Important note on NERST EQUATION

E^0 ALWAYS BECOME MORE POSITIVE FOR THE FORWARD REACTION WITH RESPECT TO LE CHATELIER'S PRINCIPLE

What happens to the electrode potential when we change the concentration of ions in a half-cell? Let us take an example of a metal/metal ion equilibrium:

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

- If $[Zn^{2+}]$ is greater than 1.00 mol dm^{-3}, the value of E becomes less negative / more positive (for example −0.61 V).
- If $[Zn^{2+}]$ is less than 1.00 mol dm^{-3}, the value of E becomes more negative / less positive (for example −0.80 V).

We can apply Le Chatelier's principle to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So the value of E becomes more positive / less negative.

If two different ions are present in the half-cell, we have to consider both ions.

Let us take the equilibrium between Fe^{3+} ions and Fe^{2+} ions as an example.

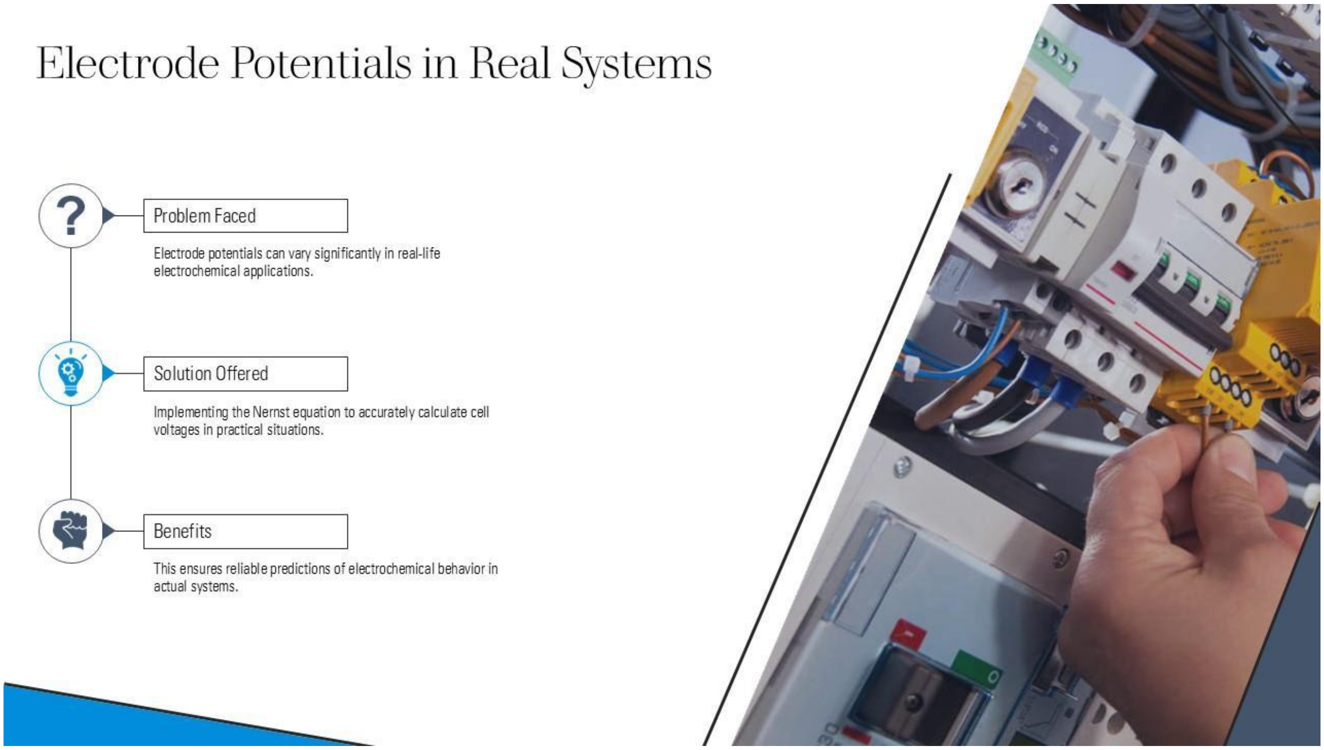
$$\underset{1.00\,mol\,dm^{-3}}{Fe^{3+}} + e^- \rightleftharpoons \underset{1.00\,mol\,dm^{-3}}{Fe^{2+}} \qquad E^\ominus = +0.77\,V$$

- If $[Fe^{3+}]$ is greater than 1.00 mol dm^{-3} (keeping $[Fe^{2+}]$ = 1.00 mol dm^{-3}) the value of E becomes more positive (for example +0.85 V).
- If $[Fe^{3+}]$ is less than 1.00 mol dm^{-3} (keeping $[Fe^{2+}]$ = 1.00 mol dm^{-3}) the value of E becomes less positive (for example +0.70 V).
- If $[Fe^{2+}]$ is greater than 1.00 mol dm^{-3} (keeping $[Fe^{3+}]$ = 1.00 mol dm^{-3}) the value of E becomes less positive (for example +0.70 V).
- If $[Fe^{2+}]$ is less than 1.00 mol dm^{-3} (keeping $[Fe^{3+}]$ = 1.00 mol dm^{-3}) the value of E becomes more positive (for example +0.85 V).

Real-World Applications of the Nernst Equation

The practical uses of the Nernst equation are diverse and impactful in various fields:

- **In Battery Technology:** It helps in understanding and predicting the changes in potential of batteries over time and use. This is crucial for the development of more efficient and long-lasting batteries.
- **For Environmental Analysis:** The equation is used in measuring the concentration of pollutants in water bodies by analysing the changes in electrode potentials. This is essential in environmental monitoring and in the study of aquatic ecosystems.
- **Bioelectrochemistry:** It plays a role in the study of biological systems, particularly in understanding ion transport across cell membranes and the electrochemical gradients that are essential for cellular processes.



Electrode Potentials in Real Systems

Problem Faced

Electrode potentials can vary significantly in real-life electrochemical applications.

Solution Offered

Implementing the Nernst equation to accurately calculate cell voltages in practical situations.

Benefits

This ensures reliable predictions of electrochemical behavior in actual systems.

Learning outcome 24.2.10

This statement deals with the relationship between standard electrode potentials and Gibbs free energy.

The key equation is:

$$\boxed{\Delta G^\circ = -\, nE^\circ_{cell}F}$$

You will often find this in books or on the web rearranged slightly as:

$$\boxed{\Delta G^\circ = -\, nFE^\circ_{cell}}$$

The terms:

- **ΔG°** is the standard Gibbs free energy change.
- **n** is the number of electrons transferred in the reaction.
- **F** is the Faraday constant, 96500 coulombs mol^{-1}.
- **E°_{cell}** is the standard cell potential in volts.

This equation links together the two conditions for feasibility you have met:

- E°_{cell} has to be positive.
- ΔG° has to be negative.

Worked Example

Calculating the standard Gibbs free energy change

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

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

Answer

- **Step 1:** Determine the two half-equations and their $E^\ominus$ using the Data booklet:

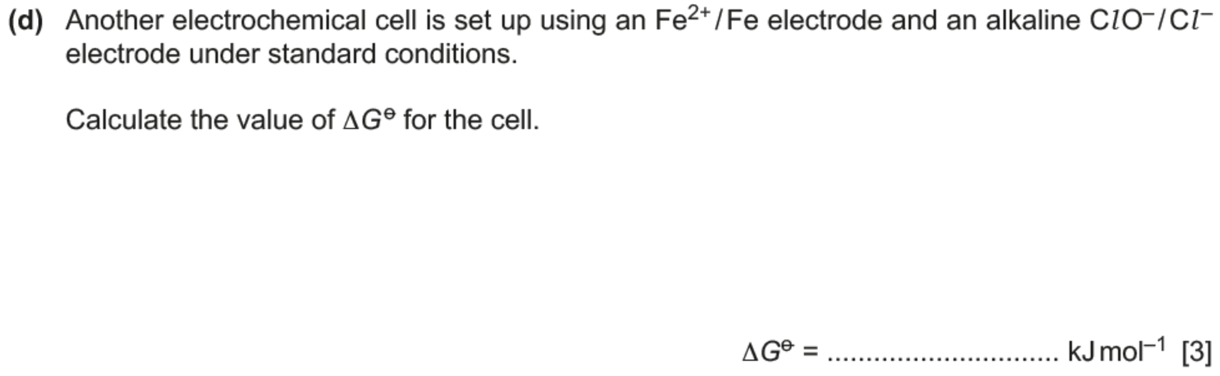
$\mathbf{Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \quad\quad E^\ominus = +0.77\ V}$

Cu^{2+} (aq) + $2e^-$ $\rightleftharpoons$ Cu (s) $\quad$ **$E^\ominus$ = +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 x (+0.43) x 96 500
  - $\Delta G^\ominus$ = -82 990 J mol^{-1} = -83 kJ mol^{-1}

This means that this reaction is feasible

Try this



(d) Another electrochemical cell is set up using an Fe^{2+}/Fe electrode and an alkaline ClO^-/Cl^- electrode under standard conditions.

Calculate the value of $\Delta G^\ominus$ for the cell.

$\Delta G^\ominus$ = ... kJ mol^{-1} [3]

Faraday's Law

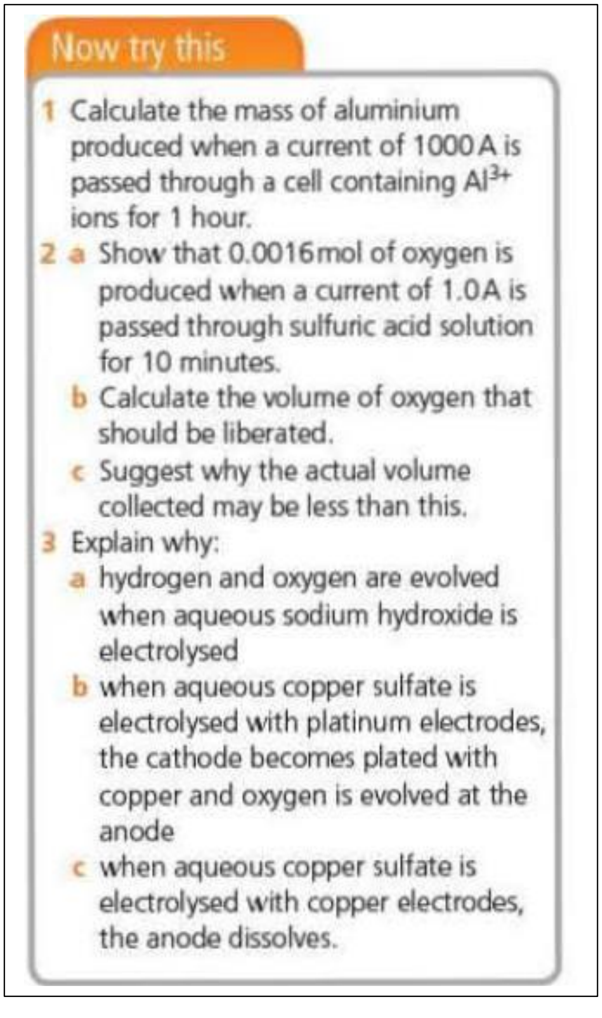
- The **amount** of substance that is formed at an electrode during **electrolysis** is proportional to:
    - The amount of **time** where a constant current to passes
    - The **amount of charge**, in coulombs, that passes through the electrolyte (strength of electric **current**)
    - The relationship between the current and time is:

Q = I x t

- **Q** = charge (coulombs, C)
    - **I** = current (amperes, A)
    - **t** = time, (seconds, s)
- The **amount** or the **quantity of electricity** can also be expressed by the **faraday (*F*)** unit
    - One faraday is the amount of **electric charge** carried by 1 mole of electrons or 1 mole of singly charged ions
    - 1 faraday is 96 500 C mol^{-1}
    - Thus, the relationship between the Faraday constant and the Avogadro constant (*L*) is:

F = L x e

- **F** = Faraday's constant (96 500 C mol^{-1})
    - **L** = Avogadro's constant (6.02 x 10^{23} mol^{-1})
    - **e** = charge on an electron



Now try this

1 Calculate the mass of aluminium produced when a current of 1000 A is passed through a cell containing Al^{3+} ions for 1 hour.

2 a Show that 0.0016 mol of oxygen is produced when a current of 1.0 A is passed through sulfuric acid solution for 10 minutes.

b Calculate the volume of oxygen that should be liberated.

c Suggest why the actual volume collected may be less than this.

3 Explain why:

a hydrogen and oxygen are evolved when aqueous sodium hydroxide is electrolysed

b when aqueous copper sulfate is electrolysed with platinum electrodes, the cathode becomes plated with copper and oxygen is evolved at the anode

c when aqueous copper sulfate is electrolysed with copper electrodes, the anode dissolves.

WORKED EXAMPLES

1 Calculate the mass of lead deposited at the cathode during electrolysis when a current of 1.50 A flows through molten lead(II) bromide for 20.0 min.
(A_r value: [Pb] = 207; $F = 96\,500\ \text{C mol}^{-1}$)

Step 1 Write the half-equation for the reaction.

$$Pb^{2+} + 2e^- \longrightarrow Pb$$

Step 2 Find the number of coulombs required to deposit 1 mole of product at the electrode.

2 moles of electrons are required per mole of Pb formed

$$\begin{aligned} &= 2F \\ &= 2 \times 96\,500 \\ &= 193\,000\ \text{C mol}^{-1} \end{aligned}$$

Step 3 Calculate the charge transferred during the electrolysis.

$$\begin{aligned} Q &= I \times t \\ &= 1.50 \times 20 \times 60 \\ &= 1800\ \text{C} \end{aligned}$$

Step 4 Calculate the mass by simple proportion using the relative atomic mass.

193 000 C deposits 1 mole Pb, which is 207 g Pb

so 1800 C deposits $\frac{1800}{193\,000} \times 207 = 1.93$ g Pb

WORKED EXAMPLES (CONTINUED)

2 Calculate the volume of oxygen produced at r.t.p. when a concentrated aqueous solution of sulfuric acid, H_2SO_4, is electrolysed for 30.0 min using a current of 0.50 A.
($F = 96\,500\ \text{C mol}^{-1}$; 1 mole of gas occupies 24.0 dm^3 at r.t.p.)

Step 1 Write the half-equation for the reaction.

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

Step 2 Find the number of coulombs required to produce 1 mole of gas.

4 moles of electrons are released per mole of O_2 formed

$$\begin{aligned} &= 4F \\ &= 4 \times 96\,500 \\ &= 386\,000\ \text{C mol}^{-1} \end{aligned}$$

Step 3 Calculate the charge transferred during the electrolysis.

$$\begin{aligned} Q &= I \times t \\ &= 0.50 \times 30 \times 60 \\ &= 900\ \text{C} \end{aligned}$$

Step 4 Calculate the volume by simple proportion using the relationship 1 mole of gas occupies 24.0 dm^3 at r.t.p.

386 000 C produces 1 mole O_2, which is 24 dm^3 O_2

so 900 C produces $\frac{900}{386\,000} \times 24.0$

$= 0.0560\ dm^3\ O_2$ at r.t.p.