

# CAIE Chemistry A-level

## 24: Electrochemistry (A-level only)

### Notes

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## Electrolysis

Electrolysis is the **decomposition of a molten or aqueous ionic compound** (an electrolyte) by passing an **electric current** through it. The solution must contain a cathode (negative electrode) and an anode (positive electrode).

### $F = Le$

The **Faraday constant** (F) is equal to the Avogadro constant (L) multiplied by the charge of an electron in coulombs (e):  $F = Le$

$$1 \text{ faraday} = 9.65 \times 10^4 \text{ C mol}^{-1} \text{ (coulombs per mole)}$$

- A **coulomb** is a quantity of electricity.  
Number of coulomb = current (amps) x time (seconds).
- **Avogadro's constant** is the **number of particles in one mole** of any substance.  
This is equal to  $6.02 \times 10^{23}$ .

### Predicting Products

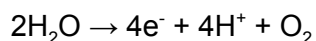
When the electrolyte is molten, cations (positive ions) move to the cathode and gain electrons to form atoms. Anions move towards the anode, lose electrons and become atoms. Examples are shown below:

- Electrolysis of aqueous NaCl:  
Cathode:  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$   
Anode:  $2\text{Cl}^- \rightarrow 2\text{e}^- + \text{Cl}_2$
- Electrolysis of molten lead(II) bromide:  
Cathode:  $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$   
Anode:  $2\text{Br}^- \rightarrow 2\text{e}^- + \text{Br}_2$

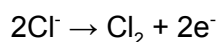
When using inert electrodes to electrolyse a solution, if the metal ions are **below hydrogen** in the **electrochemical series** (more positive  $E^\ominus$ ), the metal atoms will be produced at the cathode. If the metal is above hydrogen in the electrochemical series, hydrogen gas will be produced at the cathode.

Metals from **lead to zinc** in the electrochemical series depend on the **concentration**, with the **more concentrated ions becoming atoms**. A very dilute solution will form hydrogen and when the metal ion concentrations are similar, both may form atoms.

Generally, when a solution is electrolysed using **inert electrodes**, **oxygen** is produced at the anode:



However, if concentrated chlorine ions are present, chlorine will form:



When electrolysing a solution with **non-inert electrodes**, the same reaction takes place at the cathode. At the anode, atoms in the anode lose electrons to form ions in the electrolyte. The net charge is a transfer of an element from the **anode to the cathode**.

### Calculations

The amount of charge passed during electrolysis can be calculated using the equations  **$F=Le$**  and **number of coulombs = current x time ( $Q=It$ )**:

1. Multiplying current (amps) by time (seconds) to find the number of coulombs.
2. Convert the number of coulombs to faradays using the conversion 1 faraday =  $9.65 \times 10^4 \text{ C mol}^{-1}$ .
3. Divide the Faraday constant by the Avogadro constant to find the quantity of charge in coulombs.

To find the **mass of silver liberated** during the electrolysis of  **$\text{AgNO}_3$** :

1. Multiply the current (amps) by the time (seconds) to find the number of coulombs.
2. Use the equation at the cathode,  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ :
  - 1 mol of electrons forms 1 mol of silver
  - 1 mol electrons is 1 faraday
  - 96500 coulombs gives 108 g of silver.
3. If 96500 coulombs produces 108 g of silver, find the mass of silver produced by dividing the number of coulombs calculated in step 1 by 96500 and multiplying this by 108.

To find the **volume of hydrogen** produced during the electrolysis of  **$\text{H}_2\text{SO}_4$**  at room temperature and pressure:

1. Multiply the current (amps) by the time (seconds) to find the number of coulombs.
2. Use the equation at the cathode,  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ :
  - 2 mol of electrons forms 1 mol of hydrogen
  - 2 mol of electrons is 2 faradays
  - 2 x 96500 coulombs forms  $24 \text{ dm}^3 \text{ H}_2$  at room temperature and pressure.
3. If 2 x 96500 coulombs produces  $24 \text{ dm}^3 \text{ H}_2$ , find the volume of hydrogen produced by dividing the number of coulombs calculated in step 1 by (2 x 96500) and multiplying this by 24.

### Avogadro Constant and Electrolysis

The Avogadro constant can be determined using **electrolysis** of silver nitrate:

1. Clean two silver electrodes and weigh the anode. Pour silver nitrate solution into a beaker.
2. Set up the electrolysis experiment. Control the current and leave for a measured amount of time.
3. Switch off and remove the anode. Wash the anode in distilled water and propanone before weighing. Calculate the change in mass.



Calculating the **Avogadro constant** from experimental results:

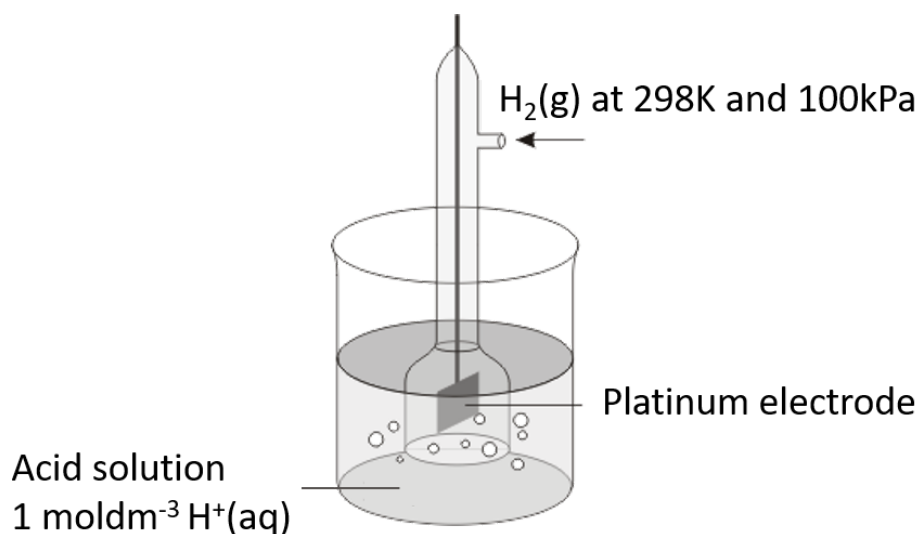
1. Multiply the current (amps) by the time (seconds) to find the number of coulombs.
2. Use the cathode reaction,  $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ :
  - 1 mol of electrons forms 1 mol of silver
3. Calculate the number of moles of silver by dividing the mass change by the atomic mass of silver (108).
4. Find the number of coulombs in one mole of electrons by dividing the calculated number of coulombs from step 1 by the number of moles in step 3.
5. To calculate the Avogadro constant, divide the number of coulombs in one mole of electrons by the charge on an electron (from the data book, this is  $1.60 \times 10^{-19}$ ).

## Electrode Potentials, Cell Potentials and the Nernst Equation

A half cell contains **an element in two oxidation states**. An **equilibrium** is established between these two oxidation states on the surface of a solid.

- **Standard electrode potential ( $E^\ominus$ )**: the emf of a half cell compared with a hydrogen half cell under standard conditions.
- **Standard cell potential ( $E^\ominus_{\text{cell}}$ )**: the emf when two half cells are connected under standard conditions
- **Emf**: electromotive force, the voltage when no current flows

### Standard Hydrogen Electrode



[File:SHE.gif, Scioly Wiki, CC BY 3.0](#)

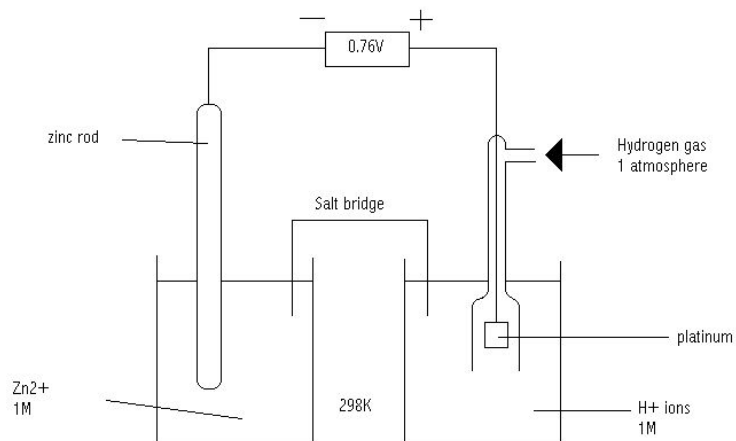
An equilibrium is set up on the surface of the platinum electrode between the hydrogen gas molecules and the hydrogen ions in solution:  $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ .



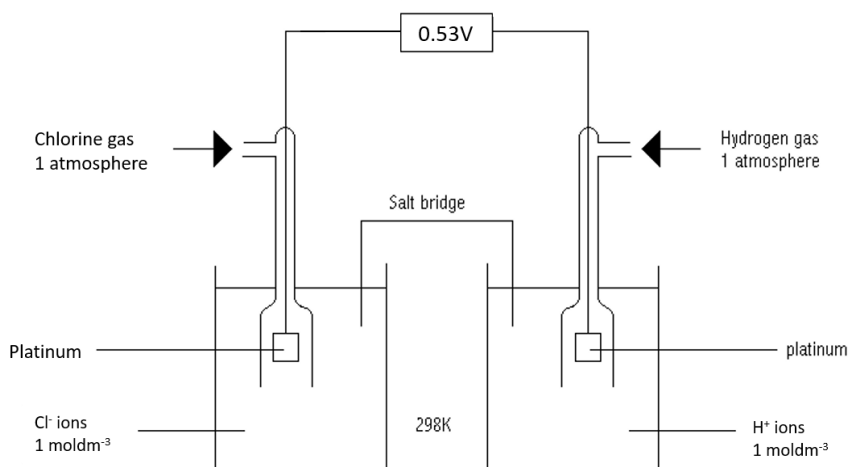
## Measuring Standard Electrode Potentials

The diagrams below show how the standard electrode potential of different half cells can be measured.

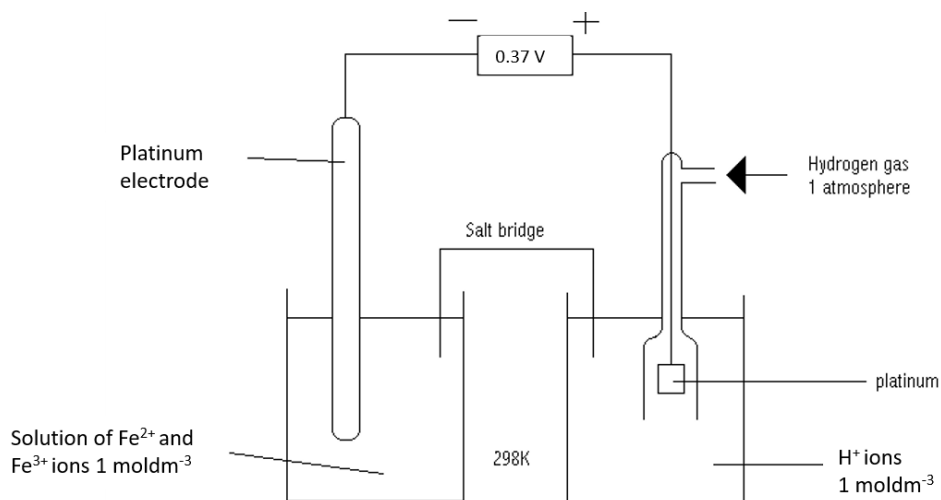
### Metal with metal ions:



### Non-metal with non-metal ions:



### Mixture of ions:



For the cells on the previous page, each half cell must contain one element in two oxidation states. To create a **closed circuit** and allow charge to flow, a **salt bridge** must be placed between the two solutions and a **wire** must connect the two electrodes. A **voltmeter** measures the potential difference of the cell.

### Calculating Standard Cell Potential

A cell can be made by connecting two half cells with **different electrode potentials**. One half cell will release electrons while the other will gain them. The half cell with the more positive  $E^\ominus$  (positive terminal) will gain electrons while the half cell with the more negative  $E^\ominus$  (negative terminal) will release electrons. The standard cell potential can be calculated in volts using the equation below:

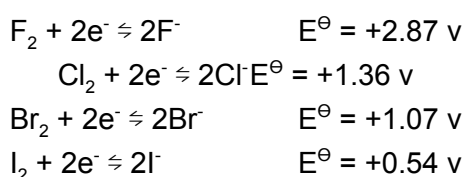
$$E^\ominus_{\text{cell}} = E^\ominus(\text{positive terminal}) - E^\ominus(\text{negative terminal}).$$

Electrons flow from the **negative terminal to the positive terminal**. This means electrons flow from the half cell with the more negative  $E^\ominus$  to the cell with the more positive  $E^\ominus$ .

A reaction is **feasible, or spontaneous**, if the cell potential is **positive**. Half cells with more negative electrode potentials are more likely to be oxidised and lose electrons. When two half cells are connected, the **more negative half cell will always undergo oxidation**.

### $E^\ominus$ and Group 17

Below are the  $E^\ominus$  values for the first four halogens:



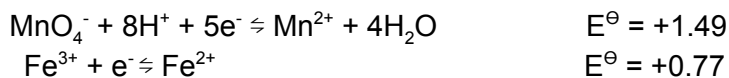
As the value of  $E^\ominus$  **becomes more positive**, the position of the equilibrium lies further to the right and the element is **more likely to be reduced**. An oxidising agent is a species which oxidises another species while being reduced. Fluorine is the **most powerful oxidising agent** in the group because it has the most positive  $E^\ominus$  value.

### Redox Equations

Half equations can be combined to form a redox equation. The number of electrons on both sides of the redox equation must be the **same** so that the **electrons are cancelled out**. An example is shown below:

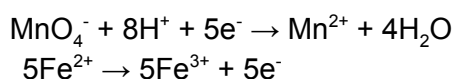


1. **Half equations:**

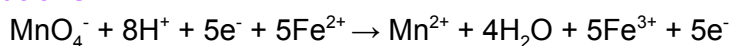


2. **Decide the positive and negative terminals:**  $\text{MnO}_4^- / \text{Mn}^{2+}$  has the more positive standard electrode potential so this is the positive terminal. Since it is the positive terminal, the forward reduction reaction occurs.  $\text{Fe}^{2+} / \text{Fe}^{3+}$  has the less positive standard electrode potential so this is the negative terminal. It is more negative and so undergoes oxidation.

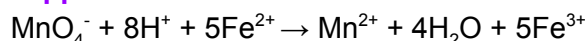
3. **Balance the electrons:**



3. **Combine equations:**



4. **Cancel species that appear on both sides:**



### Electrode Potentials and Concentrations

A half equation shows an equilibrium. If the **concentration** of a substance changes, the **position of equilibrium will shift** to minimise this change (**Le Chatelier's principle**).

The **copper half equation** is:  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$ . If the concentration of copper ions decreases, the position of equilibrium will shift left. This causes the electrode potential to become less positive because more oxidation will occur. The half cell is **no longer a standard half cell** because the concentration of the solution has changed from  $1 \text{ mol dm}^{-3}$ .

If a half cell contains two ions and the concentration of both ions is changed by the same amount, the electrode potential will remain the same because the tendencies for the equilibrium position to move will cancel out.

### Nernst Equation

The Nernst equation is used to calculate the electrode potential of a half cell when the **concentration of aqueous ions changes**. The equation is shown below:

$$E = E^\ominus + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

E - electrode potential (non-standard)

$E^\ominus$  - standard electrode potential

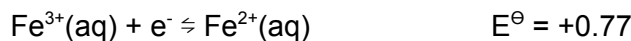
z - number of electrons transferred

[oxidised species] - concentration of the oxidised species

[reduced species] - concentration of the reduced species



**Example:** The concentration of  $\text{Fe}^{2+}$  ions is  $0.3 \text{ mol dm}^{-3}$  and  $\text{Fe}^{3+}$  ions is  $1.0 \text{ mol dm}^{-3}$ . The electrode potential for a  $\text{Fe}^{2+}/\text{Fe}^{3+}$  half cell can be calculated using the Nernst equation.  $\text{Fe}^{2+}$  is reduced and  $\text{Fe}^{3+}$  is oxidised.



$$E = E^{\ominus} + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

$$E = +0.77 + (0.059/1) \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E = +0.77 + (0.059/1) \log \frac{1}{0.3}$$

$$E = +0.77 + (0.059/1) \log(3.3333)$$

$$E = +0.80 \text{ v}$$

If the initial half equation was  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$ , **z would equal 2** because **2 electrons are transferred**. If the initial half equation was  $\text{Cl}_2(\text{aq}) + 2\text{e}^{-} \rightleftharpoons 2\text{Cl}^{-}(\text{aq})$ , the concentration of the reduced species ( $\text{Cl}^{-}$ ) would be **squared** because there are **2  $\text{Cl}^{-}$  ions in the equation**.

