

Electrochemical Calculations

Introduction

Electrochemistry involves the study of chemical reactions resulting in the movement of electrons from one chemical species to another. These reactions are known as oxidation-reduction reactions, or *redox-reactions*. Chemical species losing electrons are said to be oxidised, while those gaining electrons are said to be reduced. It is important to distinguish between the terms used when describing redox-reactions:



Key Point:

A chemical species losing electrons is oxidised and is described as a reducing agent.

A chemical species gaining electrons is reduced and is described as an oxidising agent.

Examination questions on electrochemistry consider the interaction between chemical change and electrical energy. These require students to analyse data, often in an experimental context, to either predict or explain the outcome of a chemical change.

A redox-reaction creates an *electromotive force*, or **emf**, which is the difference in electrical potential that gives rise to an electric current. This can be modelled by marbles falling from a raised platform to the floor. Figure 1 illustrates how the tendency is for the marbles to fall, rather than rise to the platform. A redox-reaction can be viewed as electrons moving from a higher electrical potential to a lower one.

Figure 1a

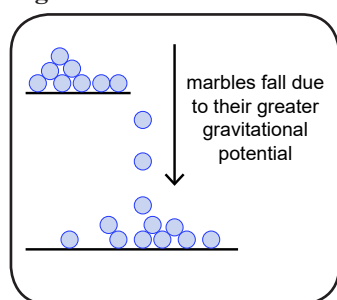
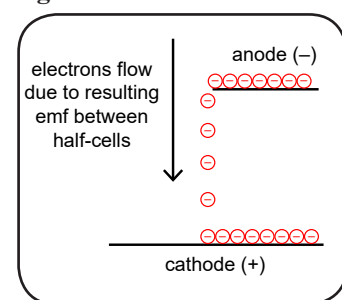
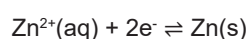
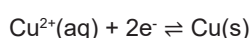


Figure 1b



Redox-reactions can be considered as two separate redox half-reactions with one redox system losing electrons and the other gaining electrons. The convention is to show each half-cell as a redox equilibria half-equation, with the reduction reaction in the forward direction. For example:



Standard Hydrogen Electrode and Standard Conditions

Two connected redox half-cells will create an emf that generates a flow of charge. It is necessary to standardise the electrochemical process to provide reproducible data that can be used to predict whether a given reaction is feasible (spontaneous) or not.



Key Point:

A spontaneous reaction occurs without intervention (e.g. without heating or any other form of energy input).

Scientists use the standard hydrogen electrode as a reference for measuring the electrode potential of other redox half-cells. Note the use of a platinum electrode to provide a surface for the hydrogen gas and hydrogen ions to interact. The value of the standard hydrogen electrode potential is zero. Figure 2 describes two pairs of electrochemical cells involving the standard hydrogen electrode and illustrates how individual redox-potentials determine the emf of the combined half-cells.

Figure 2a

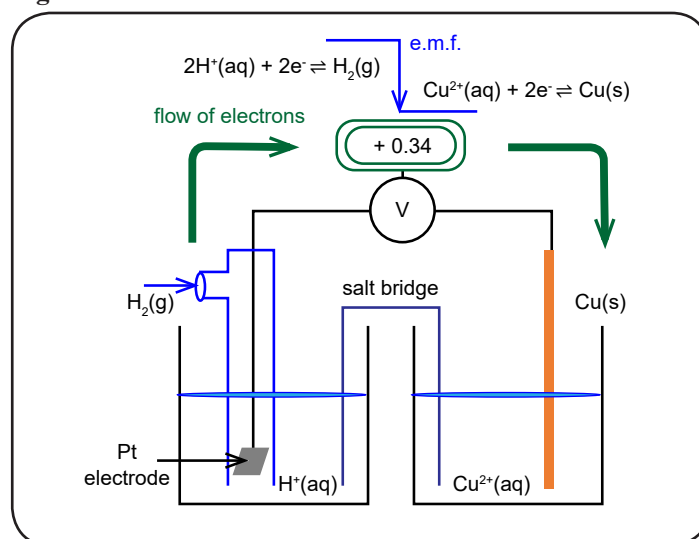
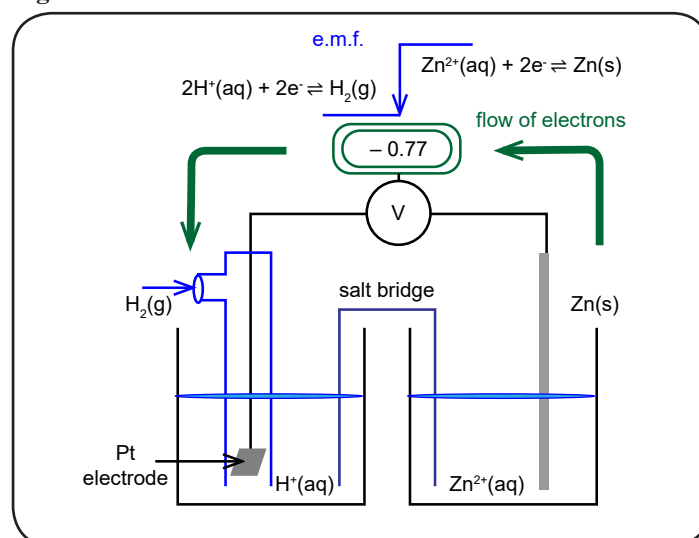


Figure 2b



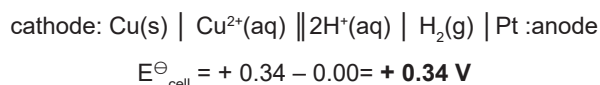
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The accuracy of electrochemical data depends on using standard conditions, which are given below:

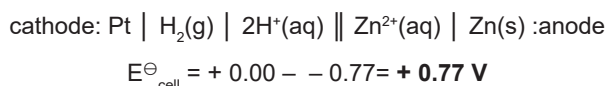
- concentration 1.0 mol dm⁻³
- temperature 25 °C (298 K)
- pressure 100 kPa (1 atm)

The salt-bridge contains an electrolyte (e.g. saturated potassium nitrate solution), and is essential to ensure a closed circuit. This is required to ensure a continuous flow of charge around the electrochemical cell.

Calculating the emf requires manipulating the standard electrode potentials to ensure there is a positive (+) value for the emf of the cell (i.e. $E_{\text{cell}}^{\ominus}$ is positive). In **Figure 2a**, the electrons flow towards the copper half-cell, i.e. the copper half-cell acts as the cathode. The electrochemical cell is written as:

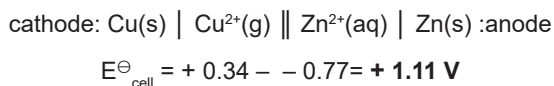


Compare this with the electrochemical cell described in **Figure 2b**, where the electrons flow in the opposite direction and the hydrogen half-cell is acting as the cathode.



Standard Electrode Potentials

The standard electrode potentials for redox half-cells can be used to predict the outcome of chemical reactions. For example, what is observed when the copper half-cell is connected to the zinc half-cell? Combining the electrochemical cells requires identifying the more positive reduction potential as the cathode (i.e. the copper half-cell).



Electrons are moving from the anode to the cathode, which results with copper(II) ions being reduced to copper metal. The chemical equation is thus:

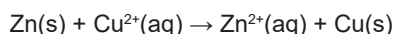


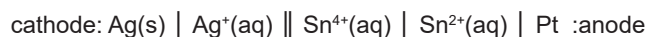
Table 1 provides the standard electrode potentials for some example redox half-reactions. These are used to determine if the $E_{\text{cell}}^{\ominus}$ value between two connected redox half-cells is positive, and thus the reaction is feasible.

Table 1 Physical data for common phosphorus allotropes

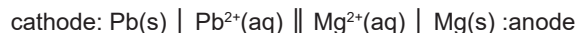
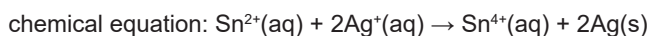
Redox potential	E^{\ominus} / V
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Mg(s)}$	-2.37
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn(s)}$	-0.77
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Pb(s)}$	-0.13
$2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	+0.15
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu(s)}$	+0.34
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag(s)}$	+0.80

The tendency is for the redox equilibria with the more positive E^{\ominus} value to shift left-to-right, and for the redox equilibria with the more negative E^{\ominus} value to shift right-to-left.

Example



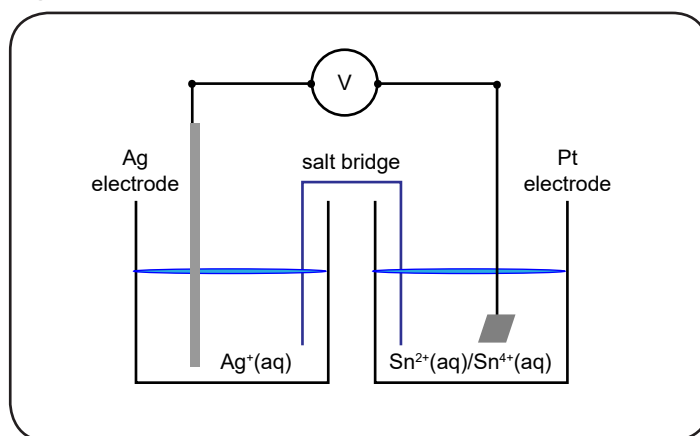
$$E_{\text{cell}}^{\ominus} = +0.80 - +0.15 = \mathbf{+0.65 \text{ V}}$$



$$E_{\text{cell}}^{\ominus} = -0.13 - -2.37 = \mathbf{+2.24 \text{ V}}$$



Figure 3



For a redox half-cell involving two ions, a platinum electrode is used to provide an inert surface on which the two ions can interact.

The electrolyte contains a 50:50 mixture of the two aqueous ions. For example, **Figure 3** shows the set-up for the $\text{Sn}^{2+}(\text{aq}) | \text{Sn}^{4+}(\text{aq})$ cell.

The electrolyte consists of 1.0 mol dm⁻³ $\text{Sn}^{2+}(\text{aq})$ and 1.0 mol dm⁻³ $\text{Sn}^{4+}(\text{aq})$.

Predicting Oxidation-Reduction Reactions

Vanadium is a transition metal that can form solutions containing vanadium ions with different oxidation states. Changes in the oxidation states of vanadium ions are observed through the colour of the solutions, see **Table 2**.

The oxidation states of aqueous vanadium ions are changed by the action of oxidising or reducing agents. **Table 3** provides the standard electrode potentials for different vanadium redox half-reactions and for the reducing agent, sulphur dioxide, SO_2 .

Table 2

vanadium ion	colour
V^{2+}	violet
V^{3+}	green
VO^{2+}	blue
VO_2^{+}	yellow

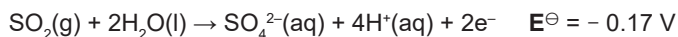
Table 3

Redox potential	E^{\ominus} / V
$\text{V}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{V(s)}$	-1.20
$\text{V}^{3+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{SO}_2(\text{g}) + 2\text{H}_2\text{O(l)}$	+0.17
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{V}^{3+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+0.34
$\text{VO}_2^{+}(\text{aq}) + 2\text{H}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{VO}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.00

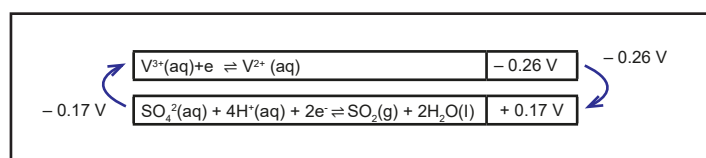
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It is important to visualise the correct direction of a redox half-reaction when applying electrochemical calculations to predict whether a given reaction is spontaneous.

For example, bubbling sulphur dioxide, SO_2 , to reduce the following vanadium ions gives the redox half-equation. Note the corresponding change in the sign for the value of E^\ominus :



a) a solution containing vanadium(III) ions, $\text{V}^{3+}(\text{aq})$;

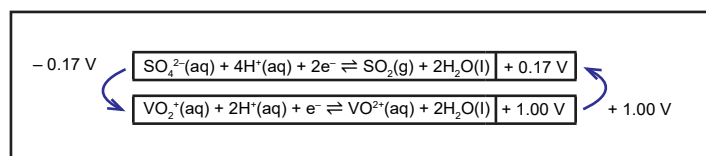


The resulting emf for this redox reaction is determined by adding the respective electrical potentials formed in the reaction:

$$-0.17 + -0.26 = -0.43 \text{ V}$$

The **negative (-)** value for E^\ominus means this reaction is **not feasible** and cannot proceed independently.

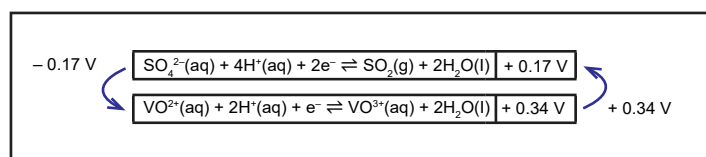
b) a solution containing vanadium(V) ions, $\text{VO}_2^+(\text{aq})$.



$$-0.17 + +1.00 = +0.83 \text{ V}$$

The resulting emf for this redox reaction is positive (+), i.e. $E^\ominus = +0.83 \text{ V}$, which means this reaction is feasible and sulphur dioxide, SO_2 , reduces vanadium(V) ions to vanadium(IV) ions.

Analysis of the standard electrode potential data suggests that if further sulphur dioxide, SO_2 , is bubbled through the reaction mixture, it will further reduce vanadium(IV) ions to vanadium(III).



$$-0.17 + +0.34 = +0.17 \text{ V}$$

Fuel Cells

Electrochemical cells transfer chemical energy into electrical energy carried by an electrical current. Hydrogen fuel cells are also electrochemical cells, but they differ from normal batteries because they require a continuous source of fuel and oxygen to sustain the chemical reaction. **Figure 4** is a diagram of a simple proton-exchange membrane fuel cell (PEMFC).

Figure 4

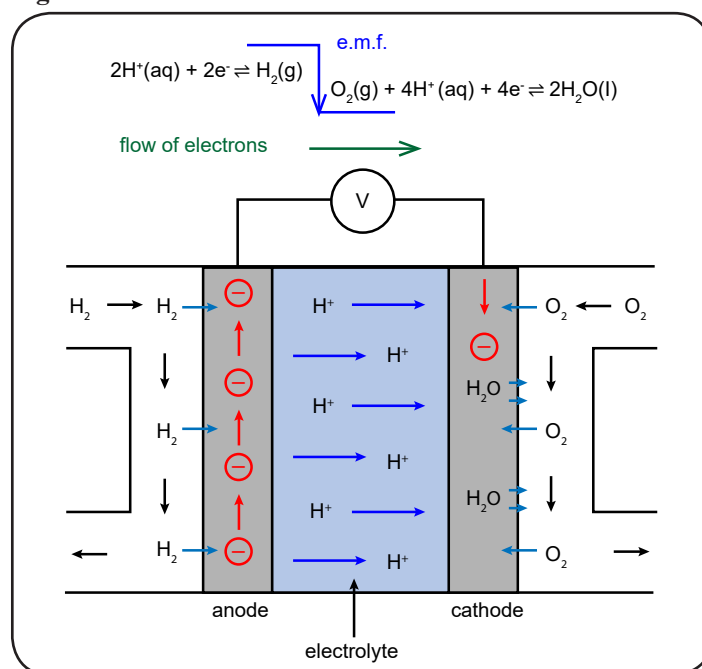
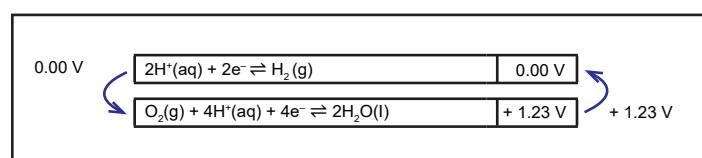


Table 4

Redox potential	E^\ominus / V
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$	-0.83
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	+0.40
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23

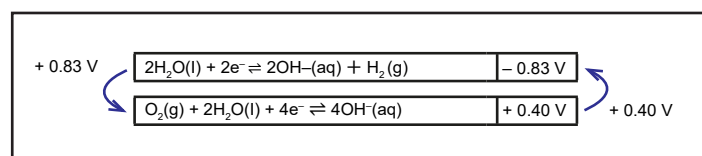
Table 4 provides the relevant standard electrode potentials for hydrogen fuel cells. The following examples show the calculated emf for the PEMFC and alkaline fuel cell.

For the simple proton-exchange membrane fuel cell:



$$0.00 + +1.23 = +1.23 \text{ V}$$

For the alkaline fuel cell:



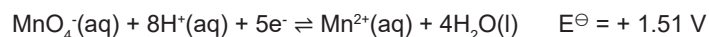
$$+0.83 + +0.40 = +1.23 \text{ V}$$

Non-Standard Conditions and the Nernst Equation

Electrochemical calculations will use standard electrode potentials measured under standard conditions. If the ion concentration used is different to 1.0 mol dm^{-3} , then the electrode potential of the cell will differ from the value measured under standard conditions. For example, the redox equilibria describing the half-cell:

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e.g.



If the concentration on the left-side of the equation is decreased, then according to Le Chatelier's principle, the equilibrium will adjust, shifting to the left. Thus, decreasing the electrical potential for the half-cell, i.e. less positive. Conversely, increasing the concentration will cause the equilibrium to shift to the right, increase in the electrical potential (i.e. more positive).

Key Point:

Le Chatelier's principle states that, in a closed system, any change in conditions applied to a system in dynamic equilibrium will lead to a shift in that equilibrium to counteract the effect of that change.

The Nernst equation, formulated by Walther Nernst, shows how the potential, E , of a given half-cell, deviates from the standard electrode potential, E^\ominus , measured against a standard hydrogen electrode.

$$E = E^\ominus + \frac{(0.059 \text{ V})}{n} \log_{10} \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

Note: n is the number of electrons transferred, and 0.059 V is a constant for $T = 298 \text{ K}$ (25°C)

The Nernst equation is used to calculate the electrode potential of a half-cell under non-standard conditions.

Example: What is the electrode potential of the $\text{MnO}_4^- (\text{aq}) \mid \text{Mn}^{2+} (\text{aq}) \mid \text{Pt}$ redox half-cell for a solution of pH 2?

$$E = +1.51 + \frac{(0.059 \text{ V})}{5} \log_{10} \frac{[\text{MnO}_4^- (\text{aq})] \times [\text{H}^+ (\text{aq})]^8}{[\text{Mn}^{2+} (\text{aq})]}$$

$\text{pH} = -\log_{10} [\text{H}^+ (\text{aq})]$
hence, $[\text{H}^+ (\text{aq})] = 10^{-\text{pH}}$

$$E = +1.51 + \frac{(0.059 \text{ V})}{5} \log_{10} [1 \times 10^{-2}]^8$$

$$E = +1.51 + 0.0118 \text{ V} \times -16$$

$$E = +1.51 + 0.0118 \text{ V} = +1.32 \text{ V}$$

Table 5

Redox potential	E^\ominus / V
$\text{Fe}^{3+} (\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+} (\text{aq})$	+ 0.77
$\text{Cl}_2 (\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^- (\text{aq})$	+ 1.33
$\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O} (\text{l})$	+ 1.51

If the reacting solution is not sufficiently acidic, then the redox reaction may not proceed as expected. The electrochemical data provided in **Table 5**, suggests oxidising chloride ions using a potassium manganate solution (with pH 2) is not feasible.

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Questions

- Use the electrochemical data provided in Table 1 to calculate the electrode potential, E^\ominus , for the following electrochemical cells:
 - $\text{Zn} (\text{s}) \mid \text{Zn}^{2+} (\text{aq}) \parallel \text{Mg}^{2+} (\text{aq}) \mid \text{Mg} (\text{s})$
 - $\text{Cu} (\text{s}) \mid \text{Cu}^{2+} (\text{aq}) \parallel \text{Ag}^+ (\text{aq}) \mid \text{Ag} (\text{s})$
 - $\text{Pb} (\text{s}) \mid \text{Pb}^{2+} (\text{aq}) \parallel \text{Sn}^{2+} (\text{aq}) \mid \text{Sn}^{2+} (\text{aq}) \mid \text{Pt}$
- The standard electrode potential for, $\text{I}_2 (\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^- (\text{aq})$ is + 0.54 V. Identify which of the redox half-cells described in Table 1 is reduced by iodide ions.
 - Calculate the electrode potential, E^\ominus .
 - Construct the overall equation for the redox reaction.
- Using the electrochemical data relating to the aluminium-oxygen fuel cell, calculate the standard cell potential of an aluminium-oxygen cell.

$\text{Al} (\text{OH})_4^- (\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al} (\text{s}) + 4\text{OH}^- (\text{aq})$	$E^\ominus = +2.31 \text{ V}$
$\text{O}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^- (\text{aq})$	$E^\ominus = +0.40 \text{ V}$

- Calculate the standard cell potential of an aluminium-oxygen cell.
 - Construct the overall cell equation for an aluminium-oxygen cell.
- Use the electrochemical data in Table 5 to confirm that it is feasible for a *neutral* solution of potassium(VII) manganate to oxidise iron(II) to iron(III).

Answers

- + 1.60 V
 - + 0.46 V
 - + 0.28 V
- $\text{Ag}^+ (\text{aq}) + \text{e}^- \rightarrow \text{Ag} (\text{s})$
 $E^\ominus = +0.26 \text{ V}$
 - $2\text{Ag}^+ (\text{aq}) + 2\text{I}^- (\text{aq}) \rightarrow 2\text{Ag} (\text{s}) + \text{I}_2 (\text{aq})$
- $E^\ominus = +2.71 \text{ V}$
 - $4\text{Al} (\text{s}) + 3\text{O}_2 (\text{g}) + 6\text{H}_2\text{O} (\text{l}) + 16\text{OH}^- (\text{aq}) \rightarrow 4\text{Al} (\text{OH})_4^- (\text{aq}) + 12\text{OH}^- (\text{aq})$
- $E = +1.51 + 0.0118 \text{ V} \log_{10} [1 \times 10^{-7}]^8 = +1.51 - 0.6608 = +0.85 \text{ V}$
Electrochemical cell is + 0.08 V. Positive value means the reaction is feasible.