

A2 (yr 13) TM Chemistry Revision Workshop

23 March 2021

Preparing for your A-level Examinations

Participants Notes

A2 TOPICS INDEX

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Post-16 Learning Resources:

(peer-produced in collaboration with world-wide UK-based research databases)

With the CCDC (chemistry); <http://tiny.cc/ccdcLR>

With the PDBe (biology & chemistry); <http://tiny.cc/proteinLR>

With LIPID MAPS (biology); <http://tiny.cc/lipidLR>

1. TRANSITION ELEMENTS

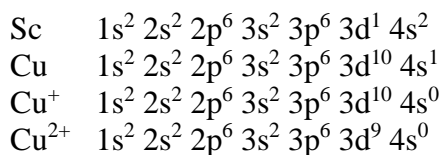
Transition Series

<u>Transition Series</u>	<u>Elements</u>	
First Series	Sc – Zn	3 d
Second Series	Y – Cd	4 d
Third Series	La – Hg	5 d

1.1 General Characteristics of Transition Metals:

1. Form complex ions
2. Form coloured ions
3. Act as catalysts
4. Form compounds with the transition element in different oxidation states

These properties are linked to the presence of an incomplete d-sub-shell in an ion. Consider:

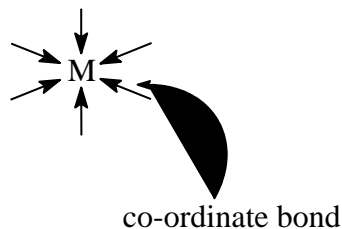


1.2 Complex Formation Definitions

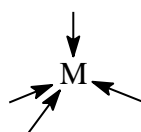
Complex	A central metal atom or ion surrounded by ions or molecules called ligands
Ligand	An ion or molecule which donates an electron pair to form a co-ordinate bond, i.e. a Lewis Base or nucleophile
Coordinate bond	A covalent bond formed using two electrons from one atom (the ligand)
Coordination number	The number of coordinate bonds formed to the central metal atom (NOT the number of ligands – see later)

1.3 Co-ordination Numbers / Shapes of Complexes

If the coordination number is 6, the shape is octahedral:



If the coordination number is 4, the shape is often tetrahedral:



If the coordination number is 2, the shape is linear:



1.4 Types of ligands

1.4.1 Unidentate ligands

These are “one-bite” ligands – **one** lone pair of electrons donated per ligand. Examples include ligands with a period 2 donor atom: H_2O , NH_3 , OH^- , CN^- or ligands with a period 3 donor atom: Cl^- , $\text{S}_2\text{O}_3^{2-}$

Examples:

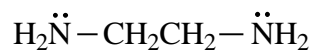
Metal Ion	Ligand	Coordination Number	Complex	Shape	Colour
Cr^{3+}	H_2O	6	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	octahedral	green
Co^{3+}	NH_3	6	$[\text{Co}(\text{NH}_3)_6]^{3+}$	octahedral	brown
Cu^{2+}	Cl^-	4	$[\text{CuCl}_4]^{2-}$	tetrahedral	green
Ag^+	$\text{S}_2\text{O}_3^{2-}$	2	$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	linear	colourless
Ag^+	NH_3	2	$[\text{Ag}(\text{NH}_3)_2]^+$	linear	colourless
Ag^+	Cl^-	2	$[\text{AgCl}_2]^-$	linear	colourless

1.4.2 Bidentate Ligands

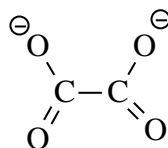
These are “two bite” ligands - **two** lone pairs of electrons donated per ligand.

Examples:

Ethanediamine (en):



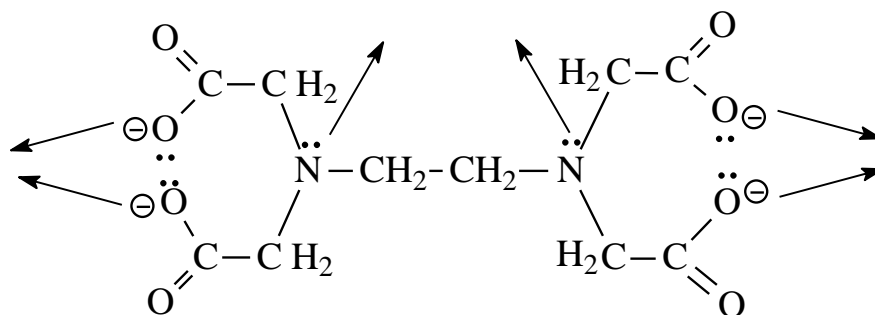
Ethanedioate anion:



1.4.3 Multidentate ligands

Examples: a **hexadentate** ligand - **six** lone pairs of electrons donated per ligand.

Ethylenediaminetetraacetate ion, EDTA⁴⁻



Example 1 $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

Example 2 $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

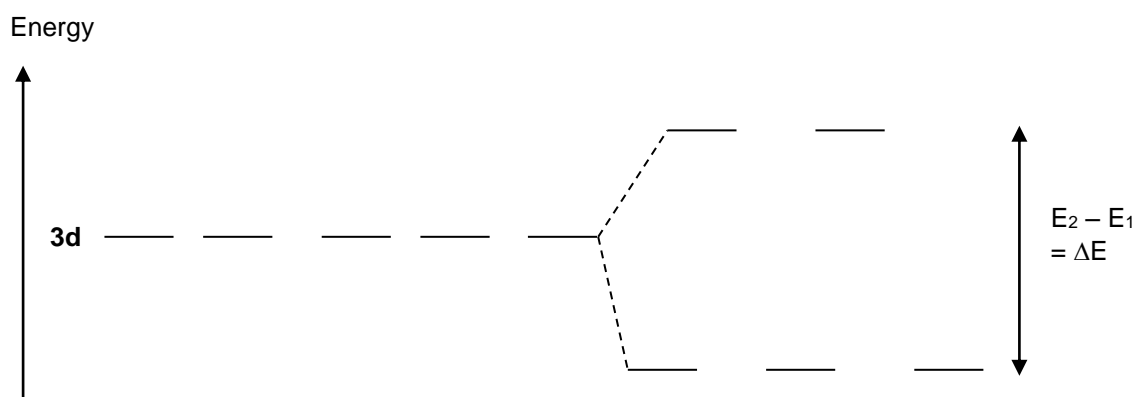
1.5 Formation of coloured ions

1.5.1 Colour depends upon:

1. The transition metal.
2. The oxidation state of the transition metal.
3. The number of ligands surrounding the transition metal ion.
4. The nature of the ligands surrounding the transition metal ion.

1.5.2 Origin of colour:

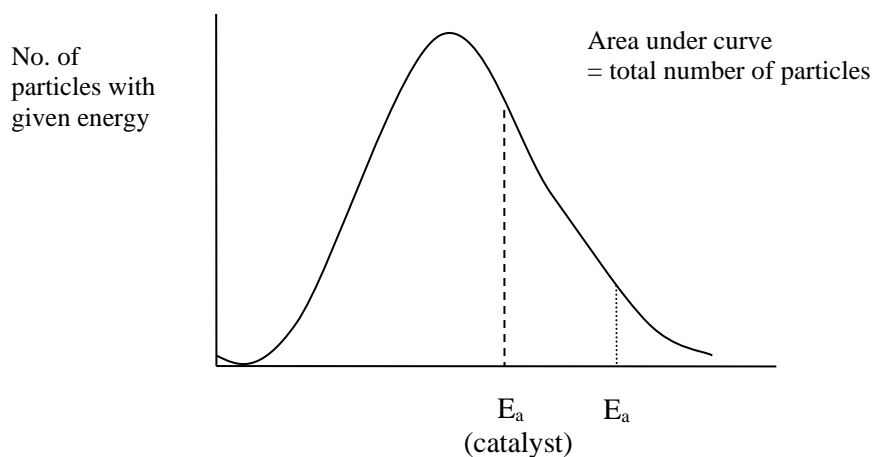
- In presence of ligand, the 5 x 3d orbitals of a transition metal ion split to form 2 slightly different energy levels
- The electrons in the lower 3d sub-level absorb visible light
- Electrons move to a higher, more excited energy state (d → d transitions)
- Difference in energy between levels is:
 $E_2 - E_1 = \Delta E = h\nu = hc / \lambda$
 (where h = Planck's constant, ν is the frequency of light absorbed, c = speed of light and λ is the wavelength).
- We see the colours which are not absorbed, i.e. the complementary colour



1.5.3 An application

- Measurement of transition metal ion concentration using a colorimeter/spectrophotometer
- Note that an intense colour is needed for accurate results and this can be achieved by use of a suitable ligand, e.g.
 Fe^{2+} (aq) absorption weak; add 2,2-bipyridyl (intense red complex)
 Fe^{3+} (aq) absorption weak; add thiocyanate (intense red complex)

1.6 Catalytic activity



The transition metal as a catalyst has the following effect on the reaction:

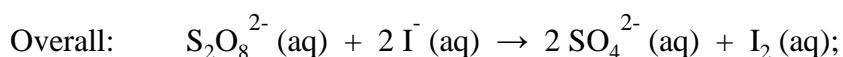
- Provides an alternative route.
- Lowers the activation energy.
- Hence more molecules can react.
- Remember the catalyst remains unchanged in amount and chemical nature.

There are 2 types of catalysts: **homogeneous** (same state) and **heterogenous** (different state):

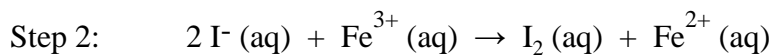
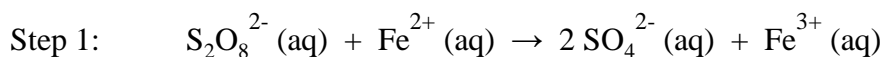
1.6.1 Examples of Homogeneous catalysis include

NB These two examples are specifically mentioned in both the AQA & Edexcel specifications! ☹

Example 1:



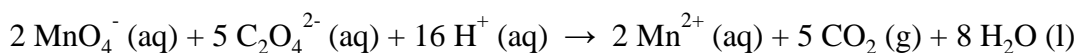
This reaction is catalysed by Fe^{2+}
(note this reaction has a high E_a due to a reaction between two like charged ions)



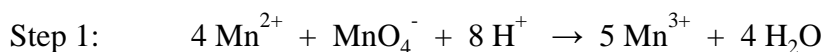
NB Fe^{2+} does not appear in the overall equation and is recovered unchanged at the end of the reaction.

Example 2:

$\text{MnO}_4^{-} / \text{C}_2\text{O}_4^{2-}$: catalysed by Mn^{2+} (NB this is an example of **autocatalysis** – the catalyst is generated in the reaction and thus the reaction speeds up as it proceeds).



Mechanism:



NB Mn^{2+} does not appear in the overall equation and is recovered unchanged at the end of the reaction.

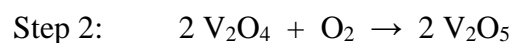
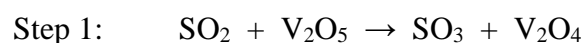
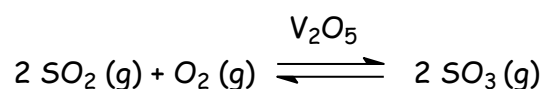
1.6.2 Examples of Heterogenous catalysis

These are reversible reactions

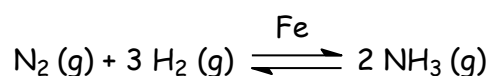
The 5 steps in heterogenous catalysis and a simple analogy:

- | | | |
|----|-------------------------|--|
| 1. | Diffusion to surface | <i>Beach party to ice cream seller</i> |
| 2. | Adsorption on surface | <i>Arriving at the counter</i> |
| 3. | Reaction on surface | <i>Making friends</i> |
| 4. | Desorption from surface | <i>Leaving the counter</i> |
| 5. | Diffusion from surface | <i>Moving away</i> |

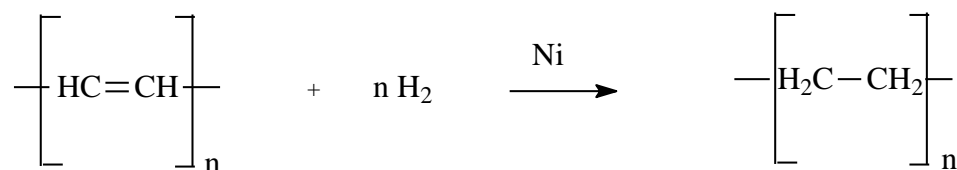
Example 1: Vanadium(V) oxide, V_2O_5 , used in the Contact Process:



Example 2: Iron on silica support, used in the Haber process to manufacture ammonia:



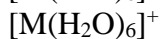
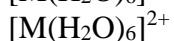
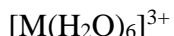
Example 3: Nickel, very finely divided, used in the hydrogenation of vegetable oil:



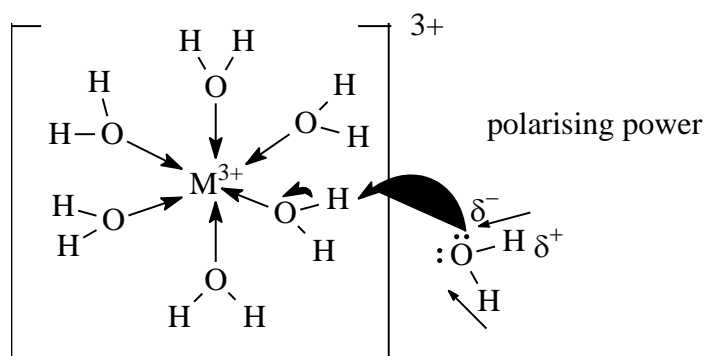
Hydrogenation causes hardening of vegetable oil forming fat. It is an important step in the manufacture of margarine. The extent of hydrogenation is linked to hardness.

1.7 Acidity reactions of metal aqua complexes (hydrolysis) (AQA ONLY)

Consider separate solutions containing the ions:



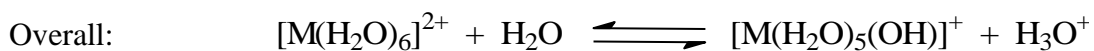
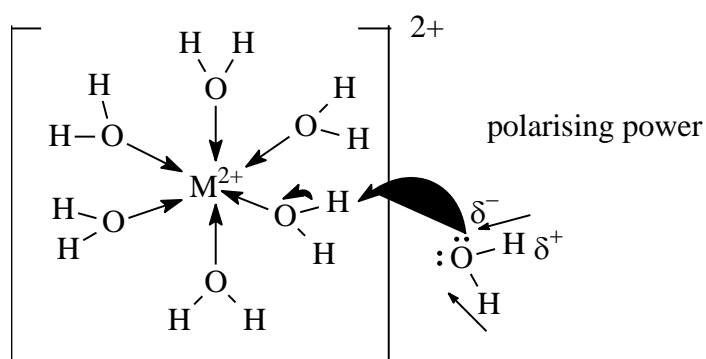
Example 1: for a solution containing approximately 1 mol dm^{-3} of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$



Approximately 1000 n 1 1

Hence: $[\text{H}^+] \sim 10^{-3}$ and $\text{pH} \sim 3$

Example 2: for a solution containing approximately 1 mol dm^{-3} of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$



Approximately 100 000 n 1 1

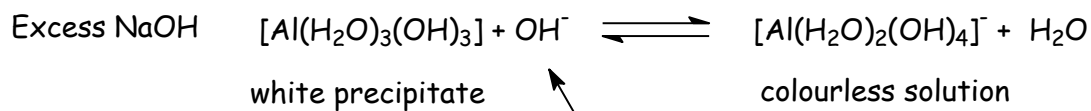
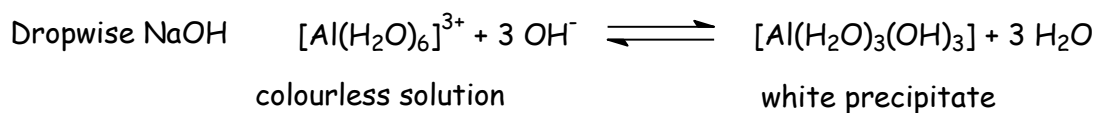
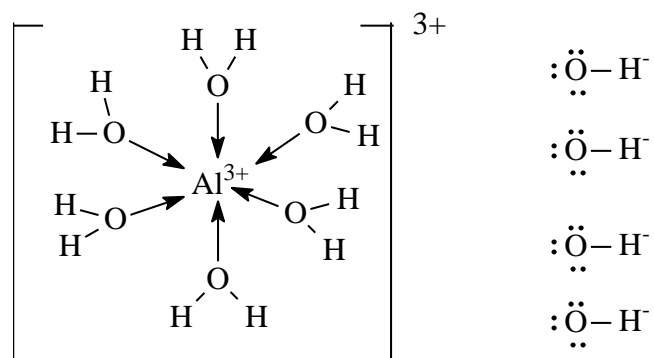
Hence: $[\text{H}^+] \sim 10^{-5}$ and $\text{pH} \sim 5$

1.8 Reactions of metal aqua complexes with other bases

Consider the relative base strengths of the following:

OH^- ; NH_3 ; CO_3^{2-}

Example 1: The addition of a 2.0 mol dm^{-3} solution of NaOH to a solution containing, e.g. $\text{Al}^{3+}(\text{aq})$



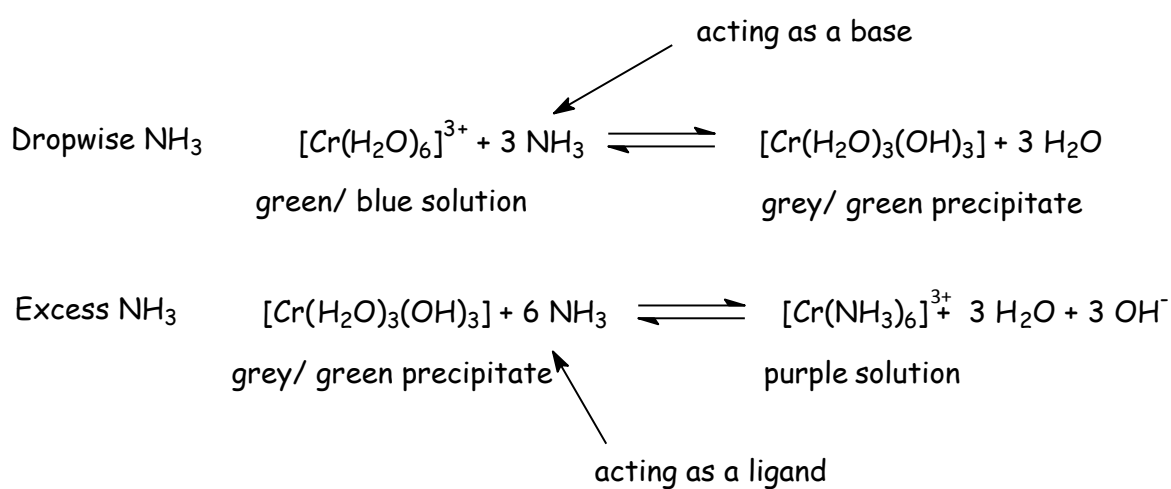
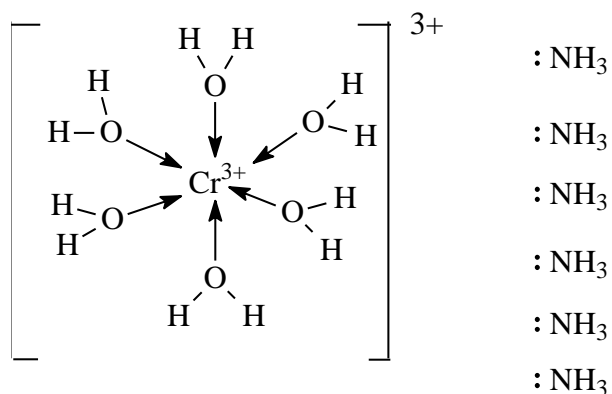
acting as a ligand

NB The $[\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4]^-$ complex ion is often more simply written as $[\text{Al}(\text{OH})_4]^-$

Summary:

- OH^- acting as a base.
- Precipitation when no repulsion; species hydrogen bond together.
- Excess OH^- (aq) forms negatively-charged species.
- Repulsion causes separation, precipitate re-dissolves.

Example 2: Addition of concentrated NH_3 (aq) to a solution containing Cr^{3+} (aq)

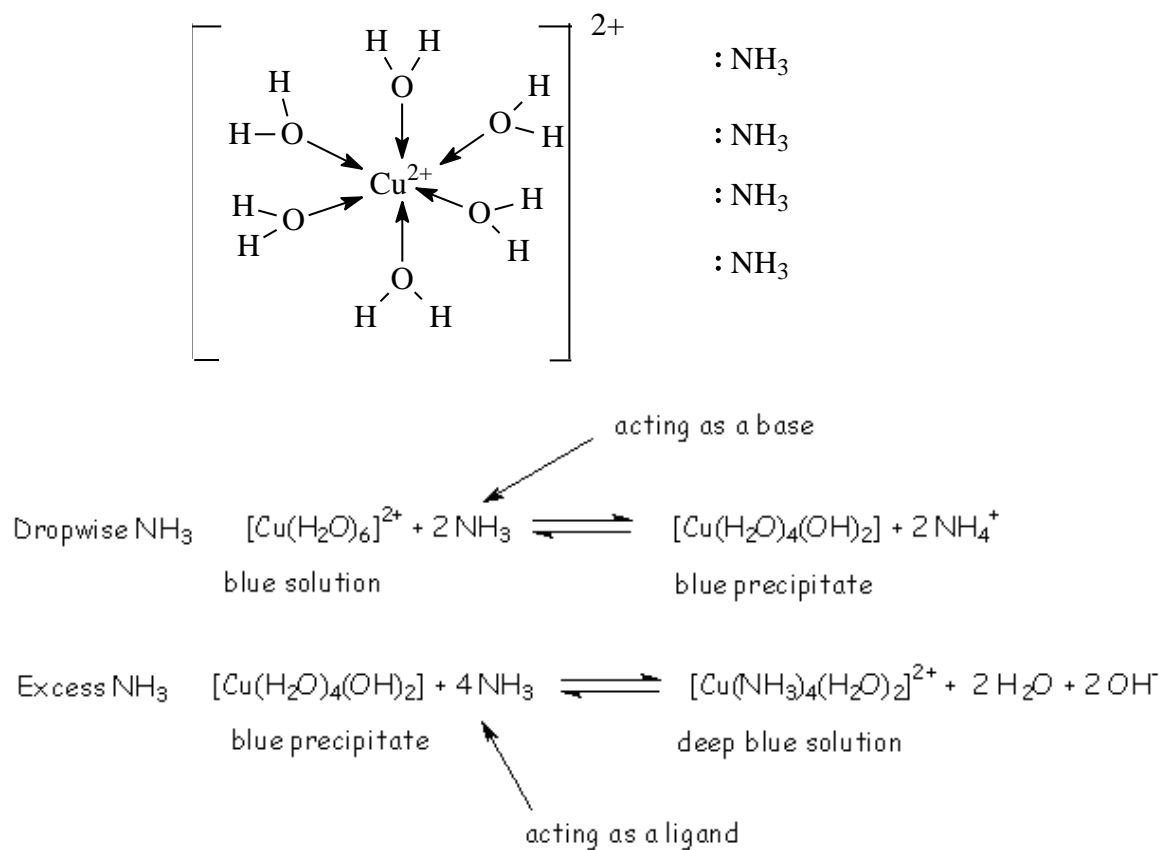


Summary:

- NH_3 is a weaker base than OH^- .
- NH_3 acts first as a base than as a ligand.
- Precipitation when no repulsion; species hydrogen bond together.
- Excess NH_3 (aq) forms positively charged species.
- Repulsion causes separation, precipitate re-dissolves.

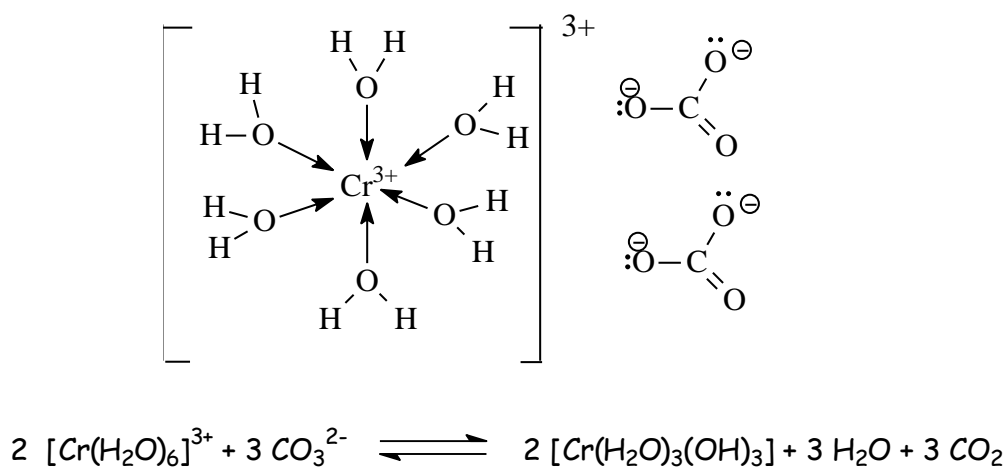
Example 3: In concentrated NH_3 (aq) the ratio $\text{H}_2\text{O}:\text{NH}_3$ is 2:1

Substitution reactions are in equilibria and sometimes not all H_2O replaced

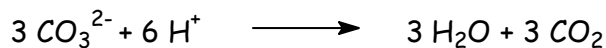


Example 4: Addition of solution containing CO_3^{2-} to solution containing M^{3+} (aq)

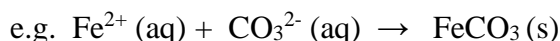
CO_3^{2-} acts only as a **base**, e.g.



The following *INCORRECT* stepwise equations aid understanding of this reaction:



NB Aqueous complex ions of metals in oxidation state (II) form simple carbonate precipitates on the addition of aqueous Na_2CO_3 . **NO** CO_2 is produced.



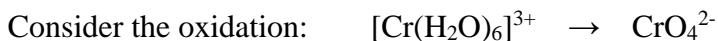
1.9 Redox reactions

Useful rules of thumb:

- High oxidation state to low oxidation state:
Reagents: acid (e.g. dilute H_2SO_4) + reducing agent (e.g. Zn or SO_2)
- Low oxidation state to high oxidation state
Reagents: base (e.g. $\text{NaOH}(\text{aq})$) + oxidising agent (e.g. H_2O_2)

Explanations:

High oxidation states are commonly found in complexes containing oxygen

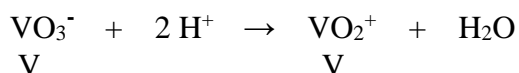


1.10 Oxidation states of vanadium (AQA & Edexcel only)

Summary table:

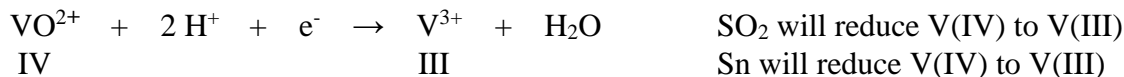
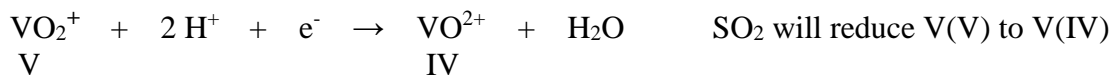
Oxidation state	Formula of species	Colour of aqueous solution
+5	VO_3^-	yellow
+5	VO_2^+	orange
+4	VO^{2+}	blue
+3	V^{3+}	green
+2	V^{2+}	violet

There are two aqueous species which are both V(V) – converted in presence of acid:

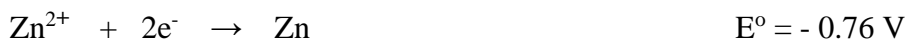
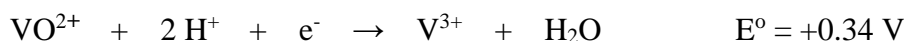
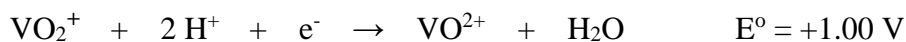


Note that this is NOT a redox reaction as there are no electrons in the overall equation.

V(V) can be reduced stepwise through the other oxidation states down to V(II) with an appropriate reducing agent, i.e:



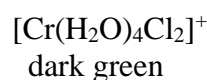
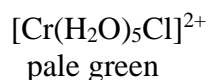
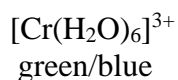
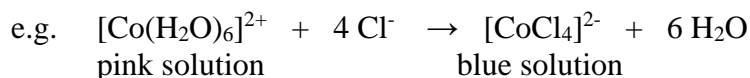
Each of these reductions can be predicted using the appropriate half-equations and E° values listed below:



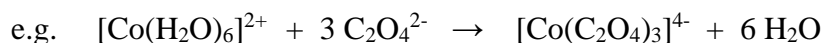
1.11 Substitution reactions

1.11.1 Substitution by chloride ligands

1. Chloride ions are larger than water and ammonia molecules (period 3 vs. period 2).
2. Substitution of all water ligands by chloride ligands results in a change in coordination number and shape.
3. The *colour* of the complex changes.
4. Since chloride ions are charged, the charge on the complex changes.
5. Substitutions are equilibria; conc. HCl (aq) gives chloro complexes (NaCl is not very soluble and does not have a sufficiently high chloride ion concentration).



1.11.2 Substitution of monodentate ligands by bidentate ligands:

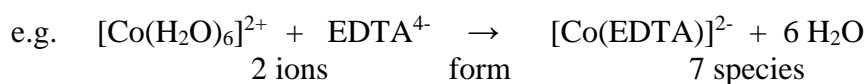


These complexes are octahedral.

NB: bidentate ligands can also bond two metal ions together acting as a bridge.

1.11.3 Substitution of monodentate ligands by the hexadentate ligand EDTA⁴⁻

1. EDTA⁴⁻ is a hexadentate ligand and forms a 6 coordinate complex.
2. A colour change usually occurs when water is replaced by EDTA⁴⁻.
3. The complexes formed are octahedral.
4. There is a large entropy change when a monodentate ligand is replaced by EDTA⁴⁻



1.12 The stability of complexes

Complexes in which bidentate or multidentate ligands are bonded to one central metal ion are known as **chelates**. Chelate stability depends on:

1. Size of ring formed by ligand with metal ion, i.e. strain.
2. Metal-ligand bond energy.
3. Number of bonds to be broken when ligand replaced, e.g. 6 for EDTA⁴⁻.
4. A reaction is feasible when Gibbs Free Energy, ΔG , is negative.

$$\Delta G = \Delta H - T\Delta S.$$

If the change in entropy, ΔS , is large and positive; and change in energy ΔH is small when bond energies are similar, then $T\Delta S \gg \Delta H$. Hence, Gibbs Free Energy (ΔG) is large and negative.

NB: The stability of EDTA⁴⁻ complexes is so high that the reactions go to completion so that, for example, no precipitate forms when NaOH (aq) is added. This is known as the **chelate effect**.

1.13 Summary Table of Aqueous Metal Ion Chemistry (AQA)

Formula & colour of species	Al³⁺	Fe²⁺	Fe³⁺	Cu²⁺
aqueous solution	[Al(H ₂ O) ₆] ³⁺ Colourless solution	[Fe(H ₂ O) ₆] ²⁺ Pale green solution	[Fe(H ₂ O) ₆] ³⁺ Brown solution	[Cu(H ₂ O) ₆] ²⁺ Light blue solution
dropwise NaOH	[Al(H ₂ O) ₃ (OH) ₃] White ppt	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NaOH	[Al(H ₂ O) ₂ (OH) ₄] ⁻ Colourless solution	No change	No change	No change
dropwise NH ₃	Al(H ₂ O) ₃ (OH) ₃ White ppt	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NH ₃	No change	No change	No change	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ Deep blue solution
excess Na ₂ CO ₃	[Al(H ₂ O) ₃ (OH) ₃] White ppt & CO ₂ produced	FeCO ₃ Green ppt	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt & CO ₂ produced	CuCO ₃ Green ppt
excess conc. HCl	X	X	X	[CuCl ₄] ²⁻ Green solution Tetrahedral
pH of aqueous solution	pH = 2 – 3 acidic	pH = 7 neutral	pH = 2 – 3 acidic	pH = 5 – 6 weakly acidic

NB. Shapes of **ALL** complexes are **octahedral** unless otherwise stated in the table.

1.13a Summary Rules for Learning Aqueous Metal Ion Chemistry (AQA)

1. With dropwise NaOH:
ALL give a ppt. of the metal hydroxide, $[M(OH)_n(H_2O)_{6-n}]$, where $n = 2$ or 3
2. With excess NaOH:
Al only dissolves and gives $[Al(OH)_4(H_2O)_2]^-$
Others don't (still metal hydroxide ppt. above)
3. With dropwise NH_3 :
ALL give a ppt. of the metal hydroxide (same as with dropwise NaOH)
4. With excess NH_3 :
ALL dissolve *except* Fe^{2+} and Fe^{3+} (still metal hydroxide ppts.)
Cu gives $[Cu(NH_3)_4(H_2O)_2]^{2+}$; Al gives $[Al(NH_3)_6]^{3+}$
5. With Na_2CO_3 :
 M^{3+} **ALL** give ppt. of metal hydroxide and effervescence of CO_2
 M^{2+} **ALL** give ppt. of metal carbonate, MCO_3
6. With c. HCl:
Cu only - gives **tetrahedral** $[CuCl_4]^{2-}$ complex ion
7. Acidity:
 M^{3+} **ALL** acidic
 M^{2+} **ALL** neutral, *except* Cu^{2+} which is only *slightly* acidic

1.14 Summary Table of Aqueous Metal Ion Chemistry (OCR-A)

Formula & colour of species	Cr³⁺	Mn²⁺	Fe²⁺	Fe³⁺	Cu²⁺
aqueous solution	[Cr(H ₂ O) ₆] ³⁺ Purple solution	[Mn(H ₂ O) ₆] ²⁺ Pale pink (colourless) solution	[Fe(H ₂ O) ₆] ²⁺ Pale green solution	[Fe(H ₂ O) ₆] ³⁺ Brown solution	[Cu(H ₂ O) ₆] ²⁺ Light blue solution
dropwise NaOH	[Cr(H ₂ O) ₃ (OH) ₃] Grey/green ppt	[Mn(H ₂ O) ₄ (OH) ₂] Pale brown ppt turns darker brown ppt in air	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NaOH	[Cr(OH) ₆] ³⁻ Green solution	No change	No change	No change	No change
dropwise NH ₃	[Cr(H ₂ O) ₃ (OH) ₃] Grey/green ppt	[Mn(H ₂ O) ₄ (OH) ₂] Pale brown ppt turns darker brown ppt in air	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NH ₃	[Cr(NH ₃) ₆] ³⁺ Purple solution	No change	No change	No change	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ Deep blue solution
excess conc. HCl	X	X	X	X	[CuCl ₄] ²⁻ Green solution Tetrahedral

NB. Shapes of **ALL** complexes are **octahedral** unless otherwise stated in the table.

1.14a Summary Rules for Learning Aqueous Metal Ion Chemistry (OCR-A)

1. With dropwise NaOH:
ALL give a ppt. of the metal hydroxide, $[M(OH)_n(H_2O)_{6-n}]$ where $n = 2$ or 3
2. With excess NaOH:
Cr only dissolves and gives $[Cr(OH)_6]^{3-}$
Others don't (still metal hydroxide ppt. above)
3. With dropwise NH_3 :
ALL give a ppt. of the metal hydroxide (same as with dropwise NaOH)
4. With excess NH_3 :
Cr & Cu only dissolve - Cr gives $[Cr(NH_3)_6]^{3+}$ and Cu gives $[Cu(NH_3)_4(H_2O)_2]^{2+}$
Others don't (still metal hydroxide ppt. as above)
5. With c. HCl:
Cu only - gives **tetrahedral** $[CuCl_4]^{2-}$ complex ion

1.15 Summary Table of Aqueous Metal Ion Chemistry (OCR-B-Salters)

Formula & colour of species	Fe²⁺	Fe³⁺	Cu²⁺
aqueous solution	[Fe(H ₂ O) ₆] ²⁺ Pale green solution	[Fe(H ₂ O) ₆] ³⁺ Brown solution	[Cu(H ₂ O) ₆] ²⁺ Light blue solution
dropwise NaOH	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NaOH	No change	No change	No change
dropwise NH ₃	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NH ₃	No change	No change	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ Deep blue solution
excess conc. HCl	X	X	[CuCl ₄] ²⁻ Green solution Tetrahedral

NB. Shapes of **ALL** complexes are **octahedral** unless otherwise stated in the table.

1.15a Summary Rules for Learning Aqueous Metal Ion Chemistry (OCR-B-Salters)

1. With dropwise NaOH:
ALL give a ppt. of the metal hydroxide, $[M(OH)_n(H_2O)_{6-n}]$ where $n = 2$ or 3
2. With excess NaOH:
ALL ppts remain (still metal hydroxide ppt. above)
3. With dropwise NH_3 :
ALL give a ppt. of the metal hydroxide (same as with dropwise NaOH)
4. With excess NH_3 :
Cu only dissolves and gives $[Cu(NH_3)_4(H_2O)_2]^{2+}$
Others don't (still metal hydroxide ppt. as above)
5. With c. HCl:
Cu only - gives **tetrahedral** $[CuCl_4]^{2-}$ complex ion

1.16 Summary Table of Aqueous Metal Ion Chemistry (Edexcel)

Formula & colour of species	Cr³⁺	Fe²⁺	Fe³⁺	Co²⁺	Cu²⁺
aqueous solution	[Cr(H ₂ O) ₆] ³⁺ Purple solution	[Fe(H ₂ O) ₆] ²⁺ Pale green solution	[Fe(H ₂ O) ₆] ³⁺ Brown solution	[Co(H ₂ O) ₆] ²⁺ Pink solution	[Cu(H ₂ O) ₆] ²⁺ Light blue solution
dropwise NaOH	[Cr(H ₂ O) ₃ (OH) ₃] Grey/green ppt	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Co(H ₂ O) ₄ (OH) ₂] Blue ppt but leave in air forms beige ppt [Co(H ₂ O) ₃ (OH) ₃]	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NaOH	[Cr(OH) ₆] ³⁻ Green solution	No change	No change	No change	No change
dropwise NH ₃	[Cr(H ₂ O) ₃ (OH) ₃] Grey/green ppt	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Co(H ₂ O) ₄ (OH) ₂] Blue ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt
excess NH ₃	[Cr(NH ₃) ₆] ³⁺ Purple solution	No change	No change	[Co(NH ₃) ₆] ²⁺ → [Co(NH ₃) ₆] ³⁺ Straw/yellow solution turns to brown solution in air	[Cu(NH ₃) ₄ (H ₂ O) ₂] ²⁺ Deep blue solution
excess conc. HCl	X	X	X	[CoCl ₄] ²⁻ Blue solution Tetrahedral	[CuCl ₄] ²⁻ Green solution Tetrahedral

NB. Shapes of **ALL** complexes are **octahedral** unless otherwise stated in the table.

1.16a Summary Rules for Learning Aqueous Metal Ion Chemistry (Edexcel)

1. With dropwise NaOH:
ALL give a ppt. of the metal hydroxide, $[M(OH)_n(H_2O)_{6-n}]$, where $n = 2$ or 3
2. With excess NaOH:
Cr only dissolves to give $[Cr(OH)_6]^{3-}$
Others don't (still metal hydroxide ppt. above)
3. With dropwise NH_3 :
ALL give a ppt. of the metal hydroxide (same as with dropwise NaOH)
4. With excess NH_3 :
ALL dissolve *except* Fe^{2+} and Fe^{3+} (still metal hydroxide ppts.)
Cr & Co give $[M(NH_3)_6]^{n+}$; Cu gives $[Cu(NH_3)_4(H_2O)_2]^{2+}$
5. With c. HCl:
Co & Cu only - give **tetrahedral** $[MCl_4]^{2-}$ complex ions

1.17 Summary Table of Aqueous Metal Ion Chemistry (WJEC)

Formula & colour of species	Cr³⁺	Fe²⁺	Fe³⁺	Cu²⁺	Co²⁺
aqueous solution	[Cr(H ₂ O) ₆] ³⁺ Purple solution	[Fe(H ₂ O) ₆] ²⁺ Pale green solution	[Fe(H ₂ O) ₆] ³⁺ Brown solution	[Cu(H ₂ O) ₆] ²⁺ Light blue solution	[Co(H ₂ O) ₆] ²⁺ Pink solution
dropwise NaOH	[Cr(H ₂ O) ₃ (OH) ₃] Grey/green ppt	[Fe(H ₂ O) ₄ (OH) ₂] Green ppt turns to brown ppt in air	[Fe(H ₂ O) ₃ (OH) ₃] Brown ppt	[Cu(H ₂ O) ₄ (OH) ₂] Blue ppt	X
excess NaOH	[Cr(OH) ₆] ³⁻ Green solution	No change	No change	No change	X
excess conc. HCl	X	X	X	[CuCl ₄] ²⁻ Green solution Tetrahedral	[CoCl ₄] ²⁻ Blue solution Tetrahedral

NB. Shapes of **ALL** complexes are **octahedral** unless otherwise stated in the table.

1.17a Summary Rules for Learning Aqueous Metal Ion Chemistry (WJEC)

1. With dropwise NaOH:
ALL give a ppt. of the metal hydroxide, $[M(OH)_n(H_2O)_{6-n}]$, where $n = 2$ or 3
2. With excess NaOH:
Cr only dissolves to give $[Cr(OH)_6]^{3-}$
Others don't (still metal hydroxide ppt. above)
3. With c. HCl:
Co & Cu only - give **tetrahedral** $[MCl_4]^{2-}$ complex ion

2. REDOX

2.1 Redox reactions

You should already know from AS Chemistry;

- That oxidation and reduction involve transfer of electrons
- Recall the acronym “**OILRIG**” to remember that:
Oxidation Is Loss and Reduction Is Gain (of electrons)
- To use OILRIG to deduce if a species has been oxidised or reduced in a reaction
- To know the difference between oxidised and an oxidising agent and reduced and a reducing agent! ☺
- Be able to write balanced half-equations when reactant and product are specified
- Be able to add two balanced half-equations to produce the overall equation (electrons cancel).

2.1.1 Writing balanced half-equations:

1. write down the reactant and product as supplied.
2. balance the equation for atoms – remember, you can use H^+ and/or H_2O to balance the loss or gain of H or O in an equation – do **NOT** write H_2 or O_2 !!
3. finally, add the appropriate number of electrons to balance the charges.

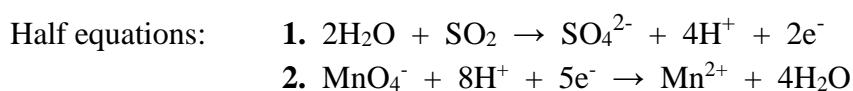
Example Deduce the half equation for the oxidation, in acid solution, of SO_2 to SO_4^{2-}



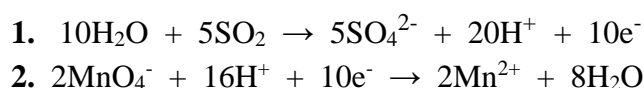
2.1.2 Writing the balanced full equation from the half-equations:

1. firstly, multiply up each half-equation as necessary to get the same number of electrons in each one.
2. add the two half equations together – the electrons will cancel out and you may find that other species such as H^+ or H_2O cancel down or out too.
3. finally, double check the final equation is balanced for the atoms of each element on each side and the charges too.

Example Deduce the full equation for the oxidation of SO_2 to SO_4^{2-} by MnO_4^- ?

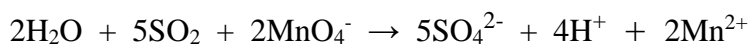


Multiply **1.** by 5 and **2.** by 2 to get same no. of electrons in each one:



Add together: $10\text{H}_2\text{O} + 5\text{SO}_2 + 2\text{MnO}_4^- + 16\text{H}^+ \rightarrow 5\text{SO}_4^{2-} + 20\text{H}^+ + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$

Cancel H^+ and H_2O on each side to produce final equation:



2.2 Redox titration calculations

2.2.1 Basic method

A reminder that most moles calculations involve the same **three** steps:

Step 1 – calculate the no. of moles (n) of the known substance;

Step 2 – use the balanced equation or stoichiometry for the reaction (always supplied) to deduce the no. moles of the unknown (the one you're asked to find in the question);

Step 3 – convert the unknown no. of moles into the required answer (mass, M_r , concentration, volume, % purity, *etc*)

We will use this method in all the calculations in this booklet.

2.2.2 Calculations

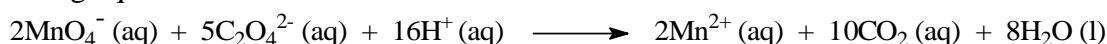
Again, these use the same basic three step method as for other moles calculations (see previous section).

– this time step 1 to calculate the known *usually* (but not always) involves the *titre* value.

e.g. 1 25.0 cm³ of an acidified solution of ethandioate, $\text{C}_2\text{O}_4^{2-}$, was found to react with exactly 22.7 cm³ of a 0.020 M solution of potassium manganate(VII). Calculate the concentration of the ethanedioate solution?

1. No. moles MnO_4^- (known) = $C \times V / 1000 = 0.020 \times 22.7 / 1000 = 4.54 \times 10^{-4}$ mol

2. Using equation:



2 mol MnO_4^- reacts with 5 mol $\text{C}_2\text{O}_4^{2-}$

1 mol MnO_4^- reacts with $5/2$ mol $\text{C}_2\text{O}_4^{2-}$

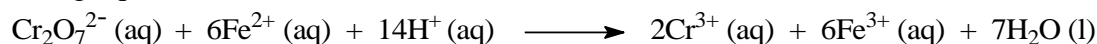
4.54×10^{-4} mol MnO_4^- reacts with $4.54 \times 10^{-4} \times 5/2 = 1.14 \times 10^{-3}$ mol $\text{C}_2\text{O}_4^{2-}$

3. Concentration (C) of $\text{C}_2\text{O}_4^{2-} = 1000 \times n / V = 1000 \times 1.14 \times 10^{-3} / 25.0 = \mathbf{0.0454 \text{ M}}$

e.g. 2 A 0.152g iron sample containing an insoluble impurity was found to react with exactly 17.3 cm³ of a 0.0160 M solution of Cr₂O₇²⁻.
Calculate the % by mass of iron in the sample?

1. No. moles Cr₂O₇²⁻ (known) = C x V / 1000 = 0.0160 x 17.3/1000 = 2.77 x 10⁻⁴ mol

2. Using equation:



1 mol Cr₂O₇²⁻ reacts with 6 mol Fe²⁺

$$2.77 \times 10^{-4} \text{ mol Cr}_2\text{O}_7^{2-} \text{ reacts with } 2.77 \times 10^{-4} \times 6 \text{ mol Fe} = 1.66 \times 10^{-3} \text{ mol}$$

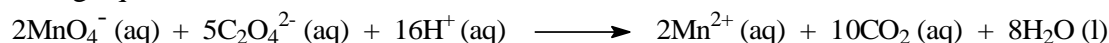
3. Mass of Fe = n x M_r = 1.66 x 10⁻³ x 55.9 = 0.0928 g

4. % Fe = 0.0928 / 0.152 x 100 = **61.1 %**

e.g. 3 Separate aqueous solutions of potassium manganate(VII) (KMnO₄) and sodium manganate(VII) (NaMnO₄) each contained 1.00 g of the compound in 250 cm³. A 25.0 cm³ sample of **one** of these solutions reacted with exactly 17.6 cm³ of a 0.100 M acidified solution of sodium ethanedioate, Na₂C₂O₄.

1. No. moles C₂O₄²⁻ (known) = C x V / 1000 = 0.100 x 17.6/1000 = 1.76 x 10⁻³ mol

2. Using equation:



5 mol C₂O₄²⁻ reacts with 2 mol MnO₄⁻

1 mol C₂O₄²⁻ reacts with ²/₅ mol MnO₄⁻

$$1.76 \times 10^{-3} \text{ mol C}_2\text{O}_4^{2-} \text{ reacts with } 1.76 \times 10^{-3} \times \frac{2}{5} \text{ mol MnO}_4^- = 7.04 \times 10^{-4} \text{ mol}$$

3. Moles of MnO₄⁻ in 250 cm³ = 7.04 x 10⁻⁴ x 10 = 7.04 x 10⁻³ mol

4. Molar mass of MMnO₄ salt, M_r = m/n = 1.00/7.04 x 10⁻³ = 142 g mol⁻¹

5. M_r (KMnO₄) = 158 g mol⁻¹ & M_r (NaMnO₄) = 142 g mol⁻¹ so **solution is NaMnO₄**

3. ELECTROCHEMISTRY

3.1 Electrode potentials

These are measured against a reference electrode, the **HYDROGEN** electrode, which is arbitrarily assigned a potential of 0.00 V.

All other half-cells have their potentials measured against this hydrogen electrode – if this is done under the usual “standard conditions”, i.e. a pressure of 100 kPa, a temperature of 298 K and a 1M solution, the electrode potential becomes the standard electrode potential for that half-cell, given the symbol E° .

We can use tables of E° values to predict:

1. if two species are capable of reacting with each other in a redox reaction.
2. the likely reaction which will occur if two half-cell systems are brought together.

We will work through an example of each type of question.

A table of common E° values is given below – you do **NOT** need to learn these – the half-equations and E° values you will need to answer an examination question will always be supplied in the question paper! ☺

Table of some common electrode potentials

$F_2(g) + 2e^-$	\longrightarrow	$2F^-(aq)$	$E^\circ = +2.56\text{ V}$
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	\longrightarrow	$Mn^{2+} + 4H_2O(l)$	$E^\circ = +1.51\text{ V}$
$Cl_2(g) + 2e^-$	\longrightarrow	$2Cl^-(aq)$	$E^\circ = +1.36\text{ V}$
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	\longrightarrow	$2Cr^{3+} + 7H_2O(l)$	$E^\circ = +1.33\text{ V}$
$Br_2(g) + 2e^-$	\longrightarrow	$2Br^-(aq)$	$E^\circ = +1.09\text{ V}$
$Ag^+(aq) + e^-$	\longrightarrow	$Ag(s)$	$E^\circ = +0.80\text{ V}$
$Fe^{3+}(aq) + e^-$	\longrightarrow	$Fe^{2+}(aq)$	$E^\circ = +0.77\text{ V}$
$I_2(g) + 2e^-$	\longrightarrow	$2I^-(aq)$	$E^\circ = +0.54\text{ V}$
$Cu^{2+}(aq) + 2e^-$	\longrightarrow	$Cu(s)$	$E^\circ = +0.34\text{ V}$
$2H^+(aq) + 2e^-$	\longrightarrow	$H_2(g)$	$E^\circ = +0.00\text{ V (defined)}$
$Pb^{2+}(aq) + 2e^-$	\longrightarrow	$Pb(s)$	$E^\circ = -0.13\text{ V}$
$Sn^{2+}(aq) + 2e^-$	\longrightarrow	$Sn(s)$	$E^\circ = -0.14\text{ V}$
$V^{3+}(aq) + e^-$	\longrightarrow	$V^{2+}(s)$	$E^\circ = -0.26\text{ V}$
$Fe^{2+}(aq) + 2e^-$	\longrightarrow	$Fe(s)$	$E^\circ = -0.44\text{ V}$
$Zn^{2+}(aq) + 2e^-$	\longrightarrow	$Zn(s)$	$E^\circ = -0.76\text{ V}$
$Mg^{2+}(aq) + 2e^-$	\longrightarrow	$Mg(s)$	$E^\circ = -2.36\text{ V}$
$Ca^{2+}(aq) + 2e^-$	\longrightarrow	$Ca(s)$	$E^\circ = -2.87\text{ V}$
$Li^+(aq) + e^-$	\longrightarrow	$Li(s)$	$E^\circ = -3.05\text{ V}$

The more +ve E° values are systems which are good **oxidisers** – they consume electrons and would form the +ve right-hand electrode of an electrochemical cell. They do the forward **reduction** reaction as written in the table above.

The more –ve E° values are systems which are good **reducers** – they produce electrons and would form the –ve left-hand electrode in an electrochemical cell. They do the reverse **oxidation** reaction to that written in the table above.

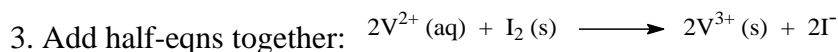
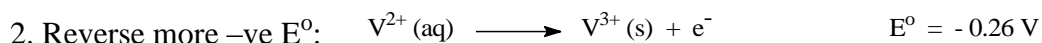
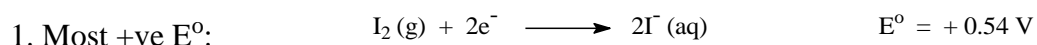
Tables of E° values are usually written in this format, with the most +ve best oxidisers at the top (on the left hand side) and the most –ve best reducers at the bottom (on the right-hand side).

It thus follows that any species on the left-hand side (a potential oxidiser) can react with any species below it on the right-hand side (a potential reducer). It also follows that species with the reverse relationship in the table can **NEVER** react together.

3.2 The Rules:

1. write down the half-equation with the most +ve E° – this is the RH electrode
2. write down the half-equation with the more –ve E° in reverse – this is the LH electrode (**DO NOT** change the sign of this E° value – a common error!).
3. Multiply electrons and then add the two half-equations together to produce the overall reaction.
4. Calculate $E_{\text{cell}}^{\circ} = E_{\text{Right}}^{\circ} - E_{\text{Left}}^{\circ}$ (**DO NOT** multiply the E° values – they are independent of the number of electrons transferred – another common error!).

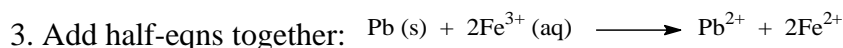
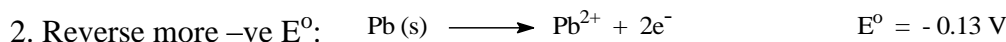
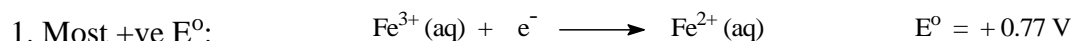
e.g 1: predict if V^{2+} can react with I_2 . Write an overall equation for the reaction and calculate the overall E_{cell}° .



4. Calculate $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = +0.54 - (-0.26) = +0.80\text{ V}$

Since $\Delta G = -nE^{\circ}F$ (you don't need to remember this equation); when E° is +ve, ΔG will be –ve and thus the reaction is feasible. Of course, if the forward reaction has a –ve E° , then the reverse reaction will have a +ve E° and be the feasible one in this case.

e.g. 2: predict the cell reaction which will occur if the Pb^{2+}/Pb and $\text{Fe}^{2+}/\text{Fe}^{3+}$ cells are connected together. Write the overall cell reaction and calculate the E_{cell} .

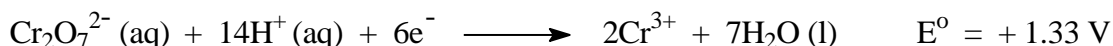


4. Calculate $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = +0.77 - (-0.13) = +0.90 \text{ V}$

3.3 An alternative approach? ☺

e.g. Deduce the overall cell reaction between $\text{Cr}_2\text{O}_7^{2-}$ and NO_3^{-} and calculate the E_{cell} ?

Half-equations & electrode potentials:

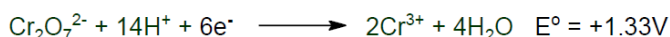


Method:

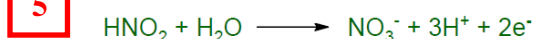
1. Sketch a horizontal scale to represent the voltage.
2. Mark on the more +ve half-cell system – this is the RH electrode and thus the +ve.
3. Mark on the more -ve half-cell system – this is the LH electrode and thus the -ve.
4. Electrons flow from the -ve cathode to the +ve anode; thus oxidation takes place at the cathode and reduction takes place at the anode as the electrons flow to there.
5. Reverse the half-equation for the cathode (LH electrode) as it produces electrons.
6. Add to produce the full equation and thus overall cell reaction.
7. $E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$.

This is a snapshot of the Powerpoint slide I went through in the workshop session:

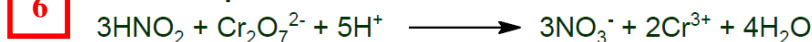
Standard electrode potentials:



Half-cell reactions:



6 **Overall equation:**



7 E_{cell}

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = +1.33 - (+0.94) = +0.39\text{V}$$