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IB Chemistry DP

YOUR NOTES

9. Redox Processes

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9.1 Redox Processes

9.1.1 Oxidation & reduction

Oxidation & Reduction

- There are three definitions of **oxidation** and **reduction** used in different branches of chemistry
- Oxidation and reduction can be used to describe any of the following processes

Definitions and Examples of Oxidation & Reduction Table

| Oxidation | Reduction |
|--|--|
| Addition of oxygen | Loss of oxygen |
| e.g. $2Mg + O_2 \longrightarrow 2MgO$ | e.g. $2CuO + C \longrightarrow 2Cu + CO_2$ |
| Loss of hydrogen | Addition of hydrogen |
| e.g. $CH_3OH \xrightarrow{[O]} CH_2O + H_2O$ | e.g. $C_2H_4 + H_2 \longrightarrow C_2H_6$ |
| Loss of electrons | Gain of electrons |
| e.g. Al → Al ³⁺ + 3e ⁻ | e.g. $F_2 + 2e^- \longrightarrow 2F^-$ |

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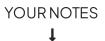
Oxidation Numbers

- The **oxidation number** of an atom is the charge that would exist on an individual atom if the bonding were completely ionic
- It is like the electronic 'status' of an element
- Oxidation numbers are used to...
 - o tell if oxidation or reduction has taken place
 - o work out what has been oxidised and/or reduced
 - o construct half equations and balance redox equations

Atoms and simple ions

- The oxidation number is the number of electrons which must be added or removed to become neutral
- The oxidation number is always written with the charge before the number

Oxidation Number of Simple Ions Table





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| Atoms | Na in Na = 0 | neutral already, no need to add any electrons | |
|---------|----------------------------|--|--|
| Cations | Na in Na ⁺ = +1 | need to add 1 electron to make Na+ neutral | |
| Anions | $ClinCl^- = -1$ | need to take 1 electron away to make Cl neutral | |

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Worked Example

What are the oxidation states of the elements in the following species?

a) C

b) Fe³⁺

c) Fe^{2+} d) O^{2-}

e) He

f) ΔI³

Answers:

a) 0 b) +3 c) +2 d) -2 e) 0 f) +3

- So, in simple ions, the oxidation number of the atom is the charge on the ion:
 - Na+, K+, H+ all have an oxidation number of +1
 - Mg²⁺, Ca²⁺, Pb²⁺ all have an oxidation number of +2
 - ∘ Cl⁻, Br⁻, l⁻ all have an oxidation number of -1
 - \circ O²⁻. S²⁻ all have an oxidation number of -2

Molecules or Compounds

• In molecules or compounds, the sum of the oxidation numbers on the atoms is zero

Oxidation Number in Molecules or Compounds Table

| Elements | H in $H_2 = 0$ | Both are the same and must add up to zero | | |
|-----------|------------------|---|--|--|
| Compounds | C in $CO_2 = +4$ | $1 \times (+4)$ and $2 \times (-2) = 0$ | | |
| Compounds | O in $CO_2 = -2$ | 14 (14) Gild 24 (2) = 0 | | |

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- Because CO₂ is a neutral molecule, the sum of the oxidation states must be zero
- For this, one element must have a positive oxidation number and the other must be negative

How do you determine which is the positive one?

- the more electronegative species will have the negative value
- electronegativity increases across a period and decreases down a group
- O is further to the right than C in the periodic table so it has the negative value



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How do you determine the value of an element's oxidation state?

- from its position in the periodic table and/or
- the other element(s) present in the formula

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Variable Oxidation Numbers

- Many atoms, such as S, N and Cl, can exist in a variety of oxidation states
- The oxidation number of these atoms can be calculated by assuming that the oxidation number of the other atom is fixed
- Here are six rules to deduce the oxidation number of an element

Oxidation Number Rules Table



| YOUR | NOTES |
|------|-------|
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| Rule | Example | |
|--|--|--|
| 1. The ox.no. of any uncombined element is zero | H ₂ Zn O ₂ | |
| 2. Many atoms or ions have fixed ox.no. in compounds | Group 1 elements are always +1 Group 2 elements are always +2 Fluorine is always -1 Hydrogen is +1 (except for in metal hydrides like NaH, where it is -1) Oxygen is -2 (except in peroxides, where it is -1 and in F ₂ O where it is +2) | |
| 3. The ox.no. of an element in a mono—atomic ion is always the same as the charge | Zn^{2+} ox.no. = +2 Fe^{3+} ox.no. = +3 Cl^{-} ox.no. = -1 | |
| 4. The sum of the ox.no. in a compound is zero | NaCl ox.no. of Na = +1 ox.no. of Cl = -1 Sum ox.no. = 0 | |
| 5. The sum of ox.no. in an ion is equal to the charge on the ion | SO_4^{2-} ox.no. of $S = +6$ ox.no. of four O atoms = $4 \times (-2)$ sum ox.no. = -2 | |
| 6. In either a compound or an ion, the more electronegative element is given the negative ox.no. | F_2O ox.no. of both F atoms = 2 x (-1) ox.no. of $O = +2$ | |



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Exam Tip

Oxidation number and oxidation state are often used interchangeably, though $\hbox{IUPAC does not distinguish between the two terms.} Oxidation numbers are$ represented by Roman numerals according to IUPAC

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Deducing Oxidation Numbers

- The oxidation numbers of all other atoms in their compounds can vary
- By following the oxidation number rules, the oxidation number of any atom in a compound or ion can be deduced
- The position of an element in the periodic table can act as a guide to the oxidation state

Oxidation Numbers & The Periodic Table

| | Have positive values in compounds |
|------------|--|
| | • Value is usually that of the Group Number Al is +3 |
| Metals | Where there are several possibilities the values go no higher than the Group No. |
| | Sn can be +2 or +4, Mn can be +2, +4, +6, +7 |
| | Mostly negative based on their usual ion |
| Non-metals | Cl usually -1 |
| Non-metals | • Can have values up to their Group No. |
| | Cl +1+3+5 or +7 |

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• Test your understanding on the following examples:

?

Worked Example

State the oxidation number of the atoms in blue in these compounds or ions

a) P₂O₅

b) SO₄²⁻

c) H₂S

d) Al₂Cl₆

e) NH₃

f) ClO₂-

Answers:



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| Example | Explanation | |
|------------------------------------|---|--|
| a. P ₂ O ₅ | ox. no. 5 O atoms Overall charge compound ox. no. of 2 P atoms ox. no of P | $= 5 \times (-2)$ = -10 = 0 = +10 = +5 |
| b. SO ₄ ²⁻ | ox. no. 4 O atoms Overall charge compound ox. no. of S | $= 4 \times (-2)$ = -8 = -2 = $+6$ |
| c. H ₂ S | ox. no. 2 H atoms Overall charge compound ox. no. of S | $= 2 \times (+1)$ = +2 = 0 = -2 |
| d. Al ₂ Cl ₆ | ox. no. 6 Cl atoms Overall charge compound ox. no. of 2 Al atoms ox. no. of Al | = Cl x (-1) = -6 = 0 = +6 = +3 |
| e. NH ₃ | ox. no. 3 H atoms Overall charge compound ox. no. of N | = 3 x (+1) = +3 = 0 = -3 |
| f. ClO ₂ | ox. no. 2 O atoms Overall charge compound ox. no. of Cl | $= 2 \times (-2)$ = -4 = -1 = +3 |

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Are oxidation numbers always whole numbers?

- The answer is yes and no
- When you try and work out the oxidation of sulfur in the tetrathionate ion ${\bf S_4O_6}^{2-}$ you get an interesting result!



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$$S_4O_6^{2-}$$

$$(? \times 4) + (-2 \times 6) = -2$$

$$(? \times 4) - 12 = -2$$

$$(? \times 4) = -2 + 12$$

$$? = \frac{+10}{4} = +2\frac{1}{2}$$
Consider 5 from the Balance of Blacks Barrane

The oxidation number of sulfur in $S_4O_6^{2-}$ is a fraction

- The fact that the oxidation number comes out to +2.5 does not mean it is possible to get half an oxidation number
- This is only a mathematical consequence of four sulfur atoms sharing +10 oxidation number
- Single atoms can only have an integer oxidation number, because you cannot have half an electron!



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9.1.3 Oxidizing & Reducing agents

Oxidizing & Reducing Agents

Oxidising agent

- An oxidising agent is a substance that oxidises another atom or ion by causing it to lose electrons
- An oxidising agent itself gets reduced gains electrons
- Therefore, the **ox. no.** of the oxidising agent **decreases**

OXIDISING AGENT AS IT OXIDISES
$$Fe^{2+} \rightarrow Fe^{3+}$$

AND GETS REDUCED ITSELF FROM $H_2O_2 \rightarrow H_2O_3$
 $2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O_3$
 $+3 -2$

Example of an oxidising agent in a chemical reaction

Reducing agent

- A reducing agent is a substance that reduces another atom or ion by causing it to gain electrons
- A reducing agent itself gets oxidised loses/donates electrons
- Therefore, the ox. no. of the reducing agent increases

REDUCING AGENT AS IT REDUCES
$$Fe^{3+} \rightarrow Fe^{2+}$$

AND GETS OXIDISED ITSELF FROM $H_2O_2 \rightarrow O_2$
 $2Fe^{3+} + H_2O_2 + 2OH^- \rightarrow 2Fe^{2+} + 2H_2O + O_2$
 $+3$ -1 $+2$ 0

Example of a reducing agent in a chemical reaction

- For a reaction to be recognised as a redox reaction, there must be both an oxidising and reducing agent
- Some substances can act both as oxidising and reducing agents
- Their nature is dependent upon what they are reacting with and the reaction conditions

Oxidising & Reducing Agents Table



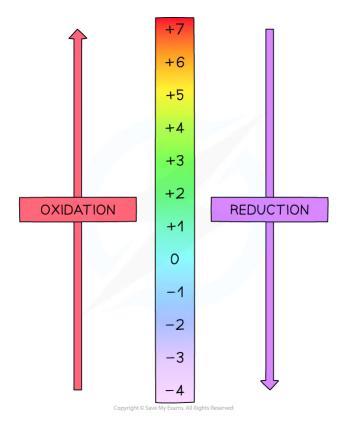
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| Oxidizing agents | Reducing agents |
|------------------------|-------------------------|
| oxidize other species | reduce other species |
| accept electrons | donate electrons |
| are themselves reduced | are themselves oxidized |

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Identifying Oxidizing & Reducing Agents

- Applying the definitions of oxidising and reducing agents allows you to identify them in chemical equations
- By deducing the oxidation numbers of the species you can determine whether it has been oxidised or reduced



A visual reminder of oxidation numbers and redox. This is like an elevator in a building going up to higher floors is oxidation and going down to the basement is reduction



Worked Example

Four reactions are shown. In which reaction is the species in blue acting as an oxidising agent?

A.
$$Cr_2O_7^{2-} + 8H^+ + \frac{3SO_3^{2-}}{3} \rightarrow 2Cr^{3+} + 4H_2O + 3SO_4^{2-}$$

B.
$$Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$$

C.
$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

D.
$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

Answer:

The correct option is **B**.





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• Oxidising agents are substances that oxidise other species, gain electrons and are themselves reduced.

• Write down the oxidation numbers of each species in the reaction

0 +2 +2 0 $\text{Mg} + \text{Fe}^{2+} \rightarrow \text{Mg}^{2+} + \text{Fe}$

 $\circ~$ In equation B, Fe^2+ oxidises Mg(0) to Mg^2+(+2) and is itself reduced from Fe^2+(+2) to Fe(0)

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9.1.4 Naming Transition Metal Compounds

Naming Transition Metal Compounds

- Transition metals are characterized by having variable oxidation numbers.
- Oxidation numbers can be used in the names of compounds to indicate which oxidation number a particular element in the compound is in
- Where the element has a **variable oxidation number**, the number is written afterwards in **Roman numerals**.
- This is called the **STOCK NOTATION** (after the German inorganic chemist Alfred Stock), but is not widely used for non-metals, so SO₂ is sulphur dioxide rather than sulphur(IV) oxide
- For example, iron can be both +2 and +3 so **Roman numerals** are used to distinguish between them
 - Fe²⁺ in FeO can be written as iron(II) oxide
 - Fe³⁺ in Fe₂O₃ can be written as iron(III) oxide



Worked Example

Can you name these transition metal compounds?

- 1.Cu₂O
- 2. MnSO₄
- 3. Na₂CrO₄
- 4. KMnO₄
- 5. Na₂Cr₂O₇

Answer:

Answer 1: copper(I) oxide:

The ox. no. of 1 O atom is -2 and Cu_2O has overall no charge so the ox. no. of Cu is +1

Answer 2: manganese(II) sulfate:

The charge on the sulfate ion is -2, so the charge on Mn and ox. no. is +2

Answer 3: sodium chromate(VI):

The ox. no. of 2 Na atoms is +2 so CrO_4 has an overall -2 charge, so the ox. no. of Cr is +6

Answer 4: potassium manganate(VII):

The ox. no. of a K atom is +1 so MnO₄ has overall -1 charge, so the ox. no. of Mn is +7

Answer 5: sodium dichromate(VI):

The ox. no. of 2 Na atoms is +2 so Cr_2O_7 has an overall -2 charge, so the ox. no. of Cr is +6. To distinguish it from CrO_4 we use the prefix di in front of the anion



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Exam Tip

The answer to No. 2 should strictly speaking being managanese (II) sulfate (VI) since sulfur is an element with a variable oxidation number. However, it is a common ion whose name and formula you should know and you are only required to name transition metal compounds using Stock Notation

9.1.5 Half Equations

Half Equations

- Oxidation numbers can be used to balance chemical equations
- Go through these steps to balance a redox equation:
 - 1. Write the unbalanced equation and identify the atoms which change in ox. no.
 - 2. Deduce the ox.no. changes
 - 3. Balance the ox.no. changes
 - 4. Balance the charges
 - 5. Balance the atoms

?

Worked Example

Manganate(VII) ions (MnO₄ $^-$) react with Fe²⁺ ions in the presence of acid (H⁺) to form Mn²⁺ ions, Fe³⁺ ions and waterWrite the overall redox equation for the reaction

Answer:

Step 1: Write the unbalanced equation and identify the atoms which change in ox. no.

$$M_{n}O_{4}^{-}(aq) + Fe^{2+}(aq) + H^{+}(aq) \longrightarrow M_{n}^{2+}(aq) + Fe^{3+}(aq) + H_{2}O(1)$$

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Step 2: Deduce the ox.no. changes

OX. NO. CHANGE = -5

$$MnO_4^-(aq) + Fe^{2+}(aq) + H^+(aq) \longrightarrow Mn^{2+}(aq) + Fe^{3+}(aq) + H_2O(l)$$
+7

OX. NO. CHANGE = +1

Step 3: Balance the ox.no. changes

OX. NO. CHANGE =
$$1 \times (-5) = -5$$
 $M_{1}O_{4}^{-}(aq) + 5Fe^{2+}(aq) + H^{+}(aq) \longrightarrow M_{1}O_{2}^{-}(aq) + 5Fe^{3+}(aq) + H_{2}O(l) + 2 + 2 + 3$

OX. NO. CHANGE = $5 \times (+1) = +5$

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Step 4: Balance the charges

$$MnO_{4}^{-}(aq) + 5Fe^{2+}(aq) + H^{+}(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + H_{2}O(l)$$

IGNORING H+

• TOTAL + CHARGE = (5 × 2+) = 10+

• TOTAL + CHARGE = 5 × (3+) + (2+)= 17+

TOTAL CHARGE REACTANTS = 9+

TOTAL CHARGE PRODUCTS = 17+

THUS 8H IONS ARE NEEDED TO BALANCE THE CHARGES ON BOTH SIDES

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Step 5: Balance the atoms

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

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9.1.6 The Activity Series

The Activity Series

- Metals can be ranked in order of reactivity -this is called the reactivity series or just activity series
- Metals higher in reactivity can **displace** less reactive metals from their compounds in solutions or from their oxides
- An example of a **metal displacement reaction** occurs between magnesium and aqueous copper (II) sulfate solution

$$Mg(s) + CuSO_4(aq) \rightarrow MgSO_4(aq) + Cu(s)$$

• What are the **redox processes** going on here? If we split the equation into half equations it's easy to see which species is **oxidized** and which is **reduced**:

Mg
$$\rightarrow$$
 Mg²⁺+2e⁻ Loss of electrons = oxidation
Cu²⁺+2e⁻ \rightarrow Cu Gain of electrons = reduction

- The more reactive metal acts as a reducing agent
- This allows metals to be ranked from most reactive (**strongest reducing agents**) to least reactive:



The more reactive a metal is the better it is at pushing electrons onto less reactive metal ions. Magnesium is better at pushing electrons onto copper(II) ions than copper is at pushing electrons onto magnesium ions



Worked Example

What is the order of decreasing reactivity of the metals (most reactive first)?

$$Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$$

 $Cu(s) + Zn^{2+}(aq) \rightarrow No Reaction$

 $Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$

 $Ag(s) + Cu^{2+}(aq) \rightarrow No Reaction$

- A. Zn > Cu > Sn > Ag
- B. Sn > Zn > Aq > Cu
- C. Ag > Cu > Zn > Sn
- **D.** Zn > Sn > Cu > Ag

Answer:

The correct option is **D**.

• The first reaction tells you that zinc is more reactive than tin (Zn > Sn):

$$Zn(s) + Sn^{2+}(aq) \rightarrow Zn^{2+}(aq) + Sn(s)$$

• The second reaction tells you that zinc is more reactive than copper (Zn > Cu):

$$Cu(s) + Zn^{2+}(aq) \rightarrow No Reaction$$

• The third reaction tells you that tin is more reactive than copper (Sn > Cu):

$$Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$$

• The fourth reaction tells you that copper is more reactive than silver (Cu > Ag):

$$Ag(s) + Cu^{2+}(aq) \rightarrow No Reaction$$

Deducing the Feasibility of a Redox Reaction

- Given the **activity series** of metals it is possible to predict whether a **displacement** reaction will take place or not (if it is **feasible**)
- For example will calcium displace lead from lead(IV) oxide?

$$PbO_2 + 2Ca \rightarrow Pb + 2CaO$$

• Deduce the **redox** half equations

$$Ca \rightarrow Ca^{2+} + 2e^{-}$$

$$Pb^{4+} + 4e^{-} \rightarrow Pb$$

- Ca is above Pb in the **activity series**, so this reaction is **feasible**
- The more reactive metal undergoes oxidation (Ca in this case)
- The less reactive metal ion undergoes reduction



Exam Tip

You don't need to learn the Activity Series for Metals as it is given to you in Section 25 of the IB Chemistry Data Booklet

9.1.7 Redox Titrations

Redox Titrations

- In a **titration**, the concentration of a solution is determined by titrating with a solution of known concentration.
- In redox titrations, an **oxidizing agent** is titrated against a **reducing agent**
- Electrons are transferred from one species to the other
- Indicators are sometimes used to show the endpoint of the titration
- However, most **transition metal ions** naturally change colour when changing **oxidation** state
- There are two common **redox titrations** you should know about **manganate(VII) titrations** and **iodine-thiosulfate titrations**

Manganate(VII) Titrations

• A redox reaction occurs between acidified manganate (VII) ions and iron (II) ions:

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

- This reaction needs no indicator as the manganate (VII) is a strong purple colour which disappears at the end point, so the titration is self-indicating
- This reaction is often used for the analysis of iron for example in iron tablets (health supplement)

lodine-Thiosulfate Titrations

• A redox reaction occurs between iodine and thiosulfate ions:

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

- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, **starch** is added to clarify the end point
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can be used to determine the concentration of an **oxidizing agent**, which **oxidizes** iodide ions to iodine molecules
- The amount of iodine is determined from **titration** against a known quantity of sodium thiosulfate solution
- This reaction can be used for the analysis of chlorine in bleach



9.1.8 The Winkler Method

The Winkler Method

- The **Winkler Method** is a technique used to measure dissolved oxygen in freshwater systems
- Dissolved oxygen is used as an indicator of the health of a water body, where higher dissolved oxygen concentrations correlate with high productivity and little pollution
- The **biological oxygen demand (BOD)** is the amount of oxygen used to decompose the organic matter in a sample of water over a specified time period, usually 5 days, at a specified temperature
- A **high BOD** indicates a greater quantity of organic waste in the water, which means a **lower level of dissolved oxygen**

Chemical analysis

- In the first step, **manganese(II) sulfate** is added to a water sample and then the solution is made alkaline with NaOH
- In the alkaline solution, dissolved oxygen will oxidize manganese(II) ions to manganese(IV)

$$2Mn^{2+}(aq) + 4OH^{-}(aq) + O_{2}(aq) \rightarrow 2MnO_{2}(s) + 2H_{2}O(l)$$

- The manganese(IV) oxide, MnO₂, appears as a brown precipitate
- In the second part, acidified **potassium iodide**, **KI**, is added to the solution
- The precipitate will dissolve back into solution, so **Mn(IV)** is reduced back to **Mn(II)** liberating iodine in the process

$$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(I)$$

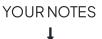
• Thiosulfate is used, with a starch indicator, to titrate the iodine liberated

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

• From the above stoichiometric equations, we can see that:

1 mole of $O_2 \rightarrow 2$ moles of MnO₂ $\rightarrow 2$ moles of $I_2 \rightarrow 4$ moles of

- Therefore, after determining the number of moles of iodine produced, we can work out the number of moles of oxygen molecules present in the original water sample
- The oxygen content is usually presented as mg/dm³ or ppm



Winkler Method Calculation

• The following calculation shows how the data from a Winkler analysis is carried out:

?

Worked Example

A sample of lake water was analysed using the Winkler Method. The size of the sample was $600\,\mathrm{cm^3}$ and the following table shows the results of a titration of the liberated iodine against $0.0500\,\mathrm{mol\,dm^{-3}}$ sodium thiosulfate solution in the final step of the analysis:

| | Trial 1 | Trial 2 | Trial 3 |
|---|---------|---------|---------|
| Final burette reading, cm³ | 20.45 | 19.35 | 21.80 |
| Initial burette reading, cm ³ | 2.10 | 1.05 | 3.40 |
| Volume of Na ₂ S ₂ O ₃ delivered, cm ³ | 18.35 | 18.30 | 18.40 |

Determine the dissolved oxygen content of the water sample in $g \, dm^{-3}$

Answer:

Step 1: Determine the average volume of delivered

Average volume $Na_2S_2O_3 = (18.35 + 18.30 + 18.40) \div 3$

Average volume $Na_2S_2O_3 = 18.35$ cm³

Step 2: Determine the number of moles of sodium thiosulfate reacted

Moles of $Na_2S_2O_3$ = volume in dm³ x concentration = 0.01835 dm³ x 0.0500 mol dm⁻³

$$= 9.175 \times 10^{-4} \text{ mol}$$

Step 3: Determine the moles of oxygen reacted

 $1 \, \text{mol of O}_2 \, \text{is equivalent to } 4 \, \text{mol of Na}_2 \, \text{S}_2 \, \text{O}_3$

Therefore, amount of oxygen in the sample is = $(9.175 \times 10^{-4}) \div 4 = 2.294 \times 10^{-4}$ mol

Step 4: Calculate the concentration of the dissolved oxygen

Concentration = mol \div volume in dm³ = (2.294 x 10⁻⁴ mol) \div 0.600 dm³

$$= 3.823 \times 10^{-4} \text{ mol dm}^{-3}$$

Convert to g dm⁻³ = 3.823×10^{-4} mol dm⁻³ x 32.00 g mol⁻¹ = 0.01223 g dm⁻³

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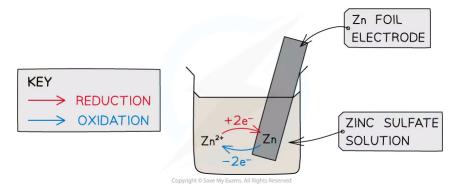
Voltaic Cells

- Voltaic (or Galvanic) cells generate electricity from spontaneous redox reactions
- For example:

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$

- Instead of electrons being transferred directly from the zinc to the copper ions a cell is built which separates the two redox processes
- Each part of the cell is called a half cell
- If a rod of metal is dipped into a solution of its own ions, an equilibrium is set up
- For example:

$$Zn(s) = Zn^{2+}(aq) + 2e^{-}$$



When a metal is dipped into a solution contains its ions an equilibrium is established between the metal and it ions

- This is a half cell and the strip of metal is an electrode
- The position of the equilibrium determines the **potential difference** between the metal strip and the solution of metal
- The Zn atoms on the rod can deposit two electrons on the rod and move into solution as Zn²⁺ions:

$$Zn(s) = Zn^{2+}(aq) + 2e^{-}$$

- This process would result in an accumulation of negative charge on the zinc rod
- Alternatively, the Zn²⁺ ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms:

$$Zn^{2+}(aq) + 2e^- \neq Zn(s)$$

- This process would result in an accumulation of positive charge on the zinc rod
- In both cases, a potential difference is set up between the rod and the solution
- This is known as an electrode potential
- A similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg CuSO₄), due to the following processes:

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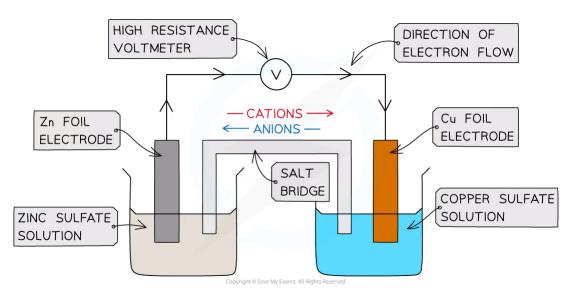
 $Cu^{2+}(aq) + 2e^{-} \neq Cu(s)$ - reduction (rod becomes positive)

 $Cu(s) \neq Cu^{2+}(aq) + 2e^{-}$ - oxidation (rod becomes negative)

- Note that a chemical reaction is not taking place there is simply a **potential difference** between the rod and the solution
- The potential difference will depend on
 - the **nature of the ions** in solution
 - the concentration of the ions in solution
 - the type of electrode used
 - the temperature

Creating an emf

- If two different electrodes are connected, the potential difference between the two electrodes will cause a current to flow between them. Thus an **electromotive force (emf)** is established and the system can generate electrical energy
- A typical electrochemical cell can be made by combining a zinc electrode in a solution of zinc sulphate with a copper electrode in a solution of copper sulphate



The zinc-copper voltaic cell (also known as the Daniell Cell)

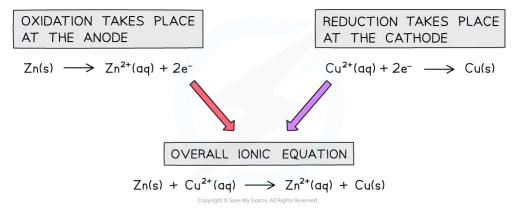
- The circuit must be completed by allowing ions to flow from one solution to the other
- This is achieved by means of a **salt bridge** often a piece of filter paper saturated with a solution of an **inert electrolyte** such as KNO₃(aq)
- The e.m.f can be measured using a voltmeter
- Voltmeters have a high resistance so that they do not divert much current from the main circuit
- The combination of two electrodes in this way is known as an **electrochemical or voltaic cell**, and can be used to generate electricity
- The **positive electrode** or **cathode** is the one which most favours **reduction**
 - In this case it is the copper electrode which is positive

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- The **negative electrode** or **anode** is the one which most favours **oxidation**
 - o In this case it is the zinc electrode which is negative
- Thus electrons flow from the zinc electrode to the copper electrode



Ionic equations for the Daniell Cell

- To maintain charge in the half cells:
 - anions flow to the negative half cell to replace the negative charge of the electrons
 - **cations** flow **to the positive** half cell since there is a surplus positive charge from the metals becoming cations in the negative half cell
- The sulphate ions flow through the salt bridge from the Cu²⁺(aq) solution to the Zn²⁺(aq) solution, to complete the circuit and compensate for the reduced Cu²⁺ concentration and increased Zn²⁺ concentration
- The overall cell reaction including spectator ions can thus be written as follows:

$$Zn(s) + CuSO_4(aq) \rightarrow Cu(s) + ZnSO_4(aq)$$

- The external connection must be made of a **metallic wire** in order to allow electrons to flow
- The salt bridge must be made of an aqueous electrolyte to allow ions to flow
- By allowing two chemical reagents to be connected electrically, but not chemically, a reaction can only take place if the electrons flow externally
- The **chemical energy** is thus converted into **electrical energy**.



Exam Tip

Students often confuse the redox process that take place in voltaic cells and electrolytic cells. An easy way to remember is the phrase RED CATS:REDuction takes place at the CAThode!



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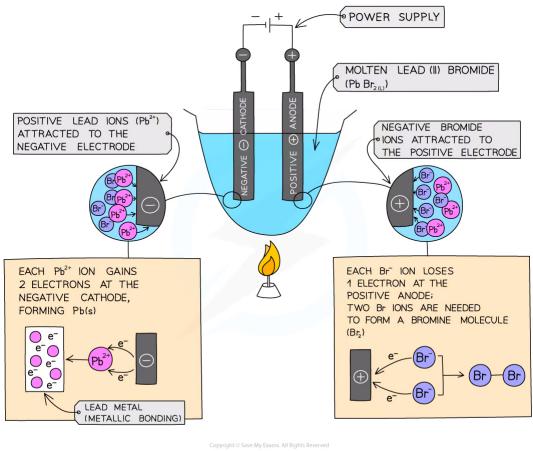
9.1.10 Electrolytic Cells

Electrolytic Cells

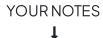
- An ionic compound conducts electricity when it is molten or in solution
- The current causes the ionic compound to split up and form new substances.
- This process is called **electrolysis**, a word which comes from Greek and means "splitting by electricity"
- Electrolysis has many uses, including:
 - purifying copper
 - o plating metals with silver and gold
 - o extracting reactive metals, such as aluminium
 - making chlorine, hydrogen and sodium hydroxide

Electrolysis cells

- Electrolysis cells can be constructed using a beaker or crucible as the cell depending whether the ionic compound is in solution or molten
- For Standard Level Chemistry we only need to look at the electrolysis of molten ionic compounds









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Electrolysis of a molten ionic compound

- In electrolysis, the substance that the current passes through and splits up is called the **electrolyte**
- The electrolyte contains positive and negative ions
- What happens to these ions during electrolysis?
 - **Negative ions** move to the **anode** and lose electrons this is **oxidation**
 - Positive ions move to the cathode and gain electrons this is reduction
 - Electrically neutral atoms or molecules are released

Electrolysis of molten lead bromide

- The reactions which take place at the electrodes can be shown by half equations
- When the positive lead ions move to the **cathode**, they gain electrons in a **reduction** reaction:

$$Pb^{2+}(aq) + 2e^- \neq Pb(s)$$

• Similarly when the negative bromide ions move to the **anode** they lose electrons in an **oxidation** reaction:

$$2Br^{-}(I) - 2e^{-} \Rightarrow Br_{2}(I)$$

- Sometimes oxidation reactions are written with '+2e-' on the right of the arrow instead of '-2e' on the left
- In this case the alternative half equation is:

$$2Br^{-}(I) \Rightarrow Br_{2}(I) + 2e^{-}$$

- Since metals are always **cations** and non-metal **anions**, it is easy to predict the products of electrolysis of molten salts:
 - Metals will always be formed at the cathode and non-metals at the anode

Comparing Voltaic & Electrolytic Cells Summary Table

| | Negative | Positive |
|-------------------|-----------|-----------|
| Voltaic cell | anode | cathode |
| Voltaic cell | oxidation | reduction |
| Electrolytic cell | cathode | anode |
| | reduction | oxidation |

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Exam Tip

Rather confusingly.....in electrolytic cells the negative electrode is called the cathode and the positive electrode is called the anode, which is the opposite to voltaic cellsThis naming confusion arises because in both cases the cathode is where reduction occurs and the anode is where oxidation occurs To avoid this confusion many people only use the words cathode and anode when talking about electrolysis and use negative and positive electrodes when talking about voltaic cells