Reactivity 3.2 HL

IB CHEMISTRY HL

25	16		6	2	25
Mn	**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
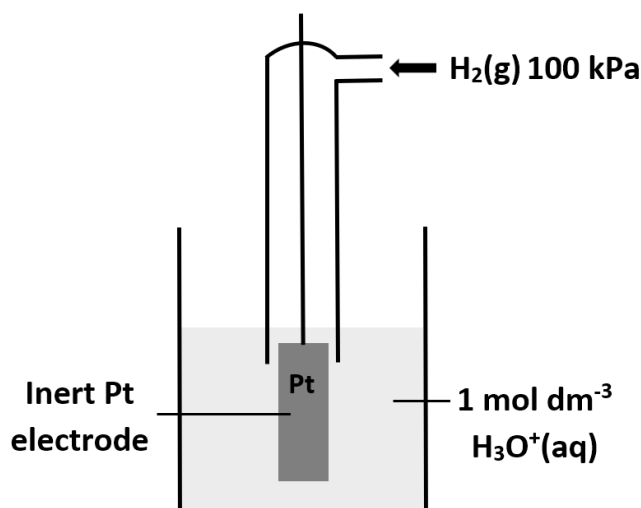
- Depending on which half-cell is connected to the hydrogen half-cell, hydrogen ions are reduced to form hydrogen gas, or hydrogen gas is oxidised to form hydrogen ions.

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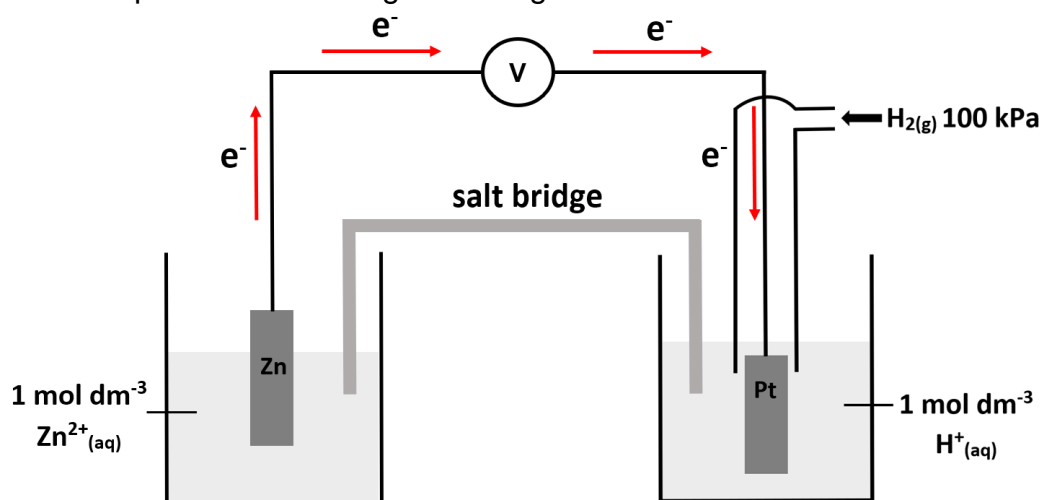
Standard electrode potential ($E^{\ominus}$)

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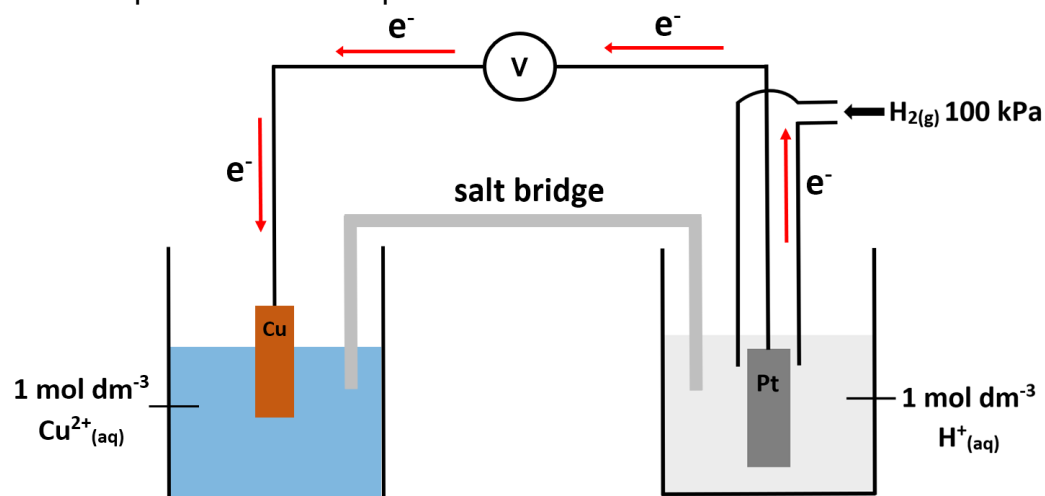
- The standard electrode potential, $E^{\ominus}$, of the copper half-cell is +0.34 V.

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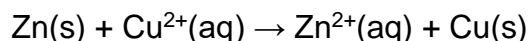
Calculating standard cell potential ($E^\ominus_{cell}$)

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

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox} \quad or \quad E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$$
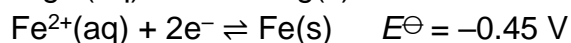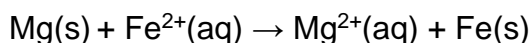
- The standard electrode potential values are the reduction potentials and must be used as given in section 19 of the data booklet.
- $E^\ominus$ values are intensive quantities and are not multiplied according to the stoichiometry of the equation.
- A reaction with a positive $E^\ominus_{cell}$ value 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.
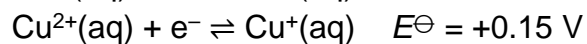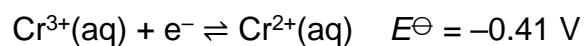
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

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

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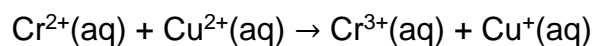
Exercises:

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

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

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

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^\ominus = -0.45 \text{ V}$$
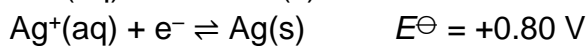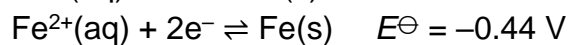
2) Calculate the $E^{\ominus}_{cell}$ for the following reaction. Comment on the spontaneity of the reaction.

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

$$Cr^{3+}(aq) + e^- \rightleftharpoons Cr^{2+}(aq) \quad E^{\ominus} = -0.41 \text{ V}$$
$$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq) \quad E^{\ominus} = +0.15 \text{ V}$$

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

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \quad E^{\ominus} = -0.26 \text{ V}$$
$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \quad E^{\ominus} = +0.80 \text{ V}$$
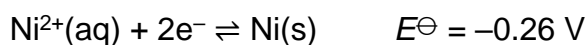
4) Calculate the standard cell potential, $E^{\ominus}_{cell}$, of a voltaic cell consisting of an aluminum half-cell and an iron half-cell.

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \quad E^{\ominus} = -1.66 \text{ V}$$
$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \quad E^{\ominus} = -0.44 \text{ V}$$
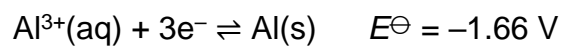
Reactivity 3.2.14
Understandings:
- The equation $\Delta G^{\ominus} = -nFE^{\ominus}$ shows the relationship between standard cell change in Gibbs energy and standard electrode potential for a reaction.

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?

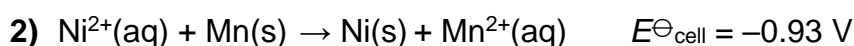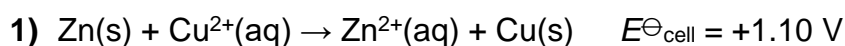## Relationship between $E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$

- 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

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

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.
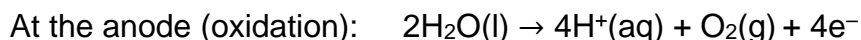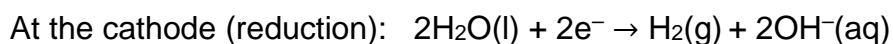
Learning outcomes:
- Deduce from standard electrode potentials the products of the electrolysis of aqueous solutions.

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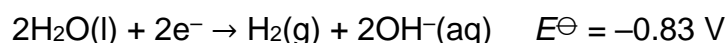
Electrolysis of aqueous solutions

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

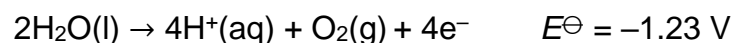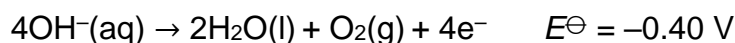At the cathode (reduction): $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

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.
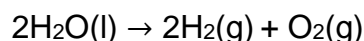
At the cathode:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad\qquad E^\ominus = -2.71 \text{ V}$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \quad E^\ominus = -0.83 \text{ V}$$

- 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:

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^- \qquad E^\ominus = -0.40 \text{ V}$$
$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \qquad E^\ominus = -1.23 \text{ V}$$

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

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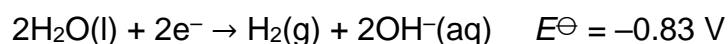$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

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 $[OH^-]$).
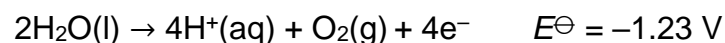
Electrolysis of aqueous sodium chloride, NaCl(aq)

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

At the cathode:

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

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

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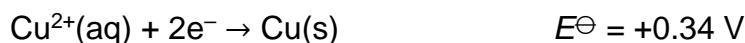
At the anode:

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

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

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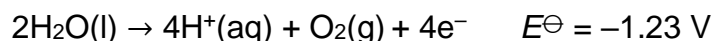- At high concentrations – concentrated NaCl(aq) – $Cl_2(g)$ is produced.

Electrolysis of aqueous copper(II) sulfate, CuSO₄(aq)

Inert (graphite electrodes)

At the cathode:

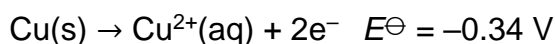$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^{\ominus} = -0.83 \text{ V}$$

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

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

(b) Copper(II) nitrate solution

(c) Concentrated magnesium chloride solution

(d) Sodium hydroxide solution

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

(a) Using copper electrodes.

(b) Using platinum electrodes.

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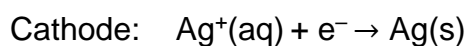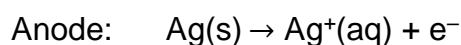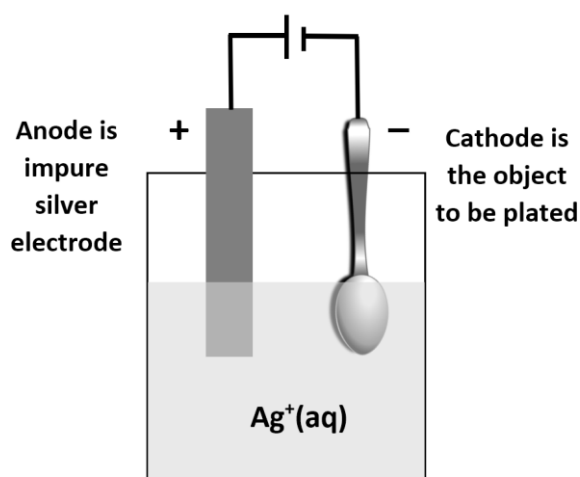
Factors that affect the amount of product in an electrolysis reaction

The factors that affect the amount of product formed in an electrolysis reaction are:
- duration of the electrolysis
- current supplied
- charge on the ion