# Reactivity 3.2 HL Answers

IB CHEMISTRY HL

| 25 | 16 | | 6 | 2 | 25 |
|---|---|---|---|---|---|
| **M**n | **S** | **J** | **C** | **He** | **M**n |
| Manganese | Sulfur | | Carbon | Helium | Manganese |
| 54.938045 | 32.065 | | 12.0107 | 4.002602 | 54.938045 |

**Reactivity 3.2.12**
**Understandings:**

- The hydrogen half-cell $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$ is assigned a standard electrode potential of zero by convention. It is used in the measurement of standard electrode potentials, $E^{\ominus}$.

**Learning outcomes:**

- Interpret standard electrode potential data in terms of ease of oxidation/reduction.

**Additional notes:**

- Standard electrode potentials are given in the data booklet.

## Hydrogen half-cell

- The hydrogen half-cell, also known as the standard hydrogen electrode (SHE), is a reference electrode used to measure the standard electrode potentials, $E^{\ominus}$, of other half-cells.
- The hydrogen half-cell is assigned a standard electrode potential ($E^{\ominus}$) of 0 V.
- The conditions of the hydrogen half-cell are:
    - Hydrogen gas ($H_2$) at a pressure of 100 kPa
    - A temperature of 298 K
    - A 1.0 mol dm$^{-3}$ of $H^+$ ions
    - An inert platinum electrode
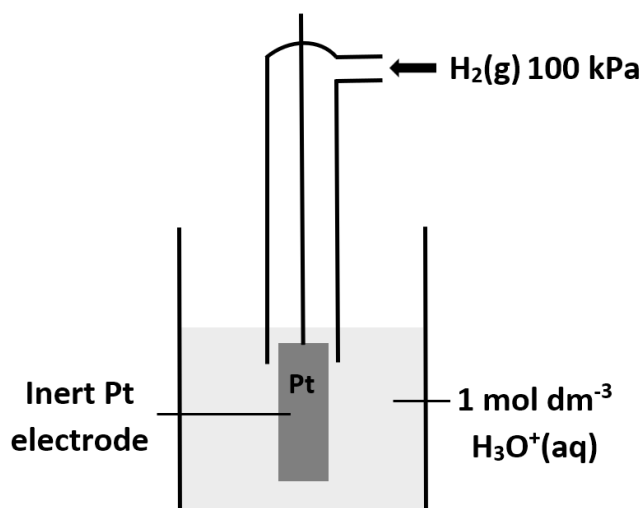


- Depending on which half-cell is connected to the hydrogen half-cell, hydrogen ions are reduced to form hydrogen gas, or hydrogen gas is oxidised to form hydrogen ions.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g) \qquad H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$
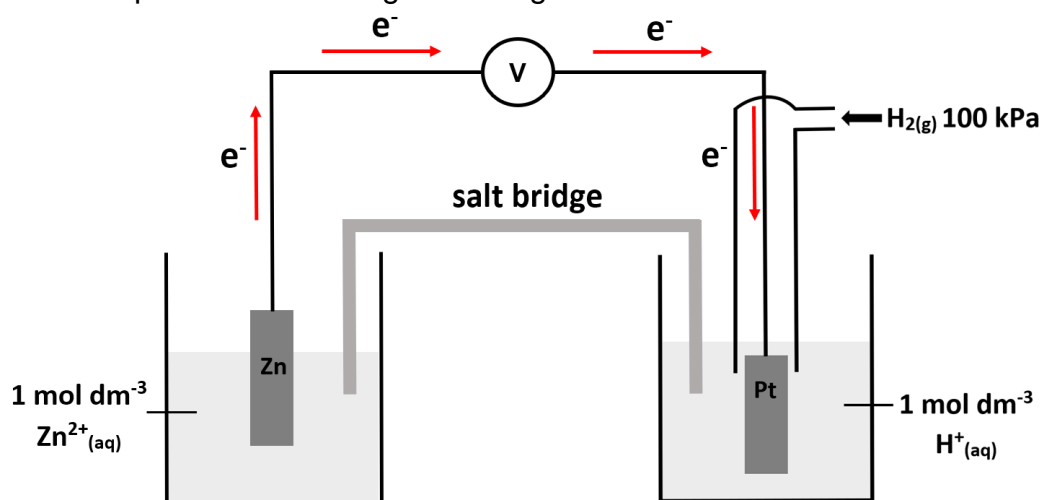
## Standard electrode potential ($E^{\ominus}$)

- The standard electrode potential, $E^{\ominus}$, is the electrode potential (in V) of a half-cell measured under standard conditions relative to the hydrogen half-cell.
- Standard electrode potential values can be found in section 19 of the data booklet.

## Standard conditions used when comparing half-cells:

- Solutions with 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, platinum is used as the electrode.

**In the diagram shown below, the hydrogen half-cell is connected to a zinc half-cell.**
- The voltage produced is 0.76 V.
- The electrons flow from the zinc half-cell to the hydrogen half-cell.
- When a half-cell above hydrogen in section 19 of the data booklet is connected to the hydrogen half-cell, electrons flow to the hydrogen half-cell and the standard electrode potential value is given a negative value.



- The standard electrode potential, $E^\ominus$, of the zinc half-cell is -0.76 V.

**In the diagram below, the hydrogen half-cell is connected to a copper half-cell.**
- The voltage produced is 0.34 V.
- The electrons flow from the hydrogen half-cell to the copper half-cell.
- When a half-cell below hydrogen in section 19 of the data booklet is connected to the hydrogen half-cell, electrons flow from the hydrogen half-cell and the standard electrode potential value is positive.
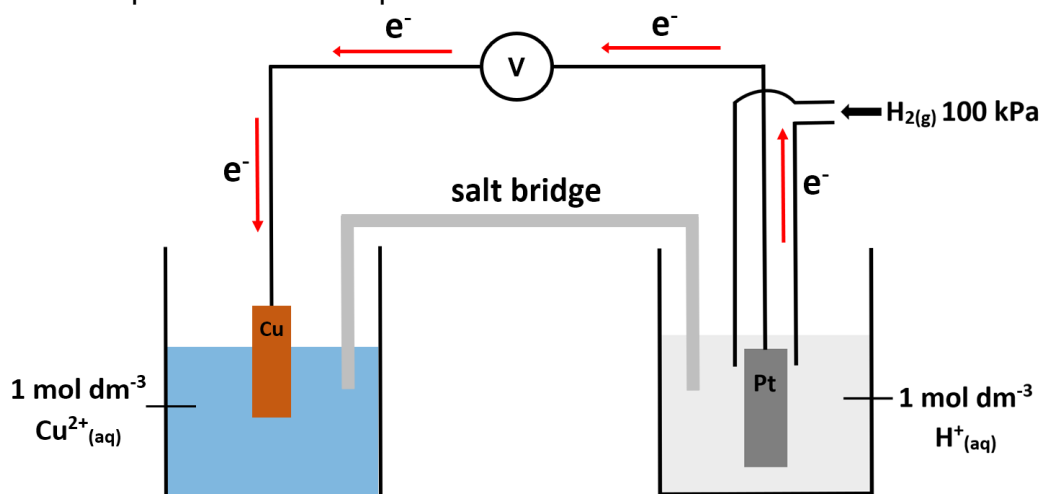


- The standard electrode potential, $E^\ominus$, of the copper half-cell is +0.34 V.

**Reactivity 3.2.13**

**Understandings:**

- Standard cell potential, $E^\ominus$, can be calculated from standard potentials. $E^\ominus$ has a positive value for a spontaneous reaction.

**Learning outcomes:**

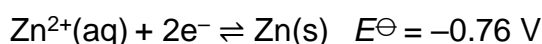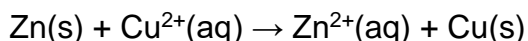- Predict whether a reaction is spontaneous in the forward or reverse direction from $E^\ominus$.

**Calculating standard cell potential ($E^\ominus_{cell}$)**

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

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} \quad or \quad E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$$

- The standard electrode potential values are the reduction potentials and must be used as given in section 19 of the data booklet.
- $E^\ominus$ values are intensive quantities and are not multiplied according to the stoichiometry of the equation.
- A reaction with a positive $E^\ominus_{cell}$ value is spontaneous as written and the reverse reaction is non-spontaneous.
- A reaction with a negative $E^\ominus_{cell}$ value is non-spontaneous as written and the reverse reaction is spontaneous.
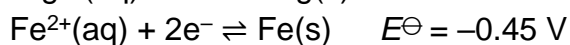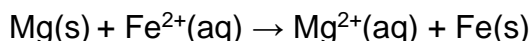
**Example:** Calculate the $E^\ominus_{cell}$ for the following reaction. Comment on the spontaneity of the reaction.

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

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

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

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

**Exercises:**

1) Calculate the $E^\ominus_{cell}$ for the following reaction. Comment on the spontaneity of the reaction.

$$Mg(s) + Fe^{2+}(aq) \rightarrow Mg^{2+}(aq) + Fe(s)$$

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \quad E^\ominus = -2.37 \text{ V}$$

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^\ominus = -0.45 \text{ V}$$

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

The $E^\ominus_{cell}$ value is positive therefore the reaction is spontaneous as written.

**2)** Calculate the $E^⊖_{cell}$ for the following reaction. Comment on the spontaneity of the reaction.

$$Cr^{2+}(aq) + Cu^{2+}(aq) \rightarrow Cr^{3+}(aq) + Cu^+(aq)$$

$$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq) \quad E^⊖ = -0.41 \text{ V}$$
$$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq) \quad E^⊖ = +0.15 \text{ V}$$
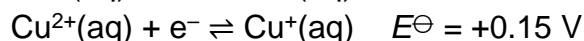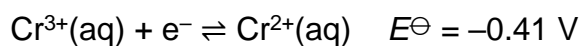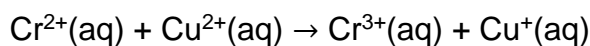
$E^⊖_{cell} = E_{red} - E_{ox}$
$E^⊖_{cell} = +0.15 - (-0.41) = +0.56$ V
The $E^⊖_{cell}$ value is positive therefore the reaction is spontaneous as written.

**3)** Calculate the standard cell potential, $E^⊖_{cell}$, of a voltaic cell consisting of a nickel half-cell and a silver half-cell.

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^⊖ = -0.26 \text{ V}$$
$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^⊖ = +0.80 \text{ V}$$
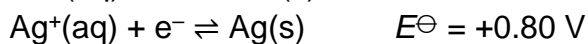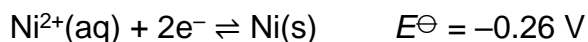
$E^⊖_{cell} = +0.80 - (-0.26) = +1.06$ V

**4)** Calculate the standard cell potential, $E^⊖_{cell}$, of a voltaic cell consisting of an aluminum half-cell and an iron half-cell.

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad E^⊖ = -1.66 \text{ V}$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^⊖ = -0.44 \text{ V}$$
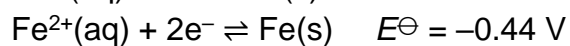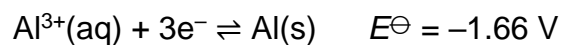
$E^⊖_{cell} = -0.44 - (-1.66) = +1.22$ V

**Reactivity 3.2.14**
**Understandings:**
- The equation $\Delta G^{\ominus} = -nFE^{\ominus}$ shows the relationship between standard cell change in Gibbs energy and standard electrode potential for a reaction.

**Learning outcomes:**
- Determine the value for $\Delta G^{\ominus}$ from $E^{\ominus}$ data.

**Additional notes:**
- The equation and the value of $F$ in C mol$^{-1}$ are given in the data booklet.

**Linking questions:**
- Reactivity 1.4 How can thermodynamic data also be used to predict the spontaneity of a reaction?

**Relationship between $E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$**

- The following equation can be found in section 1 of the data booklet:
$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$
- $n$ is the amount (in mol) of electrons transferred in the reaction
- $F$ is the Faraday constant (96500 C mol$^{-1}$).
- For a spontaneous reaction, the $\Delta G^{\ominus}$ is negative and the $E^{\ominus}_{cell}$ is positive.
- For a non-spontaneous reaction, the $\Delta G^{\ominus}$ is positive and the $E^{\ominus}_{cell}$ is negative.
- The relationship between the $E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$ is summarised in the table below.

| $\Delta G^{\ominus}$ | $E^{\ominus}_{cell}$ | Spontaneity |
|---|---|---|
| Negative | Positive | Spontaneous |
| Positive | Negative | Non-spontaneous |
| Zero | Zero | Reaction is at equilibrium |

**Exercises:** Calculate the $\Delta G^{\ominus}$ for the following reactions. Comment on the spontaneity of the reaction in each case.

1) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$     $E^{\ominus}_{cell} = +1.10$ V
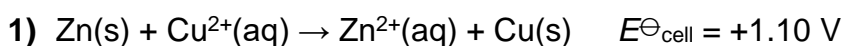
$\Delta G^{\ominus} = -2 \times 96500 \times 1.10$

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

$\Delta G^{\ominus}$ is negative therefore reaction is spontaneous as written.

2) $Ni^{2+}(aq) + Mn(s) \rightarrow Ni(s) + Mn^{2+}(aq)$     $E^{\ominus}_{cell} = -0.93$ V
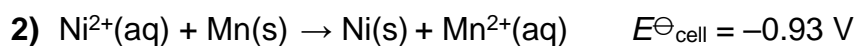
$\Delta G^{\ominus} = -2 \times 96500 \times -0.93$

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

$\Delta G^{\ominus}$ is positive therefore reaction is non-spontaneous as written.

**Reactivity 3.2.15**
**Understandings:**
- During electrolysis of aqueous solutions, competing reactions can occur at the anode and cathode, including the oxidation and reduction of water.
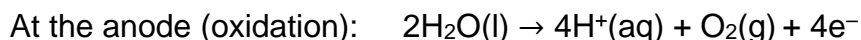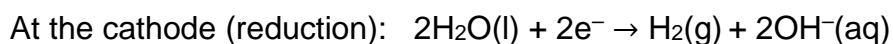
**Learning outcomes:**
- Deduce from standard electrode potentials the products of the electrolysis of aqueous solutions.

**Additional notes:**
- Electrolytic processes should include the electrolysis of water and of aqueous solutions.
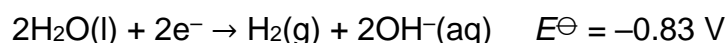
**Electrolysis of aqueous solutions**

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

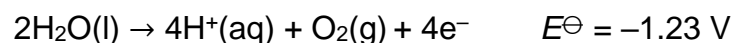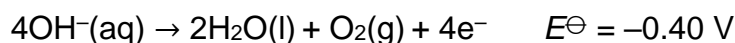At the cathode (reduction): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

At the anode (oxidation): $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

**Electrolysis of water ($H_2O$)**

- Pure water is a poor conductor of electricity, therefore NaOH or $H_2SO_4$ is added to increase its conductivity.
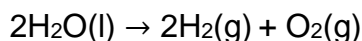
At the cathode:

$Na^+(aq) + e^- \rightarrow Na(s)$          $E^\ominus = -2.71$ V

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$     $E^\ominus = -0.83$ V

- $H_2O$ is reduced instead of $Na^+$ ions because $H_2O$ is a stronger oxidising agent / $Na^+$ is a weaker oxidising agent.

At the anode:

$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^-$     $E^\ominus = -0.40$ V

$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$     $E^\ominus = -1.23$ V

- Both reactions result in the formation of $O_2$ at the anode.

Overall equation:
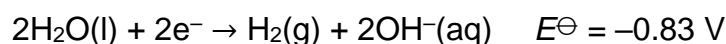
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Observed changes at the electrodes:

- A colorless gas is evolved at the anode and cathode.
- The ratio of $H_2$ to $O_2$ is 2:1
- The pH at the anode decreases (increase in $[H^+]$) and the pH at the cathode increases (increase in $[OH^-]$).
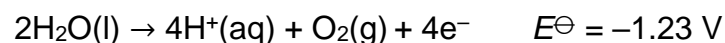
### Electrolysis of aqueous sodium chloride, NaCl(aq)

- The products of the electrolysis of aqueous solution that contain chloride ions depend on the concentration of the solution.

At the cathode:

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

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\ominus = -0.83 \text{ V}$$

- $H_2O$ is reduced instead of $Na^+$ ions because $H_2O$ is a stronger oxidising agent / $Na^+$ is a weaker oxidising agent.
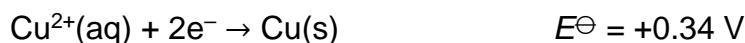
At the anode:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \qquad E^\ominus = -1.23 \text{ V}$$

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

- At low concentrations – dilute NaCl(aq) – $O_2(g)$ is produced.
- At high concentrations – concentrated NaCl(aq) – $Cl_2(g)$ is produced.

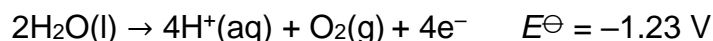### Electrolysis of aqueous copper(II) sulfate, $CuSO_4$(aq)
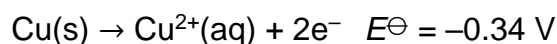
### Inert (graphite electrodes)

At the cathode:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\ominus = -0.83 \text{ V}$$

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

At the anode:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \qquad E^\ominus = -1.23 \text{ V}$$

### Copper electrodes

At the cathode:

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

At the anode:

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

Observed changes at electrodes with graphite electrodes:
- Pinky-brown colour as copper is deposited on the cathode.
- The blue color is lost because of discharge of $Cu^{2+}$ ions.

Observed changes at electrodes with copper electrodes:
- 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: $O_2(g)$   cathode: $H_2(g)$

**(b)** Copper(II) nitrate solution

anode: $O_2(g)$   cathode: $Cu(s)$

**(c)** Concentrated magnesium chloride solution

anode: $Cl_2(g)$  cathode: $H_2(g)$

**(d)** Sodium hydroxide solution

anode: $O_2(g)$   cathode: $H_2(g)$

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

**(a)** Using copper electrodes.

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

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

**(b)** Using platinum electrodes.

anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

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

**Reactivity 3.2.16**
**Understandings:**
- Electroplating involves the electrolytic coating of an object with a metallic thin layer.

**Learning outcomes:**
- Deduce equations for the electrode reactions during electroplating.

**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 electrolyte is an aqueous solution of the same ions as the anode material.



Anode:     $Ag(s) \rightarrow Ag^+(aq) + e^-$

Cathode:   $Ag^+(aq) + e^- \rightarrow Ag(s)$
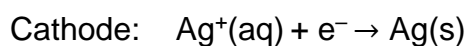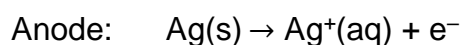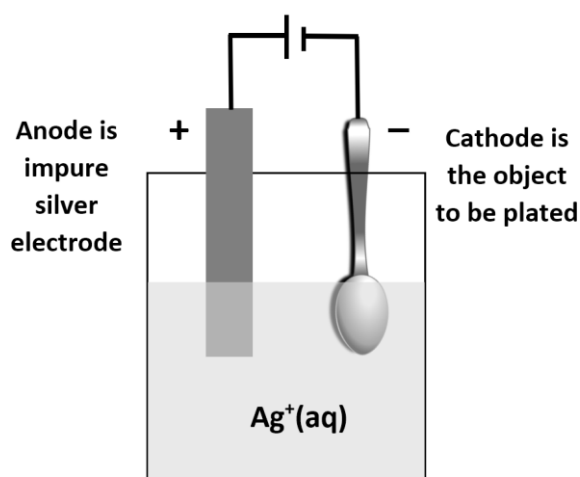
**Factors that affect the amount of product in an electrolysis reaction**

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

- duration of the electrolysis

- current supplied

- charge on the ion