Edexcel International A Level (IAL) Chemistry

Your notes

Redox Equilibria

Contents

- Reduction & Oxidation
- Standard Electrode Potential
- Measuring Standard Electrode Potential
- Conventional Cell Representation
- Thermodynamics & Electrode Potential
- Fuel Cells
- Redox Titration Calculations

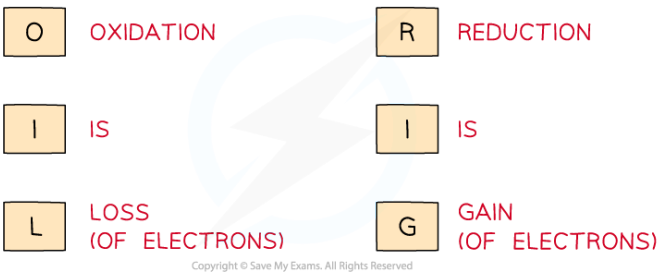
Your notes

Reduction & Oxidation in s-, p- & d-Block Elements

- To recap, 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

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



Use the acronym "Oil Rig" to help you remember the definitions of oxidation and reduction

- s-block elements are usually oxidised by losing electrons to form 1+ and 2+ ions

$$Na \rightarrow Na^+ + e^-$$

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

- p-block metals typically undergo oxidation, by losing electrons, to form positive ions
  - p-block metal ions can have a charge that is consistent with their group of the Periodic Table

$$Al \rightarrow Al^{3+} + 3e^-$$

- p-block metal ions can also form common ions with a charge that is not consistent with their group

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

- p-block non-metals are usually reduced, by gaining electrons, to form negative ions
  - p-block non-metals form ions with a charge that can be calculated by (the group number - 8)

$$F + e^- \rightarrow F^- \text{ (group 7 - 8 = -1)}$$

$$O + 2e^- \rightarrow O^{2-} \text{ (group 6 - 8 = -2)}$$

- d-block elements can form various ions due to their variable oxidation states
  - d-block elements will usually be oxidised, by losing electrons, to form positive ions, e.g. Cu^{2+}, Cr^{3+}, V^{5+}

Your notes

Your notes

Standard Electrode Potential Definition

Standard electrode potential

- The position of equilibrium and therefore the electrode potential depends on factors such as:
  - Temperature
  - Pressure of gases
  - Concentration of reagents
- So, to be able to compare the electrode potentials of different species, they all have to be measured against a common reference or standard
- **Standard conditions** also have to be used when comparing electrode potentials
- These standard conditions are:
  - Ion concentration of 1.00 mol dm^{-3}
  - A temperature of 298 K
  - A pressure of 100 kPa
- Standard measurements are made using a **high resistance voltmeter** so that no current flows and the maximum potential difference is achieved
- The electrode potentials are measured relative to a **standard hydrogen electrode**
- The standard hydrogen electrode is given a value of 0.00 V, and all other electrode potentials are compared to this standard
- This means that the electrode potentials are always referred to as a **standard electrode potential ($E^{\ominus}$)**
- The **standard electrode potential ($E^{\ominus}$)** is the potential difference (sometimes called voltage) produced when a **standard half-cell** is connected to a **standard hydrogen cell** under standard conditions
- For example, the standard electrode potential of bromine suggests that relative to the hydrogen half-cell it is more likely to get reduced, as it has a **more positive** $E^{\ominus}$ value

$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \quad E^{\ominus} = +1.09\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^{\ominus} = 0.00\ V$$

- The standard electrode potential of sodium, on the other hand, suggests that relative to the hydrogen half-cell it is less likely to get reduced as it has a **more negative** $E^{\ominus}$ value

$$Na^+(aq) + e^- \rightleftharpoons Na(s) \quad E^{\ominus} = -2.71\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^{\ominus} = 0.00\ V$$

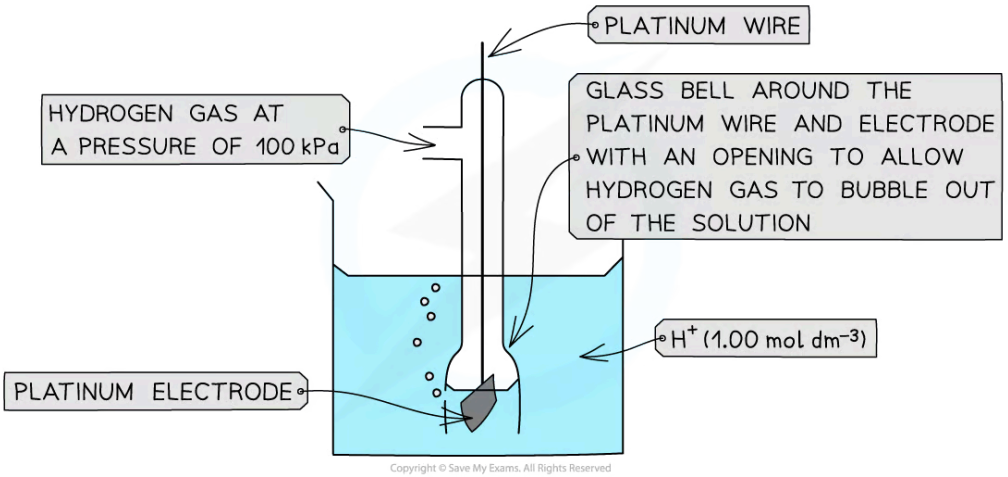
The Standard Hydrogen Electrode, SHE

Your notes

- The **standard hydrogen electrode** is a half-cell used as a **reference electrode** and consists of:
  - Hydrogen gas in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3} (at 100 kPa)

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

- An **inert platinum** electrode that is in contact with the hydrogen gas and H^+ ions
  - The inert platinum electrode often has a coating of finely divided platinum black
  - The increased surface area of the platinum black increases the rate of equilibrium between the hydrogen gas and hydrogen ions
- When the standard hydrogen electrode is connected to another half-cell, the **standard electrode potential** of that half-cell can be read off a high resistance voltmeter



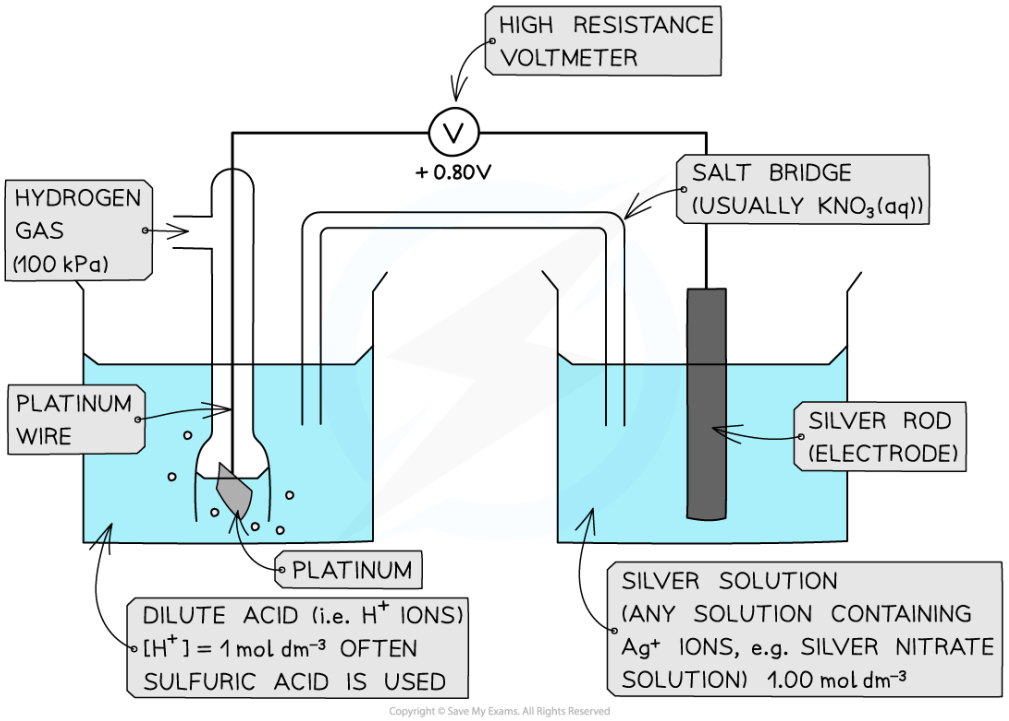
The standard electrode potential of a half-cell can be determined by connecting it to a standard hydrogen electrode

Your notes

Measuring Standard Electrode Potential

- There are three different types of half-cells that can be connected to a standard hydrogen electrode to measure standard electrode potential
  - A metal / metal ion half-cell
  - A non-metal / non-metal ion half-cell
  - An ion / ion half-cell (the ions are in different oxidation states)

Metal / metal-ion half-cell



Example of a metal / metal ion half-cell connected to a standard hydrogen electrode

- An example of a metal/metal ion half-cell is the Ag^+/ Ag half-cell
  - Ag is the metal
  - Ag^+ is the metal ion
- This half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^{\ominus} = +0.80\ V$$

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^{\ominus} = 0.00\ V$$

- Since the Ag^+/Ag half-cell has a more positive $E^{\ominus}$ value, this is the **positive pole** and the H^+/H_2 half-cell is the **negative** pole
- The **standard cell potential** ($E_{cell}^{\ominus}$) is $\boldsymbol{E_{cell}^{\ominus} = (+0.80) - (0.00) = +0.80\ V}$
- The Ag^+ ions are more likely to get **reduced** than the H^+ ions as it has a greater $E^{\ominus}$ value
  - Reduction occurs at the **positive electrode**
  - Oxidation occurs at the **negative electrode**

Your notes

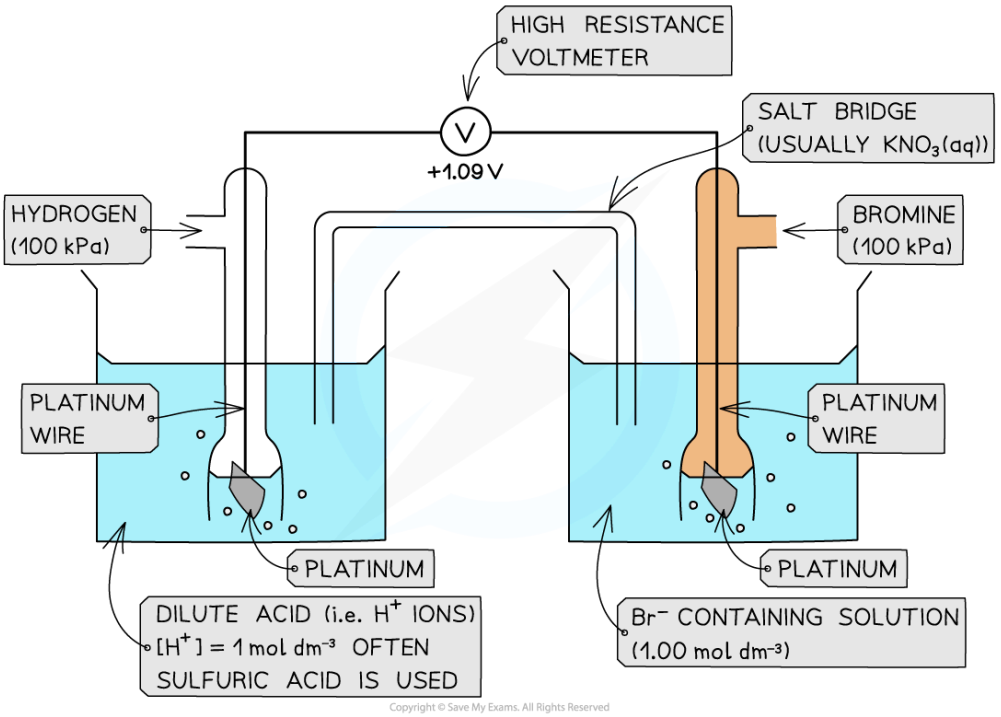
Non-metal / non-metal ion half-cell

- In a **non-metal / non-metal ion** half-cell, **platinum** wire or foil is used as an electrode to make electrical contact with the solution
  - Like graphite, platinum is inert and does not take part in the reaction
  - The redox equilibrium is established on the platinum surface
- An example of a non-metal / non-metal ion is the Br_2 / Br^- half-cell
  - Br_2 is the non-metal
  - Br^- is the non-metal ion
- The half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

$$\boldsymbol{Br_2\ (aq) + 2e^- \rightleftharpoons 2Br^-\ (aq) \quad E^{\ominus} = +1.09\ V}$$

$$\boldsymbol{2H^+\ (aq) + 2e^- \rightleftharpoons H_2\ (g) \quad E^{\ominus} = 0.00\ V}$$

- The Br_2 / Br^- half-cell is the **positive pole** and the H^+ / H_2 is the **negative** pole
- The $E_{cell}^{\ominus}$ is: $\boldsymbol{E_{cell}^{\ominus} = (+1.09) - (0.00) = +1.09\ V}$
- The Br_2 molecules are more likely to get **reduced** than H^+ as they have a greater $E^{\ominus}$ value



Example of a non-metal / non-metal ion half-cell connected to a standard hydrogen electrode

Ion / Ion half-cell

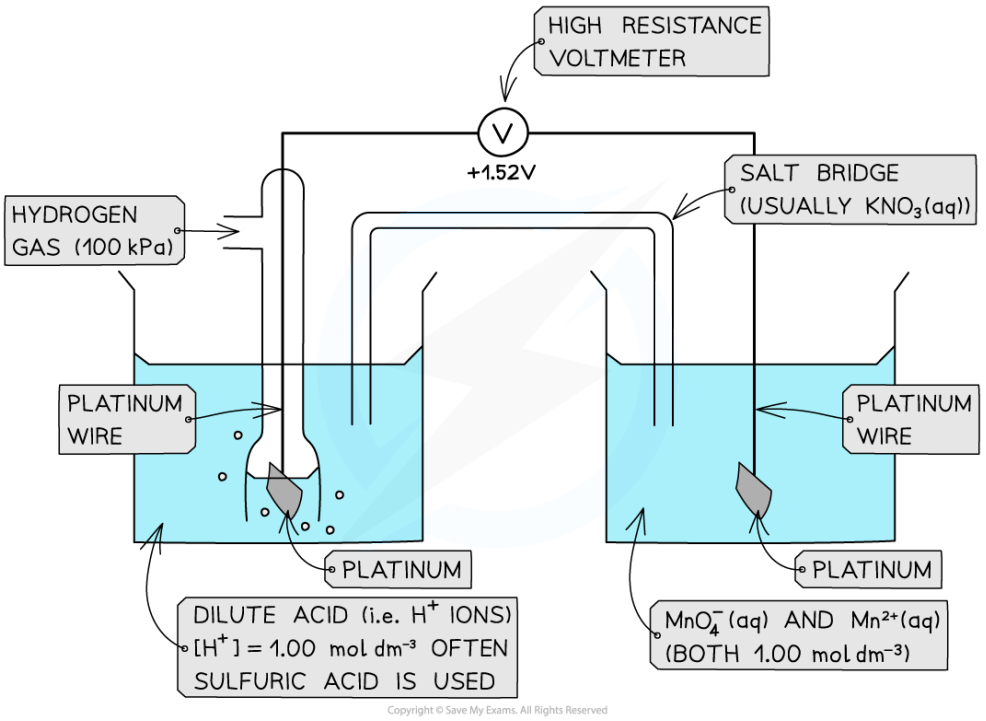
- A **platinum electrode** is again used to form a half-cell of ions that are in **different oxidation states**
- An example of such a half-cell is the MnO_4^- / Mn^{2+} half-cell
  - MnO_4^- is an ion containing Mn with oxidation state +7
  - The Mn^{2+} ion contains Mn with oxidation state +2
- This half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

$$\mathbf{MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \quad E^{\ominus} = +1.52\ V}$$

$$\mathbf{2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \quad E^{\ominus} = 0.00\ V}$$

- The H^+ ions are also present in the half-cell as they are required to convert MnO_4^- into Mn^{2+} ions
- The MnO_4^- / Mn^{2+} half-cell is the **positive pole** and the H^+ / H_2 is the **negative** pole
- The $E_{cell}^{\ominus}$ is $\mathbf{E_{cell}^{\ominus} = (+1.52) - (0.00) = +1.52\ V}$

Your notes



Ions in solution half cell

The Salt Bridge

- The salt bridge completes the circuit in a voltaic (electrochemical) cell by allowing ions to move between the two half-cells
- It helps to **balance** the charges as electrons flow through the external wire
- A metal wire must not be used as a salt bridge
  - Metals allow electrons to flow, but a salt bridge **must carry ions**, not electrons
- **Potassium chloride** and **potassium nitrate** are commonly used to make the salt bridge because **chloride** and **nitrate** ions are:
  - Highly **soluble** in water
  - **Unreactive** with most ions in the half-cells
  - Unlikely to form **precipitates**
  - This ensures smooth ion flow and prevents disruption of the redox reactions

Electromotive Force

Standard cell potential

- Once the $E^{\ominus}$ of a half-cell is known, the **potential difference** or **voltage** or **emf** of an **electrochemical cell** made up of any two half-cells can be calculated
  - These could be **any** half-cells and neither have to be a standard hydrogen electrode

Your notes

- The **standard cell potential** ($E_{cell}^{\ominus}$) can be calculated by **subtracting** the **less positive** $E^{\ominus}$ from the **more positive** $E^{\ominus}$ value
  - The half-cell with the more positive $E^{\ominus}$ value will be the **positive** pole
    - By convention this is shown on the right hand side in a conventional cell diagram, so is termed $E_{right}^{\ominus}$
  - The half-cell with the less positive $E^{\ominus}$ value will be the **negative** pole
    - By convention this is shown on the left hand side in a conventional cell diagram, so is termed $E_{left}^{\ominus}$

$$E_{cell}^{\ominus} = E_{right}^{\ominus} - E_{left}^{\ominus}$$

- Since oxidation is always on the left and reduction on the right, you can also use this version

$$E_{cell}^{\ominus} = E_{reduction}^{\ominus} - E_{oxidation}$$

Your notes

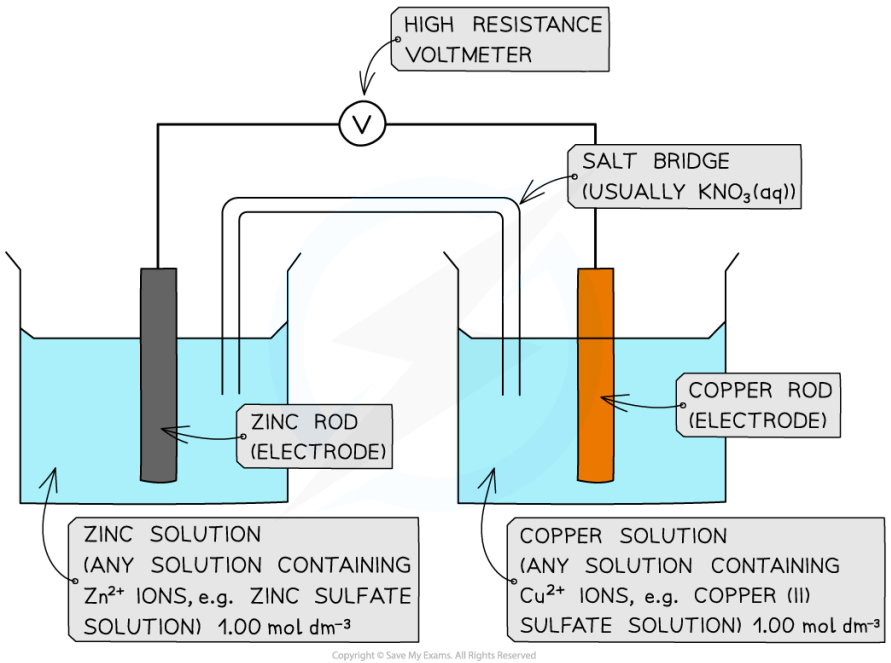
Worked Example

Calculating the standard cell potential

Calculate the standard cell potential for the electrochemical cell below and explain why the Cu^{2+} / Cu half-cell is the positive pole. The half-equations are as follows:

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus} = +0.34\ V$

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $\quad E^{\ominus} = -0.76\ V$



Answer

Step 1: Calculate the standard cell potential. The copper is more positive so must be the right hand side.

$E_{cell}^{\ominus} = E_{right}^{\ominus} - E_{left}^{\ominus}$

$E_{cell}^{\ominus} = (+0.34) - (-0.76)$

$= +1.10\ V$

The voltmeter will therefore give a value of +1.10 V

Step 2: Determine the positive and negative poles

The Cu^{2+} / Cu half-cell is the **positive** pole as its $E^{\ominus}$ is more positive than the $E^{\ominus}$ value of the Zn^{2+} / Zn half-cell

Your notes

Examiner Tips and Tricks

A helpful mnemonic for remembering redox in cells

Lio the lion goes Roor!

Lio stands for 'Left Is Oxidation' and he is saying ROOR because that is the order of species in the cell:

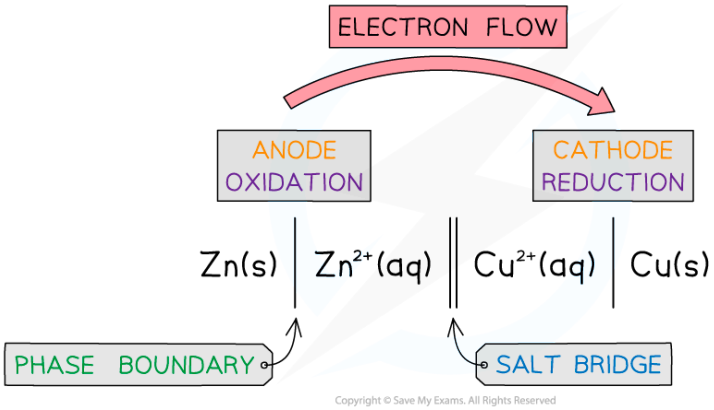
Reduced/Oxidised (salt bridge) Oxidised/Reduced

Your notes

Conventional Cell Representation

Conventional Representation of Cells

- As it is cumbersome and time-consuming to draw out every electrochemical cell in full, a system of notation is used which describes the cell in full, but does not require it to be drawn.
- An electrochemical cell can be represented in a shorthand way by a **cell diagram** (sometimes called cell representations or cell notations)



The conventional representation of voltaic cells

- By convention, the half cell with the greatest negative potential is written on the left of the salt bridge, so $E^{\ominus}_{cell} = E^{\ominus}_{right} - E^{\ominus}_{left}$
  - In this case, $E^{\ominus}_{cell} = +0.34 - -0.76 = +1.10$ V.
- The left cell is being oxidized while the right is being reduced
- If there is more than one species in solution, and the species are on different sides of the half-equation, the different species are separated by a comma
- This method of representing electrochemical cells is known as the conventional representation of a cell, and it is widely used
- If both species in a half reaction are aqueous then an inert platinum electrode is needed which is recorded on the outside of the half cell diagram

Some Examples

- For the iron(II) and iron(III) half cell reaction a platinum electrode is needed as an electron carrier
- The half equation is

$$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$$

- So the cell convention as a left hand electrode would be

$$Pt \equiv Fe^{2+}(aq), Fe^{3+}(aq)$$

- Notice the order must be Fe(II) then Fe(III) as the left side is an oxidation reaction, so Fe(II) is oxidised to Fe(III) by the loss of an electron
- The platinum electrode is separated by the phase boundary (vertical solid line), but the iron(II) and iron(III) are separated by a comma since they are in the same phase
- Non-metals will also require a platinum electrode
- If chlorine is used as an electrode the reduction reaction is

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$

- The conventional representation of the half reaction would be

$$Cl_2(g), 2Cl^-(aq) \mid Pt$$

- Notice that the half cell reaction is balanced; however, it would be also correct to write it as

$$Cl_2(g), Cl^-(aq) \mid Pt$$

- This is because conventional cell diagrams are not quantitative- they are just representations of the materials and redox processes going on
  - Most chemists tend to show them balanced anyway
- Combining these two half cells together gives

$$Pt \mid Fe^{2+}(aq), Fe^{3+}(aq) \parallel Cl_2(g) \mid 2Cl^-(aq) \mid Pt$$

- As you can see the overall cell diagram is not quantitative as the left side is a one electron transfer and the right side is a two electron transfer

Your notes

Your notes

Thermodynamic Feasibility

Feasibility

- The $E^{\ominus}$ values of a species indicate how **easily** they can get **oxidised** or **reduced**
- The **more** positive the value, the easier it is to reduce the species on the **left** of the half-equation
  - The reaction will tend to proceed in the **forward direction**
- The **less** positive the value, the easier it is to **oxidise** the species on the **right** of the half-equation
  - The reaction will tend to proceed in the backward direction
  - A reaction is **feasible** (likely to occur) when the $E_{cell}^{\ominus}$ is **positive**
- For example, two half-cells in the following electrochemical cell are:

$$Cl_2\,(g) + 2e^- \rightleftharpoons 2Cl^-\,(aq) \quad E^{\ominus} = +1.36\ V$$

$$Cu^{2+}\,(aq) + 2e^- \rightleftharpoons Cu\,(s) \quad E^{\ominus} = +0.34\ V$$

- Cl_2 molecules are **reduced** as they have a more positive $E^{\ominus}$ value
- The chemical reaction that occurs in this half cell is:

$$Cl_2\,(g) + 2e^- \rightarrow 2Cl^-\,(aq)$$

- Cu^{2+} ions are **oxidised** as they have a less positive $E^{\ominus}$ value
- The chemical reaction that occurs in this half cell is:

$$Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^-$$

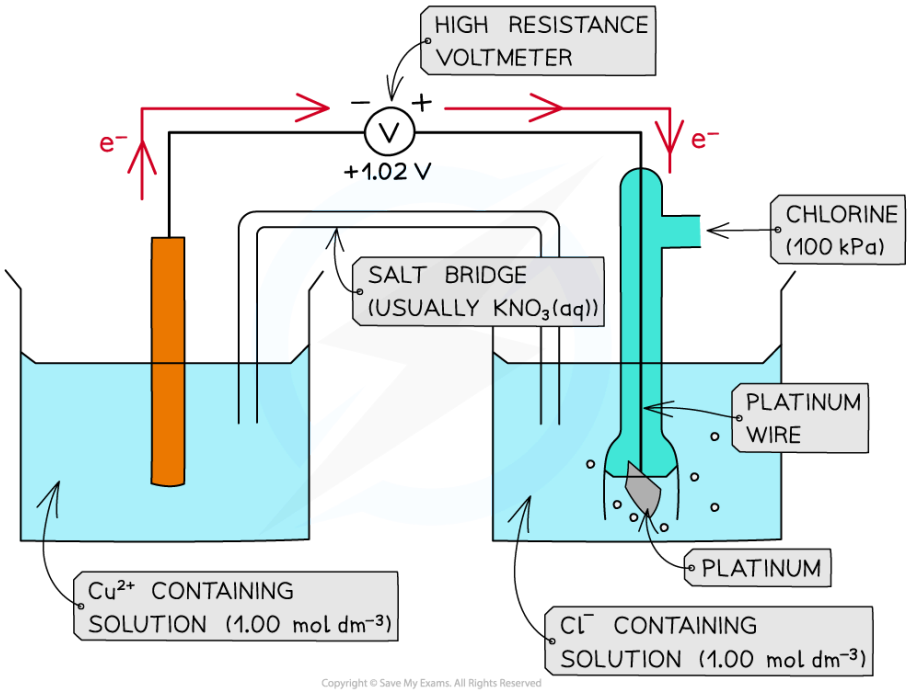
- The **overall equation** of the electrochemical cell is (after cancelling out the electrons):

$$Cu\,(s) + Cl_2\,(g) \rightarrow 2Cl^-\,(aq) + Cu^{2+}\,(aq)$$

OR

$$Cu\,(s) + Cl_2\,(g) \rightarrow CuCl_2\,(s)$$

- The **forward** reaction is **feasible** (spontaneous) as it has a **positive** $E^{\ominus}$ value of +1.02 V ((+1.36) - (+0.34))
- The **backward** reaction is **not feasible** (not spontaneous) as it has a **negative** $E^{\ominus}$ value of -1.02 ((+0.34) - (+1.36))



LESS POSITIVE
∴ OXIDATION REACTION OCCURS

MORE POSITIVE
∴ REDUCTION REACTION OCCURS

$E^\ominus = +0.34V$ $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36V$

REACTION DIRECTION (OXIDATION)

REACTION DIRECTION (REDUCTION)

HALF EQUATION 1: $Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$

HALF EQUATION 2: $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

OVERALL EQUATION: $Cl_2(g) + Cu(s) \longrightarrow 2Cl^-(aq) + Cu^{2+}(aq)$

OR...

$Cl_2(g) + Cu(s) \longrightarrow CuCl_2(s)$ $E^\ominus = +1.02V$

A reaction is feasible when the standard cell potential $E^\ominus$ is positive

Examiner Tips and Tricks

You may have to apply your understanding (from the above worked example) to questions with more than 2 equations

Your notes

- The process is still the same in terms of identifying the most positive / least negative value as the reduction reactions
- This reaction will also contain the oxidising agent on the left hand side

Your notes

Entropy Change & ln K

- Cell potential is related to both entropy, S, and the equilibrium constant, K
- A larger cell potential means a bigger change in total entropy
  - Therefore, we can say that cell potential is directly proportional to total entropy change

$$E^{\theta} \propto \Delta S_{total}$$

- The use of two equations for Gibbs free energy change can also show that:

$$E^{\theta} \propto \ln K$$

- $\Delta G = -nF E^{\theta}_{cell}$
  - $\Delta G = -RT \ln K$

Examiner Tips and Tricks

You are expected to be aware of the two directly proportional relationships described

However, you are not expected to work with the Faraday based Gibbs free energy equation

$$\Delta G = -nF E^{\theta}_{cell}$$

- The Faraday constant, F, is not given in the Data Booklet

Limitations of Standard Electrode Potential Predictions

- The **thermodynamic feasibility** of a reaction can be deduced from the electrode potential, however, it gives no information about the rate of reaction
- As standard electrode potentials are measured using solutions, we have to consider the le Châtelier's effect on concentration using non-standard conditions
  - For example, the redox equilibrium equation and standard electrode potential for the $V^{3+} | V^{2+}$ system are:

$$V^{3+}(aq) + e^{-} \rightleftharpoons V^{2+}(aq) \quad E^{\theta} = +0.26\ V$$

- If the concentration of $V^{3+}(aq)$ is greater than 1.0 mol dm^{-3}, then the equilibrium will shift to the right


Your notes

- This will remove electrons from the system, therefore, making the electrode potential less negative
- If the concentration of $V^{2+}(aq)$ is greater than 1.0 mol dm^{-3}, then the equilibrium will shift to the left
  - This will add electrons to the system, therefore, making the electrode potential more negative
- Any change to the concentration will cause a change to the electrode potential and, therefore, to the overall cell potential
  - This is true of any change to the conditions that results in non-standard conditions

- Reaction kinetics can also affect the prediction

1. The rate of reaction may simply be so slow that it looks like the reaction isn't happening, when it is
2. The reaction may have a high activation energy which inhibits the reaction, for example:

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\theta = 0.34\,V$

$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$ $E^\theta = 0.00\,V$

- The reaction of $Cu^{2+}(aq) + H_2(g) \rightarrow Cu(s) + 2H^+(aq)$ is thermodynamically feasible with an electromotive force of +0.34 V
  - However, this reaction does not occur as the activation energy is so high which means that the reactants are **kinetically stable**
- Another, more basic limitation is the fact that many redox reactions are not aqueous

Your notes

Fuel Cells

- A fuel cell is an electrochemical cell in which a fuel **donates** electrons at one electrode and oxygen **gains** electrons at the other electrode
- These cells are becoming more common in the automotive industry to replace petrol or diesel engines
- As the fuel enters the cell it becomes oxidised which sets up a **potential difference** or voltage within the cell
- Different electrolytes and fuels can be used to set up different types of fuel cells
  - Methanol and other hydrogen rich fuels can be used in fuel cells but the hydrogen-oxygen fuel cell is the most common currently
- An important cell is the **hydrogen-oxygen** fuel cell which combines both elements to release energy and water

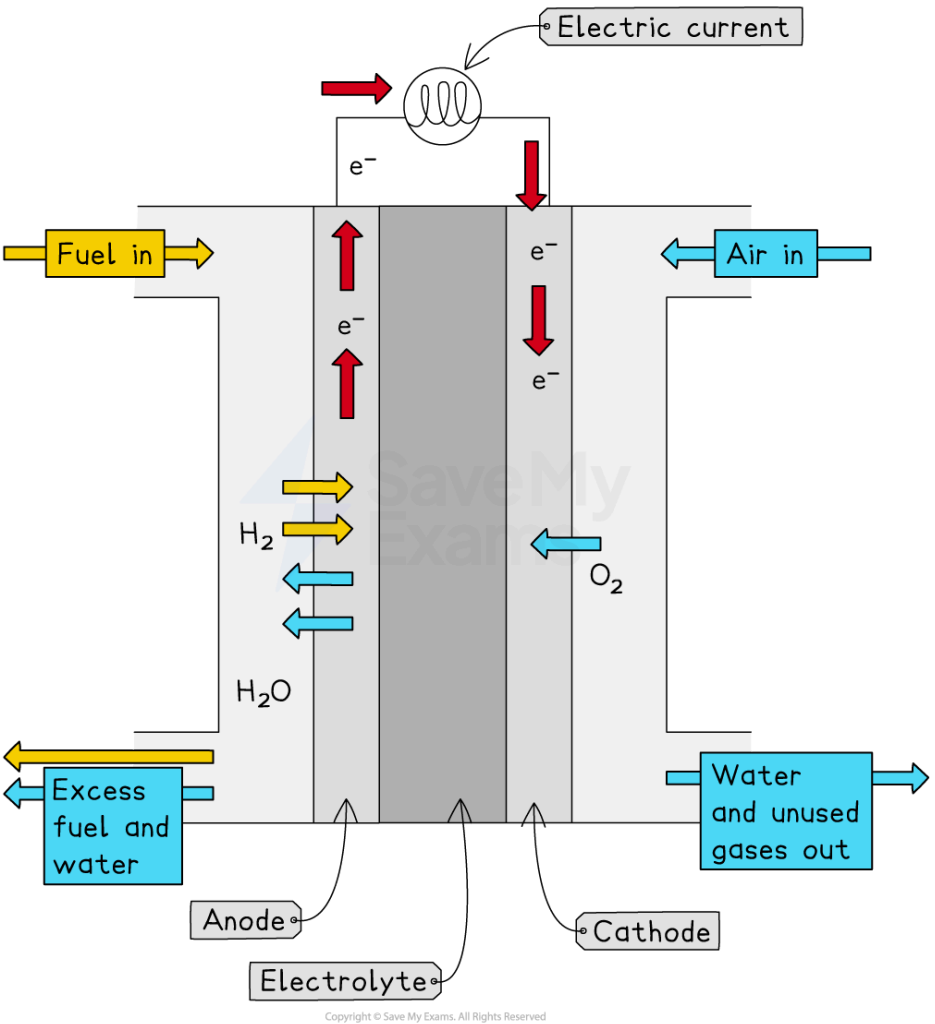


Diagram showing the movement of hydrogen, oxygen and electrons in a hydrogen-oxygen fuel cell

Your notes

- The fuel cell consists of
  - a reaction chamber with separate inlets for hydrogen and oxygen gas
  - an outlet for the product - water
  - an electrolyte
  - two metal electrodes that are coated in platinum to catalyse the reactions at the electrodes
  - a semi-permeable membrane that separates the hydrogen and oxygen gases

The alkaline hydrogen-oxygen fuel cell

- The half equations occurring at each electrode are:

Negative electrode / anode: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^- \quad E^\theta = -0.83\ V$

Positive electrode / cathode: $O_2(g) + 2H_2O + 4e^- \rightarrow 4OH^-(aq) \quad E^\theta = +0.40\ V$

- The overall reaction is found by combining the two half equations and cancelling the common terms:

$$2H_2(g) + 4OH^-(aq) + O_2(g) + 2H_2O + 4e^- \rightarrow 4H_2O(l) + 4e^- + 4OH^-(aq)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad E^\theta = +1.23\ V$$

The acidic hydrogen-oxygen fuel cell

- The half equations occurring at each electrode are:

Negative electrode / anode: $H_2(g) \rightarrow 2H^+(aq) + 2e^- \quad E^\theta = 0.00\ V$

Positive electrode / cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) \quad E^\theta = +1.23\ V$

- The overall reaction is found by combining the two half equations and cancelling the common terms:

$$2H_2(g) + O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l) + 4H^+(aq) + 4e^-$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad E^\theta = +1.23\ V$$

Benefits

- Water is the only reaction product, so fuel cells present obvious environmental advantages over other types of cells
- The reaction is the same as hydrogen combusting in oxygen, but since the reaction takes place at room temperature without combustion, all the bond energy is converted into electrical energy instead of heat and light
- There are no harmful oxides of nitrogen produced, which are usually formed in high temperature combustion reactions where air is present

- Fuel cells have been used on space craft, where the product can be used as drinking water for astronauts


Your notes

Risks and problems

- Hydrogen is a highly flammable gas and the production and storage of hydrogen carries safety hazards
- Very thick walled cylinders and pipes are needed to store hydrogen which has economic impacts
- The production of hydrogen is a by-product of the crude oil industry, which means it relies on a **non-renewable, finite resource**
- Until a cheap way is found to make hydrogen, its widespread use in fuel cells will be limited
- Hydrogen has high energy density, that is, the amount of energy contained in 1g of the fuel is high compared to other fuels, but because it is a gas, its energy density per unit volume is low which means larger containers are needed compared to liquid fuels

Examiner Tips and Tricks

- Dfferences between fuel cells and other cells include:
  - The cell operates continuously as long as there is a supply of hydrogen and oxygen; the energy is not stored in the cell
  - The anode is the negative electrode and the cathode is the positive electrode

Your notes

Redox Titration – Calculations

Redox Titrations

- In a **titration**, the concentration of a solution is determined by titrating with a solution of known concentration.
- In redox titrations, an **oxidising 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**

Potassium manganate(VII) titrations

- In these redox titrations the manganate(VII) is the oxidising agent and is reduced to $Mn^{2+}(aq)$
- The iron is the reducing agent and is oxidised to $Fe^{3+}(aq)$ and the reaction mixture must be acidified, to excess acid is added to the iron(II) ions before the reaction begins
- The choice of acid is important, as it must not react with the manganate(VII) ions, so the acid normally used is dilute sulfuric acid
  - As it does not oxidise under these conditions and does not react with the manganate(VII) ions

Worked Example

Equations

Find the stoichiometry for the reaction and complete the two half equations:

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

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

Answers:

Balance the electrons:

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

$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

Add the two half equations:

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

- Manganate(VII) titrations can be used to determine:
  - The percentage purity of iron supplements
- Percentage purity = $\frac{\text{mass of sample}}{\text{mass of impure sample}} \times 100$
  - The formula of a sample of hydrated ethanedioic acid

Your notes

Worked Example

Analysis of iron tablets

An iron tablet, weighing 0.960 g was dissolved in dilute sulfuric acid. An average titre of 28.50 cm^3 of 0.0180 mol dm^{-3} potassium manganate(VII) solution was needed to reach the endpoint.

What is the percentage by mass of iron in the tablet?

Answer:

- $MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+} \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
  - 1 : 5 ratio of MnO_4^- : Fe^{2+}
  - Number of moles of $MnO_4^-(aq) = 0.0180 \times \frac{28.50}{1000} = 5.13 \times 10^{-4}$ moles
  - Moles of iron(II) = $5 \times 5.13 \times 10^{-4} = 2.565 \times 10^{-3}$ moles
  - Mass of iron(II) = $55.8 \times 2.565 \times 10^{-3} = 0.143127$ g
  - Percentage by mass = $= \frac{0.143127}{0.960} \times 100 = 14.9\%$

Iodine-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

Worked Example

Analysis of household bleach

Chlorate(I) ions, ClO^-, are the active ingredient in many household bleaches.

10.0 cm^3 of bleach was made up to 250.0 cm^3.

25.0 cm^3 of this solution had 10.0 cm^3 of 1.0 mol dm^{-3} potassium iodide and then acidified with 1.0 mol dm^{-3} hydrochloric acid.

$$ClO^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow Cl^-(aq) + I_2(aq) + H_2O(l)$$

This was titrated with 0.05 mol dm^{-3} sodium thiosulfate solution giving an average titre of 25.20 cm^3.

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

What is the concentration of chlorate(I) ions in the bleach?

Answer:

- One mole of $ClO^-(aq)$ produces one mole of $I_2(aq)$ which reacts with two moles of $2S_2O_3^{2-}(aq)$
  - Therefore, 1 : 2 ratio of $ClO^-(aq) : S_2O_3^{2-}(aq)$
  - Number of moles of $S_2O_3^{2-}(aq) = \frac{0.05 \times 25.20}{1000} = 1.26 \times 10^{-3}$ moles
  - Number of moles of $I_2(aq)$ and $ClO^-(aq)$ in 25.0 $cm^3 = \frac{1.26 \times 10^{-3}}{2} = 6.30 \times 10^{-4}$ moles
  - Number of moles of $ClO^-(aq)$ in 250.0 $cm^3 = 6.30 \times 10^{-4} \times 10 = 6.30 \times 10^{-3}$ moles
  - The 250.0 cm^3 was prepared from 10.0 cm^3 bleach
    - 10 cm^3 bleach = 6.30×10^{-3} moles of ClO^- ions
    - 1.0 dm^3 bleach = 0.630 moles of ClO^- ions
    - Therefore, the concentration of ClO^- ions in the bleach is **0.630 mol dm^{-3}**

Examiner Tips and Tricks

General sequence for redox titration calculations

1. Write down the half equations for the oxidant and reductant
2. Deduce the overall equation
3. Calculate the number of moles of manganate(VII) or dichromate(VI) used
4. Calculate the ratio of moles of oxidant to moles of reductant from the overall redox equation
5. Calculate the number of moles in the sample solution of the reductant
6. Calculate the number of moles in the original solution of reductant

Your notes

7. Determine either the concentration of the original solution or the percentage of reductant in a known quantity of sample

Your notes

Redox Titration – Uncertainty

Percentage Uncertainties

- Percentage uncertainties are a way to compare the significance of an absolute uncertainty on a measurement
- This is not to be confused with percentage error, which is a comparison of a result to a literature value
- The formula for calculating percentage uncertainty is as follows:

$$\text{Percentage uncertainty} = \frac{\text{uncertainty}}{\text{measured value}} \times 100$$

Adding or subtracting measurements

- When you are adding or subtracting two measurements then you add together the **absolute** measurement uncertainties
- For example,
  - Using a balance to measure the initial and final mass of a container
  - Using a thermometer for the measurement of the temperature at the start and the end
  - Using a burette to find the initial reading and final reading
- In all these examples you have to read the instrument **twice** to obtain the quantity
- If each time you read the instrument the measurement is 'out' by the stated uncertainty, then your final quantity is potentially 'out' by twice the uncertainty

Reducing uncertainty in titrations

- In titrations, uncertainty can be reduced by adjusting the concentration of the known liquid, which is usually in the burette
  - This is to make it so that the burette readings are larger
- For example, if a burette had an uncertainty of ±0.1 cm^3, the initial reading was 0.0 cm^3 and the final reading was 5.0 cm^3
  - The titre is 5.0 cm^3
  - The percentage uncertainty is, therefore, $\frac{0.2}{5.0} \times 100 = 4\%$
- If the concentration of the chemical in the burette was diluted so that the initial reading was 0.0 cm^3 and the final reading was 30.0 cm^3
  - The titre is 30.0 cm^3

- The percentage uncertainty is, therefore, $\frac{0.2}{30.0} \times 100 = 0.67\%$

- Overall, to reduce the uncertainty in burette readings, you:
  - Dilute the chemical in the burette
  - This means that more will be required for the titration
  - Therefore, the overall uncertainty in the burette readings is reduced

Your notes