

FACTFILE: GCE CHEMISTRY

A2 5.6 ELECTRODE POTENTIALS



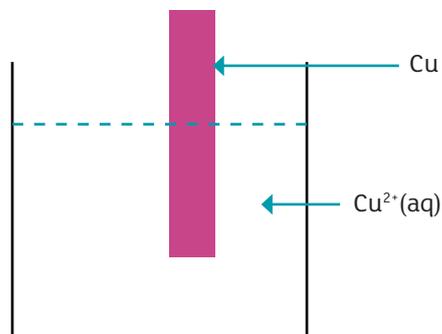
Electrode potentials

Learning Outcomes

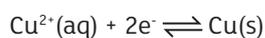
- 5.6.1 define standard electrode potential, E^\ominus , and explain the construction and significance of the hydrogen electrode and understand the importance of conditions when measuring electrode potentials;
- 5.6.2 use standard electrode potentials to predict feasibility and direction of reactions, to calculate the emf and understand the limitations of such predictions in terms of concentrations and kinetics;
- 5.6.3 use conventional representations for cells;
- 5.6.4 classify cells into non-rechargeable, rechargeable and fuel cells, and state examples of each;
- 5.6.5 demonstrate understanding of the electrode reactions in a lithium cell;
- 5.6.6 demonstrate understanding that a fuel cell uses the energy from the reaction of a fuel with oxygen to generate a voltage;
- 5.6.7 recall the electrode reactions that occur in an alkaline hydrogen-oxygen fuel cell;
- 5.6.8 recall the environmental issues associated with cells;

Electrode potentials

A half cell is a metal dipping into a metal salt solution. There is an equilibrium between the metal atoms and ions.



In this half cell the copper ions in solution are in equilibrium with the copper atoms in the metal.



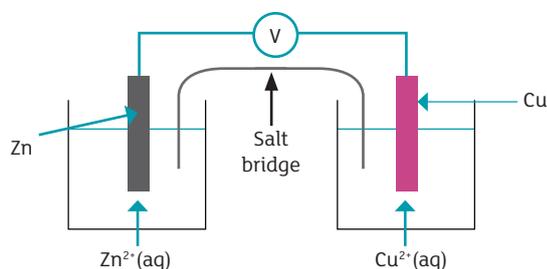
Two half cells made from two different metals, when connected by a wire, form an electrochemical cell. One cell releases electrons and the other gains electrons. The wire allows electrons to be transferred between the two half cells. A high-resistance voltmeter is connected in the external circuit to measure the emf. It reduces current flow in the wire to zero so that the potential difference measured is equal to the emf of the cell. The solutions are connected using a salt bridge. A salt bridge can be made of:

- a piece of filter paper soaked in a solution of potassium nitrate
- a U tube containing potassium chloride dissolved in gelatine

The function of a salt bridge is to:

- allow ions to pass between the solutions, allowing conduction of electricity and so completes the circuit and
- it maintains electrical neutrality in each half cell by providing cations and anions which replace those consumed at the electrodes if the current is allowed to flow.

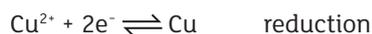
It is used instead of a piece of wire to avoid further metal/ion potentials in the circuit i.e it does not interfere with the overall reaction.



Without the high resistance voltmeter the zinc metal atoms would lose electrons.



The electrons released would pass through the external circuit wire to the copper electrode allowing copper ions to gain electrons and form copper metal.



Copper would form on the copper electrode and increases the mass, some of the zinc metal would form zinc ions and this decreases the mass of the zinc electrode. The zinc metal has a bigger build up of negative charge on its surface than copper so it has a more negative electrode potential. Relative to the zinc, the copper has a less negative electrode potential and so copper is said to be the positive electrode.

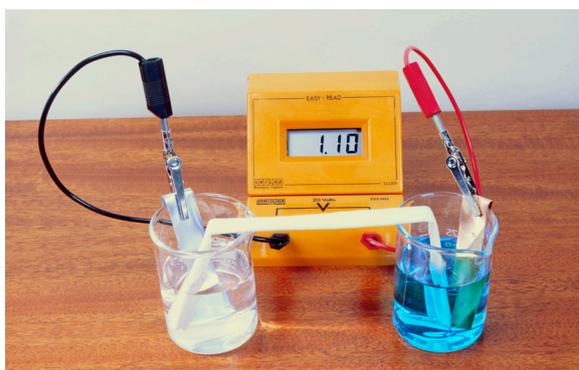
The emf is the potential difference measured when two half cells are connected

The voltmeter in this cell shows a reading (+1.1V) because electrons are trying to flow through the wire in the circuit from the zinc to the copper (from the negative to the less negative) and creating a potential difference.

The overall cell reaction is ; -



The photograph shows a zinc copper cell. The salt bridge is the white filter paper soaked in potassium chloride solution.



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Instead of drawing out a full cell diagram, conventional cell diagrams of electrochemical cells can be used:

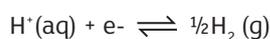
- the negative electrode, at which oxidation occurs is on the left with the components in order of being oxidised, e.g. Zn(s) then Zn²⁺(aq).
- the positive electrode at which reduction occurs is on the right with the components in order of being reduced, e.g. Cu²⁺(aq) then Cu(s).
- single vertical lines represent the boundary between two different phases e.g. Cu²⁺(aq)|Cu(s).
- a double vertical line (||) between the two electrodes represents the salt bridge.

For the cell shown in the diagram above the conventional cell diagram is



Electrons would flow from the left hand cell to the right hand cell via the external circuit so oxidation occurs in the left hand cell and reduction in the right.

A half-cell can also be made from a **non-metal and its aqueous ions**. For example a hydrogen half-cell comprises hydrogen gas H₂ in contact with H⁺ ions.



A platinum electrode must be used – platinum is inert and does not react but it allows the transfer of

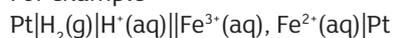
electrons from the solution in or out of the half-cell via the connecting wire.

- if a gas is used as in the hydrogen electrode, in the conventional cell diagram the platinum is included at the outside and separated by a phase boundary line. e.g. $\text{Pt(s)}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})$

Finally, a half cell may be made from ions of the same element in different oxidation states eg Fe^{2+} and Fe^{3+} ions. Again a platinum electrode is needed to dip into the equimolar solution of Fe^{2+} and Fe^{3+} .

- **In the conventional cell diagram** commas are used to separate components in an electrode which are in the same phase, e.g. $\text{Fe}^{3+}(\text{aq}), \text{Fe}^{2+}(\text{aq})$.

For example



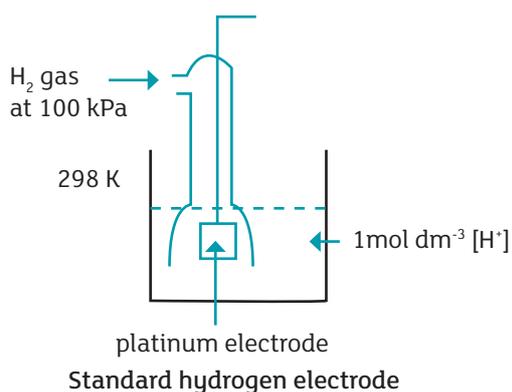
Standard electrode potentials

To measure the potential difference for a single half cell, the half cell must be connected to a standard hydrogen electrode, via a high resistance voltmeter and a salt bridge. It is important to carry out these determinations under standard conditions so that E^0 values can be compared.

Standard electrode potential is the potential difference measured when a half-cell is connected to the standard hydrogen electrode under standard conditions.

The standard conditions of the hydrogen electrode are

- hydrogen gas at 100 kPa pressure
- bubbling over a platinum electrode
- in hydrogen ions solution of concentration of 1.00 mol dm^{-3}
- at 298K

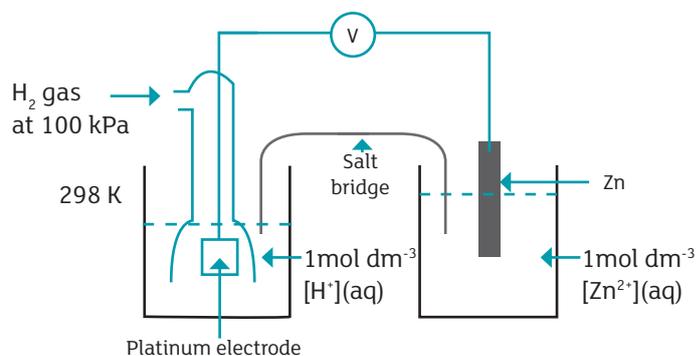


As hydrogen gas flows over the platinum, an equilibrium is set up. The electrode potential of hydrogen is assigned the value of 0.00 V

$$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g}) \quad E^0 = 0.00 \text{ V}$$

The experimental method to determine the standard electrode potential of the zinc half cell for example, is

- Set up a zinc half cell, by dipping a piece of zinc metal into a 1 mol dm^{-3} solution of zinc ions.
- Set up a standard hydrogen electrode which has hydrogen gas at 100 kPa pressure bubbling over a platinum black electrode at 298 K in a solution of 1 mol dm^{-3} hydrogen ions.
- Link these half cells with wire and a high resistance voltmeter and a salt bridge linking the solutions.
- Record the voltage and since the hydrogen half cell has a value of 0.0 V the value will be for the zinc cell.



The conventional cell diagram for this cell is $\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})||\text{Zn}^{2+}(\text{aq})|\text{Zn}(\text{s})$

Using standard electrode potentials to calculate the emf of cells.

The standard electrode potential is the difference between the standard electrode potentials of the half cells.

$$E^0 = E^0 (\text{positive electrode}) - E^0 (\text{negative electrode})$$

The positive electrode is the half cell with the more positive E^0 value. The negative electrode is the half cell with the more negative value. Electrons flow from the negative electrode to the positive.

By convention the left hand half cell is the negative electrode and the right hand half cell is the positive electrode.

Standard electrode potentials for half cells are by convention, quoted for the reduction process and are written as shown in the table .

Half cell	Standard electrode potential/V
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}$	-0.76 V
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag}$	+0.80 V
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}$	+0.34 V
$\text{Mg}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Mg}$	-2.38 V

These are reversible reactions, the direction of the reaction in a half cell depends on which half-cell it is connected to.

Example: Calculate the emf of the cell.



First look at the standard electrode potentials and determine which half cell is the negative electrode. The magnesium half cell has the more negative value (-2.38 V) so it is the negative electrode.

$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}$	-0.76 V
$\text{Mg}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Mg}$	-2.38 V

$$E^{\circ} = E^{\circ}(\text{positive electrode}) - E^{\circ}(\text{negative electrode}) \\ = -0.76 - (-2.38) = +1.62 \text{ V}$$

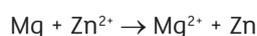
The magnesium half cell has the more negative value and has the greatest tendency to lose electrons and become oxidized. Hence the reaction occurring in this half cell is



The zinc half cell gains electrons and the reaction which occurs is



Adding these equations and canceling the electrons gives the overall equation



Electrons move from the negative electrode (magnesium half cell) through the circuit to the zinc half cell.

Example: Calculate the emf of a silver-copper cell and write the equation for the reaction which occurs.

First look at the standard electrode potentials and determine which half cell is the negative electrode.

$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Ag}$	+0.80 V
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu}$	+0.34 V

The copper half cell has the more negative value (+0.32 V) so it is the negative electrode.

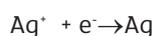
$$E^{\circ} = E^{\circ}(\text{positive electrode}) - E^{\circ}(\text{negative electrode})$$

$$= +0.8 - (0.34) = +0.46 \text{ V}$$

The copper half cell has the more negative value and has the greatest tendency to lose electrons and become oxidized. Hence the reaction occurring in this half cell is



The silver half cell gains electrons and the reaction which occurs is



This equation must be multiplied by two to balance the electrons, and then the equations can be added



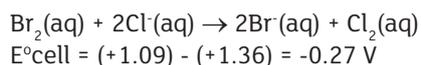
The overall equation is



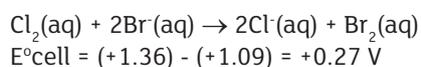
Feasibility of reactions

A positive value for emf for a cell generally means a reaction will occur.

A negative value for emf for a cell means that the reaction is happening in the opposite direction to the one written. For example, for the reaction between bromine and chloride ions



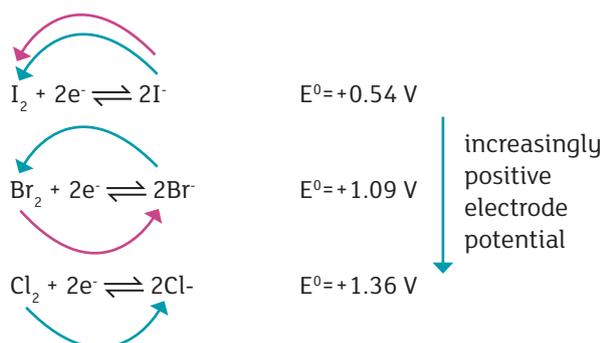
The negative value for E°_{cell} indicates the above reaction does not occur. The reaction that can occur is -



The anticlockwise rule, is a quick way to determine the feasibility of the reaction

To use the anticlockwise rule

- Arrange the redox half equations so that the smaller electrode potential (more negative) is at the top.
- The reaction which is feasible (with a positive E°) takes place anticlockwise around the half equations (i.e. the top right reacts with the bottom left).
- To calculate the emf reverse the top voltage and add the bottom of the pair.



So in the diagram above, reactions will occur between iodide ions and bromine (red arrows) and iodide ions and chlorine (blue arrows) and bromide ions and chlorine (blue arrows) because these reactions follow an anti-clockwise path. However, no reactions will occur between chloride ions and bromine or iodine and between iodine and chloride or bromide ions as these would be clockwise paths.

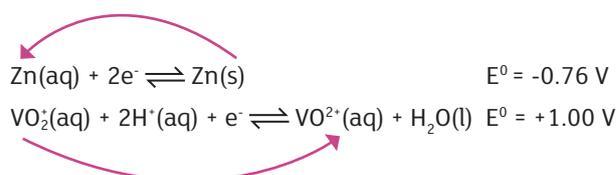
In the electrochemical series of standard electrode potentials, all equations are written as reduction processes, with the most negative E° at the top.

- The species on the left-hand side of the series can accept electrons and be reduced to a lower oxidation state. They are therefore all oxidising agents. All the species on the right-hand side of the series can give up electrons and be oxidised to a higher oxidation state, and are thus reducing agents.
- The higher a half-equation is located in the electrochemical series, the more negative the standard electrode potential and the greater the tendency to undergo oxidation. The reducing agents at the top of the series are thus very strong, and the oxidising agents very weak. The lower down a half-equation is located in the electrochemical series, the more positive the standard electrode potential and the greater the tendency to undergo reduction. The oxidising agents at the bottom of the series are thus very strong, and the reducing agents very weak. The best oxidising agent is the bottom left species.

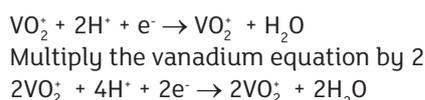
It is possible to use electrode potentials to deduce, given appropriate E° values, reagents for the interconversion of vanadium between its oxidation states and to combine half-cells to give an overall equation for a reaction. You need to know the colours of vanadium in its different oxidation states (see transition metal fact sheet).

Example: Will zinc reduce VO_2^+ to VO^{2+} ?

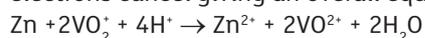
Write the equations with the more negative on to



The reaction goes anticlockwise,
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$



Add this equation to the zinc equation and the electrons cancel giving an overall equation:



The emf is +1.76 V

Limitations of predictions using standard potentials

a) In terms of Kinetics

Electrode potentials can be used effectively to predict whether or not a given reaction will take place, but they give no indication as to how fast a reaction will proceed. In many cases E°_{cell} is positive but no apparent reaction occurs. This is because the reactants are kinetically stable; the reaction has a high activation energy so is very slow at room temperature

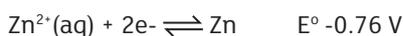
The reactions in a cell are equilibrium reactions and if the conditions are changed then the position of equilibrium changes and the electrode potential will change.

b) In terms of concentration

Standard potentials are measured at 298 K, 100 kPa pressure and using 1.0 mol dm⁻³ solutions.

It is possible to predict how the electrode potential will vary if non-standard conditions are used by using Le Chatelier's Principle.

The half equation for the zinc half-cell is



the concentration of zinc ions (oxidizing agent) is increased then the equilibrium opposes the change by moving right, removing electrons and so the electrode potential will become less negative since the reduction of zinc ions is more likely to occur.

A change in the electrode potential resulting from concentration changes means that predictions made on the basis of the standard values may not be valid.

Thus if a reaction is expected to take place but is found not to, there are two possible reasons:

- the solutions are too dilute (ie conditions are non-standard)
- the reaction is very slow (ie reactants are kinetically stable)

If a reaction is not expected to take place but does take place, then it is because the conditions are non-standard (ie the solutions are concentrated).

Commercial applications of electrochemical cells

Electrochemical cells are used as cells and batteries. Cells can be divided into three types as shown in the table.

	Non-rechargeable cells	Rechargeable cells.	Fuel cells
Description	These provide electrical energy until the chemicals have reacted and used up. The cell is then flat and cannot be used again.	The chemicals in the cell react providing electrical energy. The cell reaction can be reversed during recharging – the chemicals are regenerated and the cell can be used again.	The cell uses external supplies of a fuel and an oxidant which are consumed and need to be provided continuously
Examples	Dry cell alkaline batteries	Lithium ion cell used in cameras, laptops and mobile phones and lead acid batteries in cars	Alkaline oxygen-hydrogen fuel cell
Environmental issues associated with cells	Advantages: non-toxic materials. Disadvantages: Cannot be recycled, they may leak	Disadvantages: Lead needs to be recycled to avoid environmental contamination,	Advantages: water is the only by product – no carbon dioxide or greenhouse gases. More efficient than combustion engines, so less fuel consumption Disadvantages - Fuel cells use toxic chemicals in their manufacture; also energy is used in making the hydrogen -one strategy which is better for the environment is to use renewable energy in the production of hydrogen.

Lithium ion cell

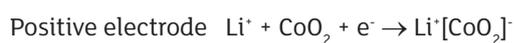
The cell has three components: a positive electrode usually made from lithium-cobalt oxide, and a negative electrode made from graphite and an electrolyte in between them.

When the battery is charging up, and absorbing power, the lithium-cobalt oxide positive electrode gives up some of its lithium ions, which move through the electrolyte to the negative, graphite electrode and remain there. The battery takes in and stores energy during this process. Electrons also flow from the positive electrode to the negative electrode, but take the longer path around the outer circuit. The electrons and ions combine at the negative electrode and deposit lithium there. When no more ions will flow, the battery is fully charged and ready to use.

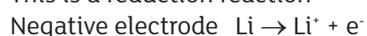
During discharging, the lithium ions flow back through the electrolyte from the negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode through the outer circuit, powering your laptop/phone etc. When the ions and electrons combine at the positive electrode, lithium is deposited there. When all the ions have moved back, the battery is fully discharged and needs charging up again.

In both cases, electrons flow in the opposite direction to the ions around the outer circuit.

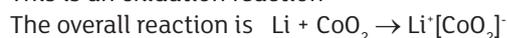
In this cell the half equations are:



This is a reduction reaction



This is an oxidation reaction



Fuel cells



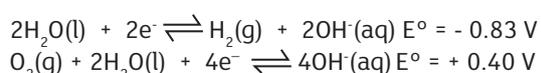
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This London bus is powered by a hydrogen fuel cell.

A fuel cell uses the energy from the reaction of a fuel with oxygen to generate a voltage. The fuel is usually hydrogen. As long as there is a supply of the fuel and oxygen into the cell, replacing those used up, the cell keeps working. Unlike a battery they do not store energy.

Alkaline hydrogen-oxygen fuel cell

In the alkaline hydrogen-oxygen fuel cell the electrolyte is an alkaline solution such as potassium hydroxide, located in the centre of the cell. It allows ions and molecules to move through it. Oxygen is the oxidising agent (gets reduced) and hydrogen fuel (gets oxidised) is the reducing agent. The redox equilibria in the cell are :



The top electrode of these two has the more negative value and is the negative electrode

$$E^\ominus = E^\ominus (\text{positive electrode}) - E^\ominus (\text{negative electrode}) \\ = -0.40 - (-0.83) = +1.23\text{V}$$

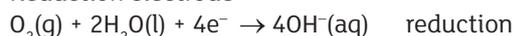
The half equations for the electrodes are :

Oxidation electrode



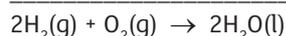
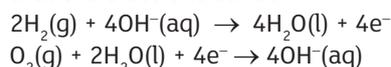
Hydrogen gas loses electrons to form hydrogen ions which immediately combine with the hydroxide ions in the electrolyte to form water.

Reduction electrode



Oxygen molecules gain electrons and in combination with water molecules are reduced to hydroxide ions.

The overall equation for the reaction in the fuel and is obtained by multiplying the first equation by two and then by adding equations 1 and 2 together so that the electrons cancel.



Water is the only product of the reaction; water is not polluting

The reaction is very efficient and the electrical energy supplied can be used to power cars and buses. The platinum catalyst is expensive.



Revision Questions

- 1 Standard electrode potentials for two half-cells are shown below:

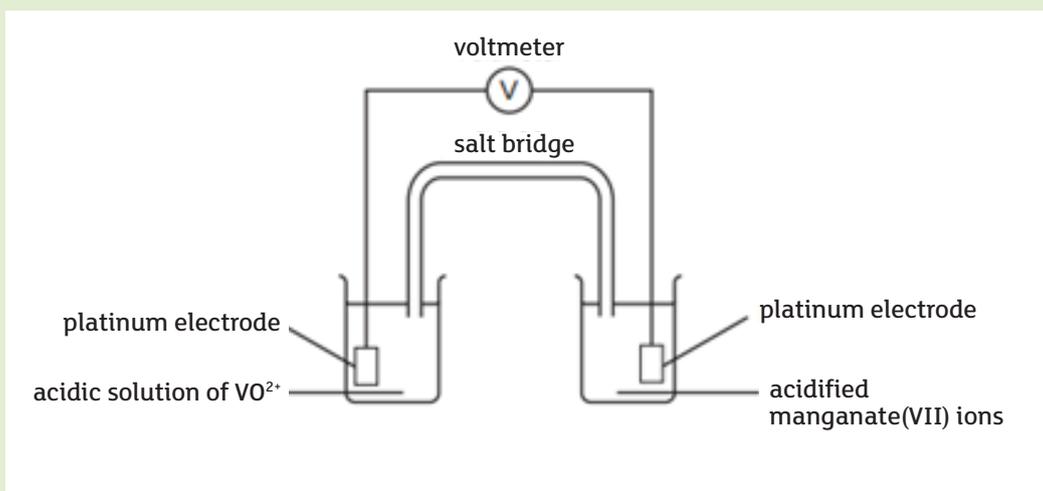
Half-cell	Standard electrode potential/V
$\text{Ce}^{3+}(\text{aq}) + 3\text{e}^{-} \rightleftharpoons \text{Ce}(\text{s})$	-2.30
$\text{Th}^{4+}(\text{aq}) + 4\text{e}^{-} \rightleftharpoons \text{Th}(\text{s})$	-1.90

Which one of the following species is the most powerful reducing agent?

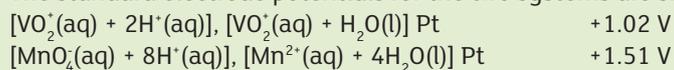
- A $\text{Ce}^{3+}(\text{aq})$
 B $\text{Ce}(\text{s})$
 C $\text{Th}^{4+}(\text{aq})$
 D $\text{Th}(\text{s})$

[1]

- 2 The cell shown below was set up to investigate the reaction between an acidic solution of VO^{2+} ions, with acidified manganate(VII) ions.



The standard electrode potentials for the two systems are shown below:



- a) Explain in which direction the electrons flow in the external circuit.

.....
 [2]

- b) The reaction taking place is a redox reaction. Explain, by referring to oxidation numbers in the cell, what is meant by the term **redox**.

.....

 [2]



Revision Questions

- 2 c) Write the equations for the reactions taking place in the two half-cells and combine them to obtain the overall equation.

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.....
.....
..... [3]

- d) i) Describe the colour change in the VO^{2+} half-cell.

..... [2]

- ii) Describe the colour change in the manganate(VII) half-cell.

..... [2]

- e) Calculate the reading that will be observed on the voltmeter.

..... [2]

- f) Explain the purpose of the salt bridge and how it works.

.....
..... [2]

- g) The electrode potentials of the half-cells are measured using a hydrogen electrode. Describe a hydrogen electrode and state the conditions under which it operates.

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.....
.....
..... [4]



Revision Questions

- 3 i) Write equations for the changes that take place at each electrode for an alkaline hydrogen – oxygen fuel cell

Hydrogen electrode

Oxygen electrode [2]

- ii) Write the overall equation for the reaction in the cell.

[1]

- iii) What is the emf of the cell?

[1]

- iv) State one difference between a fuel cell and a rechargeable cell.

[1]

