CAIE Chemistry A-level

Topic 24 - Electrochemistry

(A level only)

Flashcards

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What is the equation $F = Le$?

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What is the equation $F = Le$?

- 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.

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

Note, when the constants have a greater number of significant figures, F comes to approx. 96500 coulombs. This is the value usually used in calculations.

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What is electrolysis?

What is electrolysis?

The decomposition of a compound using an electric current.

What is an electrolyte?

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What is an electrolyte?

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

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Describe what happens at the electrodes during electrolysis

Describe what happens at the electrodes during electrolysis

Negative ions are attracted to the anode where they are then oxidised (lose electrons).

Positive ions are attracted to the cathode where they are then reduced (gain electrons).

What forms at each electrode when a molten electrolyte containing two simple ions undergoes electrolysis?

What forms at each electrode when a molten electrolyte containing two simple ions undergoes electrolysis?

- A molten electrolyte containing 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.

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What forms at each electrode when an aqueous electrolyte undergoes electrolysis?

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What forms at each electrode when an aqueous electrolyte undergoes electrolysis?

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 anode. 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.

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What happens during discharge?

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What happens during discharge?

A process in electrolysis in which ions are converted to atoms/molecules at the electrodes.

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What does discharge depend upon?

What does discharge depend upon?

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

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

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

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?

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

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?

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How does discharge depend upon the relative electrode potentials of ions?

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

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How can you calculate the quantity of charge passed during electrolysis?

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How can you calculate the quantity of charge passed during electrolysis?

$$Q = It$$

where:

Q is the charge, in coulombs

I is the current, in amps

t is the time, in seconds.

Explain how to calculate the mass of substance liberated during electrolysis using the cathode half equation for $Na_2SO_{4(aq)}$:

$$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$$

Explain how to calculate the mass of a substance liberated during electrolysis using the cathode half equation for $Na_2SO_{4(aq)}$: $Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$

- There is a 1:1 ratio of e^- to $Na_{(s)}$ so one mole of electrons are needed to form mole of $Na_{(s)}$. 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 $Na_{(s)}$ formed.
- Rearrange $n = m/M_r$ to calculate the mass of $Na_{(s)}$ formed.

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Explain how to calculate the volume of a substance liberated during electrolysis using the cathode half equation for $H_2SO_{4(aq)}$:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

Explain how to calculate the volume of a substance liberated during electrolysis using the cathode half equation for $H_2SO_{4(aq)}$: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

- 2 moles of electrons forms 1 mole of hydrogen gas so the charge transferred for every one mole of $H_{2(g)}$ 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 $H_{2(g)}$.
- Use V = n x 24 to calculate the volume of $H_{2(g)}$ produced.

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Describe how to determine a value for the Avogadro constant using the electrolysis of silver nitrate

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Describe how to determine a value for the Avogadro constant using the electrolysis of silver nitrate

- Cathode half equation: $Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$
- Measure the current (amps) and the time taken (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 $Ag_{(s)}$ formed.
- Use $n = m/M_r$ to calculate the number of moles of $Ag_{(s)}$ 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 $Ag_{(s)}$ 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.

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What must a half-cell contain?

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What must a half-cell contain?

An element in two different oxidation states.

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Describe a metal/metal ion half-cell

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Describe a metal/metal ion half-cell

- 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.

$$\text{E.g. } Zn^{2+}_{(aq)} + 2e^{-} \rightleftharpoons Zn_{(s)}$$

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Describe an ion/ion half-cell

Describe an ion/ion half-cell

- 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+}:

$$Fe^{3+}_{(aq)} + e^{-} \rightleftharpoons Fe^{2+}_{(aq)}$$

- The electrode is usually graphite or platinum.

Define standard electrode potential

Define standard electrode potential

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

Define EMF

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Define EMF

Electromotive force, the voltage when no current flows.

What are standard conditions?

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What are standard conditions?

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

What is a hydrogen half-cell?

What is a hydrogen half-cell?

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

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$$

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What is standard cell potential?

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What is standard cell potential?

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

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

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

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

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How can you predict which half-cell is being oxidised and which is being reduced?

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How can you predict which half-cell is being oxidised and which is being reduced?

- 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 reduced and the half-cell with the more negative E^{θ} is oxidised .

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Describe the flow of electrons in a simple electrochemical cell

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Describe the flow of electrons in a simple electrochemical cell

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.

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

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

- 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.

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

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

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

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

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

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.

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What must be balanced before combining half equations to write a redox equation?

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What must be balanced before combining half equations to write a redox equation?

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

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

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

$$Fe^{3+}_{(aq)} + e^{-} \rightarrow Fe^{2+}_{(aq)} \text{ (reduced)}$$

How do you combine the half equations below to write a redox equation? $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$

Balance the number of electrons:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ $2Fe^{3+}_{(aq)} + 2e^- \rightarrow 2Fe^{2+}_{(aq)}$

Combine the equations and cancel any common species: that appear on both sides of the equation:

$$Zn_{(s)} + 2Fe^{3+}_{(aq)} + \cancel{2e^-} \rightarrow Zn^{2+}_{(aq)} + \cancel{2e^-} + 2Fe^{2+}_{(aq)}$$

Overall equation:

$$Zn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$$

A half cell contains the equilibrium below:

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

How does decreasing copper ion concentration affect electrode potential?

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A half cell contains the equilibrium below:

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$

How does decreasing copper ion concentration affect electrode potential?

- 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?

What is the Nernst equation?

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

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.

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

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \qquad E^\theta = +1.36V$

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

$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ $E^\theta = +1.36V$

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

$$E = +1.36 + (0.059/2)\log\frac{[Cl^-]^2}{[Cl_2]}$$

Cl_2 is reduced and Cl^- is oxidised

2 electrons are transferred so z = 2

$[Cl^-]$ is squared because there are $2Cl^-$ in the equation