🧪 Cambridge (CIE) A Level Chemistry

Standard Electrode Potentials E⊖, Standard Cell Potentials E⊖cell & the Nernst Equation

Contents

Standard Electrode & Standard Cell Potentials
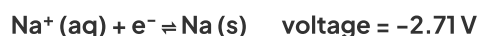
Electrode potential

- The **electrode (reduction) potential** (*E*) is a value which shows how easily a substance is **reduced**

- These are demonstrated using reversible half equations

    - This is because there is a redox equilibrium between two related species that are in different oxidation states

    - For example, if you dipped a zinc metal rod into a solution which contained zinc ions, there would be zinc atoms losing electrons to form zinc ions and at the same time, zinc ions gaining electrons to become zinc atoms

    - This would cause a redox equilibrium

Half equations

- When writing half equations for this topic, the electrons will always be written on the left-hand side (demonstrating reduction)

- The position of equilibrium is different for different species, which is why different species will have electrode (reduction) potentials

- The more **positive** (or less negative) an electrode potential, the **more likely** it is for that species to undergo **reduction**

    - The equilibrium position lies more to the **right**

- For example, the positive electrode potential of bromine below, suggests that it is likely to get reduced and form bromide (Br^-) ions

$$Br_2 \text{ (l)} + 2e^- \rightleftharpoons 2Br^- \text{ (aq)} \qquad \text{voltage} = +1.09 \text{ V}$$

- The more **negative** (or less positive) the electrode potential, the less likely it is that reduction of that species will occur

    - The equilibrium position lies more to the **left**

- For example, the negative electrode potential of sodium suggests that it is unlikely that the sodium (Na^+) ions will be reduced to sodium (Na) atoms

$$Na^+ \text{ (aq)} + e^- \rightleftharpoons Na \text{ (s)} \qquad \text{voltage} = -2.71 \text{ V}$$
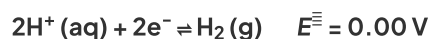
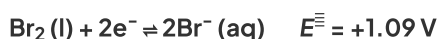## Standard electrode potential

- The position of equilibrium and therefore the electrode potential depends on factors such as:
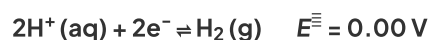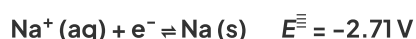
- Temperature

- 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

- **Standard conditions** also have to be used when comparing electrode potentials

- These standard conditions are:

  - An ion concentration of 1.00 mol dm^{-3}

  - A temperature of 298 K

  - A pressure of 1 atm

- The electrode potentials are measured relative to something called 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 ($E^⦵$)**

- The **standard electrode potential ($E^⦵$)** is the 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** $E^⦵$ value

$$\text{Br}_2 \text{ (l)} + 2e^- \rightleftharpoons 2\text{Br}^- \text{ (aq)} \qquad E^⦵ = +1.09 \text{ V}$$

$$2\text{H}^+ \text{ (aq)} + 2e^- \rightleftharpoons \text{H}_2 \text{ (g)} \qquad E^⦵ = 0.00 \text{ V}$$

- 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** $E^⦵$ value

$$\text{Na}^+ \text{ (aq)} + e^- \rightleftharpoons \text{Na (s)} \qquad E^⦵ = -2.71 \text{ V}$$

$$2\text{H}^+ \text{ (aq)} + 2e^- \rightleftharpoons \text{H}_2 \text{ (g)} \qquad E^⦵ = 0.00 \text{ V}$$

Standard cell potential

- Once the $E^⦵$ of a half-cell is known, the **voltage** of an **electrochemical cell** made up of two half-cells can be calculated

  - These could be **any** half-cells and neither have to be a standard hydrogen electrode

- This is also known as the **standard cell potential ($E_{cell}^⦵$)**

- The standard cell potential can be determined by two methods:

 1. Using the equation $E_{cell}^⦵ = E_{reduction}^⦵ - E_{oxidation}^⦵$

- Use of this equation does require knowledge of which reaction is reduction and which is oxidation

  - The reduction reaction has the higher / more positive $E^{\ominus}$ value
  2. $E_{cell}^{\ominus}$ is the difference in $E^{\ominus}$ between two half-cells
- For example, an electrochemical cell consisting of bromine and sodium half-cells has an $E_{cell}^{\ominus}$ of:

  - $E_{cell}^{\ominus}$ = (+1.09) – (–2.71)

  - $E_{cell}^{\ominus}$ = +3.80 V

Standard Hydrogen Electrode

- When a metal rod is placed in an aqueous solution, a **redox equilibrium** is established between the metal ions and atoms

  - For example, the copper atoms get **oxidised** and enter the solution as copper ions

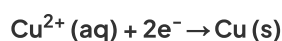$$Cu\,(s) \rightarrow Cu^{2+}\,(aq) + 2e^-$$
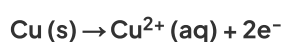
Oxidation of copper ions
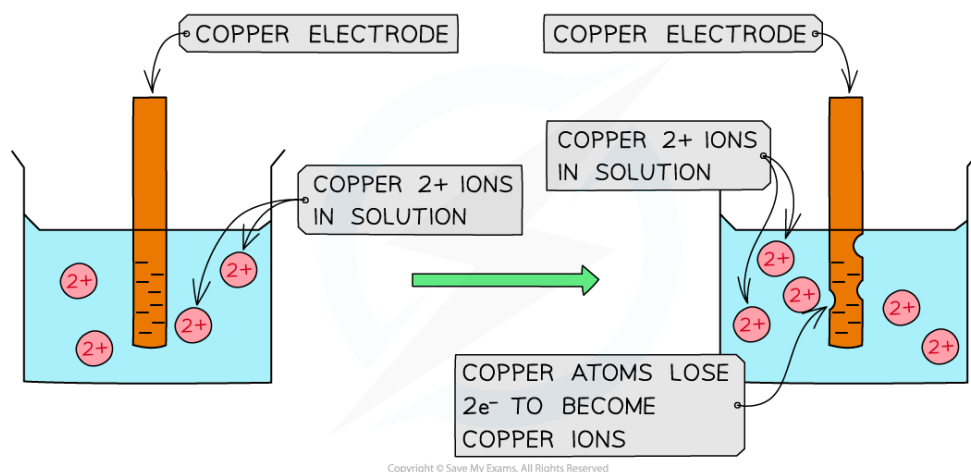
During oxidation, copper atoms lose 2 electrons to form copper ions

- The copper ions gain electrons from the metal rod and deposit as metal atoms on the rod

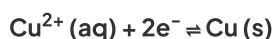$$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s)$$

Reduction of copper ions
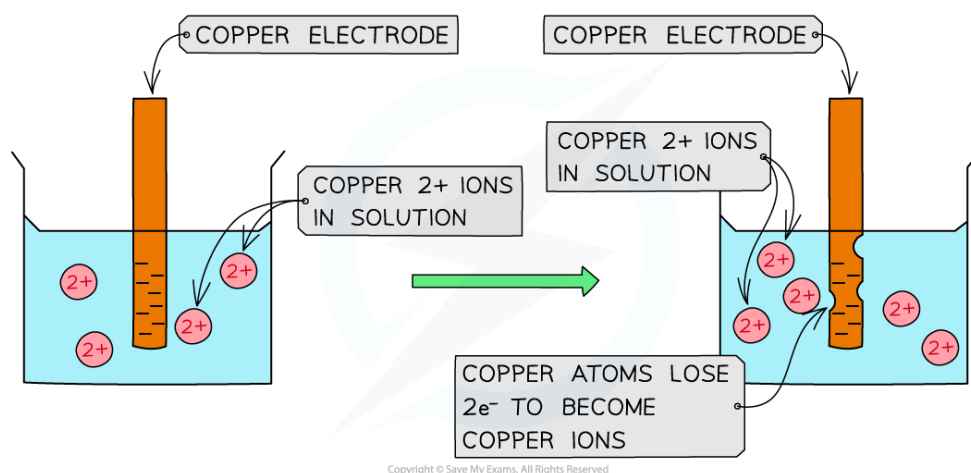
During oxidation, copper atoms lose 2 electrons to form copper ions

- When equilibrium is established, the **rate** of oxidation and reduction of copper is **equal**

- The position of the redox equilibrium is different for different metals

   - Copper is more easily **reduced**, thus the equilibrium lies further over to the **right**

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

- Vanadium is more easily **oxidised**, thus the equilibrium lies further over to the **left**

$$V^{2+} (aq) + 2e^- \rightleftharpoons V(s)$$
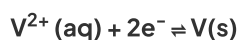
- The metal atoms and ions in solution cause an **electric potential** (**voltage**)

- This potential cannot be measured **directly** however the potential between the metal/metal ion system and **another** system **can** be measured

- This value is called the **electrode potential** (*E*) and is measured in **volts**

    - The electrode potential is the **voltage** measured for a half-cell compared to another half-cell

    - Often, the half-cell used for comparison is the **standard hydrogen electrode**

Standard hydrogen electrode

- 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 1 atm)

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g)$$
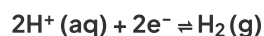
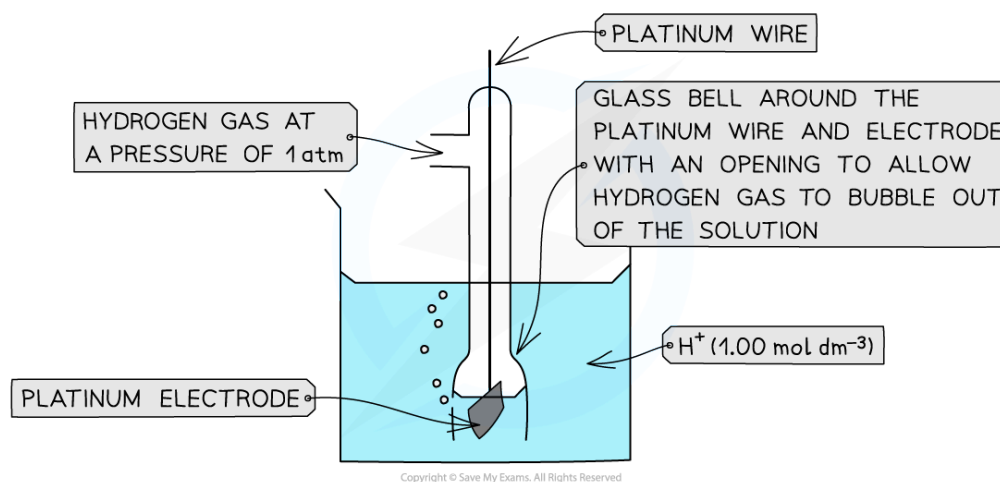- An **inert platinum** electrode that is in contact with the hydrogen gas and H^+ ions

- When the standard hydrogen electrode is connected to another half-cell, the **standard electrode potential** of that half-cell can be read off a voltmeter

The standard hydrogen electrode (SHE)

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

Measuring the Standard Electrode Potential

- There are three different types of half-cells that can be connected to a standard hydrogen electrode

    - 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)

- When a half-cell is connected to a standard hydrogen electrode, or when two half-cells are connected, a **salt bridge** is required

    - A salt bridge has **mobile ions** that complete the circuit

    - A salt bridge is typically a strip of filter paper soaked in a saturated solution of **potassium nitrate** or **potassium chloride** as nitrates and chlorides are usually soluble

    - This should ensure that no precipitates form which can affect the equilibrium position of the half-cells

Metal / metal ion half-cell

- 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:

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

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g) \quad E^{\ominus} = 0.00 \ V$$
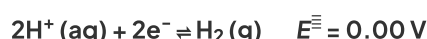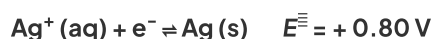
- Since the Ag^+ / Ag half-cell has a more positive $E^{\ominus}$ value, this is the **positive pole** and the H^+ / H_2 half-cell is the **negative** pole

- The **standard cell potential** ($E_{cell}^{\ominus}$) is $E_{cell}^{\ominus}$ = (+ 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 pole**

    - Oxidation occurs at the **negative pole**

Example of an electrochemical cell containing a metal / metal ion half-cell

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Under standard conditions, a metal / metal ion half-cell is connected to the standard hydrogen electrode to measure the cell potential

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 is the non-metal

    - Br^- is the non-metal ion

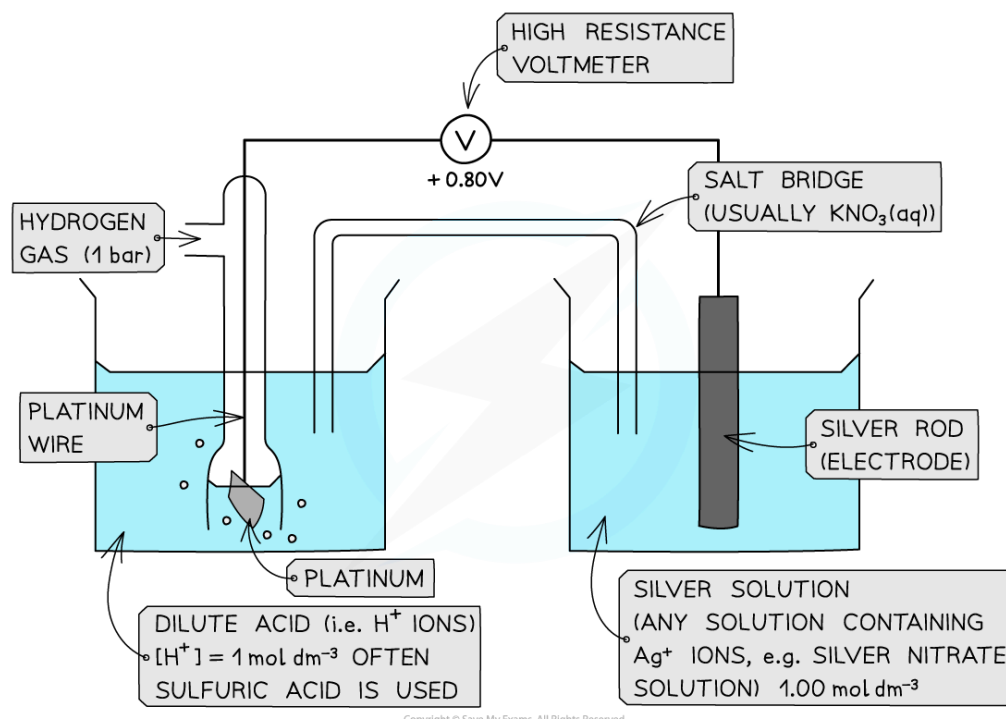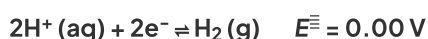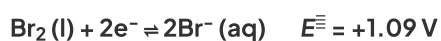- The half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

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

$$2H^+ \text{ (aq)} + 2e^- \rightleftharpoons H_2 \text{ (g)} \quad E^{\ominus} = 0.00 \text{ V}$$
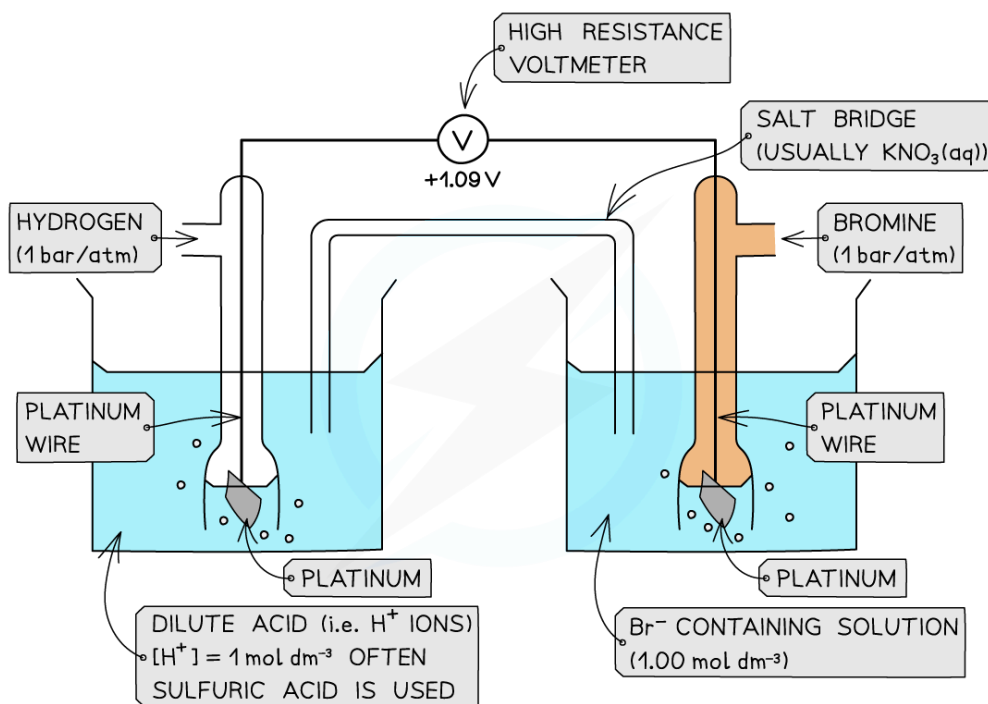
- The Br_2 / Br^- half-cell is the **positive pole** and the H^+ / H_2 is the **negative** pole

- $E_{cell}^{\ominus} = (+1.09) - (0.00) = +1.09 \text{ V}$

- The Br_2 molecules are more likely to get **reduced** than H^+ as they have a greater $E^{\ominus}$ value

Example of an electrochemical cell containing a non-metal / non-metal ion half-cell

Under standard conditions, a non-metal / non-metal ion half-cell is connected to the standard hydrogen electrode to measure the cell potential

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 an oxidation number of +7

  - The Mn^{2+} ion contains Mn with an oxidation number of +2

- This half-cell is connected to a **standard hydrogen electrode** and the two half-equations are:

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

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

- 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

- $E_{cell}^{\ominus}$ = (+ 1.52) – (0.00) = + 1.52 V

Example of an electrochemical cell containing an ion / ion half-cell

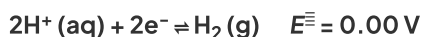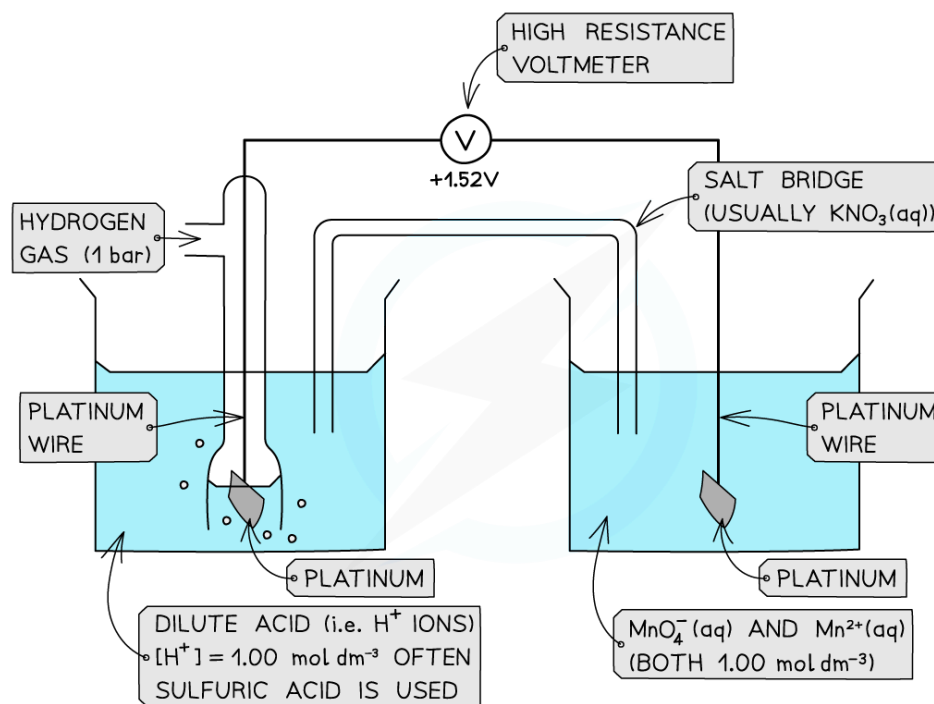*Under standard conditions, an ion / ion half-cell is connected to the standard hydrogen electrode to measure the cell potential*

Standard Cell Potential: Direction of Electron Flow & Feasibility

Direction of electron flow

- The **direction of electron flow** can be determined by comparing the $E^{\ominus}$ values of two half-cells in an electrochemical cell

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

$$Cu^{2+}\,(aq) + 2e^- \rightleftharpoons Cu\,(s) \qquad E^{\ominus} = +0.34\,V$$
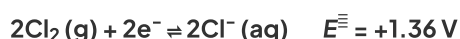
- The Cl_2 more **readily accept** electrons from the Cu^{2+}/Cu half-cell
  - This is the **positive pole**
  - Cl_2 gets more readily reduced
- The Cu^{2+} more **readily loses** electrons to the Cl_2/Cl^- half-cell
  - This is the **negative pole**
  - Cu^{2+} gets more readily oxidised
- The electrons flow from the Cu^{2+}/Cu half-cell to the Cl_2/Cl^- half-cell
- The flow of electrons is from the **negative pole** to the **positive pole**

Flow of electrons through an electrochemical cell
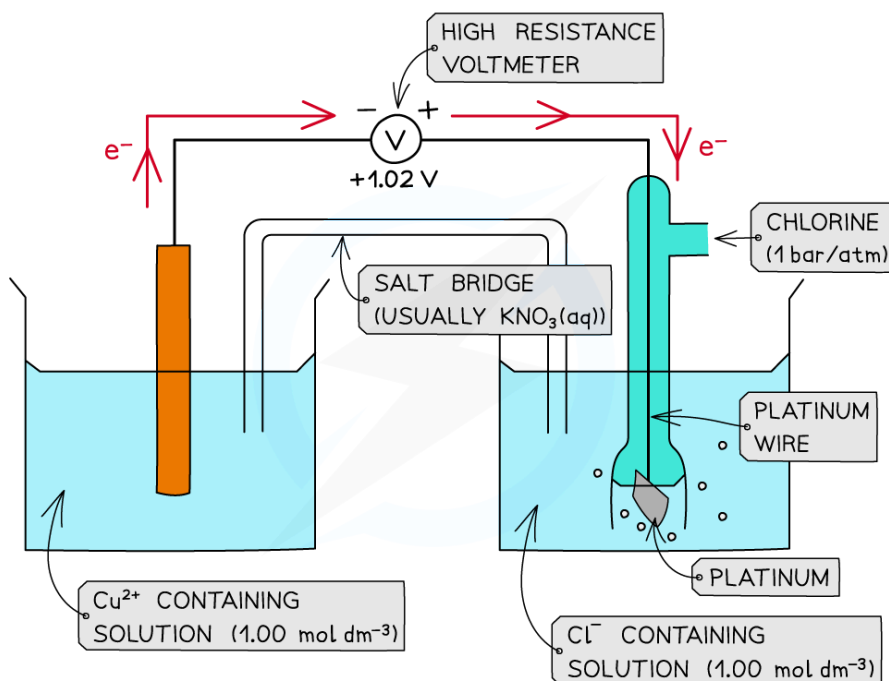
The electrons flow through the wires from the negative pole to the positive pole

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:

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

$$Cu^{2+} \text{ (aq)} + 2e^- \rightleftharpoons Cu \text{ (s)} \qquad E^{\ominus} = +0.34 \text{ V}$$
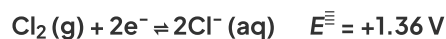
- Cl_2 molecules are **reduced** as they have a more positive $E^{\ominus}$ value

- The chemical reaction that occurs in this half-cell is:

$$Cl_2 \text{ (g)} + 2e^- \rightarrow 2Cl^- \text{ (aq)}$$
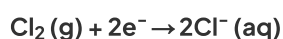
- Cu^{2+} ions are **oxidised** as they have a less positive $E^{\ominus}$ value

- The chemical reaction that occurs in this half-cell is:

$$Cu \text{ (s)} \rightarrow Cu^{2+} \text{ (aq)} + 2e^-$$
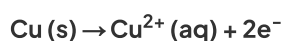
- The **overall equation** of the electrochemical cell is (after cancelling out the electrons):

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

OR

$$Cu \text{ (s)} + Cl_2 \text{ (g)} \rightarrow CuCl_2 \text{ (s)}$$

- 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))
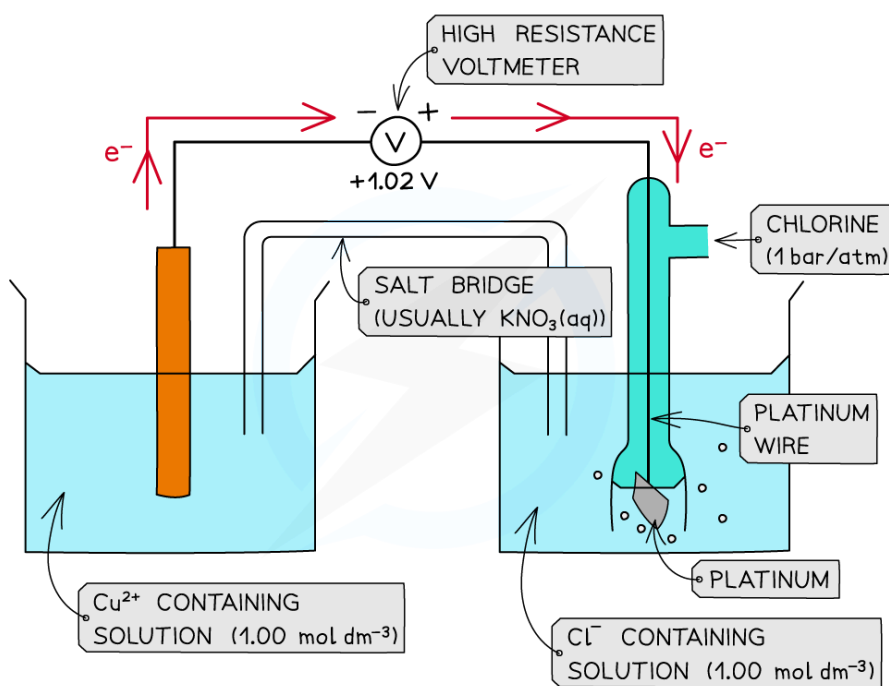
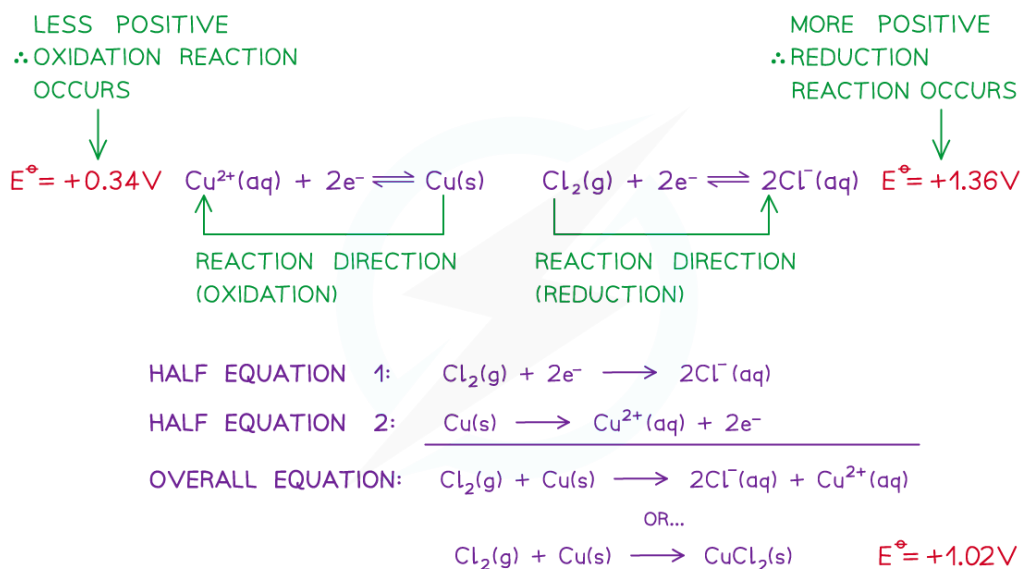# Reaction feasibility and the standard cell potential

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LESS POSITIVE
∴ OXIDATION REACTION OCCURS

MORE POSITIVE
∴ REDUCTION REACTION OCCURS

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

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...

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

A reaction is feasible when the standard cell potential E⦵ is positive

Examiner Tips and Tricks

Remember that the electrons only move through the wires in the external circuit and not through the electrolyte solution.

Redox Equations

- The main ways to construct redox equations using the relevant half-equations:

  - Using changes in oxidation numbers to help balance chemical equations

  - Using the number of electrons for each half-cell

    - Both of these are discussed in the Redox Reactions topic

  - Interpreting the information given to you and predicting any other chemicals involved in the reaction

Worked Example

Write the balanced chemical equation for hydrogen iodide reacting with sulfuric acid to form hydrogen sulfide, iodine and one other product

Answer:

- There are 2 possible methods:

  1. Using ionic half-equations

2. Interpreting the information and predicting any other chemicals involved

Using ionic half-equations method:

- **Step 1:** Identify possible half-equations from the information

    - Iodide → iodine
    - Sulfuric acid → hydrogen sulfide
- **Step 2:** Construct the half equations

    - Iodide → iodine

        - $I^- → I_2$
        - This requires 2 iodide ions and 2 electrons as products to balance the equation
        - $2I^- → I_2 + 2e^-$
    - Sulfuric acid → hydrogen sulfide

        - $H_2SO_4 → H_2S$
        - The 4 oxygen atoms will form 4 water molecules as products
        - $H_2SO_4 → H_2S + 4H_2O$
        - The 8 hydrogen atoms in the water molecules will require 8 protons as reactants
        - $H_2SO_4 + 8H^+ → H_2S + 4H_2O$
        - The 8 protons will require 8 electrons to balance the charge
        - $H_2SO_4 + 8H^+ + 8e^- → H_2S + 4H_2O$
- **Step 3:** Combine the half-equations

    - Iodide → iodine

        - $2I^- → I_2 + 2e^-$
        - The iodide half-equation needs to be multiplied by 4 to have the same number of electrons as the sulfuric acid half-equation
        - $8I^- → 4I_2 + 8e^-$
    - Sulfuric acid → hydrogen sulfide

        - $H_2SO_4 + 8H^+ + 8e^- → H_2S + 4H_2O$
    - Combining the half-equations

        - $8I^- + H_2SO_4 + 8H^+ + 8e^- → 4I_2 + 8e^- H_2S + 4H_2O$
    - Cancelling, where appropriate

        - The electrons cancel on both sides
        - The $8I^-$ and $8H^+$ can be re-written as 8HI
        - $8HI + H_2SO_4 → 4I_2 + H_2S + 4H_2O$

Interpreting and predicting method:

- **Step 1:** Start with what you know:

    - $HI + H_2SO_4 → H_2S + I_2$
- **Step 2:** Consider any elements that are not accounted for

    - The only element that is not currently considered is oxygen
- **Step 3:** Make a common and appropriate suggestion for the missing product

    - Most of these questions are in solution so there is always H_2O, H^+ and OH^- available

- Missing product suggestion = $4H_2O$
- $HI + H_2SO_4 \rightarrow H_2S + I_2 + 4H_2O$
- **Step 4:** Balance the remaining chemicals

    - $8HI + H_2SO_4 \rightarrow H_2S + 4I_2 + 4H_2O$

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Examiner Tips and Tricks

- Similar approaches can be used to balance more complicated ionic half-equations
- In these situations, you will have H_2O, H^+, OH^- and electrons available

Your notes

Standard Cell Potential Calculations

- 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

- 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

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

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

  $$E_{cell}^{\ominus} = (+0.34) - (-0.76) = +1.10\,V$$
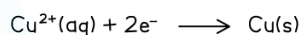
- **Step 2:** Determine the positive and negative poles

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

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

OVERALL IONIC EQUATION

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

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- 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

Examiner Tips and Tricks

- 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. OR AN OX. OXidation takes place at the ANode
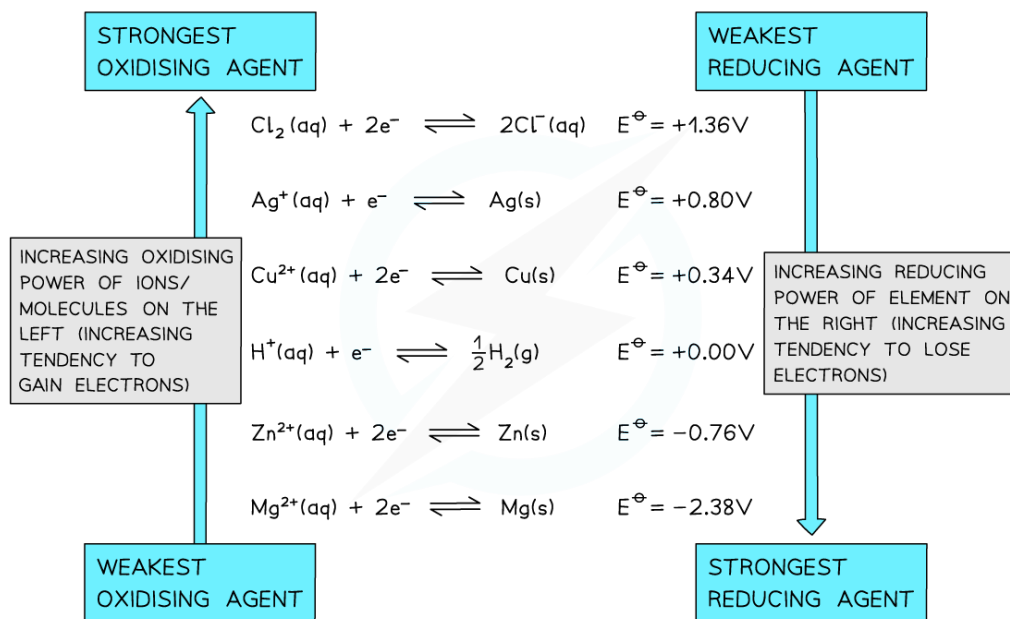
Electrochemical Series

- The $E^{\ominus}$ values of a species indicate how **easily** they can get **oxidised** or **reduced**

- In other words, they indicate the relative **reactivity** of elements, compounds and ions as **oxidising agents** or **reducing agents**

- The **electrochemical series** is a list of various **redox equilibria** in order of decreasing $E^{\ominus}$ values

- **More positive** (less negative) $E^{\ominus}$ values indicate that:

  - The species is easily **reduced**

  - The species is a better **oxidising agent**

- **Less positive** (more negative) $E^{\ominus}$ values indicate that:

  - The species is easily **oxidised**

  - The species is a better **reducing agent**

An example electrochemical series

STRONGEST OXIDISING AGENT

WEAKEST REDUCING AGENT

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

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

INCREASING OXIDISING POWER OF IONS/ MOLECULES ON THE LEFT (INCREASING TENDENCY TO GAIN ELECTRONS)

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

$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g) \quad E^{\ominus} = +0.00V$

INCREASING REDUCING POWER OF ELEMENT ON THE RIGHT (INCREASING TENDENCY TO LOSE ELECTRONS)

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

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E^{\ominus} = -2.38V$

WEAKEST OXIDISING AGENT

STRONGEST REDUCING AGENT

In this example electrochemical series the equilibria are arranged in order of decreasing $E^{\ominus}$ values. These values can then be used to identify the strongest and weakest reducing / oxidising agents.

# Effect of Concentration on Electrode Potential

- Changes in **temperature** and **concentration** of aqueous ions will affect the standard electrode potential ($E^\ominus$) of a half-cell

- Under these **non-standard conditions**, E is used as a symbol for the electrode potential instead of $E^\ominus$

Increasing the concentration of the species on the left

- If the concentration of the species on the left is increased, the position of equilibrium will shift to the **right**

- This means that the species on the left gets **more easily reduced**

- The E value becomes **more positive** (or less negative)

- Let's look at the half-cell below as an example

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

- If the concentration of Zn^{2+} (**species on the left**) is **increased**, the equilibrium position will shift to the **right**

- The species on the **left** (Zn^{2+}) will get **more easily reduced**

- Therefore, the E value becomes **less negative** and will change too, for example, –0.50 V instead

- This principle can also be applied to a half-cell with a positive $E^\ominus$ value such as:

$$Fe^{3+} \text{ (aq)} + e^- \rightleftharpoons Fe^{2+} \text{ (aq)} \qquad E^\ominus = +0.77 \text{ V}$$
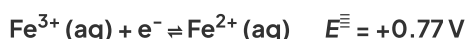
- If the concentration of Fe^{3+} (**species on the left**) is **increased**, the equilibrium position will shift to the **right**

- The species on the **left** (Fe^{3+}) will get more easily **reduced**

- Therefore, the E value becomes **more positive** and will change too, for example, +0.89 V instead

Increasing the concentration of species on the right

- If the concentration of the species on the right is increased, the position of equilibrium will shift to the **left**

- This means that the species on the left get **less easily reduced**

- The E value becomes **less positive** (or more negative)

- Let's look again at the half-cell below

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

- If the concentration of Zn (**species on the right**) is **increased**, the equilibrium position will shift to the **left**

- The species on the **left** (Zn^{2+}) will get less easily **reduced**

- Therefore, the E value becomes **more negative** and will change too, for example, –0.82 V instead

- This principle can, again, also be applied to a half-cell with a positive $E^{\ominus}$ value:

$$Fe^{3+} (aq) + e^- \rightleftharpoons Fe^{2+} (aq) \quad E^{\ominus} = +0.77 \, V$$
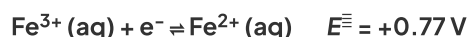
- If the concentration of Fe^{2+} (**species on the right**) is **increased**, the equilibrium position will shift to the **left**

- The species on the **left** (Fe^{3+}) will get less easily **reduced**

- Therefore, the E value becomes **less positive** and will change too, for example, +0.56 V instead

Effect of concentration on the electrode potential
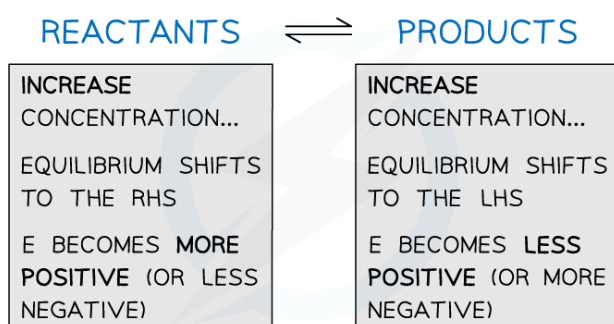
Summarising the effects of changing the concentration of reactants and products

The Nernst Equation

- Under non-standard conditions, the cell potential of the half-cells is shown by the symbol E_{cell}

- The effect of changes in **temperature** and **ion concentration** on the E_{cell} can be deduced using the **Nernst equation**

$$E = E^{\ominus} + \frac{RT}{zF} \ln \frac{[oxidised\ species]}{[reduced\ species]}$$

- **E** = electrode potential under nonstandard conditions

  - **E^{θ}** = standard electrode potential

  - **R** = gas constant ($8.31\ J\ K^{-1}\ mol^{-1}$)

  - **T** = temperature (kelvin, K)

  - **z** = number of electrons transferred in the reaction

  - **F** = Faraday constant ($96\ 500\ C\ mol^{-1}$)

  - **ln** = natural logarithm

- This equation can be simplified to

$$E = E^{\ominus} + \frac{0.059}{z} \log_{10} \frac{[oxidised\ species]}{[reduced\ species]}$$
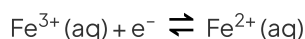
- At standard temperature, *R, T* and *F* are constant

  - $\ln x = 2.303 \log_{10} x$

- The Nernst equation only depends on **aqueous ions** and **not solids or gases**

- The concentrations of solids and gases are therefore set to $1.0\ mol\ dm^{-3}$

Worked Example

Calculating the electrode potential of a Fe^{3+} / Fe^{2+} half-cell

Calculate the electrode potential at 298K of a Fe^{3+} / Fe^{2+} half-cell.

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

- $[Fe^{3+}] = 0.034\ mol\ dm^{-3}$
- $[Fe^{2+}] = 0.64\ mol\ dm^{-3}$
- $E^{\theta} = +0.77\ V$

Answer

- From the question, the relevant values for the Fe^{3+} / Fe^{2+} half-cell are:

    - $[Fe^{3+}]$ = 0.034 mol dm^{-3}
    - $[Fe^{2+}]$ = 0.64 mol dm^{-3}
    - $E^{\ominus}$ = + 0.77 V
- The oxidised species is Fe^{3+} as it has a higher oxidation number (+3)
- The reduced species is Fe^{2+} as it has a lower oxidation number (+2)
- z is 1 as only one electron is transferred in this reaction
- The Nernst equation for this half-reaction is, therefore:

$$E \; = \; 0.77 + \frac{0.059}{1} \; \log_{10} \frac{[0.034]}{[0.64]}$$
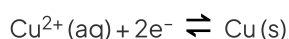
- E = (+0.77) + (−0.075)
- E = +0.69 V

Worked Example

Calculating the electrode potential of a Cu^{2+} / Cu half-cell

Calculate the electrode potential at 298K of a Cu^{2+} / Cu half-cell.

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

- $[Cu^{2+}]$ = 0.001 mol dm^{-3}
- $E^{\ominus}$ = +0.34 V

Answer

- From the question, the relevant values for the Cu^{2+} / Cu half-cell are:

    - $[Cu^{2+}]$ = 0.0010 mol dm^{-3}
    - $E^{\ominus}$ = + 0.34 V
- The oxidised species is Cu^{2+} as it has a higher oxidation number (+2)
- The reduced species is Cu as it has a lower oxidation number (0)
- Cu is solid which means that it is not included in the Nernst equation

    - Its concentration does not change and is, therefore, fixed at 1.0
- z is 2 as 2 electrons are transferred in this reaction
- The Nernst equation for this half-reaction is, therefore:

$$E \; = \; E^{\ominus} + \frac{0.059}{z} \; \log_{10} \frac{[oxidised\ species]}{[reduced\ species]}$$

$$E \; = \; 0.34 + \frac{0.059}{2} \; \log_{10} \frac{[0.0010]}{[1.0]}$$

- E = (+ 0.34) + (− 0.089)
- E = + 0.25 V

Examiner Tips and Tricks

- You need to know the Nernst equation, so make sure you learn it

    - CIE specifically ask students to learn use this version:

$$E = E^{\ominus} + \frac{0.059}{z} \ \log_{10} \frac{[oxidised\ species]}{[reduced\ species]}$$

- Make sure you always check what the temperature is
- If the temperature is **not** 298 K (or 25 °C) the full Nernst equation should be used
- You don't need to know how to **simplify** the Nernst equation
- You are only expected to use the equation when the temperature is 298 K (or 25 °C)

Calculating Free Energy Change Using Standard Electrode Potentials

- The **standard free energy change** can be calculated using the standard cell potential of an electrochemical cell

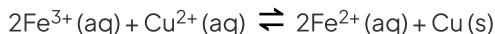$$\Delta G^{\ominus} = -\,n \times E_{cell}^{\ominus} \times F$$

- $\Delta G^{\ominus}$ = standard Gibbs free energy

    - **n** = number of electrons transferred in the reaction

    - $E_{cell}^{\ominus}$ = standard cell potential (V)

    - **F** = Faraday constant (96 500 C mol^{-1})

Worked Example

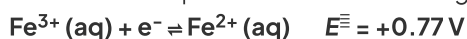**Calculating the standard Gibbs free energy change**

Calculate the standard Gibbs free energy change for the following electrochemical cell:

$$2Fe^{3+}\,(aq) + Cu^{2+}\,(aq) \rightleftharpoons 2Fe^{2+}\,(aq) + Cu\,(s)$$

Answer

- **Step 1:** Determine the two half-equations and their $E^{\ominus}$ using the Data booklet:
  $$Fe^{3+}\,(aq) + e^{-} \rightleftharpoons Fe^{2+}\,(aq) \qquad E^{\ominus} = +0.77\,V$$

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

- **Step 2:** Calculate the $E_{cell}^{\ominus}$

    - $E_{cell}^{\ominus} = E_{red}^{\ominus} - E_{ox}^{\ominus}$
    - $E_{cell}^{\ominus} = (+0.77) - (+0.34)$
    - $E_{cell}^{\ominus} = +0.43\,V$
- **Step 3:** Determine the number of electrons transferred in the reaction

    - The Cu^{2+}/Cu has a smaller $E^{\ominus}$ value which means that it gets **oxidised**
    - It **transfers** two electrons to **two** Fe^{3+} ions
    - Each Fe^{3+} ion accepts one electron so the total number of electrons transferred is **two**
- **Step 4:** Substitute the values in for the standard Gibbs free energy equation

    - $\Delta G^{\ominus} = -\,n \times E_{cell}^{\ominus} \times F$
    - $\Delta G^{\ominus} = -2 \times (+0.43) \times 96\,500$
    - $\Delta G^{\ominus} = -82\,990\,J\,mol^{-1} = -83\,kJ\,mol^{-1}$