2.5 Redox and Electrochemistry

AQA 7405 · Calculator allowed · about 185 minutes · Write-in edition

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 When chlorine gas is bubbled into cold, dilute sodium hydroxide solution, a disproportionation reaction occurs.

(a) State the oxidation state of chlorine in Cl_2, and the oxidation states of chlorine in the two chlorine-containing products of this reaction, Cl^- and ClO^-. **(2)**

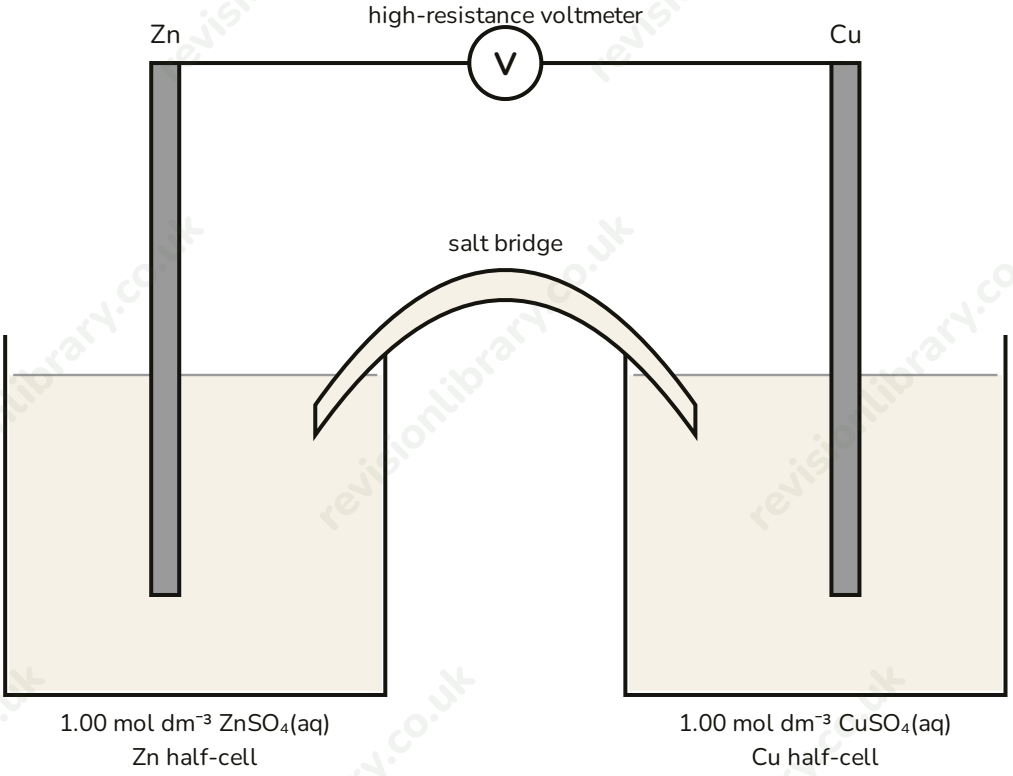
(b) Write ionic half-equations for the reduction and the oxidation processes that occur when chlorine reacts with cold, dilute hydroxide ions, OH^-. **(2)**

(c) Combine your two half-equations from part (b) to give the overall ionic equation for the reaction of chlorine with cold, dilute sodium hydroxide solution. **(2)**

(d) State the term used to describe a reaction, such as this one, in which the same element is simultaneously oxidised and reduced. **(1)**

(Total for Question 1 is 7 marks)

2 A student sets up a Daniell cell using a zinc half-cell (Zn(s) in 1.00 mol dm-3 $ZnSO_4(aq)$) and a copper half-cell (Cu(s) in 1.00 mol dm-3 $CuSO_4(aq)$) at 298 K, connected by a salt bridge. Standard electrode potentials: $E(Zn^{2+}/Zn) = -0.76$ V; $E(Cu^{2+}/Cu) = +0.34$ V



(a) Define the term 'standard electrode potential' of a half-cell. **(2)**

(b) Write the conventional cell diagram (cell notation) for this Daniell cell under standard conditions. **(2)**

(c) Calculate the standard emf of this cell. **(2)**

(d) State which electrode is the negative terminal of the cell and explain your answer. **(2)**

(Total for Question 2 is 8 marks)

3 This question is based on the required practical for measuring the emf of an electrochemical cell. A student builds the Daniell cell described in Question 2, connecting the two half-cells with a salt bridge and a high-resistance voltmeter, and measures an emf of 1.05 V, slightly lower than the theoretical value of 1.10 V.

(a) Explain why a high-resistance voltmeter, rather than an ammeter or a low-resistance meter, must be used to measure the emf of the cell. **(2)**

(b) State the purpose of the salt bridge in this cell and name one substance that could be used to make it. **(2)**

(c) Suggest two reasons, other than the voltmeter resistance, why the measured emf (1.05 V) might be lower than the theoretical value (1.10 V). **(2)**

(d) The concentration of the $CuSO_4(aq)$ in the copper half-cell is decreased to 0.0010 mol dm-3, while the zinc half-cell remains at standard conditions. State and explain the effect this has on the emf of the cell. **(3)**

(Total for Question 3 is 9 marks)

4 This question uses practical techniques from the required practical on redox titrations. A student wants to determine the percentage by mass of iron in an iron supplement tablet. One tablet, of total mass 2.50 g, is dissolved in dilute sulfuric acid and the resulting solution made up to exactly 250 cm^3 in a volumetric flask.

25.0 cm^3 portions of this solution are titrated against 0.0150 mol dm-3 potassium manganate(VII) solution. The mean titre required is 16.00 cm^3.

Equation: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(a) State the colour change observed at the end point of this titration, and explain why no external indicator is required. **(2)**

(b) Calculate the amount, in mol, of MnO_4^- used in the titration of one 25.0 cm^3 sample. **(1)**

(c) Calculate the amount, in mol, of Fe^{2+} present in the 25.0 cm^3 sample. **(1)**

(d) Calculate the total amount, in mol, of Fe^{2+} in the whole 250 cm^3 solution, and hence the mass, in g, of iron in the tablet. **(3)**

(e) Calculate the percentage by mass of iron in the tablet. **(2)**

(Total for Question 4 is 9 marks)

5 This question is about setting up and calculating the EMF of a magnesium-silver electrochemical cell.

(a) Standard electrode potentials: Mg^{2+}/Mg = -2.37 V, Ag^{+}/Ag = +0.80 V. Identify which electrode is the positive terminal (where reduction occurs) and which is the negative terminal (where oxidation occurs) in a cell combining these two half-cells. **(2)**

(b) Calculate the standard EMF, Ecell, of this cell. **(2)**

(c) Write the overall (combined) equation for the spontaneous cell reaction, ensuring electrons cancel. **(2)**

(d) Describe how this cell would be set up in the laboratory to measure Ecell experimentally, naming the key piece of apparatus needed to complete the circuit without allowing the two solutions to mix directly. **(3)**

(Total for Question 5 is 9 marks)

6 A steel spoon is electroplated with silver. The spoon (cathode) and a silver anode are placed in a solution of $AgNO_3(aq)$, and a constant current of 0.500 A is passed through the cell for 45.0 minutes.

Faraday constant, F = 96500 C mol^{-1}; Ar(Ag) = 108

(a) Write the half-equation for the reduction of silver ions at the cathode. **(1)**

(b) Calculate the total charge, in coulombs, passed through the cell. **(1)**

(c) Calculate the amount, in mol, of electrons that passed through the cell. **(1)**

(d) Calculate the mass, in g, of silver deposited on the spoon. **(2)**

(e) The silver coats the spoon evenly over a total surface area of 12.0 cm^2, and solid silver has a density of 10.5 g cm^{-3}. Calculate the thickness, in mm, of the silver coating. **(3)**

(Total for Question 6 is 8 marks)

7 A breathalyser test uses the reaction between acidified potassium dichromate(VI) and ethanol vapour from a person's breath:

$2Cr_2O_7^{2-}(aq) + 3CH_3CH_2OH(aq) + 16H^+(aq) \rightarrow 4Cr^{3+}(aq) + 3CH_3COOH(aq) + 11H_2O(l)$

$E(Cr_2O_7^{2-}/Cr^{3+}) = +1.33$ V; $E(CH_3COOH/CH_3CH_2OH) = +0.19$ V (data given for this question)

(a) State the oxidation state of chromium in $Cr_2O_7^{2-}$ and in Cr^{3+}, and state whether chromium is oxidised or reduced in this reaction. **(2)**

(b) State the colour change observed during this reaction and name the type of reaction that ethanol undergoes. **(2)**

(c) Using the E values given, calculate the E cell value for this reaction and state whether the reaction is feasible under standard conditions. **(3)**

(Total for Question 7 is 7 marks)

8 Explain, using ideas about standard electrode potentials and reaction kinetics, why a reaction between two half-cells that is predicted to be thermodynamically feasible from a positive E cell value may not actually be observed to occur, or may occur only extremely slowly, when the two solutions are mixed.

(Total for Question 8 is 6 marks)

9 A 1.20 g sample of brass (a copper-zinc alloy) is dissolved completely in excess dilute nitric acid. The resulting solution is treated with excess potassium iodide solution, which reacts with the copper(II) ions present:

$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$

The mixture is made up to exactly 250 cm^3 in a volumetric flask. A 25.0 cm^3 sample of this solution is titrated against 0.100 mol dm-3 sodium thiosulfate solution:

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$

The mean titre of sodium thiosulfate solution required is 12.30 cm^3.

(a) Deduce the change in oxidation state of copper and of iodine in the equation $2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$, and identify the oxidising agent. **(3)**

(b) Calculate the amount, in mol, of thiosulfate ions used to react with the iodine in the 25.0 cm^3 sample. **(1)**

(c) Deduce the amount, in mol, of I_2 formed and hence the amount, in mol, of Cu^{2+} that was present in the 25.0 cm^3 sample. **(2)**

(d) Calculate the total amount, in mol, of Cu^{2+} in the original 250 cm^3 solution, and hence the percentage by mass of copper in the brass sample. **(3)**

(Total for Question 9 is 9 marks)

10 This synoptic question links the EMF of the magnesium-silver cell from Question 5 to its Gibbs free energy change, and to the separate question of reaction rate.

(a) Using Ecell = +3.17 V from Question 5 (for $Mg + 2Ag^{+} \rightarrow Mg^{2+} + 2Ag$, n = 2 mol of electrons transferred) and delta G = -nFEcell, where F = 96500 C/mol, calculate delta G for this reaction. **(3)**

(b) State what the sign of delta G found in (a) confirms about this reaction. **(2)**

(c) Despite this large negative delta G, state and explain what actually determines whether this reaction proceeds at a significant rate when magnesium metal is placed in silver nitrate solution. **(2)**

(d) Suggest why, for many redox reactions between a metal and an aqueous metal ion, the activation energy tends to be relatively low compared with many organic reactions, so a large negative delta G in cases like this does typically correspond to an observable reaction at room temperature. **(2)**

(Total for Question 10 is 9 marks)

11 This question uses a redox titration with potassium dichromate(VI) to determine the percentage of iron in an ore sample.

(a) A 2.50 g sample of iron ore is dissolved in acid, and all the iron is converted to $Fe^{2+}(aq)$; the solution is made up to 250 cm^3 in a volumetric flask. A 25.0 cm^3 sample of this solution requires 18.40 cm^3 of 0.0200 mol/dm3 potassium dichromate(VI) solution to reach the end point, using the reaction $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$. Calculate the number of moles of $Cr_2O_7^{2-}$ used in the titration. **(2)**

(b) Calculate the number of moles of Fe^{2+} in the 25.0 cm^3 sample. **(2)**

(c) Calculate the total number of moles of Fe^{2+} (and hence Fe) in the original 250 cm^3 solution. **(2)**

(d) Calculate the percentage by mass of iron in the original 2.50 g ore sample (Ar of Fe = 56.0). **(3)**

(Total for Question 11 is 9 marks)

12 This question is about how ion concentration affects electrode potential, applying Le Chatelier's principle to two half-equilibria.

(a) Using the equilibrium $Ag^+(aq) + e^- \rightleftharpoons Ag(s)$ and Le Chatelier's principle, predict and explain the effect on the electrode potential of the Ag^+/Ag half-cell of decreasing the concentration of $Ag^+(aq)$ (for example, by adding chloride ions to precipitate insoluble AgCl). **(3)**

(b) For the half-equation $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$, predict and explain the effect on the electrode potential of increasing the concentration of $H^+(aq)$ (for example, by adding more acid). **(3)**

(Total for Question 12 is 6 marks)

13 This question is about the quantities involved in the electrolytic refining of copper.

(a) In the electrolytic refining of copper, a current of 15.0 A is passed through a cell for 2.50 hours. Calculate the charge, Q, passed during this time. **(2)**

(b) Calculate the number of moles of electrons passed, given the Faraday constant F = 96500 C/mol. **(2)**

(c) At the cathode, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Calculate the mass of copper deposited at the cathode (Ar of Cu = 63.5). **(3)**

(d) State and explain what happens to less reactive metal impurities (such as silver or gold) present in the impure copper anode during this process. **(2)**

(Total for Question 13 is 9 marks)

14 The standard electrode potentials predict that the reaction between acidified manganate(VII) ions and chloride ions, $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ (E = +1.51 V) combined with $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ (E = +1.36 V), giving Ecell = +0.15 V, is thermodynamically feasible, yet in practice the reaction between potassium manganate(VII) and concentrated hydrochloric acid proceeds only slowly at room temperature without gentle heating. Explain why a reaction can be thermodynamically feasible according to Ecell, yet occur only slowly at room temperature, and describe how experimental evidence could be used to determine whether a lack of observed reaction is caused by kinetics or by thermodynamics.

(Total for Question 14 is 6 marks)

15 This question analyses the measurement uncertainty in the redox titration described in Question 11.

(a) The 18.40 cm^3 titre in Question 11 was obtained using a burette that can be read to ± 0.05 cm^3 at each reading. State the absolute uncertainty in the titre volume (from the two burette readings), and calculate its percentage uncertainty. **(3)**

(b) The 25.0 cm^3 sample was measured using a pipette with an uncertainty of ± 0.06 cm^3. Calculate its percentage uncertainty. **(2)**

(c) The 2.50 g mass of ore was measured on a balance with an uncertainty of ± 0.005 g. Calculate its percentage uncertainty. **(2)**

(d) Estimate the overall percentage uncertainty in the final percentage-by-mass result from Question 11 by summing the individual percentage uncertainties found in (a)-(c), and state which measurement contributes the least to the overall uncertainty. **(2)**

(Total for Question 15 is 9 marks)

16 This question uses standard electrode potentials to predict the feasibility of redox reactions between tin, iron and iodine species.

(a) Standard electrode potentials: Fe^{3+}/Fe^{2+} = +0.77 V, Sn^{4+}/Sn^{2+} = +0.15 V. Use these values to predict whether Sn^{2+} ions can reduce Fe^{3+} ions to Fe^{2+}, writing an overall equation for any feasible reaction. **(3)**

(b) Standard electrode potential: I_2/I^- = +0.54 V. Use the electrode potentials to predict whether I^- ions can reduce Sn^{4+} ions to Sn^{2+}, explaining your reasoning. **(3)**

(c) Explain, in general terms, how the relative electrode potentials of two half-cells can be used to predict which species will act as an oxidising agent and which as a reducing agent when they are mixed. **(3)**

(Total for Question 16 is 9 marks)

Mark scheme · 2.5 Redox and Electrochemistry

Question 1

(a) Cl in Cl_2 = 0 **B1**

(a) Cl in Cl^- = -1 and Cl in ClO^- = +1 (both required) **B1**

(a) Answer: Cl_2: 0; Cl^-: -1; ClO^-: +1

(b) reduction: Cl_2 + 2e- -> $2Cl^-$ (oe multiples) **B1**

(b) oxidation: Cl_2 + $4OH^-$ -> $2ClO^-$ + $2H_2O$ + 2e- (oe multiples) **B1**

(b) Answer: Reduction: Cl_2 + 2e- -> $2Cl^-$; Oxidation: Cl_2 + $4OH^-$ -> $2ClO^-$ + $2H_2O$ + 2e-

(c) both half-equations added and divided by 2 so that 2e- cancel **M1**

(c) Cl_2 + $2OH^-$ -> Cl^- + ClO^- + H_2O cao (accept whole-number multiples) **A1**

(c) Answer: Cl_2 + $2OH^-$ -> Cl^- + ClO^- + H_2O

(d) disproportionation cao **B1**

(d) Answer: Disproportionation

Question 2

(a) the emf (potential difference) of a half-cell measured relative to a standard hydrogen electrode oe **B1**

(a) measured under standard conditions: 298 K, 100 kPa, and 1.00 mol dm-3 solution concentrations oe **B1**

(a) Answer: The potential difference (emf) between a half-cell and a standard hydrogen electrode, measured at 298 K, 100 kPa and with 1.00 mol dm-3 solutions

(b) electrodes and ions in the correct order, more negative half-cell on the left **M1**

(b) Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s) fully correct with single/double lines and state symbols cao **A1**

(b) Answer: Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq) | Cu(s)

(c) E cell = E(Cu^{2+}/Cu) - E(Zn^{2+}/Zn) = 0.34 - (-0.76) **M1**

(c) +1.10 V cao **A1**

(c) Answer: +1.10 V

(d) zinc electrode is negative **B1**

(d) zinc has the more negative (less positive) electrode potential, so it is more readily oxidised, releasing electrons into the external circuit oe **B1**

(d) Answer: The zinc electrode; zinc is oxidised more readily (more negative E value) so it supplies electrons to the circuit

Question 3

(a) a high-resistance voltmeter allows (almost) no current to flow through the cell during the measurement **B1**

(a) so the true (maximum) emf is measured without a potential drop caused by current flowing through the internal resistance of the cell oe **B1**

(a) Answer: A high-resistance voltmeter draws negligible current, so the emf measured is the true (zero-current) potential difference, unaffected by internal resistance losses

(b) allows ions to flow between the two half-cells to complete the circuit and maintain electrical neutrality, without allowing the two solutions to mix in bulk oe **B1**

(b) saturated potassium nitrate solution (in filter paper or as an agar gel) oe (accept other inert electrolyte such as ammonium nitrate) **B1**

(b) Answer: It completes the circuit by allowing ion flow (maintaining charge balance) without the solutions mixing; e.g. filter paper soaked in saturated KNO_3(aq)

(c) any one valid reason, e.g. electrode surfaces impure/oxidised, increasing contact resistance **B1**

(c) any second valid reason, e.g. solution concentrations not exactly 1.00 mol dm-3, temperature not exactly 298 K, or resistance in the salt bridge/wires causing a small voltage drop **B1**

(c) Answer: e.g. oxide layer on an electrode increasing resistance, and solution concentrations or temperature not being exactly standard

(d) the emf of the cell decreases (falls below 1.10 V) **B1**

(d) the equilibrium Cu^{2+} + 2e- ⇌ Cu shifts to oppose the decrease in [Cu^{2+}], i.e. towards the reverse (oxidation) direction oe **M1**

(d) this makes E(Cu^{2+}/Cu) less positive (lower) than +0.34 V, so E cell = E(Cu) - E(Zn) is reduced ft **A1**

(d) Answer: The cell emf decreases; lowering [Cu^{2+}] shifts the Cu^{2+} + 2e- ⇌ Cu equilibrium towards Cu^{2+} + 2e-, making E(Cu^{2+}/Cu) less positive and hence lowering E cell

Question 4

(a) colour changes from colourless (or very pale green) to a persistent pale pink/purple oe **B1**

(a) MnO_4^- is intensely coloured (purple) while Mn^{2+} is almost colourless, so $KMnO_4$ acts as its own indicator oe **B1**

(a) Answer: Colourless to persistent pale pink/purple; MnO_4^- (purple) is reduced to almost colourless Mn^{2+}, so the manganate(VII) is self-indicating

(b) 2.40 x 10^{-4} mol cao (awrt 2.40e-4) **B1**

(b) Answer: 2.40 x 10^{-4} mol

(c) 1.20 x 10^{-3} mol cao ft from (b) **B1**

(c) Answer: 1.20 x 10^{-3} mol

(d) total n(Fe^{2+}) = 1.20e-3 x (250/25.0) = 1.20 x 10^{-2} mol ft **M1**

(d) mass = 1.20e-2 x 55.8 **M1**

(d) 0.670 g cao (awrt 0.669-0.670 g) ft **A1**

(d) Answer: 0.670 g

(e) % = (0.6696/2.50) x 100 ft **M1**

(e) 26.8% cao (awrt 26.7-26.8%) ft **A1**

(e) Answer: 26.8%

Question 5

(a) Ag^+/Ag is the positive terminal, since it has the more positive electrode potential (so it is reduced) **B1**

(a) Mg^{2+}/Mg is the negative terminal, since it has the more negative electrode potential (so it is oxidised) **B1**

(a) Answer: Ag^+/Ag positive terminal; Mg^{2+}/Mg negative terminal.

(b) correct method: Ecell = E(positive terminal) - E(negative terminal) = 0.80 - (-2.37) **M1**

(b) +3.17 V, cao **A1**

(b) Answer: +3.17 V

(c) multiply the Ag^+/Ag half-equation by 2 so both half-equations involve 2 electrons **M1**

(c) $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$ **A1**

(c) Answer: $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$

(d) two half-cells (a Mg rod in $Mg^{2+}(aq)$ solution; an Ag rod in $Ag^+(aq)$ solution), connected by a wire through a voltmeter, oe **B1**

(d) a salt bridge (e.g. filter paper soaked in a saturated inert salt solution such as KNO_3) completes the circuit by allowing ion flow between the half-cells without the two solutions mixing, oe **B1**

(d) a high-resistance voltmeter is used so that negligible current flows, ensuring a true equilibrium (standard) potential is measured, oe **B1**

(d) Answer: Two half-cells joined by a wire (via a high-resistance voltmeter) and a salt bridge.

Question 6

(a) $Ag^+ + e^- \rightarrow Ag$ cao **B1**

(a) Answer: $Ag^+ + e^- \rightarrow Ag$

(b) 1350 C cao **B1**

(b) Answer: 1350 C

(c) 0.0140 mol cao (awrt 0.0140 mol) ft **B1**

(c) Answer: 0.0140 mol

(d) n(Ag) = n(e-) = 0.0140 mol (1:1 ratio) ft **M1**

(d) mass = 0.0140 x 108 = 1.51 g cao (awrt 1.51 g) ft **A1**

(d) Answer: 1.51 g

(e) volume of Ag = mass/density = 1.51/10.5 ft **M1**

(e) thickness (cm) = volume/area = 0.1439/12.0 **M1**

(e) 0.120 mm cao (awrt 0.119-0.120 mm) ft **A1**

(e) Answer: 0.120 mm

Question 7

(a) Cr in $Cr_2O_7^{2-}$ = +6 **B1**

(a) Cr in Cr^{3+} = +3, so chromium is reduced (oxidation state decreases) oe **B1**

(a) Answer: +6 in $Cr_2O_7^{2-}$, +3 in Cr^{3+}; chromium is reduced

(b) colour change from orange to green oe **B1**

(b) ethanol is oxidised (to ethanoic acid) oe **B1**

(b) Answer: Orange to green; ethanol is oxidised to ethanoic acid

(c) E cell = $E(Cr_2O_7^{2-}/Cr^{3+}) - E(CH_3COOH/CH_3CH_2OH)$ = 1.33 - 0.19 **M1**

(c) +1.14 V cao **A1**

(c) positive E cell, so the reaction is feasible (thermodynamically favourable) under standard conditions ft **B1**

(c) Answer: +1.14 V; feasible

Question 8

Level 3 A detailed and coherent explanation that links both the thermodynamic meaning of E cell (feasibility under standard conditions) and the kinetic reason (activation energy/rate) why a feasible reaction may not be observed, using correct chemical terminology throughout. **5-6**

Level 2 A explanation that covers at least one of the two key ideas (thermodynamic feasibility versus kinetics) in reasonable detail, or touches on both but with limited development or some inaccuracy. **3-4**

Level 1 Basic or isolated relevant statement(s) with little or no linkage between ideas; chemistry is underdeveloped. **1-2**

Level 0 No relevant chemistry given, or answer entirely incorrect/irrelevant. **0**

Indicative content:

- E cell values are calculated from standard electrode potentials measured under standard conditions (298 K, 100 kPa, 1.00 mol dm-3 solutions); if the actual conditions differ from standard, the real value (and occasionally even the sign) of E cell can differ from the predicted value.
- A positive E cell value shows only that a reaction is thermodynamically feasible (energetically favourable); it gives no information about how fast the reaction will occur.
- Many thermodynamically feasible reactions have a high activation energy, so the rate of reaction may be extremely slow (or immeasurably slow at room temperature) even though the reaction is energetically favourable.
- As a result the reaction may not be observed to occur within a reasonable timescale, even though it is predicted to be feasible.
- Some reactions that are feasible from E cell values only proceed at an observable rate in the presence of a suitable catalyst.
- In practice, concentrations and temperatures often differ from standard conditions, which changes the effective (non-standard) cell potential and can also affect whether the reaction is observed to proceed.

Question 9

(a) copper: +2 -> +1 (reduced) **B1**

(a) iodine: -1 -> 0 (oxidised) **B1**

(a) oxidising agent = Cu^{2+} (copper(II) ions) **B1**

(a) Answer: Cu: +2 to +1 (reduced); I: -1 to 0 (oxidised); oxidising agent = Cu^{2+}

(b) 1.23 x 10^{-3} mol cao **B1**

(b) Answer: 1.23 x 10^{-3} mol

(c) $n(I_2)$ = 1.23e-3 / 2 = 6.15 x 10^{-4} mol ft **M1**

(c) $n(Cu^{2+})$ = 2 x $n(I_2)$ = 1.23 x 10^{-3} mol ft cao **A1**

(c) Answer: $n(I_2)$ = 6.15 x 10^{-4} mol; $n(Cu^{2+})$ = 1.23 x 10^{-3} mol

(d) total $n(Cu^{2+})$ = 1.23e-3 x (250/25.0) = 1.23 x 10^{-2} mol ft **M1**

(d) mass Cu = 1.23e-2 x 63.5 **M1**

(d) % Cu = (0.781/1.20) x 100 = 65.1% cao (awrt 65.0-65.1%) ft **A1**

(d) Answer: 65.1%

Question 10

(a) correct substitution: delta G = -2 x 96500 x 3.17, ft **M1**

(a) -611800 J/mol (accept -611000 to -612000) **A1**

(a) -612 kJ/mol (correct conversion to kJ/mol, appropriate sig figs) **B1**

(a) Answer: -612 kJ/mol

(b) delta G is large and negative, confirming that the reaction is thermodynamically feasible (spontaneous) under standard conditions, oe **B1**

(b) this is consistent with the positive Ecell found in Question 5, since a positive Ecell always corresponds to a negative delta G, oe **B1**

(b) Answer: Confirms the reaction is thermodynamically feasible, consistent with the positive Ecell.

(c) the rate is governed by kinetic factors (e.g. the activation energy, or any protective oxide layer on the magnesium surface), not by delta G, oe **B1**

(c) a large negative delta G only shows the reaction is thermodynamically favourable; it does not guarantee a fast rate, oe **B1**

(c) Answer: Reaction rate is determined by kinetic factors (activation energy), not by the size of delta G.

(d) the reaction involves simple electron transfer to/from the metal surface, oe **B1**

(d) without requiring strong covalent bonds to be broken, unlike many organic reaction mechanisms, so a smaller activation energy is generally needed, oe **B1**

(d) Answer: Simple electron transfer at a metal surface needs no covalent bonds broken, so activation energy is typically low.

Question 11

(a) correct substitution: 0.0200 x (18.40/1000) **M1**

(a) 3.68 x 10^{-4} mol, cao **A1**

(a) Answer: 3.68 x 10^{-4} mol

(b) use the mole ratio $Cr_2O_7^{2-}$: Fe^{2+} = 1 : 6, ft from (a) **M1**

(b) 2.21 x 10^{-3} mol (accept 2.20-2.21 x 10^{-3}), ft **A1**

(b) Answer: 2.21 x 10^{-3} mol

(c) correct scale factor: 250/25.0 = 10, ft from (b) **M1**

(c) 0.0221 mol (accept 0.0220-0.0221), ft **A1**

(c) Answer: 0.0221 mol

(d) mass of Fe = moles (from (c)) x 56.0, ft **M1**

(d) percentage = (mass of Fe / 2.50) x 100 **M1**

(d) 49.5% (accept 49.4-49.6%), ft, cao **A1**

(d) Answer: 49.5%

Question 12

(a) the electrode potential becomes less positive (decreases), oe **B1**

(a) decreasing [Ag^+(aq)] shifts the equilibrium Ag^+ + e- ⇌ Ag to the left, by Le Chatelier's principle, oe **B1**

(a) this reduces the tendency of the half-cell to be reduced (to gain electrons), which is measured as a less positive electrode potential, oe **B1**

(a) Answer: The electrode potential becomes less positive.

(b) the electrode potential becomes more positive (increases), oe **B1**

(b) increasing [H^+(aq)] shifts the equilibrium to the right, by Le Chatelier's principle, oe **B1**

(b) this increases the tendency of the half-cell to be reduced (to gain electrons), which is measured as a more positive electrode potential, oe **B1**

(b) Answer: The electrode potential becomes more positive.

Question 13

(a) convert time to seconds: 2.50 x 3600 = 9000 s, then use Q = It **M1**

(a) 135000 C (1.35 x 10^5 C), cao **A1**

(a) Answer: 1.35 x 10^5 C

(b) correct substitution: 135000/96500, ft from (a) **M1**

(b) 1.40 mol (accept 1.39-1.40), ft **A1**

(b) Answer: 1.40 mol

(c) moles of Cu = moles of electrons / 2, ft from (b) **M1**

(c) mass = moles of Cu x 63.5 **M1**

(c) 44.4 g (accept 44.2-44.6 g), ft **A1**

(c) Answer: 44.4 g

(d) less reactive impurities do not dissolve into solution as ions and instead fall to the bottom of the cell as an anode sludge/mud, oe **B1**

(d) this sludge can be collected and processed separately to recover the valuable metals, oe **B1**

(d) Answer: Less reactive impurities do not dissolve; they collect as anode sludge, which is processed separately.

Question 14

Level 3 A detailed, correct and coherent explanation distinguishing thermodynamic feasibility (from Ecell/delta G) from reaction rate (kinetics/activation energy), with a clearly described, valid experimental method (e.g. heating or adding a catalyst) that would distinguish a kinetic barrier from thermodynamic infeasibility, and a correct interpretation of the possible outcomes. **5-6**

Level 2 A mostly correct distinction between feasibility and rate is made, with some reference to activation energy, and a broadly valid experimental suggestion, but the explanation or the interpretation of the experimental evidence is underdeveloped or contains a minor inaccuracy. **3-4**

Level 1 Some relevant, briefly stated points are made (e.g. that the reaction is 'just slow') without a clear link to activation energy, or without a valid, clearly explained experimental method to distinguish kinetic and thermodynamic causes. **1-2**

Indicative content:

- A positive Ecell (and hence a negative delta G, since delta G = -nFEcell) indicates that a reaction is thermodynamically feasible (energetically favourable), but this says nothing about how fast the reaction proceeds.
- The rate of a reaction depends on its activation energy and the fraction of collisions with sufficient energy to react, factors that are entirely separate from the size or sign of Ecell.
- A reaction with a favourable (positive) Ecell can still have a high activation energy, so at room temperature very few collisions have enough energy to react, making the reaction appear slow or seem not to occur at all.
- To test whether a lack of observed reaction is due to a kinetic barrier rather than thermodynamic infeasibility, the mixture could be heated: if the reaction then proceeds (e.g. a new product such as chlorine gas is observed), this shows the reaction was thermodynamically feasible all along but had been prevented from occurring at a significant rate by a high activation energy.
- Alternatively, adding a suitable catalyst and observing whether the reaction then proceeds at room temperature shows the same thing, since a catalyst can only speed up a reaction that is already thermodynamically feasible; it cannot make a thermodynamically unfeasible reaction occur.
- If heating or adding a catalyst still produces no observable reaction, this suggests the original Ecell-based prediction may not hold under the real experimental conditions used (which may differ from the standard conditions used to measure Ecell).

Question 15

(a) absolute uncertainty = 0.05 + 0.05 = ± 0.10 cm^3 **B1**

(a) correct substitution: (0.10/18.40) x 100 **M1**

(a) 0.54% (accept 0.5-0.55%) **A1**

(a) Answer: ± 0.10 cm^3; 0.54%

(b) correct substitution: (0.06/25.0) x 100 **M1**

(b) 0.24%, cao **A1**

(b) Answer: 0.24%

(c) correct substitution: (0.005/2.50) x 100 **M1**

(c) 0.20%, cao **A1**

(c) Answer: 0.20%

(d) total percentage uncertainty = 0.54 + 0.24 + 0.20, ft **M1**

(d) approximately 1.0% (accept 0.9-1.0%); the mass measurement (0.20%) contributes the least, oe **B1**

(d) Answer: Approximately 1.0%; the mass measurement contributes least.

Question 16

(a) identify that Fe^{3+}/Fe^{2+} has the more positive electrode potential, so Fe^{3+} is reduced and Sn^{2+} is oxidised **M1**

(a) Ecell = 0.77 - 0.15 = +0.62 V, which is positive, so the reaction is feasible **A1**

(a) $Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$ **B1**

(a) Answer: Feasible; $Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$ (Ecell = +0.62 V)

(b) correct method: Ecell = $E(Sn^{4+}/Sn^{2+}) - E(I_2/I^-)$ = 0.15 - 0.54 **M1**

(b) Ecell = -0.39 V, which is negative, so the reaction is NOT thermodynamically feasible **A1**

(b) I_2/I^- has a more positive electrode potential than Sn^{4+}/Sn^{2+}, so I^- is too weak a reducing agent to reduce Sn^{4+} (equivalently, Sn^{4+} is not a strong enough oxidising agent to oxidise I^-), oe **B1**

(b) Answer: Not feasible (Ecell = -0.39 V).

(c) the half-cell with the more positive (higher) electrode potential proceeds as written (as a reduction), so that species acts as the oxidising agent (and is itself reduced), oe **B1**

(c) the half-cell with the more negative (lower) electrode potential is forced to run in reverse (as an oxidation), so that species acts as the reducing agent (and is itself oxidised), oe **B1**

(c) a reaction is thermodynamically feasible only if Ecell (= E of the reduced half-cell minus E of the oxidised half-cell) is positive, oe **B1**

(c) Answer: The more positive half-cell is reduced (the oxidising agent); the more negative half-cell is oxidised (the reducing agent).