2.5 Redox and Electrochemistry: 1-hour Pack

AQA 7405 · Calculator allowed · about 60 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 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 1 is 8 marks)

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2 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 2 is 7 marks)

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3 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 3 is 9 marks)

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4 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 4 is 9 marks)

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5 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 5 is 6 marks)

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6 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 6 is 9 marks)

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Mark scheme · 2.5 Redox and Electrochemistry: 1-hour Pack

Question 1

(a) Ag^+ + e- -> Ag cao **B1**

(a) Answer: Ag^+ + e- -> 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 2

(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 3

(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 4

(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.

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Question 5

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 6

(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).

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