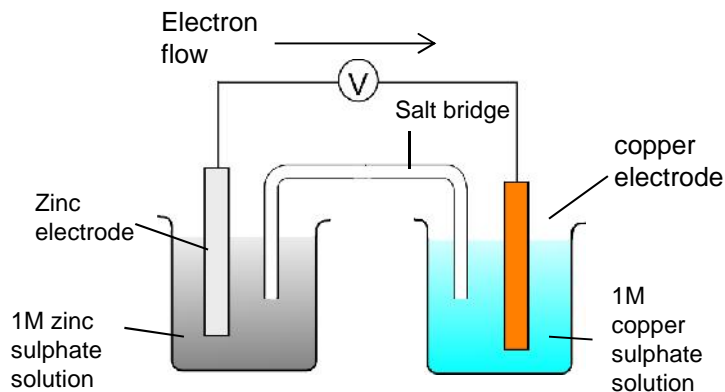


16. Redox Equilibria

Electrochemical cells

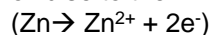
- A cell has two half-cells.
- The two half cells have to be connected with a salt bridge.
- Simple half cells will consist of a metal (acts an electrode) and a solution of a compound containing that metal (eg Cu and CuSO_4).
- These two half cells will produce a small voltage if connected into a circuit.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



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**.

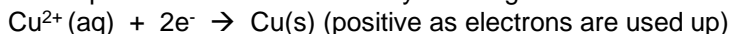
The salt should be **unreactive with the electrodes and electrode solutions**. E.g. potassium chloride would not be suitable for copper systems as Chloride ions can form complexes with copper ions.

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.

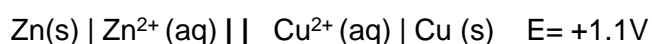


The most negative electrode will always undergo oxidation.



Cell Diagrams

Electrochemical cells can be represented by a **cell diagram**:



Most oxidised form is put next to the double line

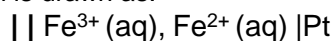
- The solid vertical line represents the boundary between **phases** e.g. solid (electrode) and solution (electrolyte)
- The double line represents the **salt bridge** between the two half cells
- the voltage produced is indicated
- the more positive half cell is written on the right if possible (but this is not essential)

Systems that do not include metals.

If a system does not include a metal that can act as an electrode, then a **platinum electrode** must be used and included in the cell diagram. It provides a **conducting surface for electron transfer**. A platinum electrode is used because it is **unreactive** and **can conduct electricity**.

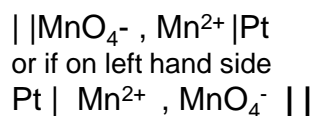
e.g. for $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$ there is no solid conducting surface, a Pt electrode must be used.

The cell diagram is drawn as:

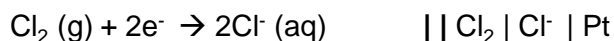
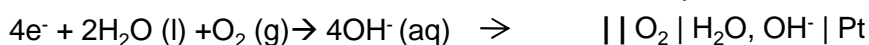


Still with more oxidised form near double line
A comma separates the oxidised from the reduced species.

If the system contains several species
e.g. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
then in the cell diagram the balancing numbers, H^+ ions and H_2O can be left out.



If a half equation has several physical states then the solid vertical line should be used between each different state boundary.



As the phase line also separates the oxidised and reduced terms a comma is not necessary here.

Measuring the electrode potential of a cell

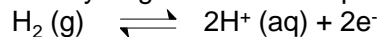
- It is not possible to measure **the** absolute potential of a half electrode on its own. It is only possible to measure the potential difference between two electrodes.
- To measure it, it has to be connected to another half-cell of known potential, and the potential difference between the two half-cells 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

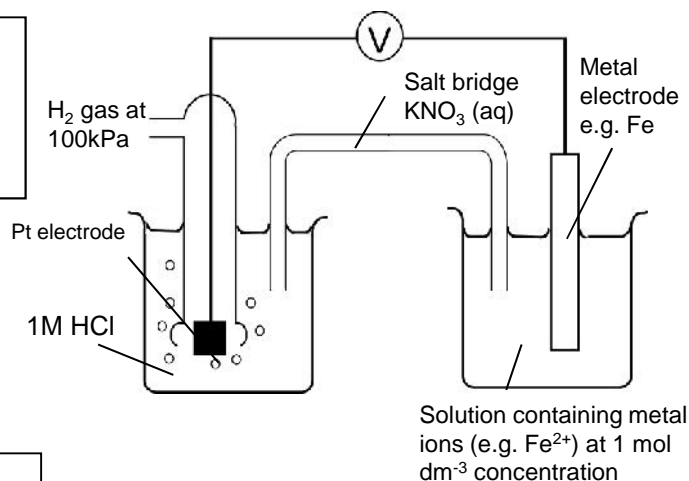
The potential of all electrodes are measured by comparing their potential to that of the standard hydrogen electrode.

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

The hydrogen electrode equilibrium is:



In a cell diagram the hydrogen electrode is represented by: $\text{Pt} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$



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

Components of a standard hydrogen electrode.

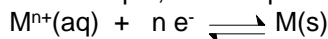
To make the electrode a standard reference electrode some conditions apply:

1. **Hydrogen gas at pressure of 100 kPa**
2. Solution containing the **hydrogen ion at 1.00 mol dm^{-3}** (solution is usually 1M 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

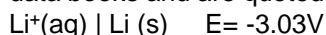


When an electrode system is connected to the hydrogen electrode system, and standard conditions apply the potential difference measured is called the standard electrode potential.

The standard conditions are :

- All ion solutions at **1.00 mol dm^{-3}**
- temperature 298K
- gases at 100kPa pressure
- No current flowing

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

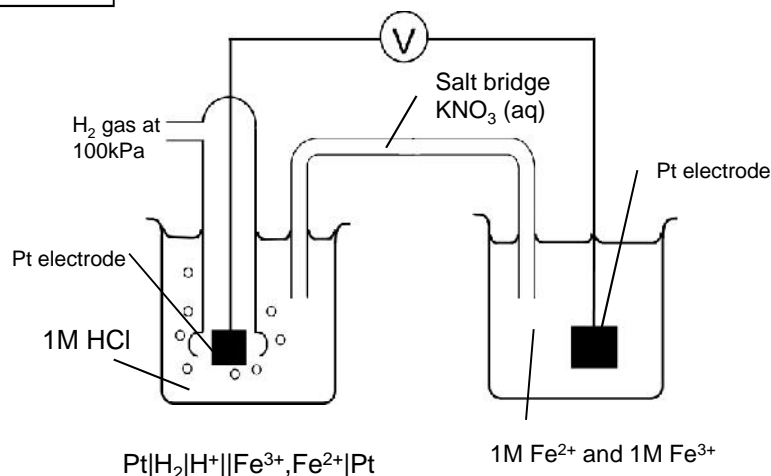


more oxidised form on left

They may also be quoted as half equations



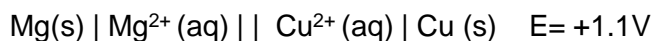
but again the more oxidised form is on the left



1M Fe^{2+} and 1M Fe^{3+}

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.

Calculating the EMF of a cell



In order to calculate the E_{cell} , we must use '**standard electrode potentials**' for the half cells.

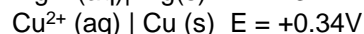
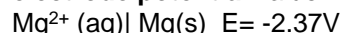
use the equation

$$E_{\text{cell}} = E_{\text{r}} - E_{\text{l}}$$

For the cell diagram above

$$E_{\text{cell}} = 0.34 - (-2.37) \\ = +2.71\text{V}$$

Each half cell has a **standard electrode potential** value



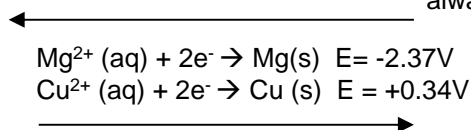
Using electrode potentials

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

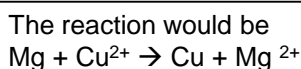
The easiest way to use electrode potentials is as follows:

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

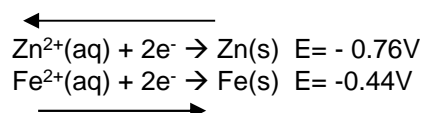
$$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$$

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 $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

Electrons are given off (lost) and travel to positive electrode

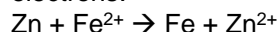


The more **positive** electrode will **reduce** and go from **left to right**

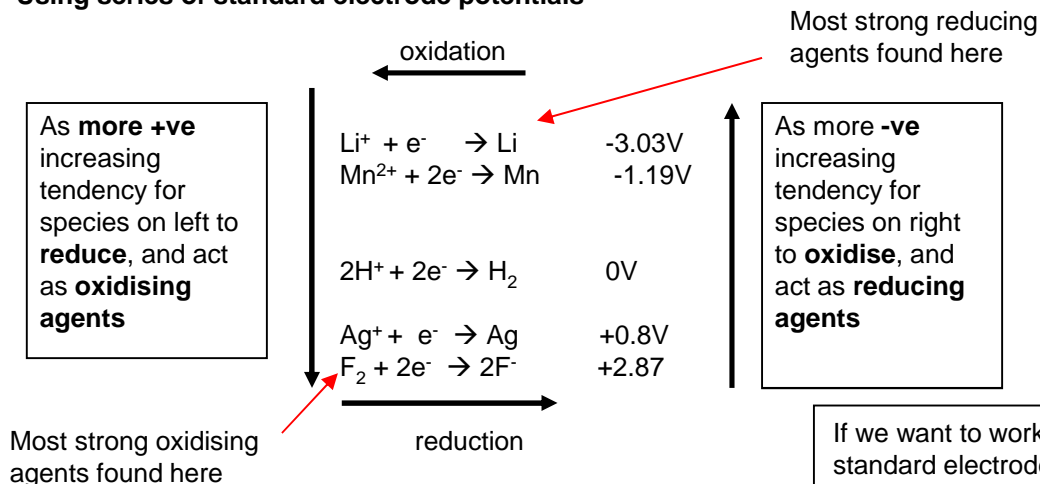
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Fe(s)}$

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.



Using series of standard electrode potentials



If we want to work out the E_{cell} from two standard electrode potentials then use $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$

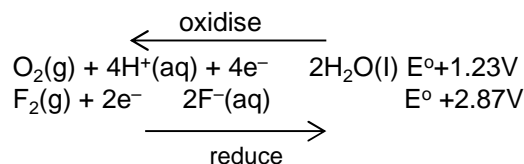
The most **powerful reducing agents** will be found at the most **negative** end of the series on the right (ie the one with the lower oxidation number)

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)

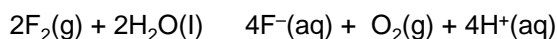


Explanation to write

As $E^\circ \text{F}_2/\text{F}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, and E_{cell} is a positive value of +1.64V, F_2 will oxidise H_2O to O_2

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

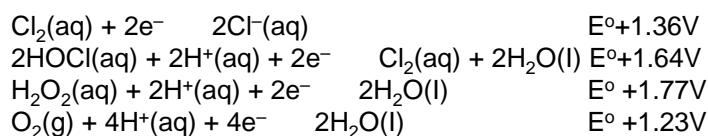
Equation



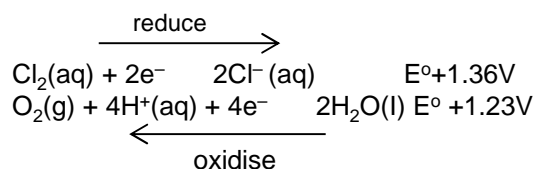
Remember to cancel out electrons in full equation

Example 2

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



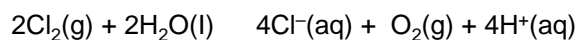
First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

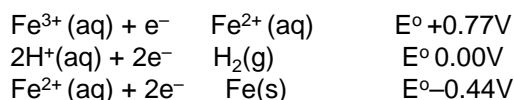
As $E^\circ \text{Cl}_2/\text{Cl}^- > E^\circ \text{O}_2/\text{H}_2\text{O}$, and E_{cell} is a positive value of +0.13V, Cl_2 will oxidise H_2O to O_2

Equation

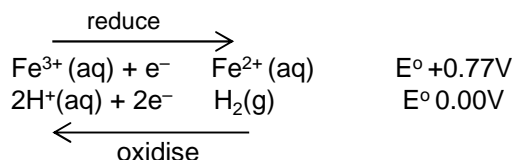


Example 3

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.



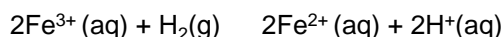
First select relevant half equations by considering the E° values and applying the idea that more positive E° will reduce (go forward) and more negative E° will oxidise (go backwards)



Explanation to write

Fe^{3+} will be reduced to Fe^{2+} by H_2 oxidising to H^+ because $E^\circ \text{Fe}^{3+}/\text{Fe}^{2+} > E^\circ \text{H}^+/\text{H}_2$ and E_{cell} is a positive value of +0.77V

Equation

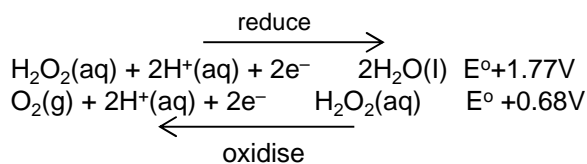


Example 4 Disproportionation

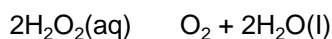
Use the half-equations to explain in terms of oxidation states what happens to hydrogen peroxide when it is reduced.

Explanation to write

As $E^\circ \text{H}_2\text{O}_2/\text{H}_2\text{O} > E^\circ \text{O}_2/\text{H}_2\text{O}_2$ and E_{cell} is a positive value of +1.09V, H_2O_2 disproportionates from -1 oxidation state to 0 in O_2 and -2 in H_2O

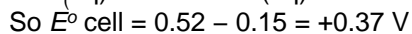
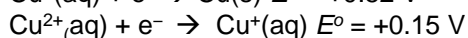


Equation



Disproportionation of copper(I) iodide

Copper(I) iodide when reacting with sulphuric acid will disproportionate to Cu^{2+} and Cu metal



As $E^\circ_{\text{Cu}^+/\text{Cu}} > E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}$ and E_{cell} has a positive value of +0.37V, Cu^+ disproportionates from +1 oxidation state to 0 in Cu and +2 in Cu^{2+}

E_{cell} is directly proportional to the total entropy change and to $\ln K$ (where K is equilibrium constant) for a reaction

A positive E_{cell} will lead to a positive total entropy change

Effect of conditions on Cell voltage E_{cell}

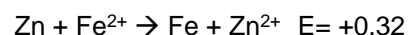
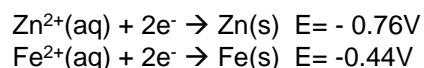
The effects of changing conditions on E_{cell} can be made by applying Le Chatelier's principle.

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

Effect of concentration on E_{cell}

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

E_{cell} is a measure of how far from equilibrium the cell reaction lies. The more positive the E_{cell} 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 E_{cell}

Most cells are exothermic in the spontaneous direction so applying Le Chatelier to a temperature rise to these would result in a decrease in E_{cell} because the equilibrium reactions would shift backwards.

If the E_{cell} 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 does not happen.

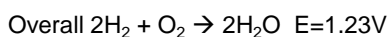
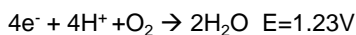
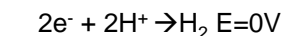
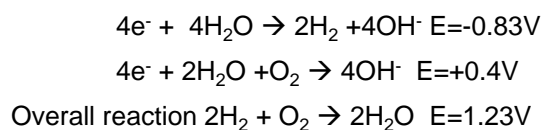
If the reaction has a high activation energy the reaction will not occur.

Also if the reaction is carried out at non-standard conditions the E_{cell} using standard conditions may deviate

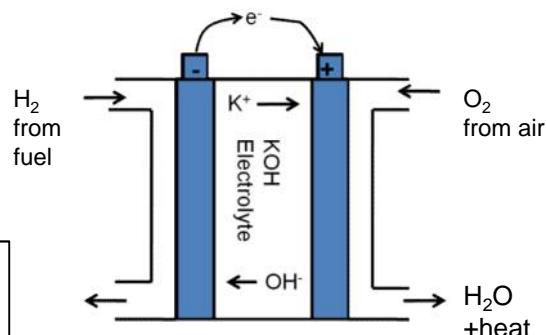
Fuel cell

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

Hydrogen Fuel cell (potassium hydroxide electrolyte)



In acidic conditions these are the electrode potentials. The Ecell 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 O_2 and H_2 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

- (i) less pollution and less CO_2 . (Pure hydrogen emits only water whilst hydrogen-rich fuels produce only small amounts of air pollutants and CO_2 .)
- (ii) greater efficiency;

Limitations of hydrogen fuel cells

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

Hydrogen is readily available by the electrolysis of water, but this is expensive. To be a green fuel the electricity needed would need to be produced from renewable resources

Hydrogen can be stored in fuel cells

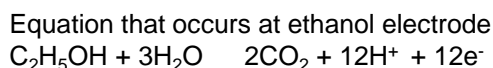
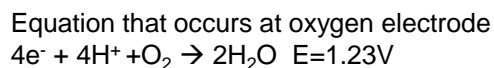
- (i) as a liquid under pressure,
- (ii) adsorbed on the surface of a solid material,
- (iii) absorbed within a solid material;

Ethanol fuel cells

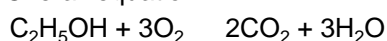
Ethanol fuel cells have also been developed. Compared to hydrogen fuel cells they have certain advantages including. Ethanol can be made from renewable sources in a carbon neutral way

Raw materials to produce ethanol by fermentation are abundant

Ethanol is less explosive and easier to store than hydrogen. New petrol stations would not be required as ethanol is a liquid fuel.



Overall equation

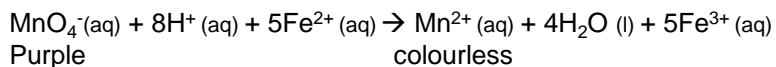


Methanol can also be used in fuel cells

Redox titrations

Manganate redox titration

The redox titration between Fe^{2+} with MnO_4^- (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 meniscus in the burette

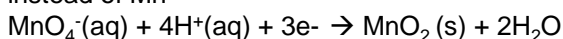
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour
Colourless \rightarrow purple

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 sulphuric acid** for manganate titration

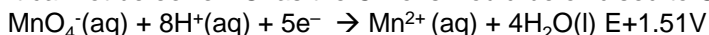
Insufficient volumes of sulphuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+}



The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of Manganate being used in the titration

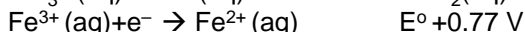
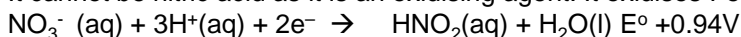
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H^+)

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$



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.

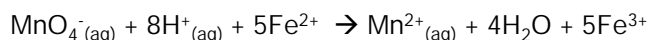
Manganate titration example

A 2.41g nail made from an alloy containing iron is dissolved in 100cm^3 acid. The solution formed contains $\text{Fe}(\text{II})$ ions.

10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02M.

9.80cm^3 of KMnO_4 were needed to react with the solution containing the iron.

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



Step 1 : find moles of KMnO_4

moles = conc x vol

$$0.02 \times 9.8/1000$$

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

Step 2 : using balanced equation find moles Fe^{2+} in 10cm^3

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

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

Step 3 : find moles Fe^{2+} in 100cm^3

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

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

Step 4 : find mass of Fe in $9.8 \times 10^{-3} \text{ mol}$

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

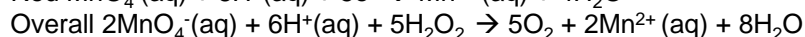
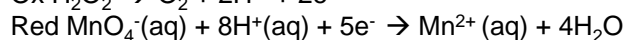
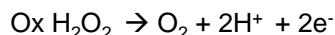
Step 5 ; find % mass

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

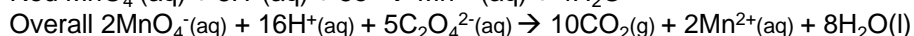
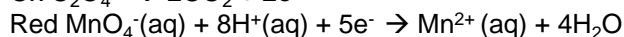
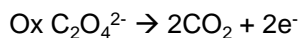
$$= 22.6\%$$

Other useful manganate titrations

With hydrogen peroxide

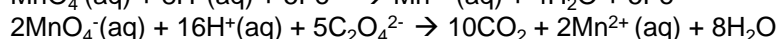
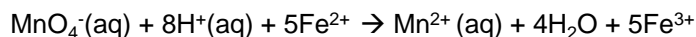


With ethanedioate

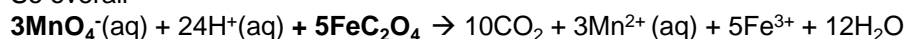


The reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is slow to begin with (as the reaction is between two negative ions) To do as a titration the conical flask can be heated to 60°C to speed up the initial reaction.

With Iron (II) ethanedioate both the Fe^{2+} and the $\text{C}_2\text{O}_4^{2-}$ react with the MnO_4^-
 1MnO_4^- reacts with 5Fe^{2+} and 2MnO_4^- reacts with $5\text{C}_2\text{O}_4^{2-}$



So overall



So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4

A 1.412 g sample of impure $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in an excess of dilute sulphuric acid and made up to 250 cm^3 of solution. 25.0 cm^3 of this solution decolourised 23.45 cm^3 of a $0.0189 \text{ mol dm}^{-3}$ solution of potassium manganate(VII).

What is the percentage by mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the original sample?

Step 1 : find moles of KMnO_4

moles = conc x vol

$$0.0189 \times 23.45/1000 \\ = 4.43 \times 10^{-4} \text{ mol}$$

Step 2 : using balanced equation find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 25 cm^3

$$= \text{moles of } \text{KMnO}_4 \times 5/3 \text{ (see above for ratio)} \\ = 7.39 \times 10^{-4} \text{ mol}$$

Step 3 : find moles $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in 250 cm^3

$$= 7.39 \times 10^{-4} \text{ mol} \times 10 \\ = 7.39 \times 10^{-3} \text{ mol}$$

Step 4 : find mass of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in $7.39 \times 10^{-3} \text{ mol}$

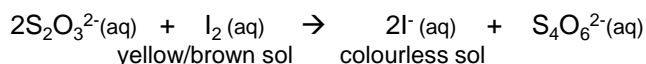
$$\text{mass} = \text{moles} \times \text{Mr} = 7.39 \times 10^{-3} \times 179.8 = 1.33 \text{ g}$$

Step 5 ; find % mass

$$\% \text{mass} = 1.33/1.412 \times 100 \\ = 94.1\%$$

Thiosulphate redox titration

The redox titration between I_2 and thiosulphate $\text{S}_2\text{O}_3^{2-}$ 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

The starch should **not** be added until nearly all the iodine has reacted because the blue complex formed with high concentrations of iodine is insoluble and does not re-dissolve as more thiosulfate is added

Uncertainty

Readings and Measurements

Readings

the values found from a single judgement when using a piece of equipment

Measurements

the values taken as the difference between the judgements of two values (e.g. using a burette in a titration)

The uncertainty of a reading (one judgement) is at least ± 0.5 of the smallest scale reading.
The uncertainty of a measurement (two judgements) is at least ± 1 of the smallest scale reading.

Calculating Apparatus Uncertainties

Each type of apparatus has a sensitivity uncertainty

- balance ± 0.001 g
- volumetric flask ± 0.1 cm³
- 25 cm³ pipette ± 0.1 cm³
- burette ± 0.05 cm³

Calculate the percentage error for each piece of equipment used by

$$\% \text{ uncertainty} = \pm \frac{\text{uncertainty}}{\text{Measurement made on apparatus}} \times 100$$

e.g. for pipette

$$\% \text{ uncertainty} = 0.05 / 25 \times 100$$

To calculate the maximum percentage apparatus uncertainty in the final result add all the individual equipment uncertainties together.

To decrease the apparatus uncertainties you can either decrease the sensitivity uncertainty by using apparatus with a greater resolution (finer scale divisions) or you can increase the size of the measurement made.

Uncertainty of a measurement using a burette.

If the burette used in the titration had an uncertainty for each reading of ± 0.05 cm³ then during a titration two readings would be taken so the uncertainty on the titre volume would be ± 0.10 cm³.

Reducing uncertainties in a titration

Replacing measuring cylinders with pipettes or burettes which have lower apparatus uncertainty will lower the error

To reduce the uncertainty in a burette reading it is necessary to make the titre a larger volume. This could be done by: increasing the volume and concentration of the substance in the conical flask or by decreasing the concentration of the substance in the burette.

If looking at a series of measurements in an investigation the experiments with the smallest readings will have the highest experimental uncertainties.

Reducing uncertainties in measuring mass

Using a more accurate balance or a larger mass will reduce the uncertainty in weighing a solid
Weighing sample before and after addition and then calculating difference will ensure a more accurate measurement of the mass added.

Calculating the percentage difference between the actual value and the calculated value

If we calculated an Mr of 203 and the real value is 214, then the calculation is as follows:

Calculate difference $214 - 203 = 11$

$$\% = 11 / 214 \times 100$$

$$= 5.41\%$$

If the %uncertainty due to the apparatus $<$ percentage difference between the actual value and the calculated value then there is a discrepancy in the result due to other errors.

If the %uncertainty due to the apparatus $>$ percentage difference between the actual value and the calculated value then there is no discrepancy and all errors in the results can be explained by the sensitivity of the equipment.