

## 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
<b>Addition of oxygen</b> e.g. $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$	<b>Loss of oxygen</b> e.g. $2\text{CuO} + \text{C} \rightarrow 2\text{Cu} + \text{CO}_2$
<b>Loss of hydrogen</b> e.g. $\text{CH}_3\text{OH} \xrightarrow{[\text{O}]}$ $\text{CH}_2\text{O} + \text{H}_2\text{O}$	<b>Addition of hydrogen</b> e.g. $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$
<b>Loss of electrons</b> e.g. $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	<b>Gain of electrons</b> e.g. $\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$

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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...
  - tell if oxidation or reduction has taken place
  - work out what has been oxidised and/or reduced
  - 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

<b>Atoms</b>	Na in Na = 0	neutral already, no need to add any electrons
<b>Cations</b>	Na in $\text{Na}^+$ = +1	need to add 1 electron to make $\text{Na}^+$ neutral
<b>Anions</b>	Cl in $\text{Cl}^-$ = -1	need to take 1 electron away to make $\text{Cl}^-$ neutral

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### Worked example

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

a) C      b) Fe<sup>3+</sup>      c) Fe<sup>2+</sup>      d) O<sup>2-</sup>      e) He      f) Al<sup>3+</sup>

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<sup>+</sup>, K<sup>+</sup>, H<sup>+</sup> all have an oxidation number of +1
  - Mg<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup> all have an oxidation number of +2
  - Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> all have an oxidation number of -1
  - O<sup>2-</sup>, S<sup>2-</sup> 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

<b>Elements</b>	H in H <sub>2</sub> = 0	Both are the same and must add up to zero
<b>Compounds</b>	C in CO <sub>2</sub> = +4	1 × (+4) and 2 × (-2) = 0
	O in CO <sub>2</sub> = -2	

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- Because CO<sub>2</sub> 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

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

## 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

Rule	Example
1. The ox.no. of any uncombined element is zero	H <sub>2</sub> Zn O <sub>2</sub>
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 <sub>2</sub> 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 <sup>2+</sup> ox.no. = +2 Fe <sup>3+</sup> ox.no. = +3 Cl <sup>-</sup> 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 <sub>4</sub> <sup>2-</sup> ox.no. of S = +6 ox.no. of four O atoms = 4 x (-2) sum ox.no. = -2
6. In either a compound or an ion, the more electronegative element is given the negative ox.no.	F <sub>2</sub> O ox.no. of both F atoms = 2 x (-1) ox.no. of O = +2

**Exam Tip**

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

## 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

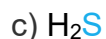
<b>Metals</b>	◦ Have positive values in compounds
	◦ Value is usually that of the Group Number Al is +3
	◦ Where there are several possibilities the values go no higher than the Group No.
	Sn can be +2 or +4, Mn can be +2, +4, +6, +7
<b>Non-metals</b>	◦ Mostly negative based on their usual ion
	Cl usually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



d)  $\text{Al}_2\text{Cl}_6$ e)  $\text{NH}_3$ f)  $\text{ClO}_2^-$ 

Answers:

Example	Explanation
a. $\text{P}_2\text{O}_5$	$\text{ox. no. 5 O atoms} = 5 \times (-2)$ $= -10$ Overall charge compound = 0 $\text{ox. no. of 2 P atoms} = +10$ $\text{ox. no of P} = +5$
b. $\text{SO}_4^{2-}$	$\text{ox. no. 4 O atoms} = 4 \times (-2)$ $= -8$ Overall charge compound = -2 $\text{ox. no. of S} = +6$
c. $\text{H}_2\text{S}$	$\text{ox. no. 2 H atoms} = 2 \times (+1)$ $= +2$ Overall charge compound = 0 $\text{ox. no. of S} = -2$
d. $\text{Al}_2\text{Cl}_6$	$\text{ox. no. 6 Cl atoms} = \text{Cl} \times (-1)$ $= -6$ Overall charge compound = 0 $\text{ox. no. of 2 Al atoms} = +6$ $\text{ox. no. of Al} = +3$
e. $\text{NH}_3$	$\text{ox. no. 3 H atoms} = 3 \times (+1)$ $= +3$ Overall charge compound = 0 $\text{ox. no. of N} = -3$
f. $\text{ClO}_2^-$	$\text{ox. no. 2 O atoms} = 2 \times (-2)$ $= -4$ Overall charge compound = -1 $\text{ox. no. of Cl} = +3$

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  $\text{S}_4\text{O}_6^{2-}$  you get an interesting result!

$$\begin{array}{c}
 \text{S}_4\text{O}_6^{2-} \\
 \downarrow \qquad \qquad \qquad \searrow \\
 (? \times 4) + (-2 \times 6) = -2 \\
 (? \times 4) - 12 = -2 \\
 (? \times 4) = -2 + 12 \\
 ? = \frac{+10}{4} = +2\frac{1}{2}
 \end{array}$$

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*The oxidation number of sulfur in  $\text{S}_4\text{O}_6^{2-}$  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!

## Oxidizing & Reducing Agents

### Oxidising agent

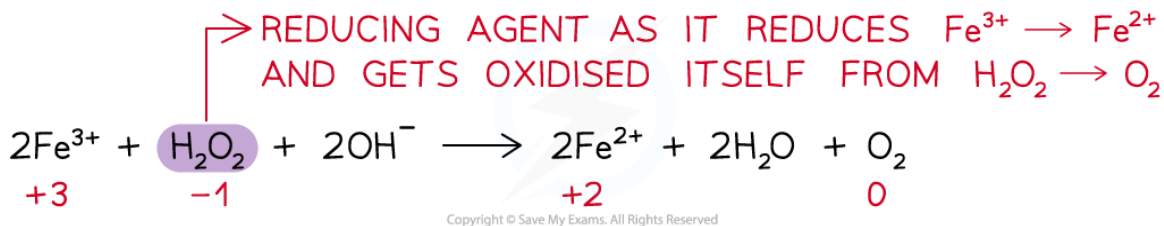
- An oxidising agent is a substance that oxidises another atom or ion by causing it to lose electrons
- An oxidising agent itself gets reduced – gains electrons
- Therefore, the ox. no. of the oxidising agent decreases



*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



*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

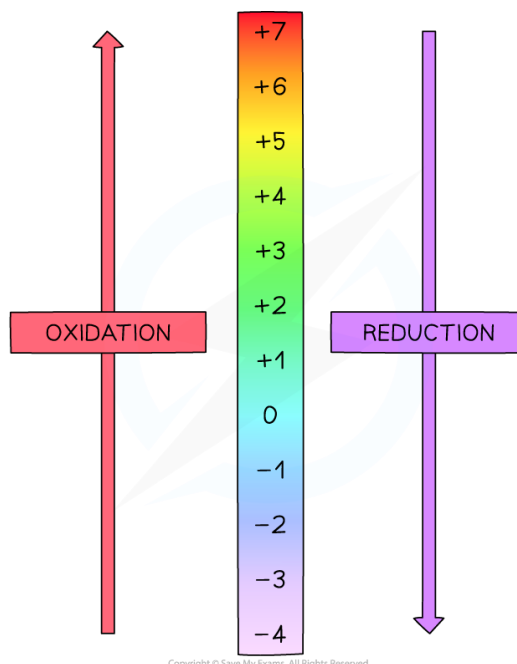
Oxidising & Reducing Agents Table

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.  $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{SO}_3^{2-} \rightarrow 2\text{Cr}^{3+} + 4\text{H}_2\text{O} + 3\text{SO}_4^{2-}$
- B.  $\text{Mg} + \text{Fe}^{2+} \rightarrow \text{Mg}^{2+} + \text{Fe}$
- C.  $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$
- D.  $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

Answer:

The correct option is B.

- 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



- In equation B,  $\text{Fe}^{2+}$  oxidises  $\text{Mg}(0)$  to  $\text{Mg}^{2+}(+2)$  and is itself reduced from  $\text{Fe}^{2+}(+2)$  to  $\text{Fe}(0)$

## 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  $\text{SO}_2$  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
  - $\text{Fe}^{2+}$  in  $\text{FeO}$  can be written as iron(II) oxide
  - $\text{Fe}^{3+}$  in  $\text{Fe}_2\text{O}_3$  can be written as iron(III) oxide

### Worked example

Can you name these transition metal compounds?

1.  $\text{Cu}_2\text{O}$
2.  $\text{MnSO}_4$
3.  $\text{Na}_2\text{CrO}_4$
4.  $\text{KMnO}_4$
5.  $\text{Na}_2\text{Cr}_2\text{O}_7$

Answer:

Answer 1: copper(I) oxide:

The ox. no. of 1 O atom is -2 and  $\text{Cu}_2\text{O}$  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  $\text{CrO}_4$  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  $\text{MnO}_4$  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  $\text{Cr}_2\text{O}_7$  has an overall -2 charge, so the ox. no. of Cr is +6. To distinguish it from  $\text{CrO}_4$  we use the prefix di in front of the anion

### Exam Tip

The answer to No. 2 should strictly speaking being manganese(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

## Half Equations

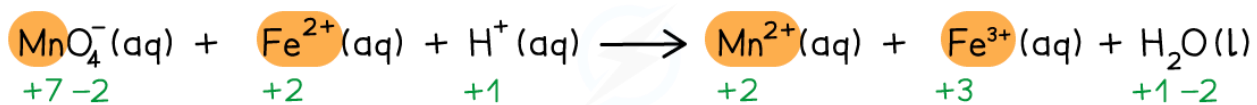
- Oxidation numbers can be used to balance chemical equations
- Go through these steps to balance a redox equation:
  1. Write the unbalanced equation and identify the atoms which change in ox. no.
  2. Deduce the ox.no. changes
  3. Balance the ox.no. changes
  4. Balance the charges
  5. Balance the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

### Worked example

Manganate(VII) ions ( $\text{MnO}_4^-$ ) react with  $\text{Fe}^{2+}$  ions in the presence of acid ( $\text{H}^+$ ) to form  $\text{Mn}^{2+}$  ions,  $\text{Fe}^{3+}$  ions and water. Write the overall redox equation for the reaction

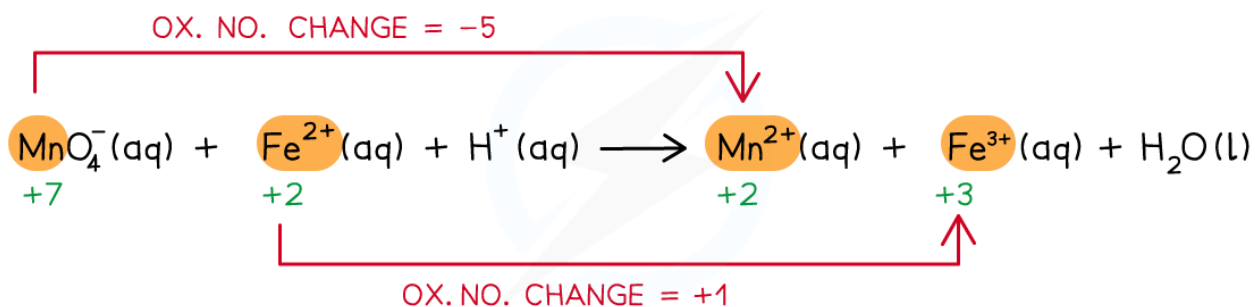
Answer:

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



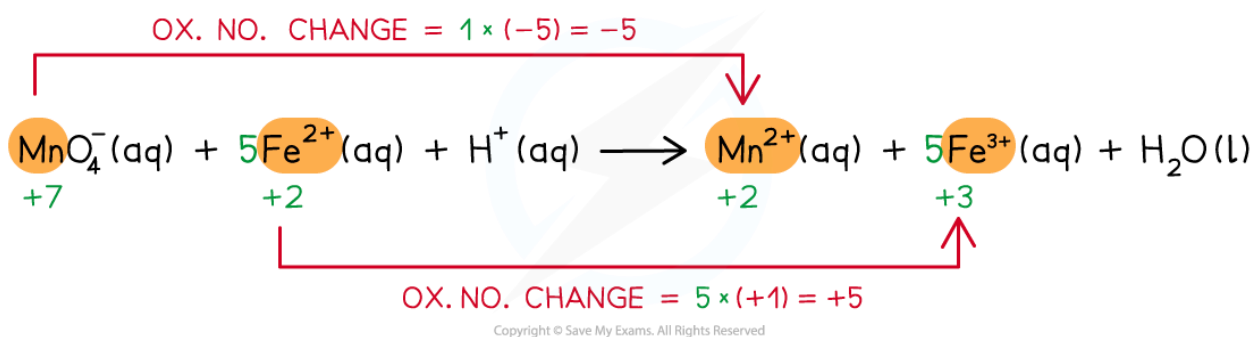
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Step 2: Deduce the ox.no. changes

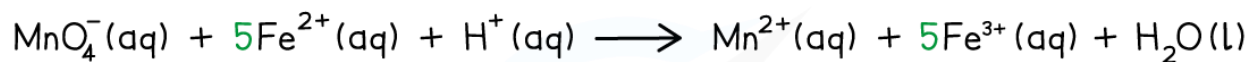


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Step 3: Balance the ox.no. changes



Step 4: Balance the charges



IGNORING  $\text{H}^+$

• TOTAL  $\oplus$  CHARGE =  $(5 \times 2+) = 10+$

• TOTAL  $\oplus$  CHARGE =  $5 \times (3+) + (2+) = 17+$

• TOTAL  $\ominus$  CHARGE =  $1-$

• TOTAL  $\ominus$  CHARGE =  $0$

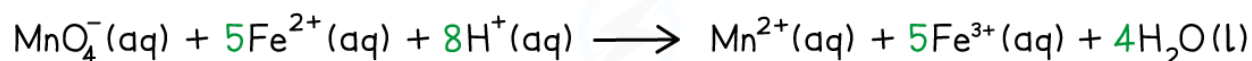
TOTAL CHARGE REACTANTS =  $9+$

TOTAL CHARGE PRODUCTS =  $17+$

THUS  $8\text{H}^+$  IONS ARE NEEDED TO BALANCE THE CHARGES ON BOTH SIDES

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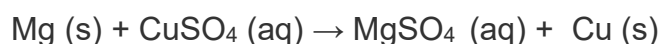
Step 5: Balance the atoms



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## 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



- 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:





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

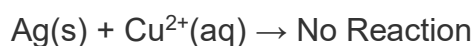
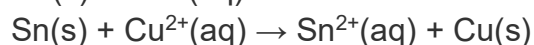
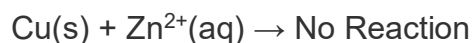
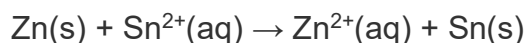


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*The more reactive a metal is the better it is at pushing electrons onto less reactive metal ions. Magnesium is better at pushing electrons onto copper(II) ions than copper is at pushing electrons onto magnesium ions*

### Worked example

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

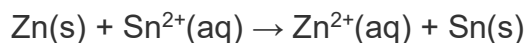


- A. Zn > Cu > Sn > Ag
- B. Sn > Zn > Ag > Cu
- C. Ag > Cu > Zn > Sn
- D. Zn > Sn > Cu > Ag

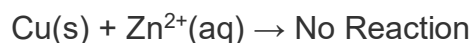
Answer:

The correct option is D.

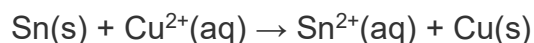
- The first reaction tells you that zinc is more reactive than tin (Zn > Sn):



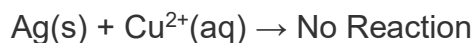
- The second reaction tells you that zinc is more reactive than copper (Zn > Cu):



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

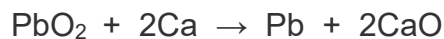


- The fourth reaction tells you that copper is more reactive than silver (Cu > Ag):



## 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?



- Deduce the redox half equations



- 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

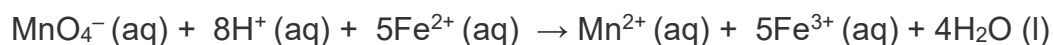
You don't need to learn the Activity Series for Metals as it is given to you in Section 25 of the IB Chemistry Data Booklet

## 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

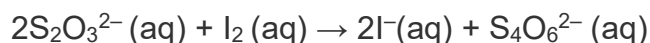
- A redox reaction occurs between acidified manganate (VII) ions and iron (II) ions:



- 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)

### Iodine-Thiosulfate Titrations

- A redox reaction occurs between iodine and thiosulfate ions:



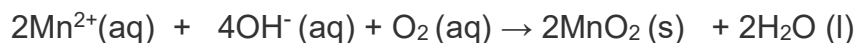
- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, starch is added to clarify the end point
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can 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

## 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

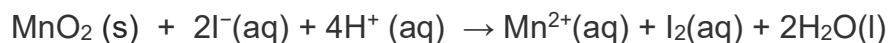
### Chemical analysis

- 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)

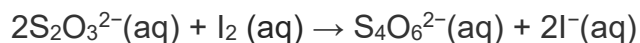


- The manganese(IV) oxide,  $\text{MnO}_2$ , appears as a brown precipitate
- In the second part, acidified potassium iodide, KI, is added to the solution

- The precipitate will dissolve back into solution, so Mn(IV) is reduced back to Mn(II) liberating iodine in the process



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



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



- 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  $\text{mg/dm}^3$  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  $600 \text{ cm}^3$  and the following table shows the results of a titration of the liberated iodine against  $0.0500 \text{ mol dm}^{-3}$  sodium thiosulfate solution in the final step of the analysis: Determine the dissolved oxygen content of the water sample in  $\text{g dm}^{-3}$

	Trial 1	Trial 2	Trial 3
Final burette reading, $\text{cm}^3$	20.45	19.35	21.80
Initial burette reading, $\text{cm}^3$	2.10	1.05	3.40
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ delivered, $\text{cm}^3$	18.35	18.30	18.40

Answer:

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Step 1: Determine the average volume of delivered

$$\text{Average volume Na}_2\text{S}_2\text{O}_3 = (18.35 + 18.30 + 18.40) \div 3$$

$$\text{Average volume Na}_2\text{S}_2\text{O}_3 = 18.35 \text{ cm}^3$$

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

$$\begin{aligned} \text{Moles of Na}_2\text{S}_2\text{O}_3 &= \text{volume in dm}^3 \times \text{concentration} = 0.01835 \text{ dm}^3 \times 0.0500 \text{ mol dm}^{-3} \\ &= 9.175 \times 10^{-4} \text{ mol} \end{aligned}$$

Step 3: Determine the moles of oxygen reacted

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

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

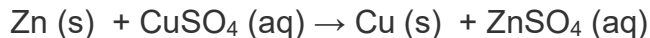
Step 4: Calculate the concentration of the dissolved oxygen

$$\begin{aligned} \text{Concentration} &= \text{mol} \div \text{volume in dm}^3 = (2.294 \times 10^{-4} \text{ mol}) \div 0.600 \text{ dm}^3 \\ &= 3.823 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

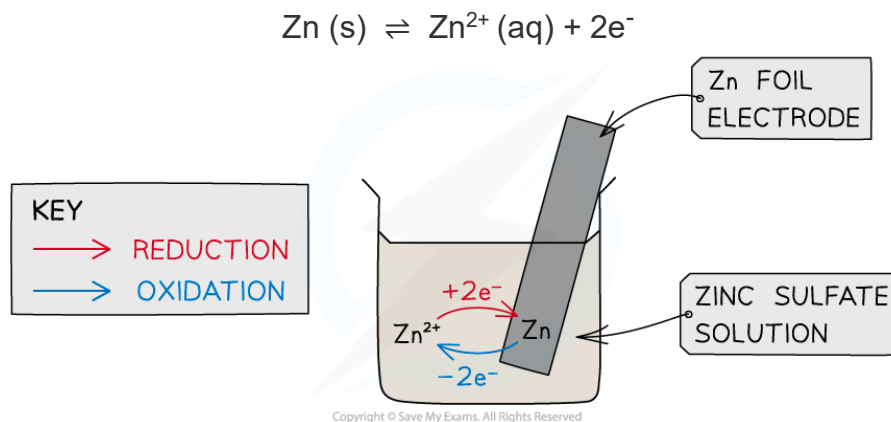
$$\text{Convert to g dm}^{-3} = 3.823 \times 10^{-4} \text{ mol dm}^{-3} \times 32.00 \text{ g mol}^{-1} = 0.01223 \text{ g dm}^{-3}$$

## Voltaic Cells

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

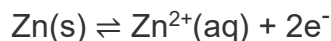


- Instead of electrons being transferred directly from the zinc to the copper ions a cell is built which separates the two redox processes
- Each part of the cell is called a half cell
- If a rod of metal is dipped into a solution of its own ions, an equilibrium is set up
- For example:



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

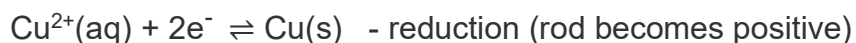
- This is a half cell and the strip of metal is an electrode
- The position of the equilibrium determines the potential difference between the metal strip and the solution of metal
- The Zn atoms on the rod can deposit two electrons on the rod and move into solution as  $\text{Zn}^{2+}$  ions:



- This process would result in an accumulation of negative charge on the zinc rod
- Alternatively, the  $\text{Zn}^{2+}$  ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms:



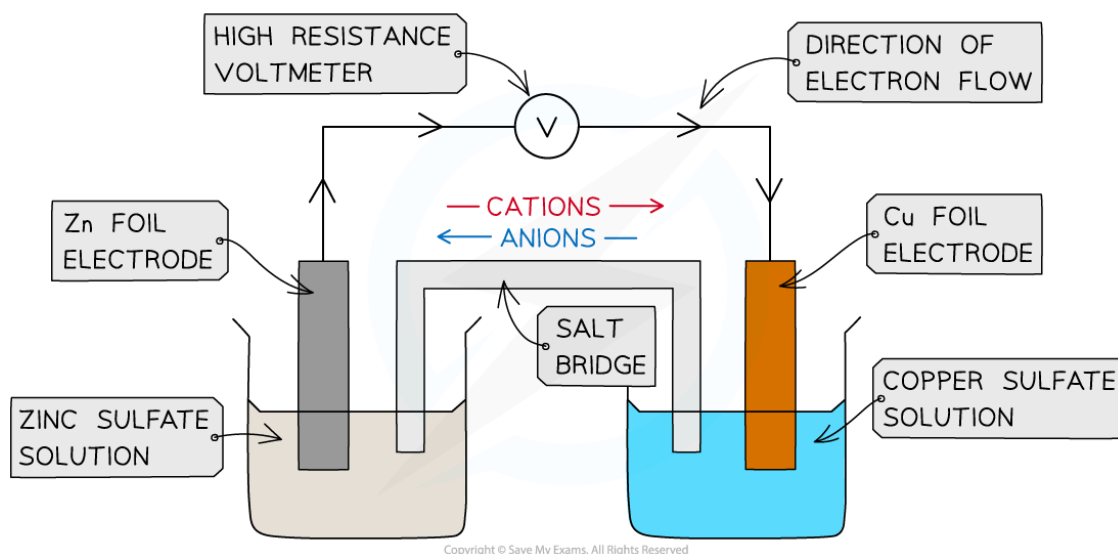
- This process would result in an accumulation of positive charge on the zinc rod
- In both cases, a potential difference is set up between the rod and the solution
- This is known as an electrode potential
- A similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg  $\text{CuSO}_4$ ), due to the following processes:



- 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

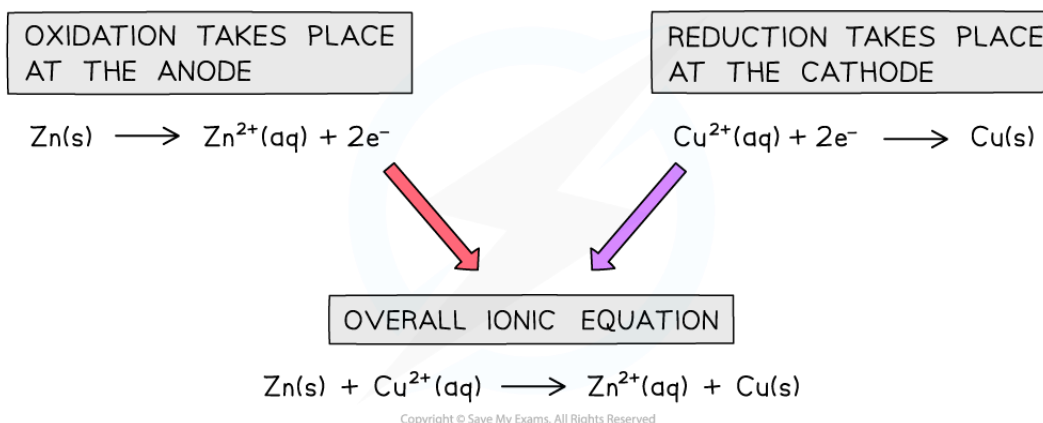
### Creating an emf

- 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



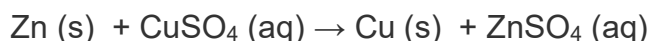
*The zinc-copper voltaic cell ( also known as the Daniell Cell)*

- 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  $\text{KNO}_3(\text{aq})$
- 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
- The negative electrode or anode is the one which most favours oxidation
  - 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  $\text{Cu}^{2+}(\text{aq})$  solution to the  $\text{Zn}^{2+}(\text{aq})$  solution, to complete the circuit and compensate for the reduced  $\text{Cu}^{2+}$  concentration and increased  $\text{Zn}^{2+}$  concentration
- The overall cell reaction including spectator ions can thus be written as follows:



- 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

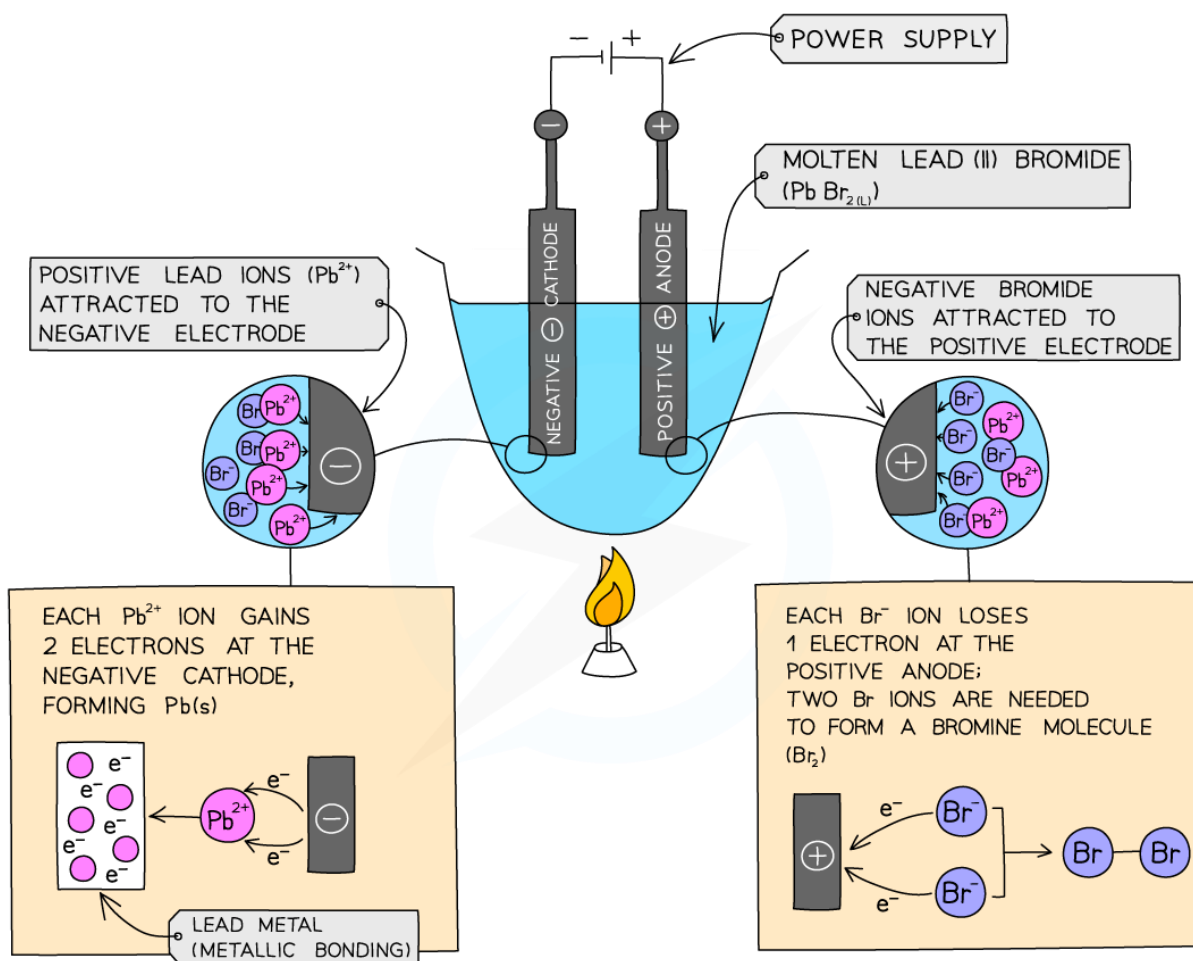
Students often confuse the redox process that take place in voltaic cells and electrolytic cells. An easy way to remember is the phrase RED CATS:REDuction takes place at the CAThode !

## 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
  - plating metals with silver and gold
  - 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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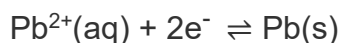


### *Electrolysis of a molten ionic compound*

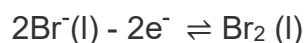
- In electrolysis, the substance that the current passes through and splits up is called the electrolyte
- The electrolyte contains positive and negative ions
- What happens to these ions during electrolysis?
  - Negative ions move to the anode and lose electrons - this is oxidation
  - Positive ions 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:



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



- 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:



- 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
	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 cells. This 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