Chemistry (A-level)

Electrochemistry (Chapter 6)

- **Electrolysis** is the decomposition of a compound into its elements by an electric current; usually carried out in an electrolysis cell:

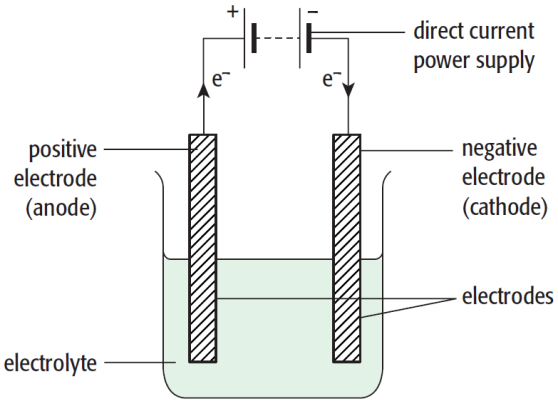


Figure 20.2 The main parts of an electrolysis cell. The actual structure of the cell will vary according to the element extracted. The e⁻ shows the direction of travel of the electrons around the external circuit.

- In the electrolysis cell:
  - The **electrolyte** is the compound being decomposed, either molten ionic compound or a concentrated aqueous solution of ions
  - The **electrodes** are rods, made from carbon or metal, which conducts electricity to and from the electrolyte:
    - Anode: positive electrode (oxidation)
    - Cathode: negative electrode (reduction)
  - Power supply: d.c.
- Cathode reactions:
  - Molten:
    - $M^{x+} + xe^- \rightarrow M$
  - Aqueous solution:
    - Cation: Group I, II, Al Mn (reactive metals, not reduced)
      - $2H^+ + 2e^- \rightarrow H_2$
    - Cation: others
      - $M^{x+} + xe^- \rightarrow M$
- Anode reactions:
  - Inert electrode (Pt, C, Au)
    - Anion (Cl^-, Br^-, I^-)
      - $2X^- \rightarrow X_2 + 2e^-$
    - Oxyanion (SO_4^{2-}, PO_4^{3-}, NO_3^-, F^-)
      - $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
  - Non-inert electrode (other metals / M)
    - Anion:
      - $M \rightarrow M^{x+} + xe^-$
      - E.g. $Cu \rightarrow Cu^{2+} + 2e^-$
- The mass of a substance produced at an electrode during electrolysis is proportional to the quantity of electricity (in coulombs) which passes through the electrolyte ($m \propto Q$):
  - The time over
  - The strength of the electric current

$$Q = I \times t$$

- **1 Faraday** is the quantity of electric charge carried by 1 mole of electrons or 1 mole of singly charged ions (96 500 $Cmol^{-1}$) (F = Q / mol of e^-)

$$\underset{1\text{ mol}}{Cu^{2+}} + \underset{2\text{ mol}}{2e^-} \longrightarrow \underset{1\text{ mol}}{Cu}$$

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu^{2+} ions. So it requires 2 Faradays of electricity (2 × 96 500 C) to deposit 1 mole of copper.

$$\underset{1\text{ mol}}{Ag^+} + \underset{1\text{ mol}}{e^-} \longrightarrow \underset{1\text{ mol}}{Ag}$$

1 Faraday of electricity (96 500 C) is required to deposit 1 mole of silver.

$$\underset{2\text{ mol}}{2Cl^-} \longrightarrow \underset{1\text{ mol}}{Cl_2} + \underset{2\text{ mol}}{2e^-}$$

The equation shows that 2 moles of electrons are released when 1 mole of chlorine gas is formed from 2 moles of Cl^- ions. So it requires 2 Faradays of electricity (2 × 96 500 C) to produce 1 mole of Cl_2.

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

The equation shows that 4 moles of electrons are released when 1 mole of oxygen gas is formed from 4 moles of OH^- ions. So it requires 4 Faradays of electricity (4 × 96 500 C) to produce 1 mole of O_2.

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 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

$= 2F$

$= 2 \times 96\,500$

$= 193\,000\text{ C mol}^{-1}$

Step 3 Calculate the charge transferred during the electrolysis.

$Q = I \times t$

$= 1.50 \times 20 \times 60$

$= 1800\text{ C}$

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 $\frac{1800}{193\,000} \times 207 = 1.93\text{ g Pb}$

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 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

$= 4F$

$= 4 \times 96\,500$

$= 386\,000\text{ C mol}^{-1}$

Step 3 Calculate the charge transferred during the electrolysis.

$Q = I \times t$

$= 0.50 \times 30 \times 60$

$= 900\text{ C}$

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 $\frac{900}{386\,000} \times 24.0$

$= 0.0560\text{ dm}^3\text{ O}_2$ at r.t.p.

- Electrolytic method can be used to find a value for the Avogadro constant, *L*, by calculating the charge associated with 1 mole of electrons:

$$L = \frac{\text{charge on 1 mole of electrons}}{\text{charge on 1 electron}}$$

where L = F / e or **$F = L \times e$**

- The determination of a value of the Avogadro constant by an electrolytic method:

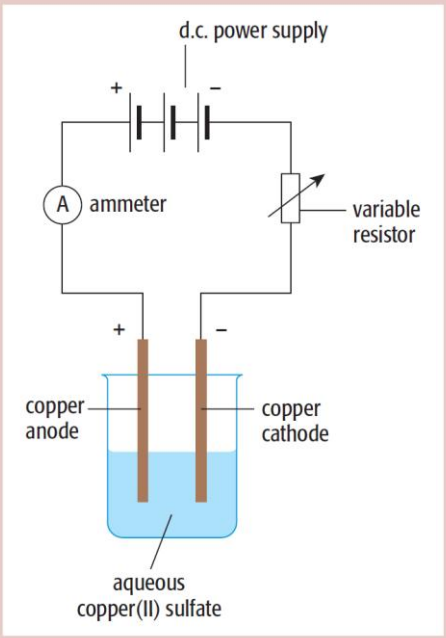


Figure 20.3 Apparatus for calculating the mass of copper deposited during the electrolysis of aqueous copper(II) sulfate.

The procedure is:

- weigh the pure copper anode and pure copper cathode separately
- arrange the apparatus as shown in Figure 20.3; the variable resistor is used to keep the current constant
- pass a constant electric current for a measured time interval
- remove the cathode and anode and wash and dry them with distilled water and then with propanone
- reweigh the cathode and anode.

The cathode increases in mass because copper is deposited. The anode decreases in mass because the copper goes into solution as copper ions. The decrease in mass of the anode is measured. This is preferred because the copper does not always 'stick' to the cathode very well.

A sample calculation is shown below, using a current of 0.20 A for 34 min.

- mass of anode at start of the experiment = 56.53 g
- mass of anode at end of experiment = 56.40 g
- mass of copper removed from anode = 0.13 g
- quantity of charge passed $Q = I \times t$
  $= 0.20 \times 34 \times 60$
  $= 408\,C$

To deposit 0.13 g of copper requires 408 C, so to deposit 1 mole of copper (63.5 g) requires $\frac{63.5}{0.13} \times 408\,C$

But the equation for the electrolysis shows that 2 moles of electrons are needed to produce 1 mole of copper:

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

The charge on 1 mole of electrons $= \frac{63.5}{0.13} \times 408 \times \frac{1}{2}$
$= 99\,600\,C$

If the charge on one electron is 1.60×10^{-19} C,

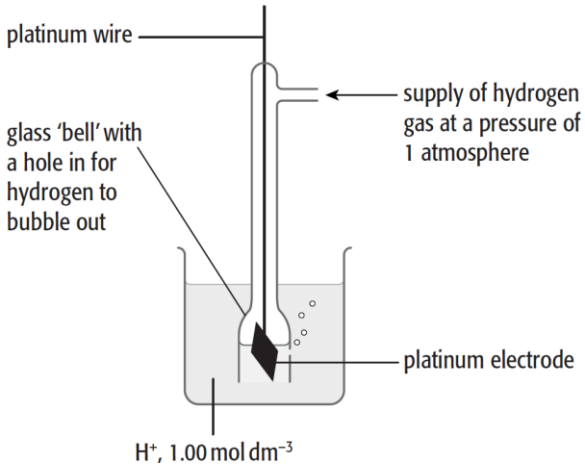
$$L = \frac{99\,600}{1.60 \times 10^{-19}} = 6.2 \times 10^{23}\,mol^{-1}$$

(to 2 significant figures)

This is in good agreement with the accurate value of $6.02 \times 10^{23}\,mol^{-1}$.

Salt bridge (strip of filter paper soaked in a saturated solution of potassium nitrate) should be soluble and has no. ppt

- **Electrode potential**: the voltage measured for a half-cell compared with another half-cell
- The **standard hydrogen electrode** is a half-cell that can be used as reference electrode:



- The electrode consist of:
  - Hydrogen gas at 101kPa pressure in equilibrium with
  - H^+ ions of concentration 1.00 mol dm^{-3}
  - A platinum electrode in contact with the hydrogen gas and the H^+ ions
- The half-equation for the hydrogen electrode:

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

- An electrochemical cell is made from two half-cells connected by:
  - Wires connecting the metal rods in each half-cell to a high-resistance voltmeter
  - A salt bridge allowing the movement of ions between the two half-cells, to maintain the ionic balance

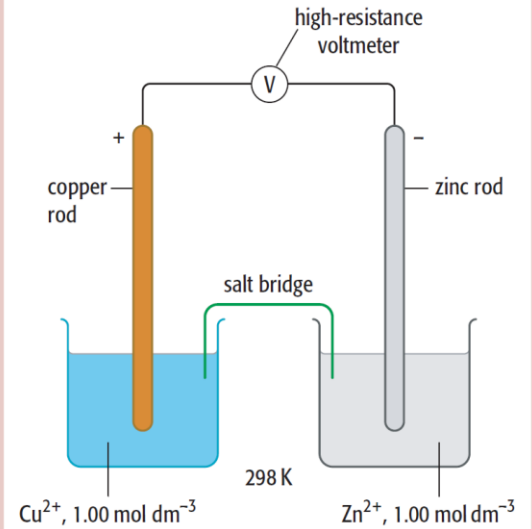


Figure 20.7 One type of electrochemical cell is made by connecting a Cu^{2+}/Cu half-cell to a Zn^{2+}/Zn half-cell. The voltage generated by this cell is +1.10 V.

- The **standard electrode potential**, $E^{\ominus}$, for a half-cell is the voltage measured under standard conditions (concentration of ions at 1.00 mol dm^{-3}, temperature of 298 K, at 1 atmospheric pressure (101kPa)) with a standard hydrogen electrode as the other half-cell
- <u>Metal/metal ion half-cell:</u>

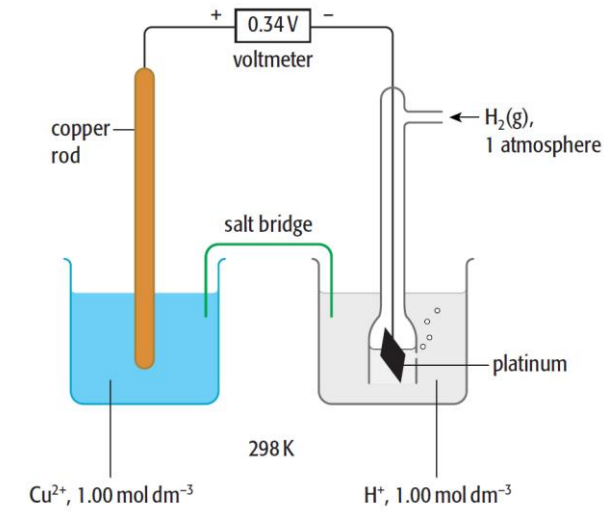


Figure 20.8 Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell.

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

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

- The copper is the positive terminal (cathode – reduction) of the cell and the hydrogen electrode is the negative terminal (anode – oxidation)

- Non-metal/non-metal ion half-cell:
  - Electrical contact with the solution made by using platinum electrode, which must come in contact with both the element and the aqueous solution of its ions

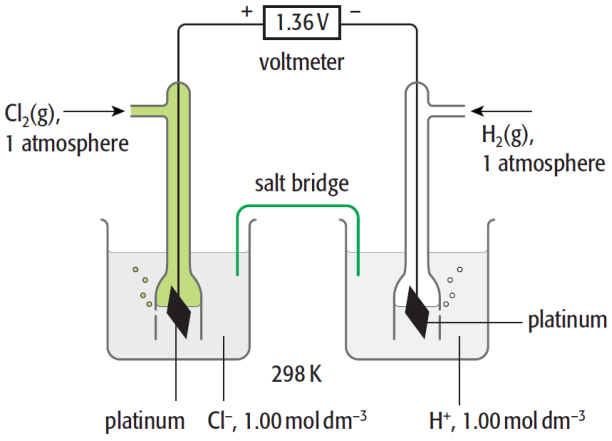


Figure 20.11 Measuring the standard electrode potential of a Cl_2/Cl^- half-cell.

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^\ominus = +1.36\,V$$

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

  - Cl_2/Cl^- half-cell forms at the positive terminal (cathode – reduction), and the hydrogen electrode at the negative terminal(anode – oxidation)

- Ion/ion half-cell (same element at different oxidation states):
  - E.g. a mixture of Fe^{3+} and Fe^{2+} ions can form a half-cell using platinum electrode:

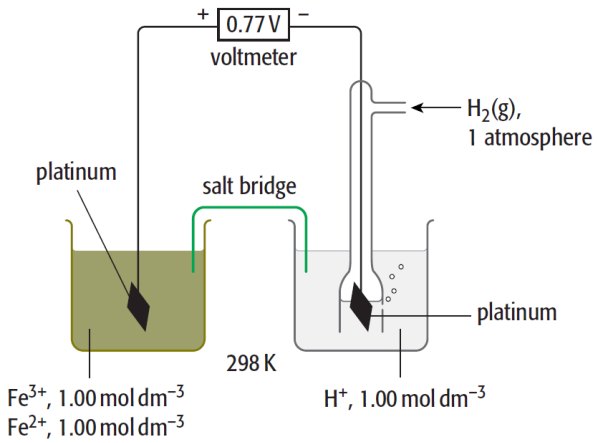


Figure 20.13 Measuring the standard electrode potential of the Fe^{3+}/Fe^{2+} half-cell.

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

  - Involving several ionic species, e.g. MnO_4^-/Mn^{2+}

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

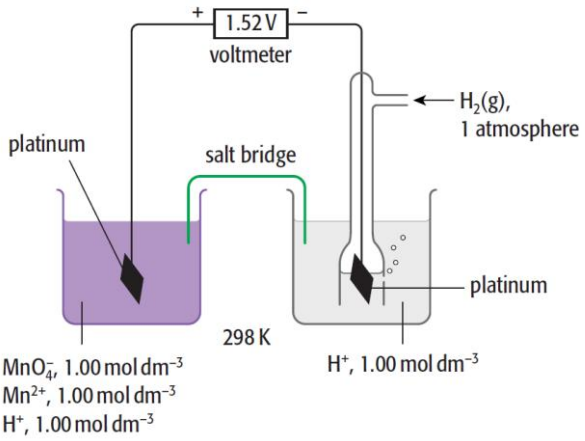


Figure 20.14 Measuring the standard electrode potential of the MnO_4^-/Mn^{2+} half-cell.

- **Standard cell potential**: the difference in standard electrode potential between two half-cells

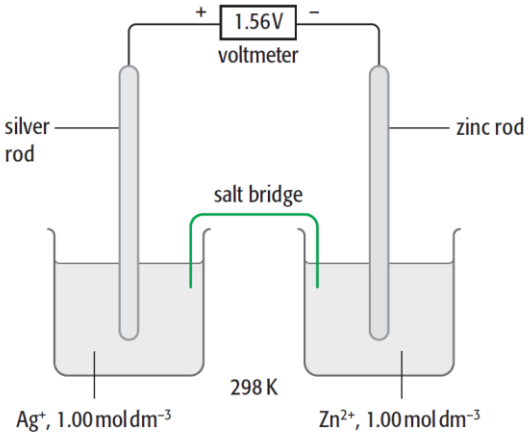


Figure 20.15 An Ag^+/Ag, Zn^{2+}/Zn electrochemical cell.

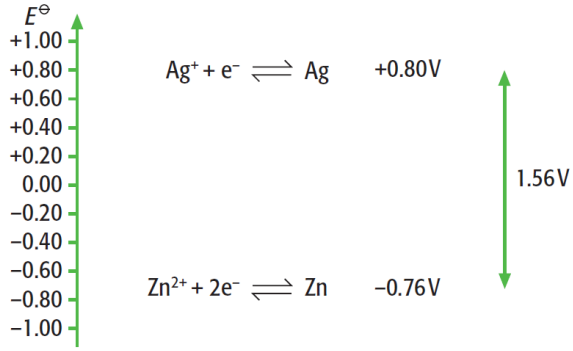


Figure 20.16 The difference between +0.80 V and −0.76 V is +1.56 V.

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E^\ominus = +0.80\,V$$

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

- Zn metal will lose electrons to the Ag^+/Ag half-cell
- Ag^+ ions will accept electrons from the Zn^{2+}/Zn half-cell.

The voltage of this cell is $+0.80 - (-0.76) = +1.56\,V$

- The $E^\ominus$ value for the Fe^{3+}/Fe^{2+} half-cell is more positive than for the Cu^{2+}/Cu half-cell. So the Fe^{3+}/Fe^{2+} half-cell is the positive pole and the Cu^{2+}/Cu half-cell is the negative pole of the cell:

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

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

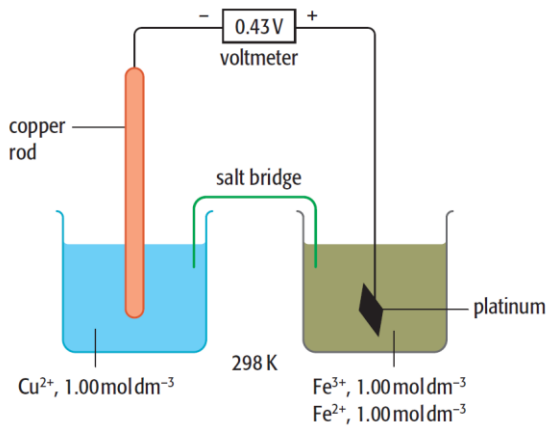


Figure 20.17 An Cu^+/Cu, Fe^{3+}/Fe^{2+} electrochemical cell.

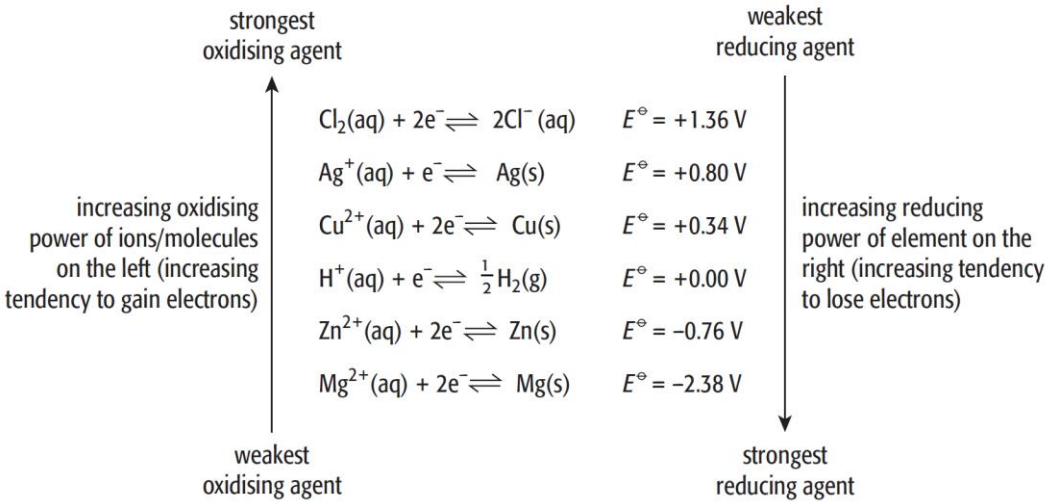


Figure 20.18 Standard electrode potentials for some oxidising and reducing agents.

- If the value of the standard cell potential is positive, the reaction is feasible
- The standard electrode potentials for the halogens are:

$\frac{1}{2}F_2 + e^- \rightleftharpoons F^-$ $E^\ominus = +2.87\,V$

$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$ $E^\ominus = +1.36\,V$

$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-$ $E^\ominus = +1.07\,V$

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ $E^\ominus = +0.54\,V$

- Based on these $E^\ominus$ values, down Group 17, the oxidising ability of the halogen decreases and the ability to act as reducing agents increases
- Effect of change in ion concentration to $E^\ominus$:

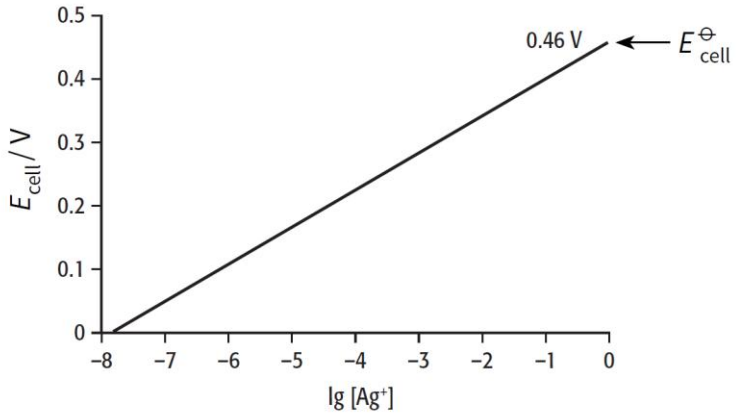


Figure 20.23 Increasing the concentration of silver ions in the cell reaction $Cu(s) + 2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ makes the value of E_{cell} more positive.

- The effects of concentration on the value of E_{cell} can be deduced using the Nernst equation:

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

(reactant) / (product)

- E is the electrode potential under non-standard conditions
- $E^{\ominus}$ is the standard electrode potential
- z is the number of electrons transferred in the reaction
- E_{cell} (reactant) - E_{cell} (product)
- $E^{\ominus}_{cell}$ (reactant) + (0.059/z) log (reactant) - $E^{\ominus}_{cell}$ (product) + (0.059/z) log (product)
- Cathode -anode

- A fuel cell (hydrogen-oxygen fuel cells) is an electrochemical cell in which a fuel gives up electrons at one electrode and oxygen gains electrons at the other electrode
  - Negative electrode (anode reaction):

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

  - Positive electrode (cathode reaction):

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

- Advantages and disadvantages of using fuel cells to power road vehicles compared to hydrocarbon fuels such as petrol:
  - Advantages:
    - Less pollution; less dependence on fossil fuels / finite resources
  - Disadvantages:
    - More expensive; takes up more space; poor power-to-volume ration; hydrogen is difficult to store or transport