Topic 14: Redox II

Edexcel A Level Chemistry • Paper 1 (9CH0/01)

14.1 Know that standard electrode potential, $E^{\ominus}$, is measured relative to the standard hydrogen electrode (SHE) under standard conditions.

Standard electrode potential ($E^{\ominus}$) is the potential difference between a half-cell and the standard hydrogen electrode (SHE) under standard conditions (298 K, 100 kPa, 1.00 mol dm^{-3} solutions).

The SHE is assigned $E^{\ominus} = 0.00$ V by convention. It consists of $H_2(g)$ at 100 kPa bubbling over a platinum electrode in 1.00 mol dm^{-3} $H^+(aq)$: $H^+(aq) + e^- \quad \frac{1}{2}H_2(g)$, $E^{\ominus} = 0.00$ V.

All standard electrode potentials are given as reduction potentials (written as reduction half-equations).

14.2 Understand the principles of measuring standard electrode potential, including the role of a salt bridge.

To measure $E^{\ominus}$ of a half-cell: connect it to a SHE using a high-resistance voltmeter (to prevent current flow) and a salt bridge (e.g. $KNO_3(aq)$ in a gel). The salt bridge allows ion flow to complete the circuit and maintain electrical neutrality without mixing the solutions. The reading on the voltmeter is $E^{\ominus}$ for the half-cell.

For metal/metal ion half-cells: the metal electrode dips into a solution of its ions. For non-metal half-cells (e.g. Cl_2/Cl^-): a platinum electrode is used.

14.3 Be able to use standard electrode potentials to calculate the standard EMF of an electrochemical cell: $E^{\ominus}cell = E^{\ominus}cathode - E^{\ominus}anode$.

$E^{\ominus}cell = E^{\ominus}cathode - E^{\ominus}anode$

$= E^{\ominus}(more\ positive\ half\text{-}cell) - E^{\ominus}(less\ positive\ half\text{-}cell)$

The more positive half-cell is the cathode (reduction occurs). The less positive half-cell is the anode (oxidation occurs). $E^{\ominus}cell$ is always positive for a spontaneous cell reaction.

14.4 Be able to use standard electrode potentials to predict the feasibility of a reaction and deduce the direction of electron flow.

A reaction is feasible if $E^{\ominus}cell > 0$ (positive). The species with the more positive $E^{\ominus}$ is the stronger oxidising agent and is reduced (gains electrons). Electrons flow through the external circuit from the anode (more negative $E^{\ominus}$, oxidation) to the cathode (more positive $E^{\ominus}$, reduction). In the cell diagram: anode || cathode. Overall cell reaction: reverse the anode half-equation (multiply as needed), add to the cathode half-equation.

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14.5 Know the limitations of using standard electrode potentials to predict the feasibility of reactions.

Standard electrode potentials predict thermodynamic feasibility only – they say nothing about the rate of reaction. A reaction with a positive $E^{\ominus}_{cell}$ may be kinetically too slow to observe (high activation energy). Also, $E^{\ominus}$ values only apply under standard conditions (298 K, 1 mol dm^{-3}, 100 kPa) – non-standard conditions will change electrode potentials and may reverse predictions.

14.6 Be able to write the overall cell equation and represent a cell using cell notation.

Cell notation: anode | anode solution || cathode solution | cathode

Vertical lines represent phase boundaries; double vertical lines represent the salt bridge.

E.g. $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

For half-cells involving gases or non-metals: include Pt electrode. E.g. $Pt \mid H_2(g) \mid H^+(aq) \parallel \ldots$

Overall equation: combine the two half-equations (multiply to balance electrons, do not multiply $E^{\ominus}$ values).

14.7 Understand how electrochemical cells can be used as a commercial source of electrical energy.

Electrochemical cells convert chemical energy directly into electrical energy via redox reactions. Primary cells: non-rechargeable (e.g. alkaline battery). Secondary cells: rechargeable (e.g. lithium-ion battery). Fuel cells: continuously supplied with fuel (e.g. H_2) and oxidant (O_2); produce electricity, water, and heat. Advantages of fuel cells: high efficiency, no combustion emissions (H_2 fuel cell produces only water), continuous operation.

14.8 Know the principles of the hydrogen fuel cell, including the reactions at each electrode.

Hydrogen fuel cell (acidic electrolyte):

Anode (oxidation): $H_2 \rightarrow 2H^+ + 2e^-$

Cathode (reduction): $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

Alkaline electrolyte:

Anode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Platinum catalyst is used at both electrodes. The fuel cell produces electricity, water, and heat.

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14.9 Know the electrode reactions during electrolysis of: (i) molten NaCl, (ii) aqueous NaCl, (iii) aqueous $CuSO_4$ using copper electrodes.

(i) Molten NaCl: cathode: $Na^+ + e^- \rightarrow Na$; anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

(ii) Aqueous NaCl: cathode: $2H^+ + 2e^- \rightarrow H_2$ (H^+ from water preferentially discharged over Na^+ as Na^+ has a very negative $E^{\ominus}$); anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (Cl^- discharged preferentially over OH^- at high concentration).

(iii) Aqueous $CuSO_4$ with copper electrodes: cathode: $Cu^{2+} + 2e^- \rightarrow Cu$; anode: $Cu \rightarrow Cu^{2+} + 2e^-$ (copper anode dissolves, replenishing Cu^{2+} in solution). Used in electroplating and copper purification.

14.10 Know that the amount of substance deposited or liberated during electrolysis is related to the charge passed: $Q = It$.

$Q = It$ where Q = charge (C), I = current (A), t = time (s).

Moles of electrons = Q / F, where F = Faraday's constant = 96,500 C mol^{-1}.

Moles of substance deposited = moles of electrons / number of electrons transferred per ion.

E.g. $Cu^{2+} + 2e^- \rightarrow Cu$: 2 moles of electrons needed per mole of Cu deposited.

14.11 Be able to calculate the mass of substance deposited or released during electrolysis.

Method: (1) Calculate $Q = It$. (2) Calculate moles of electrons = Q / 96,500. (3) Use the half-equation to find moles of substance (divide by the number of electrons in the half-equation). (4) Calculate mass: $m = n \times Mr$.

E.g. 5 A for 10 min through $CuSO_4$: $Q = 5 \times 600 = 3000$ C; moles $e^- = 3000/96500 = 0.0311$; moles Cu = 0.0311/2 = 0.01555; mass = $0.01555 \times 63.5 = 0.987$ g.

14.12 Understand the industrial importance of electrolysis in the chlor-alkali industry.

Chlor-alkali process: electrolysis of brine (concentrated NaCl(aq)) produces three important industrial chemicals:

- Chlorine (Cl_2): at the anode – used to make PVC, solvents, bleach, disinfectants.
- Hydrogen (H_2): at the cathode – used as a fuel and in the Haber process.
- Sodium hydroxide (NaOH): formed in the electrolyte – used in soap making, paper production, and cleaning products.

Membrane cell: uses an ion-exchange membrane to prevent mixing of Cl_2 and NaOH.

14.13 Know that the standard electrode potential is affected by changes in temperature, concentration and pressure.

Non-standard conditions alter electrode potentials (Le Chatelier's Principle applied to the equilibrium in the half-cell). E.g. increasing $[Cu^{2+}]$ makes E more positive (equilibrium shifts to the right, favouring reduction). This can affect the predicted feasibility of a cell reaction and may even reverse it. Electrode potentials only equal $E^{\ominus}$ at standard conditions.

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14.14 Be able to suggest reasons why $E^{\ominus}_{cell}$ may not give a realistic indication of the voltage produced by a commercial cell.

Commercial cells differ from standard conditions because:

- Concentrations are not 1 mol dm^{-3} (change as cell is used).
- Temperature may not be 298 K.
- Internal resistance of the cell causes a voltage drop under load.
- Electrode surfaces may become passivated (e.g. oxide layers form).
- Junction potentials at phase boundaries.

Therefore, the measured voltage in a real cell is often lower than $E^{\ominus}_{cell}$.

14.15 Understand the principles of storage cells and fuel cells, including lithium-ion cells.

Lithium-ion cells (secondary/rechargeable): lithium ions move between the anode (graphite, where Li intercalates) and cathode (metal oxide, e.g. $LiCoO_2$) through the electrolyte. During discharge: Li → $Li^+ + e^-$ at the anode; $Li^+ + e^-$ absorbed at the cathode. High energy density, lightweight, rechargeable. Used in phones, laptops, electric vehicles.

14.16 Know the advantages and disadvantages of hydrogen fuel cells compared with conventional batteries.

Advantages of H_2 fuel cells: high efficiency (~60%+), only product is water (no CO_2 emissions during use), continuous operation while fuel is supplied, no recharging time needed.

Disadvantages: H_2 is explosive and difficult to store safely, requires infrastructure for distribution, currently expensive to produce H_2 from renewable sources, Pt catalyst is expensive, cells can be damaged by impure H_2.

14.17 Know the advantages and disadvantages of using electrochemical cells as a source of energy.

Advantages: portable energy source, quiet operation, no combustion products at point of use, can be rechargeable.

Disadvantages: limited energy density compared to fossil fuels, disposal of batteries causes environmental issues (heavy metals), expensive to manufacture, performance decreases at low temperatures, self-discharge over time.

14.18 Understand the relationship between $E^{\ominus}_{cell}$ and ΔG: $\Delta G = -nFE^{\ominus}_{cell}$.

$\Delta G = -nFE^{\ominus}_{cell}$ where n = moles of electrons transferred, F = 96,500 C mol^{-1}, $E^{\ominus}_{cell}$ in volts.

If $E^{\ominus}_{cell}$ is positive: ΔG is negative (feasible/spontaneous).

If $E^{\ominus}_{cell}$ is negative: ΔG is positive (not feasible under standard conditions).

This links electrochemistry directly to thermodynamics – a positive cell voltage means the reaction releases free energy.

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14.19 Be able to use $\Delta G = -nFE^{\ominus}_{cell}$ to calculate ΔG from $E^{\ominus}_{cell}$ and vice versa.

Method: (1) Write the balanced overall cell equation. (2) Identify n (moles of electrons transferred). (3) Calculate $E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$. (4) Apply $\Delta G = -nFE^{\ominus}_{cell}$. Units: n (dimensionless), F = 96,500 C mol^{-1}, E in V → ΔG in J mol^{-1} (divide by 1000 for kJ mol^{-1}).

Rearranging: $E^{\ominus}_{cell} = -\Delta G / nF$.

Measuring Standard Electrode Potentials

Electrolysis of Copper Sulfate Solution

ABOUT THESE NOTES

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