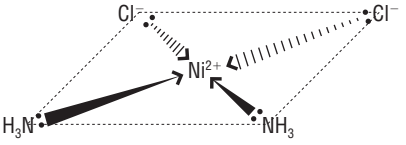
A **ligand** is a molecule or ion which *donates a pair of electrons* to the transition metal ion in a complex to form a dative covalent (or coordinate) bond.

An example of a complex ion is **$[Cu(H_2O)_6]^{2+}$**.

This formula is used to show that Cu^{2+} is surrounded by six H_2O molecules. The H_2O molecules are the ligands. Square brackets go round the whole complex and the total charge of the complex ion goes outside these square brackets. The ligands are shown in normal brackets, with the number of ligands at the end. The number of coordinate bonds round the central ion is called the **coordination number.**

Shapes of complex ions

Complex ions occur in various shapes. The three most common shapes are shown in the table below:

Octahedral Coordination number 6 Bond angle 90°	Tetrahedral Coordination number 4 Bond angle 109.5°	Square planar Coordination number 4 Bond angle 90°
e.g. $[Cu(H_2O)_6]^{2+}$ 	e.g. $CuCl_4^{2-}$ 	e.g. $[Ni(NH_3)_2Cl_2]$ 

✔ *Quick check 2*

Examiner tip

When you draw a complex ion, make sure you show clearly which atom in the ligand forms the coordinate bond.

Types of ligand

- Ligands can be neutral or anionic (negatively charged).
- Ligands can donate *one* pair of electrons (*mono*dentate), *two* pairs of electrons (*bi*dentate) or *several* pairs of electrons (*multi*dentate).

Here are the most common ligands you will come across.

Water	H_2O	monodentate
Ammonia	NH_3	monodentate
Chloride ion	Cl^-	monodentate
Hydroxide ion	OH^-	monodentate
Cyanide ion	CN–	monodentate
Ethane-1,2-diamine (abbreviated to en)	$H_2NCH_2CH_2NH_2$	bidentate
$EDTA^{4-}$		multidentate (hexadentate)

Examiner tip

EDTA is commonly used in shampoos and other cleaning agents.

✔ *Quick check 3*

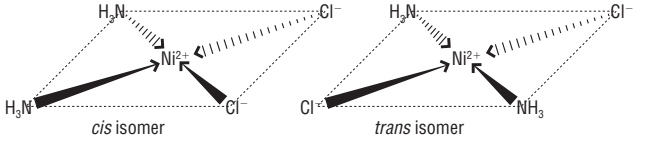
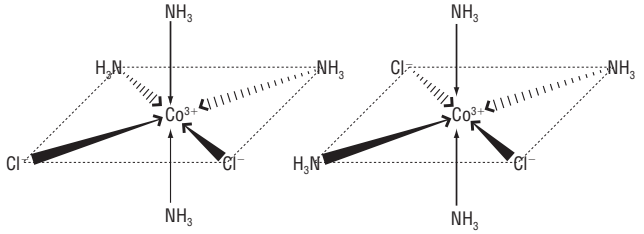
Stereoisomerism in transition metal complexes

There are two types of stereoisomerism and you will have come across both types when you studied alkenes at AS level (*cis–trans* as a special case of *E/Z* isomerism) and stereoisomerism (optical isomerism) at A2.

Cis–trans isomerism

Cis–trans isomerism in transition metals is different from that found in the alkenes because there is no double bond present, just the arrangement of ligands around a central transition metal ion. The *cis* isomer has two identical groups lying on one side of the metal ion (with a bond angle of 90° between them), whilst the *trans* isomer has two identical groups lying on opposite sides of the ion (180° apart).

The two examples below illustrate how *cis–trans* isomerism can occur for square planar and octahedral complexes.

Square planar complex – $[Ni(NH_3)_2Cl_2]$	Octahedral complex
	
One stereoisomer of another square planar complex, platin or $[Pt(Cl)_2(NH_3)_2]$, is used as an anti-cancer drug. The *cis* isomer (*cis*-platin) binds to DNA, stopping replication and therefore cell division.	

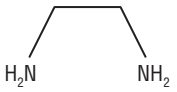
Module 3

Optical isomerism

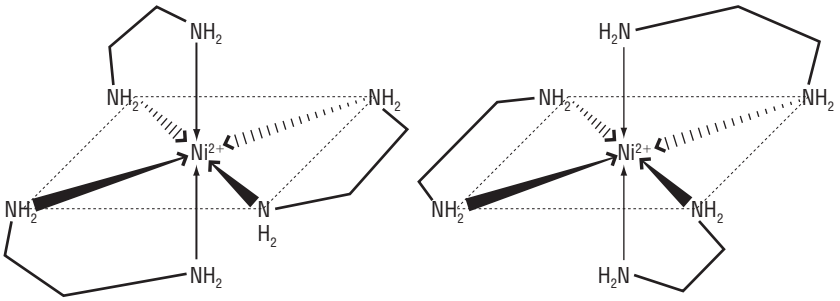
✔ *Quick check 4*

In optical isomerism there are two isomers that are non-superimposable mirror images of each other. An example of this is the $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ complex.

The $H_2NCH_2CH_2NH_2$ ligand is a bidentate ligand and can be represented as shown opposite when drawing complexes.



The two isomers of $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ are shown below.



✔ *Quick check 5*

QUICK CHECK QUESTIONS

1 Using $[Cu(H_2O)_6]^{2+}$ as an example, explain the terms ligand, complex, octahedral and coordination number.

2 Draw the following complexes:
(a) $[Fe(H_2O)_6]^{2+}$
(b) $CoCl_4^{2-}$.

3 Using $H_2NCH_2CH_2NH_2$ as an example, explain the term bidentate ligand.

4 Draw the two isomers of $[Pt(NH_3)_2Cl_2]$.

5 Draw the two optical isomers of $[CoCl_2(H_2NCH_2CH_2NH_2)_2]$.

UNIT 2

Ligand substitution

Key words

- ligand substitution
- stability constant

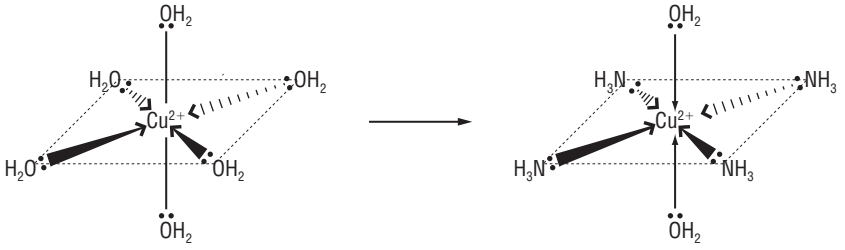
Some ligands combine more strongly with transition metal ions than others. A ligand that binds strongly can displace a ligand that binds more weakly. This is called ***ligand substitution***. You can see ligand substitution in experiments because *different ligands change the colour of the solution as a different complex is formed.*

There are certain ligand substitution reactions you must know, along with the colour changes accompanying them. These are illustrated below. The diagrams show the structures of the complexes and the colour changes occurring.

Example 1 Ammonia solution is added to a solution of aqueous copper(II) ions (e.g. aqueous copper(II) sulfate solution):

Examiner tip

Both these complexes have six ligands, so they are octahedral in shape.



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

blue → **deep blue**

✔ *Quick check 1*

Example 2 Concentrated hydrochloric acid (Cl^-) is added to aqueous copper(II) ions:

$[Cu(H_2O)_6]^{2+} + 4Cl^-(aq)$ → ***Green*** due to a mixture of the two complexes → $CuCl_4^{2-}(aq) + 4H_2O(l)$

blue → **yellow**

✔ *Quick check 2*

Example 3 Water is added to a solution of $CoCl_4^{2-}$ ions:

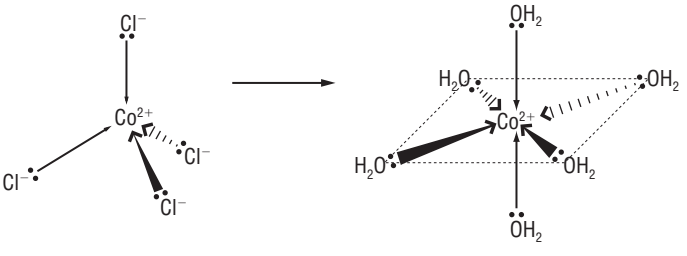
Examiner tip

This is used as a test for water. The $CoCl_4^{2-}$ ion is on cobalt chloride paper. When water is added it turns from blue to pink.

Examiner tip

To get the overall charge on the complex $CoCl_4^{2-}$ ion you add together the charge on the metal ion and the charges on the ligands.

Overall charge = charge on metal ion + charges on ligands.



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

blue → **pink**

Haemoglobin

In haemoglobin a central Fe^{2+} ion is the ion in an octahedral complex comprising four dative covalent bonds from the nitrogens in a porphyrin ring, and one from a nitrogen on one of the amino acids on the globin molecule, which is the protein part of the haemoglobin molecule. *The sixth ligand in the complex is oxygen.*

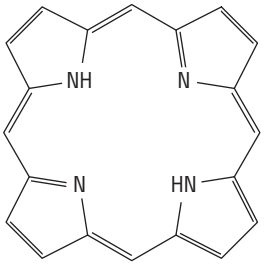
Carbon monoxide is toxic because it binds to the central Fe^{2+} ion more strongly than oxygen and replaces it in the complex. This means that oxygen cannot be carried around the body, causing asphyxiation.

The reaction is $HbO_2(aq) + CO(g) \rightleftharpoons HbCO(aq) + O_2(g)$

✔Quick check 3

Examiner tip

The structure of the porphyrin ring is shown below. The nitrogens have lone-pair electrons and can therefore form coordinate bonds with the central metal ion.



Examiner tip

Haemoglobin can be written as Hb.

Stability constants and ligand substitution

When a ligand is added to a solution of the complex formed between water and a transition metal ion, an equilibrium is established as ligand substitution takes place. You have to be able to write the equilibrium constant for this equilibrium, called the **stability constant.**

■ WORKED EXAMPLE

How do we write the stability constant when Cl^- substitutes for water molecules?

STEP 1 *Write the equation for the reaction*. This always concerns the complex containing water as a reactant:

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

STEP 2 Write the equilibrium constant for the reaction.

$$K_c = \frac{[CuCl_4^{2-}]\,[H_2O]^6}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

STEP 3 *Simplify this by omitting the concentration of water as a factor.* This is because the concentration is a constant. The new equilibrium constant is the stability constant.

$$K_{stab} = \frac{[CuCl_4^{2-}]}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

STEP 4 Add the units to your expression. In this case we have:

$$\text{units} = \frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^4} = \frac{1}{(\text{mol dm}^{-3})^4} = \text{dm}^{12}\,\text{mol}^{-4}$$

The magnitude of the stability constant is a measure of how strongly the ligand binds to the central metal ion. The greater K_{stab} the stronger the binding.

The strength of binding of some ligands to Cu^{2+} follows the following trend:

$$EDTA^{4-} > NH_3 > Cl^- > H_2O$$

✔Quick check 1

Examiner tip

Learn this useful trend in ligand strength.

QUICK CHECK QUESTIONS

1 Using the reaction
$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$:
   (a) Explain the term 'ligand substitution'.
   (b) Write the expression for the stability constant.

2 Give the colour changes occurring when Cl^- ions are added to a solution of $[Cu(H_2O)_6]^{2+}(aq)$ ions.

3 Explain why carbon monoxide poisoning is caused by ligand substitution.

UNIT 2

Redox reactions and titration calculations

Key words

- redox reactions
- titrations

You have met redox reactions before in the AS course (AS Revision Guide page 16) and on page 72 of this book. Now you will study some redox reactions involving transition metal ions. There are many of these, because transition elements have *several different oxidation states*.

Often *half-equations* and *ionic equations* are used to show redox behaviour.

Redox behaviour in iron

$$\underset{\text{Yellow}}{Fe^{3+}(aq)} + e^- \rightleftharpoons \underset{\text{Pale green}}{Fe^{2+}(aq)}$$

Species	Oxidation number of Fe
Fe^{2+}	+2
Fe^{3+}	+3

Examiner tip

Use the terms oxidising, reducing, oxidising agent and reducing agent carefully – it's easy to get muddled. The best way of working out what is oxidised and what is reduced is to use *oxidation numbers*.

Iron can change from:

oxidation state +2 to +3 (oxidation) if an oxidising agent is added to it.

oxidation state +3 to +2 (reduction) if a reducing agent is added to it.

- Fe^{3+} is itself an oxidising agent, because it can oxidise other species by gaining an electron.
- Fe^{2+} is itself a reducing agent, because it can reduce other species by donating an electron.

Example:

$$Fe^{3+}(aq) + 2I^-(aq) \rightarrow Fe^{2+}(aq) + I_2(aq)$$

✔ *Quick check 1*

You can tell by the colour change that this reaction has happened. Fe^{3+} is yellow-orange, Fe^{2+} is pale green and I_2 is brown. The brown colour of the I_2 masks the pale green of Fe^{2+}, so the colour change is pale orange to brown.

Redox behaviour in manganese

$$\underset{\substack{\text{manganate(VII) ion}\\\text{purple}}}{MnO_4^-(aq)} + 8H^+(aq) + 5e^- \rightarrow \underset{\substack{\text{manganese(II) ion}\\\text{very pale pink}}}{Mn^{2+}(aq)} + 4H_2O(l)$$

Examiner tip

The state symbols have been left out of these equations to make them clearer.

This reaction takes place in acid solution, as you can see by the presence of $H^+(aq)$ ions in the equation.

Species	Oxidation number of Mn
MnO_4^-	+7
Mn^{2+}	+2

Manganese is reduced in this reaction, so the manganate(VII) ion is an oxidising agent.

Example:

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

The colour change here is from purple (MnO_4^-) to yellow (Fe^{3+}) – the very pale pink of the Mn^{2+} does not show.

Redox behaviour in chromium

$$\underset{\substack{\text{dichromate(VI) ion}\\\text{orange}}}{Cr_2O_7^{2-}(aq)} + 14H^+(aq) + 6e^- \rightarrow \underset{\substack{\text{chromium(III) ion}\\\text{green}}}{2Cr^{3+}} + 7H_2O$$

Examiner tip

Notice that all these reactions take place in acid solution.

This reaction is frequently used in organic chemistry, where the orange → green colour change tells you the organic substance has been oxidised (see page 9 and AS Revision Guide page 62).

Species	Oxidation number of Cr
$Cr_2O_7^{2-}$	+6
Cr^{3+}	+3

Module 3

Titration calculations

You must revise *titration calculations* because they will be tested!

$KMnO_4$ titrations

Make sure you are familiar with the redox titration between MnO_4^- and Fe^{2+} in aqueous acid solution.

- The equation for this reaction is:
  $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
- The *purple* aqueous MnO_4^- is added from the burette to the aqueous Fe^{2+}. It immediately goes *colourless* as it reacts with the Fe^{2+} (the very pale pink of $Mn^{2+}(aq)$ and the pale yellow of dilute $Fe^{3+}(aq)$ do not show at these low concentrations).
- The end point is when all the Fe^{2+} has reacted and a *permanent pink colour* can be seen.
- Remember the acid! It takes part in the reaction, so without acid the reaction will not happen.

Examiner tip

See page 15 of Revise AS Chemistry for OCR.

Examiner tip

Remember the colour change at the end point is *colourless → pink*.

✔ *Quick check 2*

Thiosulfate titrations

Sodium thiosulfate (containing the $S_2O_3^{2-}$ ion) is a useful reagent because it can be titrated against iodine. It is particularly useful in linked reactions. For example, it can used to estimate the concentration of Cu^{2+} ions in a solution.

Firstly, excess iodide ions are added to the solution of copper(II) ions:

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

The iodine liberated is then titrated against standard sodium thiosulfate solution:

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

From these two equations it can be seen that:

$2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-}$

Therefore $2Cu^{2+} \equiv 2S_2O_3^{2-}$

Therefore the number of thiosulfate ions = the number of copper(II) ions.

We can then use our equations for moles in solution to find the concentration of the copper.

Examiner tip

Starch is used as the indicator in this reaction and the end point is *blue-black → colourless*.

✔ *Quick check 3*

Examiner tip

Use $n = C \times V$ in your calculation.

QUICK CHECK QUESTIONS

1 Hydrogen peroxide, H_2O_2, is an oxidising agent.

$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$

Construct the equation for the reaction between hydrogen peroxide and Fe^{2+} ions in aqueous solution.

2 A student weighed out 5.56 g of $FeSO_4 \cdot 7H_2O$, dissolved it in dilute sulfuric acid and made up the solution to 250 cm^3 in a volumetric flask using distilled water. She then titrated 25 cm^3 samples of this solution against potassium manganate(VII) solution. The iron(II) sulfate solution required 20.0 cm^3 for complete reaction.

(a) Calculate the concentration of the Fe^{2+} ion in the iron(II) sulfate solution.

(b) Calculate the concentration of the potassium manganate solution.

3 Brass is an alloy of copper and zinc. To find the percentage of copper in a sample of brass, a student dissolved 2.20 g of the brass in concentrated nitric acid and made the resulting solution up to 250 cm^3 in a volumetric flask. He then took 25.0 cm^3 samples of this solution, added excess potassium iodide solution and then titrated the iodine liberated against a standard, 0.100 mol dm^{-3} solution of sodium thiosulfate. Starch was used as the indicator. The solution required 22.5 cm^3 of sodium thiosulfate for complete reaction.

(a) Give the equations for the reaction of Cu^{2+} ions with I^- ions and the reaction of iodine with thiosulfate ions.

(b) Calculate the concentration of copper ions in the solution and the percentage composition of the sample of brass. (NOTE: zinc does not react with I^- ions.)

UNIT 2

End-of-unit questions

1 Copper readily forms complexes with water, ammonia and chloride ions, and pairs of these ions can coexist in different equilibria.

(a) Concentrated hydrochloric acid is added to a solution containing $[Cu(H_2O)_6]^{2+}(aq)$ until there is a high concentration of Cl^-.

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

pale blue — yellow

(i) Using one or both of the two complexes given above, explain what is meant by the following terms:

I coordinate bonding [2]

II ligand [2]

III complex [2]

(ii) Draw the two complexes described in the equilibrium. [4]

(b) (i) State le Chatelier's principle. [2]

(ii) For the equilibrium shown, use le Chatelier's principle to deduce what is observed as the acid is added. [3]

(c) The equilibrium constant, K_c, for the equilibrium in (**a**) may be written as:

$$K_c = \frac{[[CuCl_4]^{2-}]\,[H_2O]^6}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

It is possible in aqueous solution to simplify this expression to:

$$K'_c = \frac{[[CuCl_4]^{2-}]}{[[Cu(H_2O)_6]^{2+}]\,[Cl^-]^4}$$

The numerical value of K'_c for this equilibrium, at 25 °C, is 4.17×10^5.

(i) What are the units of K'_c? [1]

(ii) An equilibrium mixture, at 25 °C, contained 1.17×10^{-5} mol dm^{-3} $[Cu(H_2O)_6]^{2+}(aq)$ and 0.800 mol dm^{-3} Cl^-.
Calculate the equilibrium concentration of $[CuCl_4]^{2-}(aq)$. [2]

(iii) Suggest why, in aqueous solution, it is possible to simplify K_c to K'_c. [2]

[TOTAL 20 marks]

2 (a) (i) With the aid of examples, explain the meaning of the terms *strong acid* and *weak acid*. [2]

(ii) Using the ethanoic acid/sodium ethanoate mixture as an example, explain how a buffer solution works. [5]

(b) Assuming the temperature to be 25 °C, what is the pH of:

(i) 0.05 mol dm^{-3} hydrochloric acid [1]

(ii) 0.01 mol dm^{-3} sodium hydroxide? [2]

(c) Benzoic acid, C_6H_5COOH, is a weak acid with an acid dissociation constant, K_a, of 6.3×10^{-5} mol dm^{-3} at 25 °C.

(i) Calculate the pH of 0.020 mol dm^{-3} benzoic acid at this temperature. [3]

(ii) Draw a sketch graph of the change in pH which occurs when 0.020 mol dm^{-3} potassium hydroxide is added to 25 cm^3 of 0.020 mol dm^{-3} benzoic acid until in excess. [3]

(iii) The pK_a values of some indicators are:

thymol blue	1.7
congo red	4.0
thymolphthalein	9.7

Which of these indicators would be most suitable for determining the end point of the titration between the benzoic acid and potassium hydroxide in **(ii)**? Explain your answer [2]

[TOTAL 18 marks]

3 Methanol, CH_3OH, is used as an alternative fuel to petrol in racing cars. Although methanol is less volatile than petrol, its combustion in these engines is more complete.

(a) Enthalpy changes can be determined indirectly using standard enthalpy changes of formation.

(i) Write the balanced equation for the combustion of methanol. [1]

(ii) Calculate the standard enthalpy change of combustion of methanol using the following data.

Compound	ΔH_f/kJ mol^{-1}
$CH_3OH(l)$	–239
$CO_2(g)$	–394
$H_2O(l)$	–286

[3]

(iii) The molar entropies of the reactants and products involved in the reaction are given below:

	ΔS J K mol^{-1}
$CH_3OH(l)$	127
$CO_2(g)$	214
$H_2O(l)$	70
$O_2(g)$	127

Using these values calculate the standard entropy change for the reaction. [2]

(b) Calculate the molar free energy change for the reaction at 298 K and hence explain whether or not it is a spontaneous reaction at this temperature. [4]

(c) At 298 K the combustion of methanol requires, for example, a lighted spill or a spark from an ignition coil. In the light of your answer to part **(c)**, explain this fact. [2]

(d) One of the consequences of the heat generated by a car engine is the formation of nitrogen oxide, NO.

When the nitrogen monoxide leaves the car engine it is oxidised to a gas in which the oxidation number of the nitrogen is +4.

(i) Identify the product and write the balanced symbol equation for the reaction. [3]

(ii) Explain why it is a redox reaction. [2]

In an experiment to investigate the effects of changing concentrations on the rate of reaction, the following results were obtained.

Experiment number	Initial concentration $O_2/10^{-2}$ mol dm^{-3}	Initial concentration NO/10^{-2} mol dm^{-3}	Initial rate of disappearance of NO/10^{-4} mol dm^{-3}s^{-1}
1	1.0	1.0	0.7
2	1.0	2.0	2.8
3	1.0	3.0	6.3
4	2.0	2.0	5.6
5	3.0	3.0	18.9