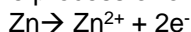


5.2.3 Electrode Potentials and Fuel Cells

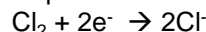
Redox

oxidation is the process of **electron loss**:



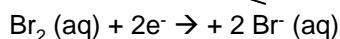
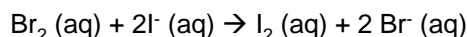
It involves an increase in oxidation number

reduction is the process of **electron gain**:



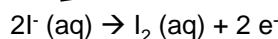
It involves a decrease in oxidation number

Redox equations and half equations



Br has reduced as it has gained electrons

A reduction half equation only shows the parts of a chemical equation involved in reduction
The electrons are on the left



I has oxidised as it has lost electrons

An oxidation half equation only shows the parts of a chemical equation involved in oxidation
The electrons are on the right

reducing agents are electron donors

oxidising agents are electron acceptors

The oxidising agent is Bromine water. It is an **electron acceptor**

The reducing agent is the iodide ion. It is an **electron donor**

An oxidising agent (or oxidant) is the species that causes another element to oxidise. It is itself reduced in the reaction

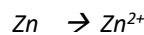
A reducing agent (or reductant) is the species that causes another element reduce. It is itself oxidised in the reaction.

When naming oxidising and reducing agents always refer to full name of substance and not just name of element

Balancing Redox equations

Writing half equations

1. Work out oxidation numbers for element being oxidised/ reduced



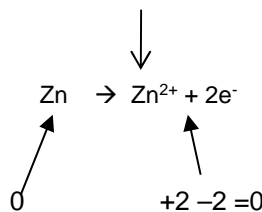
Zn changes from 0 to +2

2. Add electrons equal to the change in oxidation number

For reduction add e's to reactants

For oxidation add e's to products

3. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side



More complex Half equations

If the substance that is being oxidised or reduced contains a varying amount of O (eg $\text{MnO}_4^{-} \rightarrow \text{Mn}^{2+}$) then the half equations are balanced by adding H^{+} , OH^{-} ions and H_2O .

In acidic conditions use H^{+} and H_2O

Example: Write the half equation for the change $\text{MnO}_4^{-} \rightarrow \text{Mn}^{2+}$

1. Balance the change in O.N. with electrons

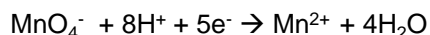
Mn changes from +7 to +2
Add 5 electrons to reactants



2. Add H_2O in products to balance O's in MnO_4^{-}



3. Add H^{+} in reactants to balance H's in H_2O



4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

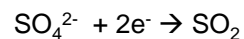
$$-1 + 8 - 5 = +2$$

$$+2$$

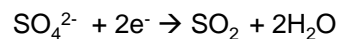
Example: Write the half equation for the change $\text{SO}_4^{2-} \rightarrow \text{SO}_2$

1. Balance the change in O.N. with electrons

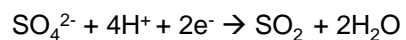
*S changes from +6 to +4
Add 2 electrons to reactants*



2. Add H_2O in products to balance O's in SO_4^{2-}



3. Add H^+ in reactants to balance H's in H_2O



4. check to see that the sum of the charges on the reactant side equals the sum of the charges on the product side

$$-4 + 4 = 0$$

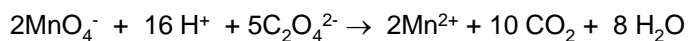
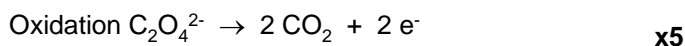
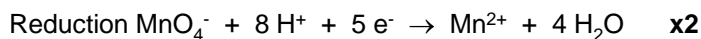
$$0$$

Combining half equations

To make a full redox equation combine a reduction half equation with a oxidation half equation

To combine two half equations there must be equal numbers of electrons in the two half equations so that the electrons cancel out

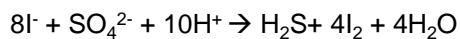
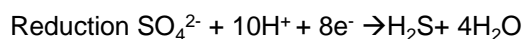
Example 1



Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

Example 2



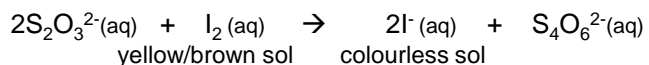
Multiply the half equations to get equal electrons

Add half equations together and cancel electrons

Redox titrations

Thiosulfate redox titration

The redox titration between I₂ and thiosulfate S₂O₃²⁻ is a common exercise.

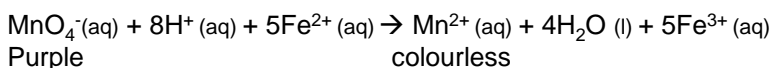


A starch indicator is added near the end point when the iodine fades a pale yellow to emphasise it.

With starch added the colour change is from blue/black to colourless

Manganate redox titration

The redox titration between Fe²⁺ with MnO₄⁻ (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product



The purple colour of manganate can make it difficult to see the bottom of the meniscus in the burette.

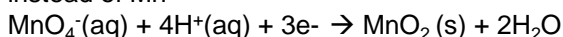
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.
Colourless → purple

Choosing correct acid for manganate titrations.

The acid is needed to supply the 8H⁺ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulfuric acid** for manganate titration

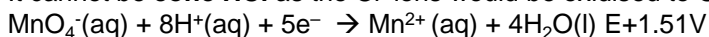
Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO₂ will be produced instead of Mn²⁺



The brown MnO₂ will mask the colour change and lead to a greater (inaccurate) volume of manganate being used in the titration

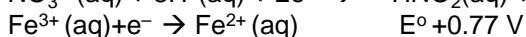
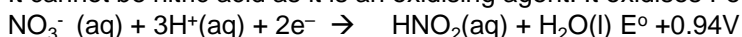
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H⁺)

It cannot be **conc HCl** as the Cl⁻ ions would be oxidised to Cl₂ by MnO₄⁻ as the E^o MnO₄⁻/Mn²⁺ > E^o Cl₂/Cl⁻



This would lead to a greater volume of manganate being used and poisonous Cl₂ being produced

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe²⁺ to Fe³⁺ as E^o NO₃⁻/HNO₂ > E^o Fe³⁺/Fe²⁺



This would lead to a smaller volume of manganate being used

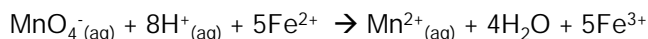
be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.

Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm³ acid. The solution formed contains Fe(II) ions.

10cm³ portions of this solution are titrated with potassium manganate (VII) solution of 0.02M. 9.80cm³ of KMnO₄ were needed to react with the solution containing the iron.

What is the percentage of Iron by mass in the nail?



Step1 : find moles of KMnO₄

moles = conc x vol

$$0.02 \times 9.8/1000$$

$$= 1.96 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles Fe²⁺ in 10cm³

$$= \text{moles of KMnO}_4 \times 5$$

$$= 9.8 \times 10^{-4} \text{ mol}$$

Step 3 : find moles Fe²⁺ in 100cm³

$$= 9.8 \times 10^{-4} \text{ mol} \times 10$$

$$= 9.8 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of Fe in 9.8x10⁻³ mol

$$\text{mass} = \text{moles} \times \text{RAM} = 9.8 \times 10^{-3} \times 55.8 = 0.547\text{g}$$

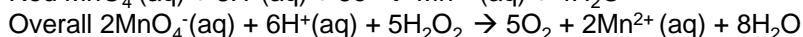
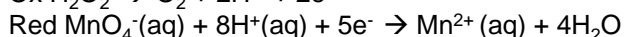
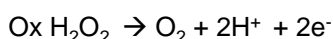
Step 5 ; find % mass

$$\% \text{mass} = 0.547/2.41 \times 100$$

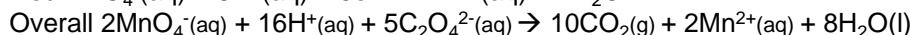
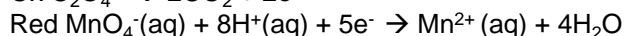
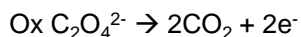
$$= 22.6\%$$

Other useful manganate titrations

With hydrogen peroxide

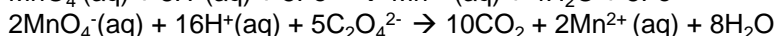
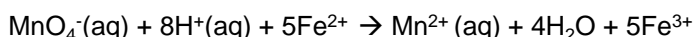


With ethanedioate

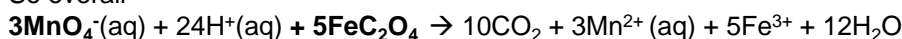


The reaction between MnO₄⁻ and C₂O₄²⁻ is slow to begin with (as the reaction is between two negative ions) To do as a titration the conical flask can be heated to 60° C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe²⁺ and the C₂O₄²⁻ react with the MnO₄⁻
1MnO₄⁻ reacts with 5Fe²⁺ and 2 MnO₄⁻ reacts with 5C₂O₄²⁻



So overall



So overall the ratio is 3 MnO₄⁻ to 5 FeC₂O₄

A 1.412 g sample of impure FeC₂O₄.2H₂O was dissolved in an excess of dilute sulfuric acid and made up to 250 cm³ of solution. 25.0 cm³ of this solution decolourised 23.45 cm³ of a 0.0189 mol dm⁻³ solution of potassium manganate(VII).

What is the the percentage by mass of FeC₂O₄.2H₂O in the original sample?

Step1 : find moles of KMnO₄

moles = conc x vol

$$0.0189 \times 23.45/1000$$

$$= 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles FeC₂O₄.2H₂O in 25cm³

$$= \text{moles of KMnO}_4 \times 5/3 \text{ (see above for ratio)}$$

$$= 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles FeC₂O₄.2H₂O in 250 cm³

$$= 7.39 \times 10^{-4} \text{ mol} \times 10$$

$$= 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of FeC₂O₄.2H₂O in 7.39x10⁻³ mol

$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33\text{g}$$

Step 5 ; find % mass

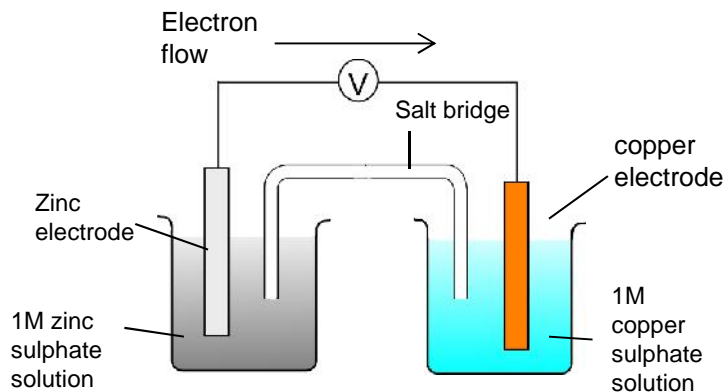
$$\% \text{mass} = 1.33/1.412 \times 100$$

$$= 94.1\%$$

Electrode Potentials

Electrochemical cells

- A cell has two half-cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts an electrode) and a solution of a compound containing that metal (eg Cu and CuSO_4).
- These two half cells will produce a small voltage if connected into a circuit. (i.e. become a Battery or cell).



Why does a voltage form?

In the cell pictured above

When connected together the zinc half-cell has more of a tendency to oxidise to the Zn^{2+} ion and release electrons than the copper half-cell. ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$)

More electrons will therefore build up on the zinc electrode than the copper electrode.

A potential difference is created between the two electrodes.

The zinc strip is the negative terminal and the copper strip is the positive terminal.

This potential difference is measured with a high resistance voltmeter, and is given the symbol **E**. The E for the above cell is $E = +1.1\text{V}$.

Why use a High resistance voltmeter?

The voltmeter needs to be of very high resistance to stop the current from flowing in the circuit. In this state it is possible to measure the maximum possible potential difference (E).

The reactions will not be occurring because the very high resistance voltmeter stops the current from flowing.

Salt Bridge

The salt bridge is used to connect up the circuit. The **free moving ions** conduct the charge.

A salt bridge is usually made from a piece of filter paper (or material) soaked in a salt solution, usually **Potassium Nitrate**.

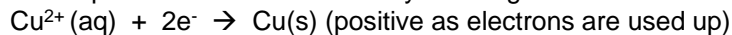
The salt should be **unreactive with the electrodes and electrode solutions**. E.g. potassium chloride would not be suitable for copper systems as chloride ions can form complexes with copper ions.

A wire is not used because the metal wire would set up its own electrode system with the solutions.

What happens if current is allowed to flow?

If the voltmeter is removed and replaced with a bulb or if the circuit is short circuited, a current flows. The reactions will then occur separately at each electrode. The voltage will fall to zero as the reactants are used up.

The most positive electrode will always undergo reduction.



The most negative electrode will always undergo oxidation.



Measuring the electrode potential of a cell

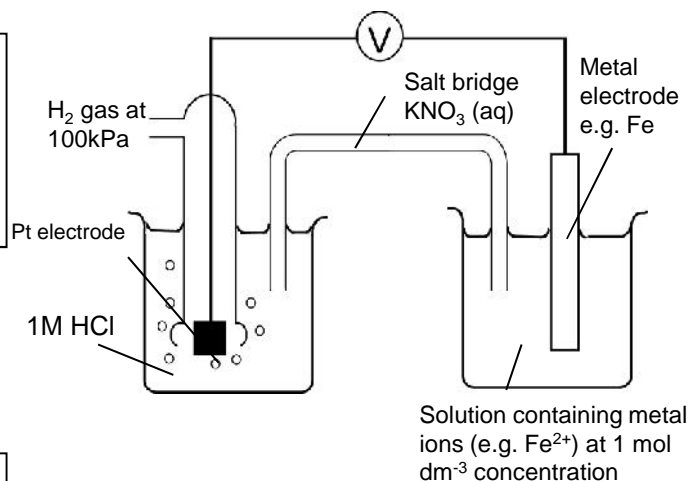
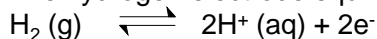
- It is not possible to measure **the** absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.
- To measure it, it has to be connected to another half-cell of known potential, and the potential difference between the two half-cells measured.
- by convention we can assign a relative potential to each electrode by linking it to a reference electrode (hydrogen electrode), which is given a potential of zero Volts

The standard hydrogen electrode

The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.

The **standard hydrogen electrode (SHE)** is assigned the potential of 0 volts.

The hydrogen electrode equilibrium is:



Solution containing metal ions (e.g. Fe^{2+}) at 1 mol dm^{-3} concentration

Components of a standard hydrogen electrode.

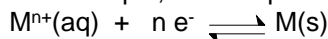
To make the electrode a standard reference electrode some conditions apply:

1. **Hydrogen gas at pressure of 100kPa**
2. Solution containing the **hydrogen ion at 1 mol dm^{-3}** (solution is usually 1 mol dm^{-3} HCl)
3. Temperature at **298K**

Because the equilibrium does not include a conducting metal surface a platinum wire is used which is coated in finely divided platinum. (The platinum black acts as a catalyst, because it is porous and can absorb the hydrogen gas.)

Standard conditions are needed because the position of the redox equilibrium will change with conditions.

For example, in the equilibrium:



an increase in the concentration of M^{n+} would move the equilibrium to the right, so making the potential more positive.

Secondary standards

The Standard Hydrogen Electrode is difficult to use, so often a different standard is used which is easier to use.

These other standards are themselves calibrated against the SHE.

This is known as using a **secondary standard** - i.e. a standard electrode that has been calibrated against the primary standard.

The common ones are:

| | |
|--------------------------|-----------------------|
| silver / silver chloride | $E = +0.22 \text{ V}$ |
| calomel electrode | $E = +0.27 \text{ V}$ |

Standard Electrode Potentials

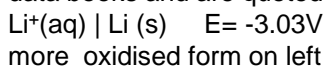
E^\ominus

When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the **standard electrode potential**.

The standard conditions are :

- All ion solutions at 1 mol dm^{-3}
- temperature 298K
- gases at 100kPa pressure
- No current flowing

Standard electrode potentials are found in data books and are quoted as

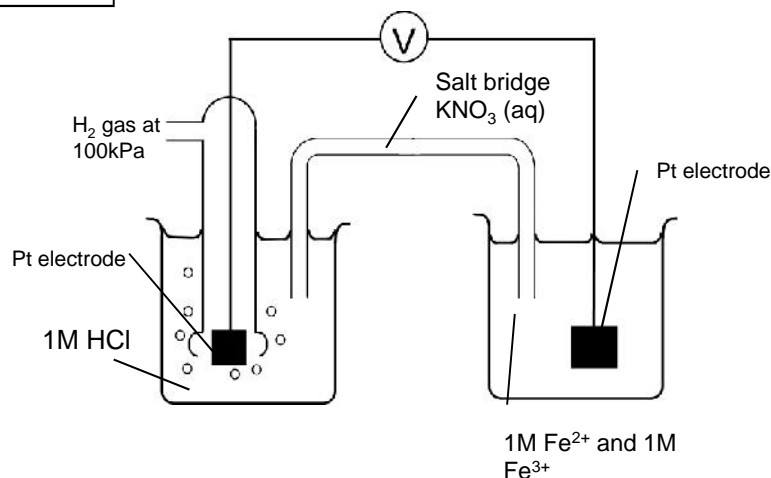


more oxidised form on left

They may also be quoted as half equations



but again the more oxidised form is on the left



Note: in the electrode system containing two solutions it is necessary to use a platinum electrode and **both** solutions must be of a 1M concentration.

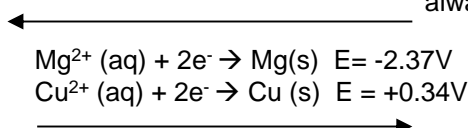
Using electrode potentials

The most useful application of electrode potentials is to show the direction of spontaneous change for redox reactions

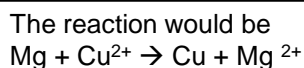
The easiest way to use electrode potentials is as follows:

For any two half equations

The more **negative** half cell will always **oxidise** (go backwards)

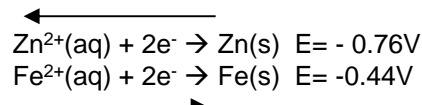


The more **positive** half cell will always **reduce** (go forwards)



If we want to work out the E_{cell} that corresponds to this spontaneous change then use **E_{cell} = E_{red} - E_{ox}**
 A spontaneous change will always have a positive E_{cell}

The most **negative** electrode will **oxidise** and go from **right to left**
 The half equation is therefore $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
 Electrons are given off (lost) and travel to positive electrode



The more **positive** electrode will **reduce** and go from **left to right**
 $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe}(\text{s})$
 Electrons arrive at this electrode and are absorbed (gained)

To get the full equation of the reaction add the two half reactions together, cancelling out the electrons.
 $\text{Zn} + \text{Fe}^{2+} \rightarrow \text{Fe} + \text{Zn}^{2+}$

Using series of standard electrode potentials

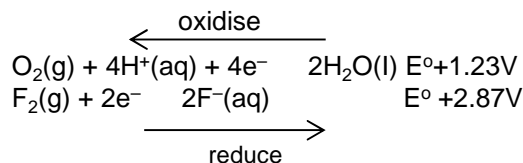
| | | |
|---|---|---|
| | oxidation \longleftarrow | |
| As more +ve increasing tendency for species on left to reduce , and act as oxidising agents | $\text{Li}^{+} + \text{e}^{-} \rightarrow \text{Li} \quad -3.03\text{V}$ $\text{Mn}^{2+} + 2\text{e}^{-} \rightarrow \text{Mn} \quad -1.19\text{V}$ $2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2 \quad 0\text{V}$ $\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag} \quad +0.8\text{V}$ $\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-} \quad +2.87$ | As more -ve increasing tendency for species on right to oxidise , and act as reducing agents |
| Most strong oxidising agents found here \uparrow | reduction \longrightarrow | Most strong reducing agents found here \downarrow |
| If we want to work out the E _{cell} from two standard electrode potentials then use E_{cell} = E_{red} - E_{ox} | | |

The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (ie the one with the lower oxidation number)
 The most **powerful oxidising agents** will be found at the most **positive** end of the series on the left (ie the one with the higher oxidation number)

Example 1

Use electrode data to explain why fluorine reacts with water.
Write an equation for the reaction that occurs.

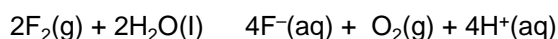
First apply idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

As $E^\circ \text{F}_2/\text{F}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, F_2 will oxidise H_2O to O_2

Equation

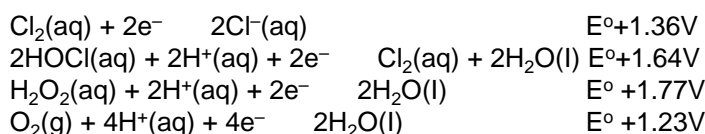


Can also work out E_{cell} and quote it as part of your answer
 $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = 2.87 - 1.23 = 1.64\text{V}$

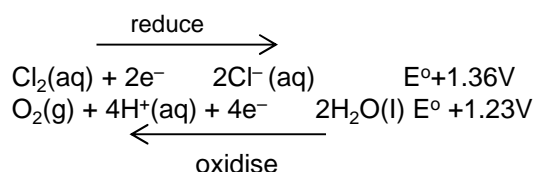
Remember to cancel out electrons in full equation

Example 2

Use data from the table to explain why chlorine should undergo a redox reaction with water. Write an equation for this reaction.



First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

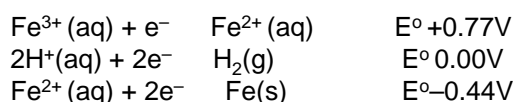
As $E^\circ \text{Cl}_2/\text{Cl}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, Cl_2 will oxidise H_2O to O_2

Equation

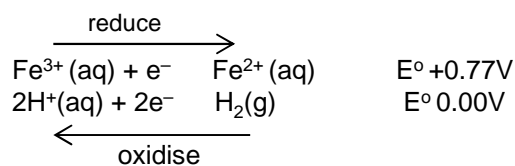


Example 3

Suggest what reactions occur, if any, when hydrogen gas is bubbled into a solution containing a mixture of iron(II) and iron(III) ions. Explain your answer.



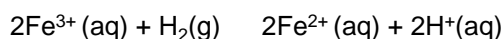
First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

Fe^{3+} will be reduced to Fe^{2+} by H_2 oxidising to H^+ because $E^\circ \text{Fe}^{3+}/\text{Fe}^{2+} > E^\circ \text{H}^+/\text{H}_2$

Equation

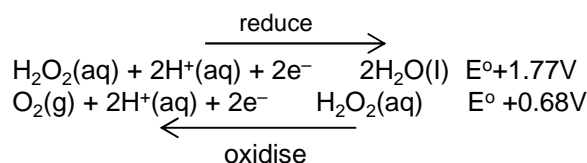


Example 4

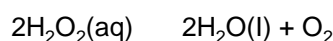
Use the half-equations to explain in terms of oxidation states what happens to hydrogen peroxide when it is reduced.

Explanation to write

As $E^\circ \text{H}_2\text{O}_2/\text{H}_2\text{O} > E^\circ \text{O}_2/\text{H}_2\text{O}_2$, H_2O_2 disproportionates from -1 oxidation state to 0 in O_2 and -2 in H_2O



Equation



Effect of conditions on cell e.m.f

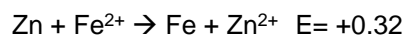
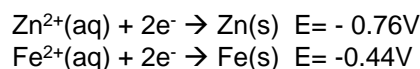
The effects of changing conditions on cell e.m.f can be made by applying Le Chatelier's principle

If current is allowed to flow, the cell reaction will occur and the emf will fall to zero as the reaction proceeds and the reactant concentrations drop

Effect of concentration on cell e.m.f

Looking at cell reaction is a straight forward application of Le Chatelier. So increasing concentration of 'reactants' would increase EMF and decreasing them would cause EMF to decrease

E.m.f. is a measure of how far from equilibrium the cell reaction lies. The more positive the e.m.f. the more likely the reaction is to occur.



Increasing the concentration of Fe^{2+} and decreasing the concentration of Zn^{2+} would cause E_{cell} to increase

Effect of temperature on cell e.m.f

Most E_{cell} are exothermic in the spontaneous direction so applying Le Chatelier to a temperature rise to these would result in a decrease in E_{cell}

If the E_{cell} is positive it indicates a reaction might occur, there is still a possibility, however, that the reaction will not occur or will occur so slowly that effectively it doesn't happen.
If the reaction has a high activation energy the reaction will not occur.

Explaining homogeneous catalysis using E values

The reaction between I^{-} and $\text{S}_2\text{O}_8^{2-}$ catalysed by Fe^{2+}
overall $\text{S}_2\text{O}_8^{2-} + 2\text{I}^{-} \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$

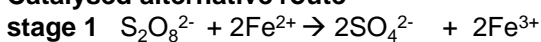


You do not need to learn the detail about this reaction

The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

For a substance to act as a homogeneous catalyst its electrode potential must lie in between the electrode potentials of the two reactants, so it can first reduce the reactant with the more positive electrode potential and then in the second step oxidize the reactant with the more negative electrode potential

Catalysed alternative route



Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

Cells

You should be able to work out E_{cell} for given half reactions.

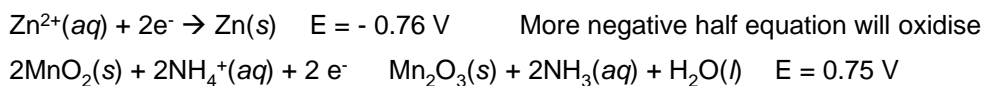
Electrochemical cells can be used as a commercial source of electrical energy
Cells can be non-rechargeable (irreversible), rechargeable and fuel cells

You do not need to learn the details of these cells. Relevant cell information will be given. You should be able to convert between standard electrode potential half cells, full cell reactions and be able to calculate potentials from given data

Example primary non rechargeable cells

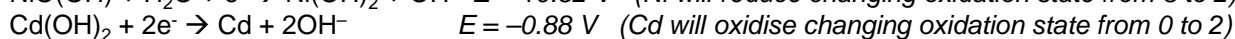
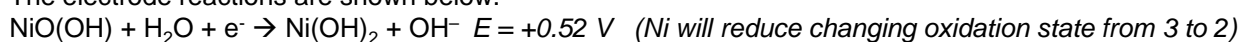
Cells are non-rechargeable when the reactions that occur with in them are non-reversible

Dry Cell



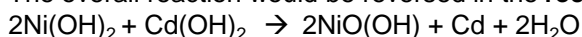
Example secondary Nickel–cadmium cells are used to power electrical equipment such as drills and shavers. They are rechargeable cells.

The electrode reactions are shown below.



$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = +0.52 - (-0.88) = +1.40 \text{ V}$$

The overall reaction would be reversed in the **recharging** state



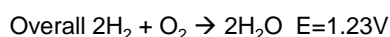
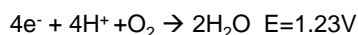
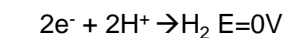
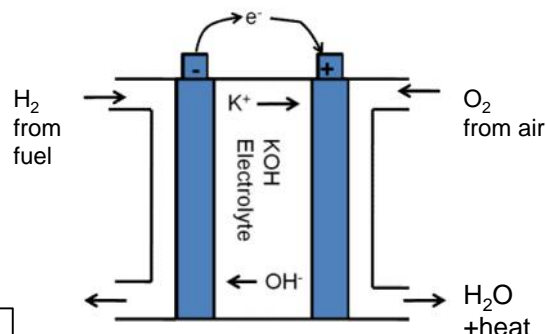
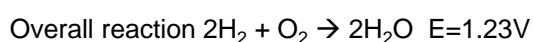
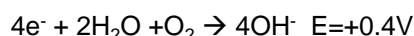
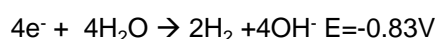
Fuel cell

A fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage

Scientists in the car industry are developing fuel cell vehicles, fuelled by:

- hydrogen gas,
- hydrogen-rich fuels;

Hydrogen Fuel cell (potassium hydroxide electrolyte)



In acidic conditions these are the electrode potentials. The E_{cell} is the same as alkaline conditions as the overall equation is the same

Using standard conditions: The rate is too slow to produce an appreciable current.

Higher temperatures are therefore used to increase rate but the reaction is exothermic so by applying Le Chatelier would mean the emf falls.

A higher pressure can help counteract this

Fuel cells will maintain a **constant voltage** over time as they are continuously fed with fresh O₂ and H₂ so maintaining constant concentration of reactants. This differs from ordinary cells where the voltage drops over time as the reactant concentrations drop

Advantages of Fuel cells over conventional petrol or diesel-powered vehicles

- less pollution and less CO₂. (Pure hydrogen emits only water whilst hydrogen-rich fuels produce only small amounts of air pollutants and CO₂).
- greater efficiency;

Limitations of hydrogen fuel cells

- storing and transporting hydrogen, in terms of safety, feasibility of a pressurised liquid and a limited life cycle of a solid 'adsorber' or 'absorber'
- limited lifetime (requiring regular replacement and disposal) and high production costs,
- use of toxic chemicals in their production