

CIE Chemistry A-Level

Topic 6 - Electrochemistry

Flashcards

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What are the rules for assigning oxidation states?



What are the rules for assigning oxidation states?

Element	Oxidation number
Group 1 metals	+1
Group 2 metals	+2
Oxygen	-2 (usually)
Hydrogen	-1 (usually)
Fluorine	-1
Oxygen with fluorine	+2

- Uncombined elements have an oxidation state of 0.
- In neutral compounds, the sum of oxidation states is 0.
- The oxidation state of common basic ions is equal to their charge.
- For highly electronegative species, the more electronegative element is negative.



What are some exceptions to the rule for oxidation states?



What are some exceptions to the rule for oxidation states?

- Hydrogen in metal hydrides has an oxidation state of -1 (instead of +1).
- Oxygen in peroxides has an oxidation state of -1 (instead of -2).

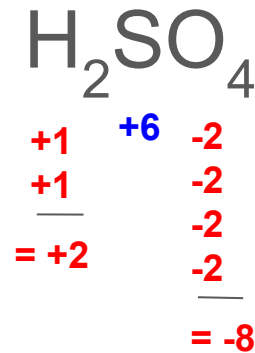


Calculate the oxidation state of sulfur in
 H_2SO_4



Calculate the oxidation state of sulfur in H_2SO_4

- Oxidation state of oxygen = -2
4 oxygen atoms so $-2 \times 4 = -8$
- Oxidation state of hydrogen = +1
2 hydrogen atoms so $+1 \times 2 = +2$
- Overall charge on the compound is 0 so the sum of oxidation states must equal 0.
- X is the oxidation state of sulfur:
 $+2 + X + -8 = 0$
 $X - 6 = 0$
 $X = 6$
- Oxidation state of S in H_2SO_4 is +6.



What is oxidation?



What is oxidation?

Loss of electrons / increase in oxidation number



What is reduction?



What is reduction?

Gain of electrons / decrease in oxidation number



What is the equation $F = Le$?
(A level only)



What is the equation $F = Le$? **(A level only)**

- L is the Avogadro constant (6.02×10^{23})
- e is the charge of an electron (1.6×10^{-19} coulombs)
- F is the Faraday constant, the charge of 1 mole of electrons.

- $$F = 6.02 \times 10^{23} \times 1.6 \times 10^{-19}$$
$$= 96320 \text{ coulombs}$$

*When the constants have a greater number of significant figures, F comes to approx. 96500 coulombs. 96500 coulombs is usually used in calculations.



What is electrolysis? **(A level only)**



What is electrolysis? **(A level only)**

The decomposition of a compound using an electric current.



What is an electrolyte?

(A level only)



What is an electrolyte? **(A level only)**

The molten ionic compound or aqueous solution of ions that is decomposed during electrolysis.



Describe what happens at the electrodes
during electrolysis
(A level only)



Describe what happens at the electrodes during electrolysis **(A level only)**

- Negative ions are attracted to the **anode** where they are then **oxidised** (lose electrons) to become neutral.
- Positive ions are attracted to the **cathode** where they are then **reduced** (gain electrons) to become neutral.



What forms at each electrode when a molten electrolyte containing two simple ions undergoes electrolysis?
(A level only)



What forms at each electrode when a molten electrolyte containing two simple ions undergoes electrolysis? **(A level only)**

- A molten electrolyte containing with two simple ions will contain metal and non-metal ions.
- A metal will form at the cathode and a non-metal will form at the anode.



What forms at each electrode when an aqueous electrolyte undergoes electrolysis?
(A level only)



What forms at each electrode when an aqueous electrolyte undergoes electrolysis? **(A level only)**

- H^+ and OH^- ions are present from the water as well as the metal and non-metal ions from the ionic compound.
- Generally, if a halogen is present, it will form at the anode. If not, oxygen is produced.
- At the cathode, atoms of substance with the more positive E^θ will form (either the metal or hydrogen). Metals from lead to zinc in the electrochemical series depend on concentration with the more concentrated ions becoming atoms.



What happens during discharge?

(A level only)



What happens during discharge? **(A level only)**

Ions are converted to atoms / molecules
at electrodes in electrolysis.



What does discharge depend upon?
(A level only)



What does discharge depend upon? **(A level only)**

1. The concentrations of the ions.
2. Position in the redox series i.e.
relative electrode potentials of the
ions.



How concentration affect discharge at the cathode when aqueous solutions undergo electrolysis?
(A level only)



How concentration affect discharge at the cathode when aqueous solutions undergo electrolysis?

(A level only)

From around lead to zinc in the electrochemical series:

- If the solution is very concentrated then the metal will form.
- If the solution is very dilute then hydrogen will form.
- If the concentration of metal and hydrogen ions is similar, both may form.



How does concentration affect discharge
at the anode when aqueous solutions
undergo electrolysis?
(A level only)



How does concentration affect discharge at the anode when aqueous solutions undergo electrolysis? **(A level only)**

Generally, if a halogen is present, it will form at the anode. If not, oxygen is produced.

However, for example, when a more concentrated solution of NaCl is electrolysed, more chlorine is produced at the anode. If the solution is dilute, little chloride would be produced and the product would mostly be oxygen.



How does discharge depend upon the
relative electrode potentials of ions?
(A level only)



How does discharge depend upon the relative electrode potentials of ions? **(A level only)**

- The cation is more easily reduced when E^\ominus is positive.
- The anion is more easily oxidised when E^\ominus is negative.
- If the cation has a greater E^\ominus than hydrogen, the cation is discharged. If not, hydrogen is discharged.



How do you calculate the quantity of charge passed during electrolysis?
(A level only)



How do you calculate the quantity of charge passed during electrolysis? **(A level only)**

Using $Q = It$

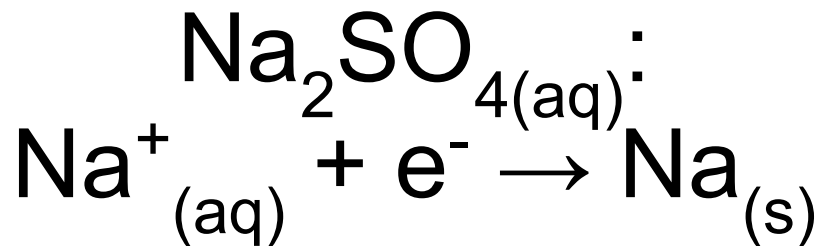
Where:

- Q is the charge, in coulombs
- I is the current, in amps
- t is the time, in seconds.

Calculations using the Faraday constant may also be required.
Remember: $F = Le$



Explain how to calculate the mass of substance liberated during electrolysis using the cathode half equation for



(A level only)

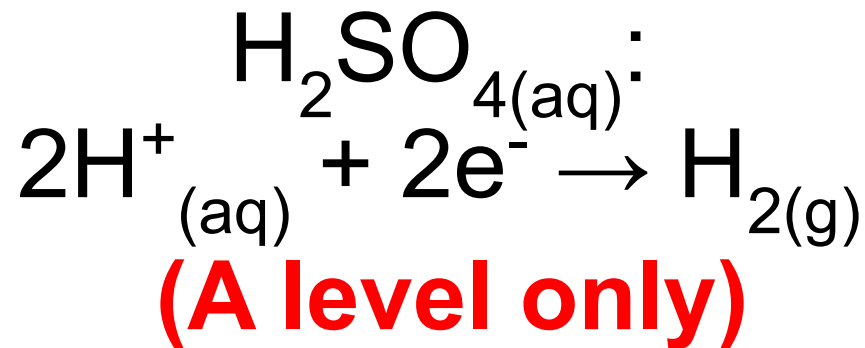


Explain how to calculate the mass of a substance liberated during electrolysis using the cathode half equation for $\text{Na}_2\text{SO}_{4(aq)}$: $\text{Na}^+_{(aq)} + e^- \rightarrow \text{Na}_{(s)}$ **(A level only)**

- 1:1 ratio of e^- to $\text{Na}_{(s)}$ so one mole of electrons is needed to form mole of $\text{Na}_{(s)}$. The charge transferred is 1F.
- Use the current and time (these will be given to you) to calculate the actual charge transferred using $Q = It$.
- Divide Q by F to get the number of moles of $\text{Na}_{(s)}$ formed.
- Rearrange $n = m/M_r$ to calculate the mass of $\text{Na}_{(s)}$ formed.



Explain how to calculate the volume of a substance liberated during electrolysis using the cathode half equation for



Explain how to calculate the volume of a substance liberated during electrolysis using the cathode half equation for $\text{H}_2\text{SO}_{4(aq)}$: $2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}$ **(A level only)**

- 2 moles of electrons forms 1 mole of hydrogen gas.
- Hence the charge transferred for every one mole of $\text{H}_{2(g)}$ produced is $2F$ (where F is the faraday constant).
- Use the time and the current (these will be given to you) to calculate the actual charge transferred using $Q = It$.
- Divide Q by $2F$ to find the number of moles of $\text{H}_{2(g)}$.
- Use $V = n \times 24$ to calculate the volume of $\text{H}_{2(g)}$ produced.



Describe how to determine a value for the Avogadro constant using the electrolysis of silver nitrate **(A level only)**



Describe how to determine a value for the Avogadro constant using the electrolysis of silver nitrate **(A level only)**

- Cathode half equation: $\text{Ag}^+_{(\text{aq})} + \text{e}^- \rightarrow \text{Ag}_{(\text{s})}$
- Measure the current (I in amps) and the time taken (t in seconds).
- Calculate the charge transferred using $Q = It$.
- Measure the mass of the cathode before and after electrolysis. The difference in mass = the mass of $\text{Ag}_{(\text{s})}$ formed.
- Use $n = m/M_r$ to calculate the number of moles of $\text{Ag}_{(\text{s})}$ formed.
- The ratio of no. of moles of electrons to silver is 1:1 so Q/n will give the charge transferred for every mole of $\text{Ag}_{(\text{s})}$ formed.
- This gives an estimate for the value of F. Divide this by e (1.6×10^{-16}) to find a value for the Avogadro constant, L.



What must a half-cell contain?
(A level only)



What must a half-cell contain? **(A level only)**

An element in two different oxidation states.



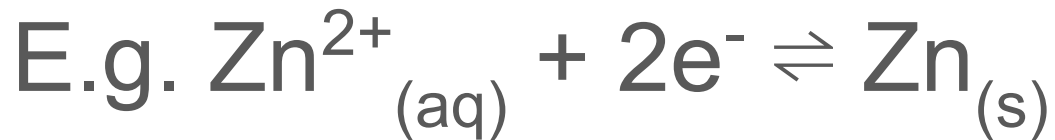
Describe a metal/metal ion half-cell

(A level only)



Describe a metal/metal ion half-cell **(A level only)**

- A solid metal rod is dipped into a solution containing ions of the metal.
- An equilibrium will be set up on the surface of the metal.



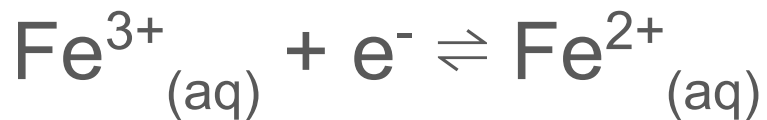
Describe an ion/ion half-cell

(A level only)



Describe an ion/ion half-cell **(A level only)**

- An ion/ion half cell contains a solution of ions of the same element but of different oxidation states e.g. Fe^{2+} and Fe^{3+} :



- The electrode is usually graphite or platinum.



Define standard electrode potential (A level only)



Define standard electrode potential **(A level only)**

The EMF of a half-cell compared with a hydrogen half-cell under standard conditions.



Define EMF (A level only)



Define EMF **(A level only)**

Electromotive force, the voltage when no current flows.



What are standard conditions?

(A level only)



What are standard conditions? **(A level only)**

- Pressure: 101 kPa / 1 atm.
- Temperature: 298 K / 25 °C.
- Solution concentrations: 1 mol dm⁻³.



What is a hydrogen half-cell?

(A level only)



What is a hydrogen half-cell? **(A level only)**

- A half-cell containing hydrogen gas and a solution of hydrogen ions.
- An inert platinum electrode provides a surface for the equilibrium.



What is standard cell potential?

(A level only)



What is standard cell potential? **(A level only)**

The EMF when two half cells are connected under standard conditions.



How do you use standard electrode potentials to calculate standard cell potential, E^{θ}_{cell} ?
(A level only)



How do you use standard electrode potentials to calculate standard cell potential, E^θ_{cell} ?

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



How do you predict which half-cell is
being oxidised and which is being
reduced?
(A level only)



How do you predict which half-cell is being oxidised and which is being reduced? **(A level only)**

- A system has a greater tendency to be oxidised when E^θ is more negative.
- A system has a greater tendency to be reduced when E^θ is more positive.
- Hence the half-cell with the more positive E^θ is oxidised and the half-cell with the more negative E^θ is reduced.



Describe the flow of electrons in a simple electrochemical cell

(A level only)



Describe the flow of electrons in a simple electrochemical cell **(A level only)**

Electrons flow from the negative electrode (where they are lost) to the positive electrode (where they are gained) due to the redox reactions that take place at these electrodes.



How can you predict the feasibility of a redox reaction in an electrochemical cell?

(A level only)



How can you predict the feasibility of a redox reaction in an electrochemical cell? **(A level only)**

- The reaction is feasible if the oxidising agent (the substance being reduced) has a lower standard cell potential than the reducing agent (the substance being oxidised).
- The greater the difference in E^θ value, the more likely the reaction is to occur.



It has been predicted using standard electrode potentials that a redox reaction is feasible. Why might this reaction not occur spontaneously?

(A level only)



It has been predicted using standard electrode potentials that a redox reaction is feasible. Why might this reaction not occur spontaneously?

(A level only)

- Non-standard conditions.
- Ambient energy of the system is lower than the activation energy.



How can standard cell/electrode potentials be used to deduce the relative reactivity of the halogens?
(A level only)



How can standard cell/electrode potentials be used to deduce the relative reactivity of the halogens?

(A level only)

- As you go down group 17 (7), standard electrode potentials decrease.
- This means halogens further down the group are more likely to be oxidised/ less likely to be reduced.
- Therefore, oxidising ability decreases. This also means that reactivity decreases down the group.



What must be balanced before
combining half equations to write a redox
equation?
(A level only)

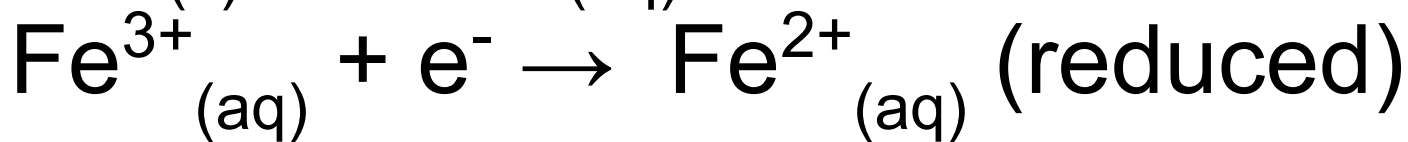
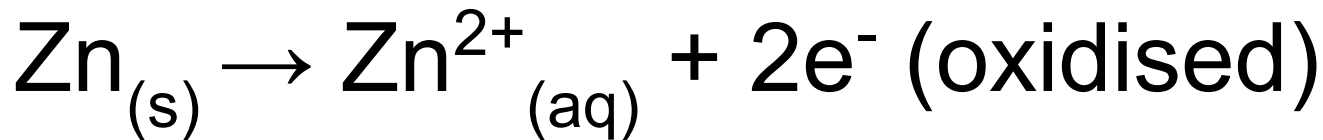


What must be balanced before combining half equations to write a redox equation? **(A level only)**

The number of electrons must be the same in both half equations



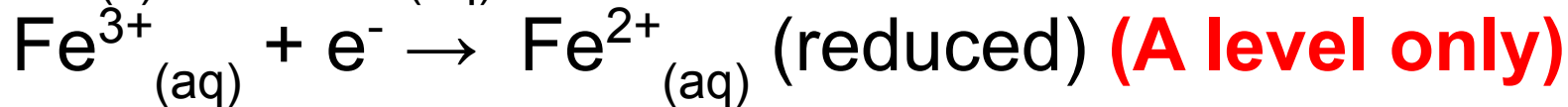
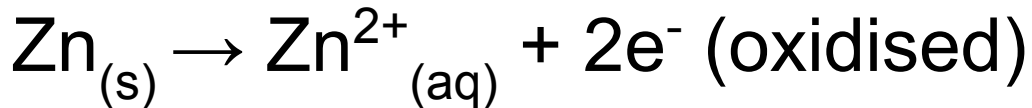
How do you combine the half equations below to write a redox equation?



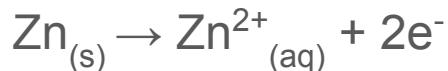
(A level only)



How do you combine the half equations below to write a redox equation?



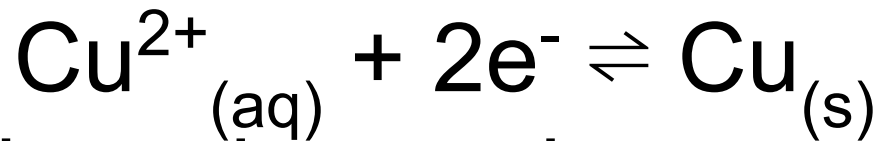
- Balance the number of electrons:



- Combine the equations and cancel any common species that appear on both sides of the equation: $\text{Zn}_{(s)} + 2\text{Fe}^{3+}_{(aq)} + \cancel{2e^{-}} \rightarrow \text{Zn}^{2+}_{(aq)} + \cancel{2e^{-}} + 2\text{Fe}^{2+}_{(aq)}$
- Overall redox equation: $\text{Zn}_{(s)} + 2\text{Fe}^{3+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + 2\text{Fe}^{2+}_{(aq)}$



A half cell contains the equilibrium below:

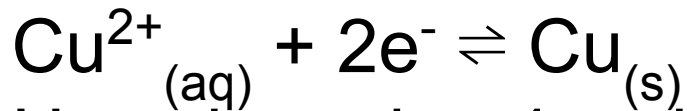


How does decreasing copper ion concentration affect electrode potential?

(A level only)



A half cell contains the equilibrium below:



How does decreasing copper ion concentration affect electrode potential? **(A level only)**

- If the concentration of copper ions decreases, there are fewer copper ions in the solution so the position of equilibrium shifts to the left to minimise this change.
- This causes the electrode potential to become less positive because the reverse reaction (oxidation) occurs more.



What is the Nernst equation?

(A level only)



What is the Nernst equation? **(A level only)**

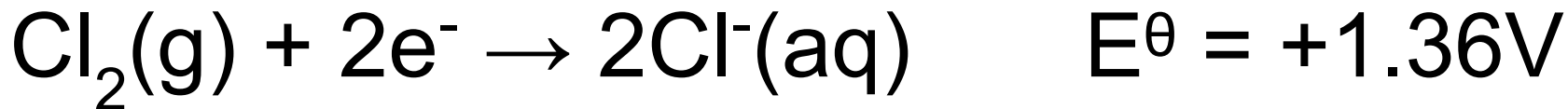
$$E = E^{\theta} + (0.059/z) \log \frac{[\text{Oxidised species}]}{[\text{Reduced species}]}$$

The standard cell potential only applies if the concentration of the solutions is 1 mol dm^{-3} . If concentrations are different, we can use the Nernst equation to calculate the electrode potential (E).

- Oxidised species = species with greater oxidation state.
- Reduced species = species with lower oxidation state.
- Z = the number of electrons transferred.



How can the Nernst equation be used to calculate the electrode potential for the half-equation below?



(A level only)



How can the Nernst equation be used to calculate the electrode potential for the half-equation below?



$$E = E^\theta + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

$$E = +1.36 + (0.059/2) \log \frac{[\text{Cl}^-]^2}{[\text{Cl}_2]}$$

Cl_2 is reduced and Cl^- is oxidised

2 electrons are transferred so
 $z = 2$

$[\text{Cl}^-]$ is squared because there are 2Cl^- in the equation



List some advantages of H_2/O_2 fuel cells
(A level only)



List some advantages of H_2/O_2 fuel cells (A level only)

- Only waste product is water.
- High efficiency conversion.
- No pollutants (such as CO_2).
- Potentially renewable (if H_2 is obtained from water).
- Don't have to be recharged.
- Run continuously provided there is a constant supply of fuel and oxygen.
- No need for fossil fuels.



List some advantages of secondary cells
(A level only)



List some advantages of secondary cells **(A level only)**

Examples include nickel-metal hydride and lithium-ion batteries.

- These are rechargeable.
- More cost efficient long term as fewer batteries need to be bought.
- Saves wasting finite and expensive resources.

