

Redox HL (answers)

IB CHEMISTRY HL

19.1 Electrochemical cells

Understandings:

- A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the cell potential (E°).
- The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential (E°) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol dm^{-3} or 100 kPa for gases. E° of the SHE is 0 V.
- When aqueous solutions are electrolysed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.
- $\Delta G^\circ = -nFE^\circ$. When E° is positive, ΔG° is negative indicative of a spontaneous process. When E° is negative, ΔG° is positive indicative of a non-spontaneous process. When E° is 0, then ΔG° is 0.
- Current, duration of electrolysis and charge on the ion affect the amount of product formed at the electrodes during electrolysis.
- Electroplating involves the electrolytic coating of an object with a metallic thin layer.

Applications and skills:

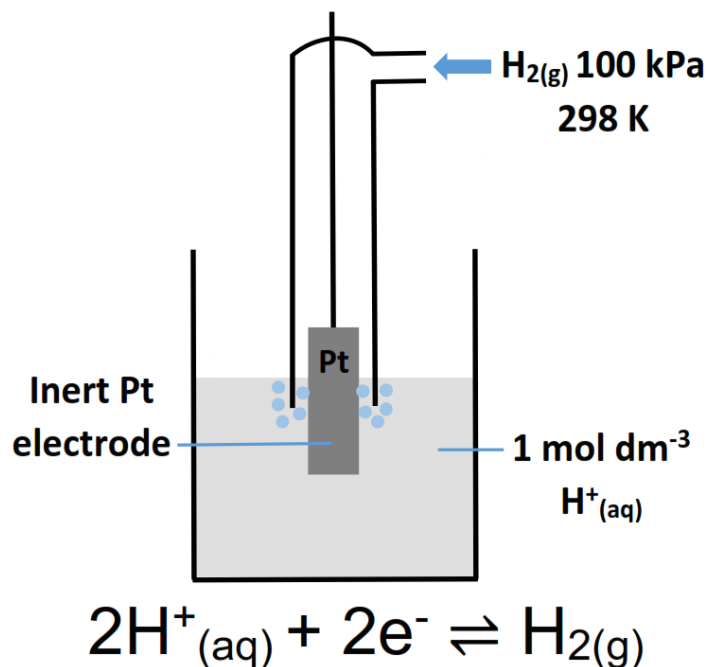
- Calculation of cell potentials using standard electrode potentials.
- Prediction of whether a reaction is spontaneous or not using E° values.
- Determination of standard free-energy changes (ΔG°) using standard electrode potentials.
- Explanation of the products formed during the electrolysis of aqueous solutions.
- Perform lab experiments that could include single replacement reactions in aqueous solutions.
- Determination of the relative amounts of products formed during electrolytic processes.
- Explanation of the process of electroplating.

Guidance:

- Electrolytic processes to be covered in theory should include the electrolysis of aqueous solutions (eg sodium chloride, copper(II) sulfate etc) and water using both inert platinum or graphite electrodes and copper electrodes. Explanations should refer to E° values, nature of the electrode and concentration of the electrolyte.
- $\Delta G^\circ = -nFE^\circ$ is given in the data booklet in section 1.
- Faraday's constant = $96\,500\text{ C mol}^{-1}$ is given in the data booklet in section 2.
- The term "cells in series" should be understood.

Standard hydrogen electrode (SHE)

- The SHE is used as a reference to measure the electrode potential of other half-cells.
- The standard hydrogen electrode (SHE) is assigned an electrode potential (E^\ominus) of 0 V.
- Conditions of the SHE are: hydrogen gas (H_2) at 100 kPa, temperature of 298 K, $1.00 \text{ mol dm}^{-3} H^+$, inert platinum electrode.



- Depending on which half-cell is connected to the SHE, either hydrogen ions (H^+) are reduced to form hydrogen gas, or hydrogen gas is oxidized to form hydrogen ions.

Standard electrode potential (E^\ominus)

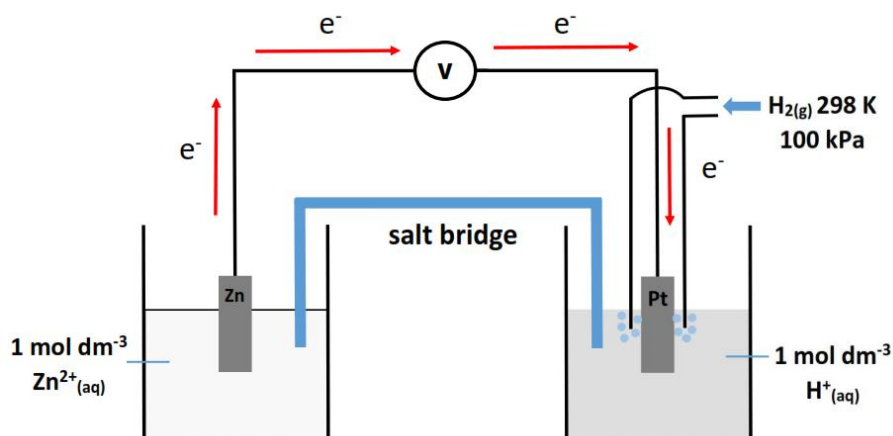
- The standard electrode potential E^\ominus is the electrode potential (V) measured under standard conditions relative to the SHE.
- Standard electrode potential values can be found in section 24 of the data booklet.

Standard conditions used when comparing half-cells:

- Solutions have a concentration of 1.00 mol dm^{-3}
- Gases at a pressure of 100 kPa.
- All substances must be pure.
- Temperature of 298 K
- If the half-cell does not include a solid metal, then platinum is used as the electrode.

In the diagram below, the SHE is connected to a zinc half-cell.

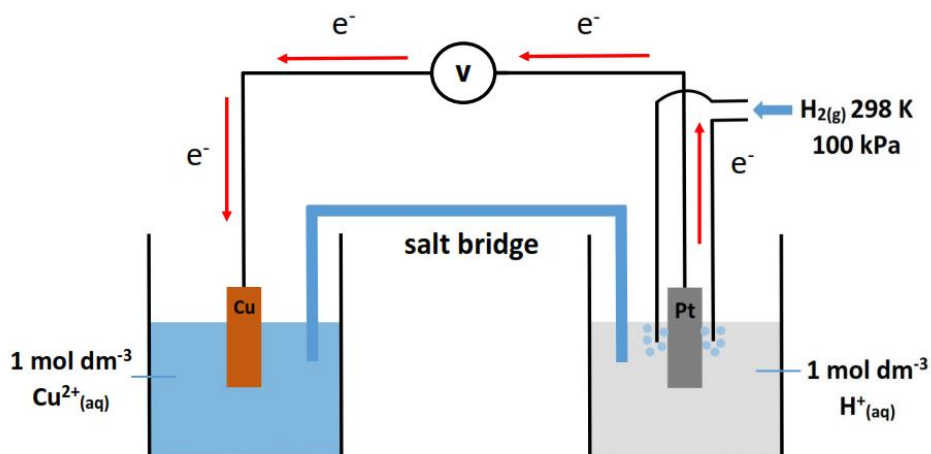
- The voltage produced is 0.76 V.
- The electrons flow from the zinc half-cell to the SHE.
- When a half-cell with a metal above hydrogen in section 24 of the data booklet is connected to the SHE, electrons flow from the metal half-cell to the SHE and the standard electrode potential value is negative.



- The zinc half-cell is the anode and undergoes oxidation.
- The SHE is the cathode and the hydrogen ions undergo reduction to form hydrogen gas.

In the diagram below, the SHE is connected to a copper half-cell.

- The voltage produced is 0.34 V.
- The electrons flow from the SHE to the copper half-cell.
- When a half-cell with a metal below hydrogen in section 24 of the data booklet is connected to the SHE, electrons flow from the SHE to the metal half-cell and the standard electrode potential value is positive.



- The copper half-cell is the cathode and undergoes reduction.
- The SHE is the anode and the hydrogen undergoes oxidation to form hydrogen ions.

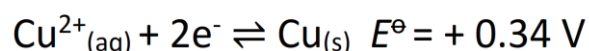
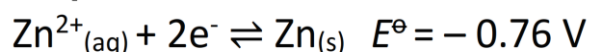
Calculating cell potential (E^\ominus_{cell})

- The following equation is used to calculate the cell potential (E^\ominus_{cell}).

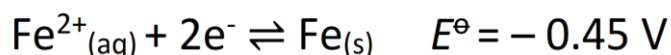
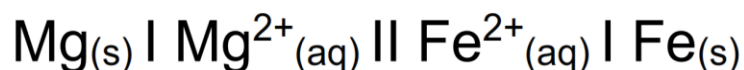
$$E^\ominus_{\text{cell}} = E^\ominus_{\text{red}} - E^\ominus_{\text{ox}}$$

- The standard electrode potential values are the reduction potentials and must be used as given in section 24 of the data booklet.
- The E^\ominus values are intensive quantities and are not multiplied according to the stoichiometry of the equation.

Example: Calculate the E^\ominus_{cell} for the following reactions.



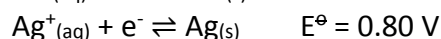
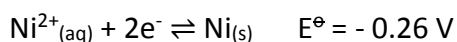
$$E^\ominus_{\text{cell}} = 0.34 - (-0.76) = +1.10 \text{ V}$$



$$E^\ominus_{\text{cell}} = -0.45 - (-2.37) = +1.92 \text{ V}$$

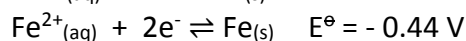
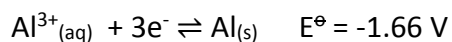
Exercises:

- Calculate the standard cell potential of a voltaic cell consisting of a nickel electrode in contact with a solution of Ni^{2+} ions and a silver electrode in contact with a solution of Ag^+ ions.



$$E^\ominus_{\text{cell}} = 0.80 - (-0.26) = +1.06 \text{ V}$$

- Calculate the standard cell potential of a voltaic cell consisting of an aluminum electrode in contact with a solution of Al^{3+} ions and an iron electrode in contact with a solution of Fe^{2+} ions.

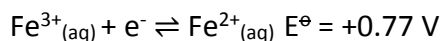
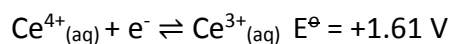
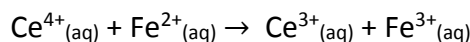


$$E^\ominus_{\text{cell}} = -0.44 - (-1.66) = +1.22 \text{ V}$$

Determining spontaneity of a reaction

- A reaction with a positive E^\ominus_{cell} value is spontaneous as written.
- A reaction with a negative E^\ominus_{cell} value is non-spontaneous as written and the reverse reaction is spontaneous.

Example: Determine the spontaneity of the following reaction using the E^\ominus values below.



According to the reaction, the Ce^{4+} ions are being reduced (decrease in oxidation number) and the Fe^{3+} ions are being oxidized (increase in oxidation number).

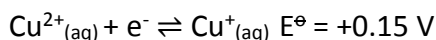
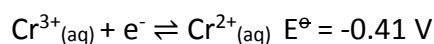
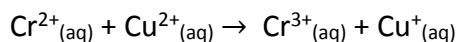
Calculate the E_{cell} for the reaction as it is written:

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

$$E_{\text{cell}} = 1.61 - 0.77 = +0.84 \text{ V}$$

The E_{cell} value is positive, therefore the reaction is spontaneous as written.

Exercise: Determine the spontaneity of the following reaction using the E^\ominus values below.



According to the reaction, the Cu^{2+} ions are being reduced (decrease in oxidation number) and the Cr^{2+} ions are being oxidized (increase in oxidation number).

Calculate the E_{cell} for the reaction as it is written:

$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

$$E_{\text{cell}} = 0.15 - (-0.41) = +0.56 \text{ V}$$

The E_{cell} value is positive, therefore the reaction is spontaneous as written.

Relationship between E^\ominus_{cell} and ΔG^\ominus

- The following equation can be found in section 1 of the data booklet:

$$\Delta G^\ominus = -nFE^\ominus_{\text{cell}}$$

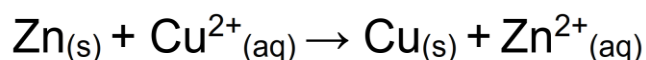
n = moles of electrons transferred in the reaction

F = Faraday constant (96500 C mol^{-1})

- The relationship between the E^\ominus_{cell} and ΔG^\ominus is shown in the table below.

E^\ominus_{cell}	ΔG^\ominus	Spontaneity
positive	negative	spontaneous
negative	positive	non-spontaneous
zero	zero	at equilibrium

Exercises: Calculate the ΔG^\ominus for the following reactions. Comment on the spontaneity of the reaction.

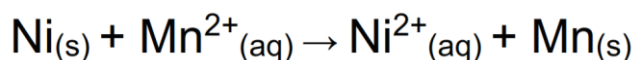


$$E^\ominus_{\text{cell}} = +1.10 \text{ V}$$

$$\Delta G^\ominus = -2 \times 96500 \times 1.10$$

$$\Delta G^\ominus = -212 \text{ kJ mol}^{-1}$$

ΔG^\ominus is negative therefore reaction is spontaneous



$$E^\ominus_{\text{cell}} = -0.93 \text{ V}$$

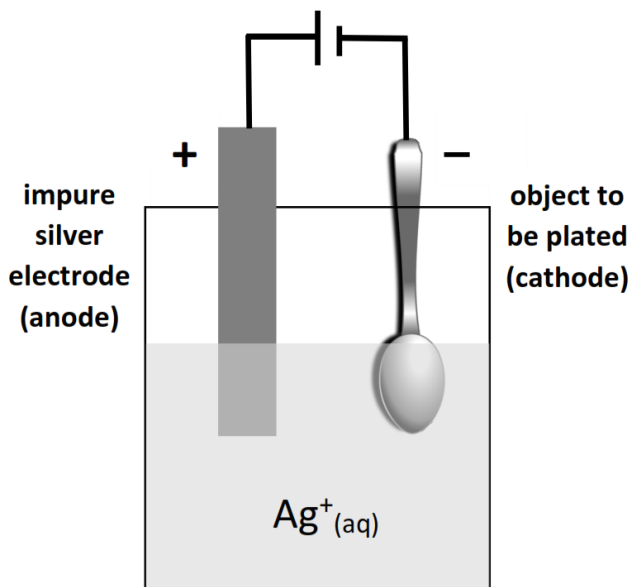
$$\Delta G^\ominus = -2 \times 96500 \times -0.93$$

$$\Delta G^\ominus = +179 \text{ kJ mol}^{-1}$$

ΔG^\ominus is positive therefore reaction is non-spontaneous

Electroplating

- Electroplating involves the electrolytic coating of an object with a thin layer of metal.
- The object to be coated is the cathode, the metal coated is the anode in a solution of aqueous metal ions.



The equation $Q = IT$ can be used to determine the charge that is passed through the cell, where Q is charge in coulombs, I is the current in amps and T is time in seconds.

Example: A current of 2.00 A is passed through a solution of AgNO_3 for 10.0 minutes. Calculate the mass of Ag plated on the spoon.

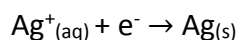
$$Q = IT$$

$$Q = 2.00 \times 600$$

$$Q = 1200 \text{ C}$$

1 mol of electrons has a charge of 96500 C

1 mol of silver ions requires 1 mol of electrons to form 1 mol of solid silver



$$\text{Amount in mol of silver plated} = 1200 \div 96500 = 0.0124 \text{ mol}$$

$$\text{Mass of silver plated} = 0.0124 \times 107.89 = 1.34 \text{ g}$$

Factors that affect the amount of product in an electrolysis reaction

The factors that affect the amount of product formed in an electrolysis reaction are:

- duration of the electrolysis (s)
- current supplied
- charge on the ion

Exercises:

1. A 40.0 amp current flows through molten iron(III) chloride for 60.0 minutes. Determine the mass of iron and chlorine gas (measured at 273 K and 100 kPa) produced at the electrodes.

$$Q = IT$$

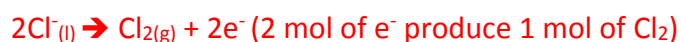
$$Q = 40.0 \times (60.0 \times 60)$$

$$Q = 144000 \text{ C}$$



$$144000 \div (3 \times 96500) = 0.497 \text{ mol Fe}$$

$$0.497 \times 55.85 = 27.7 \text{ g Fe}$$

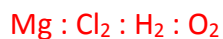
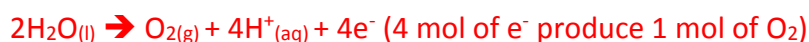
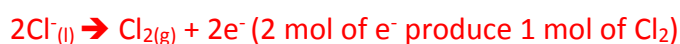
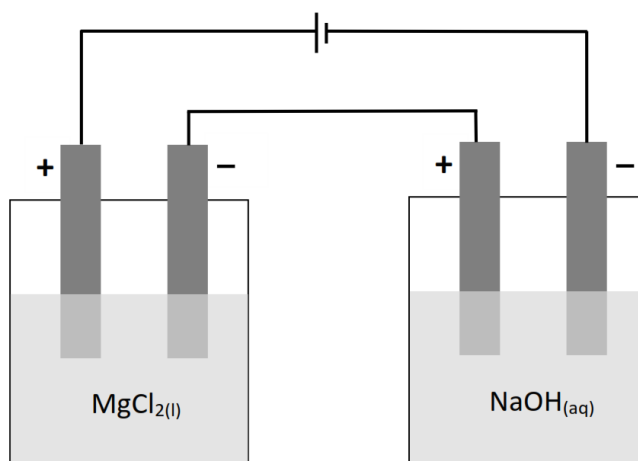


$$144000 \div (2 \times 96500) = 0.746 \text{ mol Cl}_2$$

$$0.746 \times 70.9 = 52.9 \text{ g Cl}_2$$

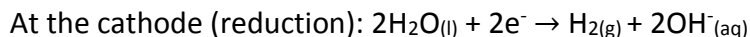
2. Two electrolytic cells are connected in series and the same amount of electricity passes through both cells. Determine the molar ratio of the products formed at the electrodes.

electrolytic cells in series



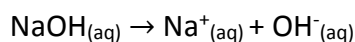
Electrolysis of aqueous solutions

- When aqueous solutions are electrolysed, water can be oxidised at the anode or reduced at the cathode.

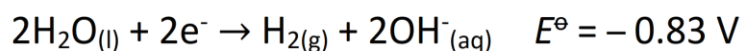


Electrolysis of water (H₂O)

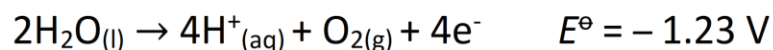
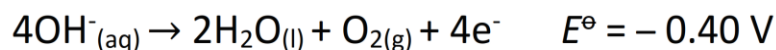
- Pure water is a very poor conductor of electricity, therefore NaOH is added to increase its conductivity.



At the cathode (-)



At the anode (+)



Overall equation:

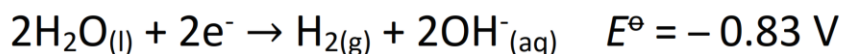


Observed changes at the electrodes:

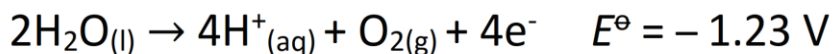
- A colorless gas is evolved at the anode and cathode.
- The ratio of H₂ to O₂ is 2:1
- The pH at the anode decreases (due to increase in [H⁺]) and the pH at the cathode increases (due to increase in [OH⁻]).

Electrolysis of aqueous sodium chloride – NaCl_(aq)

At the cathode (-)



At the anode (+)

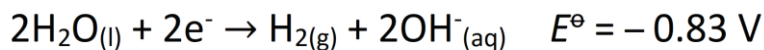


- At low concentration (dilute NaCl_(aq)) – O_{2(g)} is discharged
- At high concentration (concentrated NaCl_(aq)) – Cl_{2(g)} is discharged

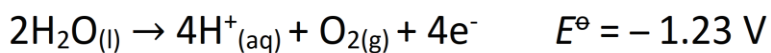
Electrolysis of aqueous copper(II) sulfate - CuSO_{4(aq)}

Inert (graphite electrodes)

At the cathode (-)

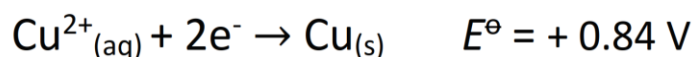


At the anode (+)

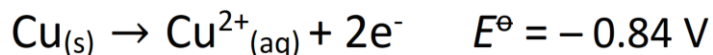


Copper electrodes

At the cathode (-)



At the anode (+)



Observed changes at electrodes (graphite):

- Pinky-brown color as copper is deposited on the cathode.
- The blue color is lost because of discharge of Cu^{2+} ions.

Observed changes at electrodes (copper):

- Pinky-brown color develops as copper is deposited on the cathode.
- Copper anode loses mass.
- No change in pH
- No change in blue color because Cu^{2+} ions are formed and removed from the solution, so the concentration remains constant.

Exercises:

1) Predict the products at the anode and cathode when the following aqueous solutions are electrolysed using platinum electrodes.

- a** dilute sodium iodide solution

anode: O_2 cathode: H_2

- b** copper nitrate solution

anode: O_2 cathode: Cu

- c** concentrated magnesium chloride solution

anode: Cl_2 cathode: H_2

- d** sodium hydroxide solution

anode: O_2 cathode: H_2

2) Write half equations for the reactions that occur at the electrodes when copper sulfate solution is electrolysed:

- a** using copper electrodes

anode: $\text{Cu}_{(s)} \rightarrow \text{Cu}^{2+}_{(aq)} + 2\text{e}^-$

cathode: $\text{Cu}^{2+}_{(aq)} + 2\text{e}^- \rightarrow \text{Cu}_{(s)}$

- b** using platinum electrodes

anode: $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^{+}_{(aq)} + 4\text{e}^-$

cathode: $\text{Cu}^{2+}_{(aq)} + 2\text{e}^- \rightarrow \text{Cu}_{(s)}$

3) When water containing a small amount of sulfuric acid is electrolysed for 30 minutes, 22.0 cm^3 of oxygen is produced. Predict, with a reason, the volume of hydrogen that is produced at STP. Ratio of H_2 to O_2 is 2:1, therefore 44 cm^3 of H_2 will be produced.

4) When a copper nitrate solution is electrolysed for 1 hour using platinum electrodes, 0.636 g of copper is produced. Calculate the volume of oxygen produced measured at STP. $n = 0.636 \div$

$63.55 = 0.0100 \text{ mol}$

Ratio of Cu to O_2 is 2: 1

$0.0100 \div 2 = 0.00500$

$0.00500 \times 22.7 = 0.114 \text{ dm}^3 \text{ O}_2$