

Redox equilibria

The electrochemical series

Good **reducing agents** (good at losing electrons)

Reduction half equation	E^\ominus / V
$\text{Li}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Li}(\text{s})$	-3.03
$\text{Ba}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Ba}(\text{s})$	-2.90
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
$\text{Al}^{3+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{V}^{3+}(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{H}_2(\text{aq})$	0.00
$\text{Cu}^{2+}(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Cu}^+(\text{aq})$	+0.15
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{VO}^{2+}(\text{aq}) + 2 \text{H}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
$\text{Cu}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.52
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightleftharpoons 2 \text{I}^-(\text{aq})$	+0.54
$\text{MnO}_4^-(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}(\text{aq})$	+0.56
$\text{MnO}_4^{2-}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 4 \text{OH}^-(\text{aq})$	+0.59
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Fe}^{3+}(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{VO}_2^+(\text{aq}) + 2 \text{H}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+1.00
$\text{Br}_2(\text{g}) + 2 \text{e}^- \rightleftharpoons 2 \text{Br}^-(\text{aq})$	+1.07
$\frac{1}{2} \text{O}_2(\text{g}) + 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \rightleftharpoons 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightleftharpoons 2 \text{Cl}^-(\text{aq})$	+1.36
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{HClO}(\text{g}) + \text{H}^+(\text{aq}) + 1 \text{e}^- \rightleftharpoons \frac{1}{2} \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+1.59
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$	+1.77
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightleftharpoons 2 \text{F}^-(\text{aq})$	+2.87

Good **oxidising agents** (good at gaining electrons)

Redox reactions

Faisal has written the following notes on redox reactions in preparation for his AS exams. However there are a few mistakes, many of which are commonly seen in exam answers. Help Faisal learn from his mistakes by correcting the errors so that he has an accurate set of notes to revise from.

(10 marks)

Redox reactions

Oxidation is the loss of electrons; the oxidation state decreases
Reduction is the gain of electrons; the oxidation state increases
An oxidising agent oxidises something and is itself reduced
A reducing agent reduces something and is itself oxidised

e.g. $\overset{+3}{\text{Fe}}_2\text{O}_3 + 3 \overset{+1}{\text{C}}\text{O} \rightarrow 2 \overset{+1}{\text{Fe}} + 3 \overset{+2}{\text{C}}\text{O}_2$

Fe_2O_3 is reduced and is therefore acting as a **reducing agent**;
 CO is oxidised and is therefore acting as an **oxidising agent**.

Rules for balancing redox reactions

- Use oxidation states to identify the species undergoing oxidation or reduction.
 $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$ reduction $\text{CO} \rightarrow \text{CO}_2$ oxidation
- Balance the atoms undergoing oxidation or reduction.
 $\text{Fe}_2\text{O}_3 \rightarrow 2 \text{Fe}$ $\text{CO} \rightarrow \text{CO}_2$
- Balance the oxygen atoms by adding H_2O .
 $\text{Fe}_2\text{O}_3 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2$
- Balance the hydrogen atoms by adding H^+ .
 $6 \text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + 2 \text{H}^+$
- Balance the electrons.
 $6 \text{e}^- + 6 \text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$ $2 \text{e}^- + \text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + 2 \text{H}^+$
- Multiply either half equation to make sure that the no. of electrons in each half equation match.
 $6 \text{e}^- + 6 \text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O}$ $6 \text{e}^- + 3 \text{H}_2\text{O} + 3 \text{CO} \rightarrow \text{CO}_2 + 6 \text{H}^+$
- Combine to get the full redox equation.
 $6 \text{e}^- + 6 \text{H}^+ + \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O} + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O} + 3 \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^-$
- Cancel out anything that appears on both sides of the equation.
 ~~$6 \text{e}^- + 6 \text{H}^+ + \text{Fe}_2\text{O}_3 + 3 \text{H}_2\text{O} + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{H}_2\text{O} + 3 \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^-$~~
 $\text{Fe}_2\text{O}_3 + 3 \text{CO} \rightarrow 2 \text{Fe} + 3 \text{CO}_2$

Standard electrode potentials

We can measure how readily something gives away electrons by measuring its standard electrode potential, E^\ominus .

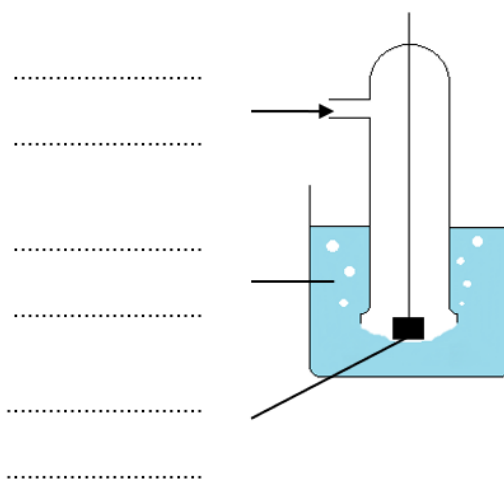
1. Standard electrode potentials are measured by connecting a half cell containing the equilibrium, the potential of which is to be measured to a standard hydrogen electrode at 298 K.

(a) Label the diagram below showing the standard hydrogen electrode.

(3 marks)

(b) Complete the diagram to show the complete cell you would use if you wished to measure E^\ominus for a zinc electrode.

(4 marks)



2. Cells can be represented in shorthand form using a series of standard conventions.

(a) Match up the symbol to its meaning when used to represent an electrochemical cell;

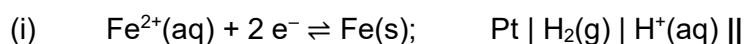
| Shows a salt bridge

|| Indicates a phase boundary

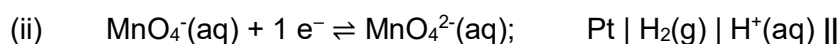
(1 mark)

(b) For each half cell, the species in the highest oxidation state in the redox equilibrium is written next to the salt bridge.

Use this convention to complete the shorthand representation of the cells produced when half cells containing each of the equilibria below are connected to a standard hydrogen electrode.



(1 mark)

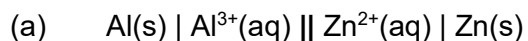


(1 mark)

Calculations involving electrochemical cells

1. For each of the electrochemical cells described below;
- Calculate the emf of the cell as written,
 - Identify the reaction occurring at the positive and negative electrodes,
 - Write an equation for the overall cell reaction which occurs when the electrodes are connected

Assume standard conditions. Use the table of standard electrode potentials provided at the start of this chapter for reference.



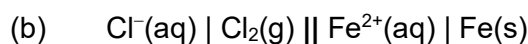
$E^{\ominus}_{\text{cell}}$

Positive electrode half equation

Negative electrode half equation

Overall cell reaction

(4 marks)



$E^{\ominus}_{\text{cell}}$

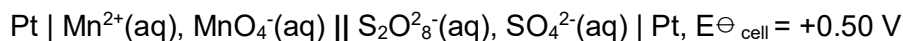
Positive electrode half equation

Negative electrode half equation

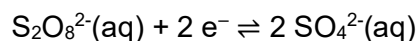
Overall cell reaction

(4 marks)

2. The electrochemical cell shown below is set up;



- (a) Calculate the standard electrode potential for the following half-reaction;



(1 mark)

- (b) For the standard electrode potentials, all ion concentrations must be 1 mol dm^{-3} .

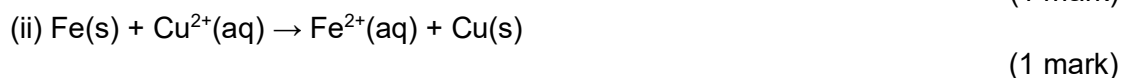
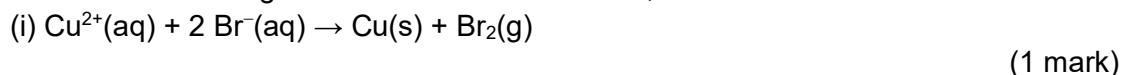
Deduce what effect an increase in the concentration of $\text{S}_2\text{O}_8^{2-}(\text{aq})$ ions to higher than 1 mol dm^{-3} would have on $E^{\ominus}_{\text{cell}}$.

(1 mark)

Using E_{sat} values to predict reactions

We can use standard electrode potentials to predict if reactions will happen. Remember the more negative the electrode potential the better the species on the right of the reduction half equation is as a reducing agent.

1. (a) Predict if the following reactions are feasible or not;



(b) Choose a halogen that could be used to oxidise $\text{Fe}^{2+}(\text{aq})$ ions to $\text{Fe}^{3+}(\text{aq})$ ions. Explain your choice.

(2 marks)

(c) When carrying out oxidation reactions, a solution of $\text{MnO}_4^{-}(\text{aq})$ cannot be acidified by HCl whereas a solution of $\text{Cr}_2\text{O}_7^{2-}$ in theory can.

Explain why, using your understanding of standard electrode potentials.

(2 marks)

2. For each of the following combination of reagents, choose from the options below the final colour of the solution. Write an equation to represent the overall reaction occurring.

Green blue yellow orange lilac

(a) Addition of tin powder to a solution of VO_2^{+} ions in acidic conditions.

[$\text{V}^{2+}(\text{aq})$ is lilac; $\text{V}^{3+}(\text{aq})$ is green; $\text{VO}^{2+}(\text{aq})$ is blue and $\text{VO}_2^{+}(\text{aq})$ is yellow]

(2 marks)

(b) Addition of silver powder to a solution of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions in acidic conditions.

[$\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ is orange; $\text{Cr}^{3+}(\text{aq})$ is green; $\text{Cr}^{2+}(\text{aq})$ is blue]

(2 marks)

Applications of electrochemical cells

Technically a **battery is two or more simple cells connected together**. However in everyday speech we rarely make the distinction.

There are a wide variety of batteries available today. The table below shows some details of the chemistry involved in just a few.

Battery type	Half equations with electrode potentials	$E_{\text{cell}} / \text{V}$
Zinc/carbon	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$ $E \approx -0.8 \text{ V}$ $2 \text{NH}_4^{+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{H}_2(\text{g})$ $E \approx +0.7 \text{ V}$
Nickel/cadmium	$\text{Cd}(\text{OH})_2(\text{s}) + 2 \text{e}^{-} \rightleftharpoons \text{Cd}(\text{s}) + 2 \text{OH}^{-}(\text{aq})$ $E \approx -0.8 \text{ V}$ $\text{NiO}(\text{OH})(\text{s}) + \text{H}_2\text{O}(\text{l}) + 1 \text{e}^{-} \rightleftharpoons \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^{-}(\text{aq})$ $E \approx +0.5 \text{ V}$
Lead-acid	$\text{PbSO}_4(\text{s}) + 2 \text{e}^{-} \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$ $E \approx -0.35 \text{ V}$ $\text{PbO}_2(\text{s}) + 4 \text{H}^{+}(\text{aq}) \rightleftharpoons \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^{-}$ $E \approx +1.70 \text{ V}$
Fuel cell	$2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$ $E \approx 0.0 \text{ V}$ $4 \text{H}^{+}(\text{aq}) + \text{O}_2(\text{g}) + 4 \text{e}^{-} \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$ $E \approx +1.2 \text{ V}$

1. Complete the table above by calculating the e.m.f. for each of the different cell types. (4 marks)

2. Consider the nickel/cadmium cell in more detail.

(a) Identify the element which undergoes a change in oxidation state at the positive electrode and state the oxidation state change.

(2 marks)

(b) Write the conventional representation of the cell.

(2 marks)

(c) The nickel-cadmium cell is rechargeable. Write an equation for the overall reaction that occurs when the battery is being **recharged**.

(1 mark)

(d) Nickel/cadmium cells must be carefully disposed of. Suggest one reason why.

(1 mark)

Redox equilibria – Answers

Redox reactions

Corrections shown in red and circled.

(10 marks; 1 mark for each correct correction made)

Redox reactions

Oxidation is the loss of electrons; the oxidation state **increases**

Reduction is the gain of electrons; the oxidation state **decreases**

An **oxidising agent** oxidises something and is itself reduced

A **reducing agent** reduces something and is itself oxidised

reduction

$$\text{e.g. } \overset{+3}{\text{Fe}_2\text{O}_3} + \overset{+2}{3\text{CO}} \rightarrow \overset{0}{2\text{Fe}} + \overset{+4}{3\text{CO}_2}$$

oxidation

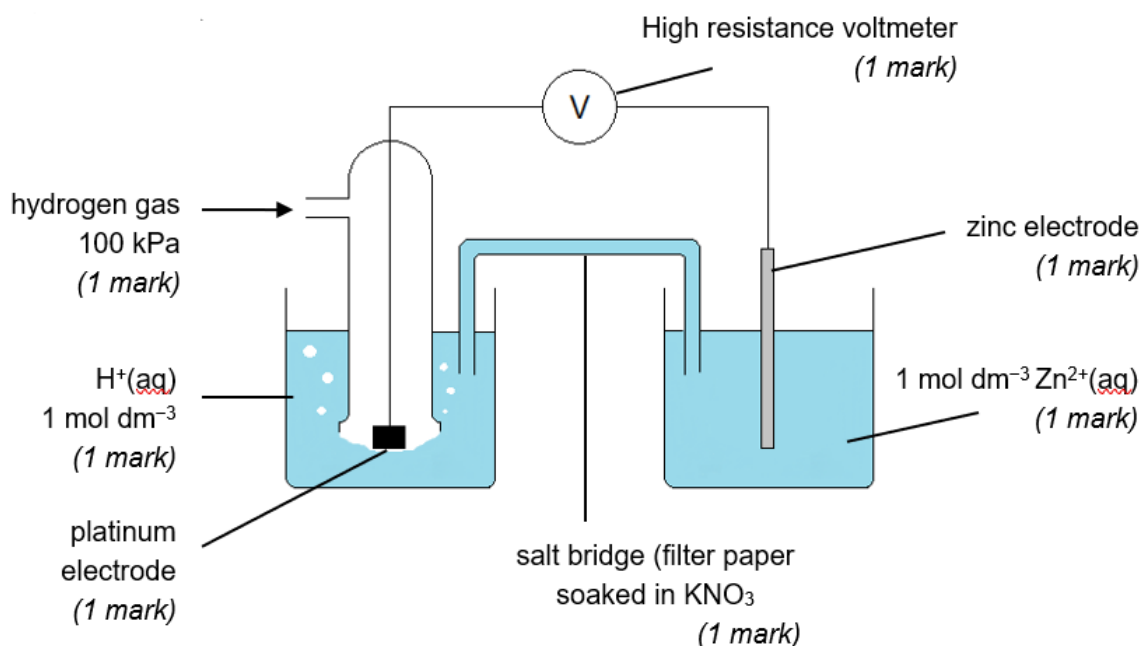
Fe_2O_3 is reduced and is therefore acting as an **oxidising agent**;

CO is oxidised and is therefore acting as a **reducing agent**.

Rules for balancing redox reactions

- Use oxidation states to identify the species undergoing oxidation or reduction.
 $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$ reduction $\text{CO} \rightarrow \text{CO}_2$ oxidation
- Balance the atoms in each undergoing oxidation or reduction.
 $\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}$ $\text{CO} \rightarrow \text{CO}_2$
- Balance the oxygen atoms by adding H_2O .
 $\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2$
- Balance the hydrogen atoms by adding H^+ .
 $6\text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + 2\text{H}^+$
- Balance the electrons.
 $6\text{e}^- + 6\text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$ $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$
- Multiply either half equation to make sure that the no. of electrons in each half equation match.
 $6\text{e}^- + 6\text{H}^+ + \text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$ $3\text{H}_2\text{O} + 3\text{CO} \rightarrow 3\text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$
- Combine to get the full redox equation.
 $6\text{e}^- + 6\text{H}^+ + \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} + 3\text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$
- Cancel out anything that appears on both sides of the equation.
 $6\text{e}^- + 6\text{H}^+ + \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} + 3\text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$
 $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$

Standard electrode potentials



2. (a) Shows a salt bridge
- Indicates a phase boundary (1 mark)
- (b) (i) $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq}) || \text{Fe}^{2+}(\text{aq}) | \text{Fe}(\text{s})$ (1 mark)
- (ii) $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq}) || \text{MnO}_4^-(\text{aq}), \text{MnO}_4^{2-}(\text{aq}) | \text{Pt}$ (1 mark)

Calculations involving electrochemical cells

1. (a) $E^\ominus_{\text{cell}} = -0.76 - (-1.66) = \underline{+0.90 \text{ V}}$ (1 mark)
- Positive electrode: $\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s}) \times 3$ (1 mark)
- Negative electrode: $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \times 2$ (1 mark)
- Overall cell reaction: $3 \text{Zn}^{2+}(\text{aq}) + 2 \text{Al}(\text{s}) \rightarrow 3 \text{Zn}(\text{s}) + 2 \text{Al}^{3+}(\text{aq})$ (1 mark)
- (b) $E^\ominus_{\text{cell}} = -0.44 - (+1.36) = \underline{-1.80 \text{ V}}$ (1 mark)
- Positive electrode: $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$ (1 mark)
- Negative electrode: $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^-$ (1 mark)
- Overall cell reaction: $\text{Cl}_2(\text{g}) + \text{Fe}(\text{s}) \rightarrow 2 \text{Cl}^-(\text{aq}) + \text{Fe}^{2+}(\text{aq})$ (1 mark)

2. (a) $+0.50 \text{ V} = E^{\ominus}_{\text{RHS}} - (+1.51 \text{ V})$, $\therefore E^{\ominus}_{\text{RHS}} = +2.01 \text{ V}$ (1 mark)

(b) According to Le Chatelier's principle, an increase in the concentration of $\text{S}_2\text{O}_8^{2-}(\text{aq})$ ions causes the equilibrium to shift to the right (using up electrons) and therefore E^{\ominus}_{RHS} will become more positive. Since $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{RHS}} - E^{\ominus}_{\text{LHS}}$, the more positive E^{\ominus}_{RHS} the more positive $E^{\ominus}_{\text{cell}}$. Therefore $E^{\ominus}_{\text{cell}}$ will increase / become more positive.

(1 mark)

Using E_{sat} values to predict reactions

1. (a) (i) $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$ $E^{\ominus} = +0.34 \text{ V}$, so $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-}$
 $\text{Br}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{Br}^{-}(\text{aq})$ $E^{\ominus} = +1.07 \text{ V}$, so $\text{Br}_2(\text{g}) + 2 \text{e}^{-} \rightarrow 2 \text{Br}^{-}(\text{aq})$

Hence the reaction, $\text{Cu}^{2+}(\text{aq}) + 2 \text{Br}^{-}(\text{aq}) \rightarrow \text{Cu}(\text{s}) + \text{Br}_2(\text{g})$ is not feasible

(1 mark)

(ii) $\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Fe}(\text{s})$ $E^{\ominus} = -0.44 \text{ V}$, so $\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^{-}$
 $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$ $E^{\ominus} = +0.34 \text{ V}$, so $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$

Hence the reaction, $\text{Fe}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ is feasible

(1 mark)

(b) $\text{Fe}^{3+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{Fe}^{2+}(\text{aq})$ $E^{\ominus} = +0.77 \text{ V}$
 $\text{F}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{F}^{-}(\text{aq})$ $E^{\ominus} = +2.87 \text{ V}$
 $\text{Cl}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{Cl}^{-}(\text{aq})$ $E^{\ominus} = +1.36 \text{ V}$
 $\text{Br}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{Br}^{-}(\text{aq})$ $E^{\ominus} = +1.07 \text{ V}$
 $\text{I}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{I}^{-}(\text{aq})$ $E^{\ominus} = +0.54 \text{ V}$

For the halogen to oxidise the Fe^{3+} ions, +0.77 V must be the more negative reduction potential. Therefore any of fluorine, chlorine or bromine would be a suitable oxidising agent.

(2 marks)

(c) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^{+}(\text{aq}) + 6 \text{e}^{-} \rightleftharpoons 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$ $E^{\ominus} = +1.33 \text{ V}$
 $\text{MnO}_4^{-}(\text{aq}) + 8 \text{H}^{+}(\text{aq}) + 5 \text{e}^{-} \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$ $E^{\ominus} = +1.51 \text{ V}$
 $\text{Cl}_2(\text{g}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{Cl}^{-}(\text{aq})$ $E^{\ominus} = +1.36 \text{ V}$

Comparing initially at the reduction potentials for $\text{MnO}_4^{-}/\text{Mn}^{2+}$ and $\text{Cl}_2/\text{Cl}^{-}$, the latter has the more negative value and hence the chloride ions in the hydrochloric acid will be oxidised by the MnO_4^{-} to produce chlorine gas which is toxic. Hence a solution of MnO_4^{-} cannot be acidified by HCl.

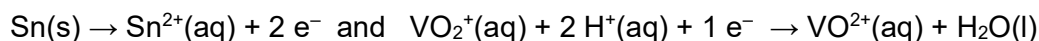
(1 mark)

Comparing now at the reduction potentials for $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ and $\text{Cl}_2/\text{Cl}^{-}$, the former now has the more positive value and hence the chloride ions cannot be oxidised by $\text{Cr}_2\text{O}_7^{2-}$ (this of course assumes standard conditions).

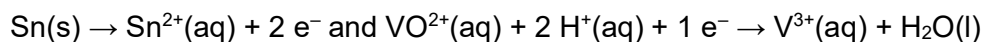
(1 mark)

2. (a) $\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Sn}(\text{s})$ $E^{\ominus} = -0.14 \text{ V}$
 $\text{V}^{3+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$ $E^{\ominus} = -0.26 \text{ V}$
 $\text{VO}^{2+}(\text{aq}) + 2 \text{H}^{+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $E^{\ominus} = +0.34 \text{ V}$
 $\text{VO}_2^{+}(\text{aq}) + 2 \text{H}^{+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $E^{\ominus} = +1.00 \text{ V}$

Between $\text{VO}_2^+ / \text{VO}^{2+}$ and $\text{Sn}^{2+} / \text{Sn}$ the latter has the more negative electrode potential and so Sn will act as a reducing agent, reducing VO_2^+ to VO^{2+} ;



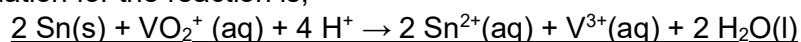
Between $\text{VO}^{2+} / \text{V}^{3+}$ and $\text{Sn}^{2+} / \text{Sn}$ again the latter has the more negative electrode potential and so Sn will act as a reducing agent, reducing VO^{2+} to V^{3+} ;



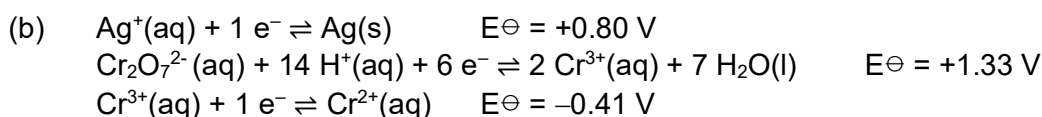
Finally between $\text{V}^{3+} / \text{V}^{2+}$ and $\text{Sn}^{2+} / \text{Sn}$ the former has the more negative electrode potential and so no further reaction will occur.

The colour of the final solution will therefore be green owing to the presence of $\text{V}^{3+}(\text{aq})$ ions.

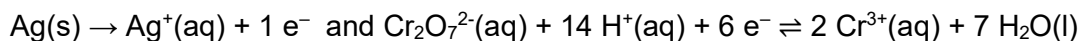
The overall equation for the reaction is;



(1 mark for the identification of the correct final colour, 1 mark for the overall equation)



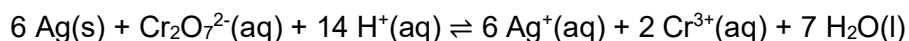
Between Ag^+/Ag and $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$, the former has the more negative electrode potential and so Ag will act as a reducing agent, reducing $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} ;



Between Ag^+/Ag and $\text{Cr}^{3+}/\text{Cr}^{2+}$, the latter has the more negative electrode potential and so no further reaction can occur i.e. the Ag cannot reduce any Cr^{3+} ions formed to Cr^{2+} ions.

Therefore the final colour of the solution will be green owing to the presence of $\text{Cr}^{3+}(\text{aq})$ ions.

The overall equation for the reaction is;



(1 mark for the identification of the correct final colour, 1 mark for the overall equation)

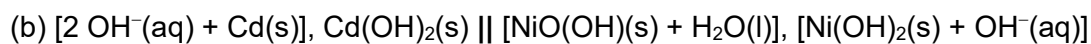
Applications of electrochemical cells

Battery type	Half equations with electrode potentials	$E_{\text{cell}} / \text{V}$
Zinc/carbon	$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$ $E \approx -0.8 \text{ V}$ $2 \text{NH}_4^{+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{H}_2(\text{g})$ $E \approx +0.7 \text{ V}$	± 1.5
Nickel/cadmium	$\text{Cd}(\text{OH})_2(\text{s}) + 2 \text{e}^{-} \rightleftharpoons \text{Cd}(\text{s}) + 2 \text{OH}^{-}(\text{aq})$ $E \approx -0.8 \text{ V}$ $\text{NiO}(\text{OH})(\text{s}) + \text{H}_2\text{O}(\text{l}) + 1 \text{e}^{-} \rightleftharpoons \text{Ni}(\text{OH})_2(\text{s}) + \text{OH}^{-}(\text{aq})$ $E \approx +0.5 \text{ V}$	± 1.3
Lead-acid	$\text{PbSO}_4(\text{s}) + 2 \text{e}^{-} \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$ $E \approx -0.35 \text{ V}$ $\text{PbO}_2(\text{s}) + 4 \text{H}^{+}(\text{aq}) \rightleftharpoons \text{PbSO}_4(\text{s}) + 2 \text{H}_2\text{O}(\text{l}) + \text{SO}_4^{2-}(\text{aq}) + 2 \text{e}^{-}$ $E \approx +1.70 \text{ V}$	± 2.05
Fuel cell	$2 \text{H}^{+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$ $E \approx 0.0 \text{ V}$ $4 \text{H}^{+}(\text{aq}) + \text{O}_2(\text{g}) + 4 \text{e}^{-} \rightleftharpoons 2 \text{H}_2\text{O}(\text{l})$ $E \approx +1.2 \text{ V}$	± 1.2

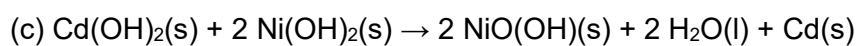
(4 marks)

2. (a) Nickel, from +3 in NiO(OH) to +2 in Ni(OH)₂

(2 marks)



(2 marks, 1 for each side correct)



(1 mark)

- (d) Nickel / cadmium are both toxic metals.

(1 mark)