AC5D Redox and Electrochemistry: Depth and Exam Drill

AQA 7405 · Calculator allowed · about 150 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests key definitions used throughout the redox and electrochemistry topic.

(a) Define oxidation in terms of electron transfer. **(1)**

(b) Define an oxidising agent. **(1)**

(c) State the conditions that define a standard electrode potential. **(2)**

(Total for Question 1 is 4 marks)

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2 This question is about the redox reaction between acidified potassium dichromate(VI) and iron(II) ions.

(a) Write the balanced half-equation for the reduction of dichromate(VI) ions, $Cr_2O_7^{2-}$, to Cr^{3+} ions in acidic solution. **(2)**

(b) Write the half-equation for the oxidation of Fe^{2+} ions to Fe^{3+} ions. **(1)**

(c) Combine the two half-equations to give the overall ionic equation for the reaction between acidified dichromate(VI) ions and Fe^{2+} ions, ensuring the electrons cancel. **(2)**

(d) State the colour change observed during this reaction, and identify the oxidising agent and the reducing agent. **(3)**

(Total for Question 2 is 8 marks)

3 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 Fe2+(aq); the solution is made up to 250 cm3 in a volumetric flask. A 25.0 cm3 sample of this solution requires 18.40 cm3 of 0.0200 mol/dm3 potassium dichromate(VI) solution to reach the end point, using the reaction $Cr2O7^{2}$- + 14H+ + 6Fe2+ -> 2Cr3+ + 7H2O + 6Fe3+. Calculate the number of moles of $Cr2O7^{2}$- used in the titration. **(2)**

(b) Calculate the number of moles of Fe2+ in the 25.0 cm3 sample. **(2)**

(c) Calculate the total number of moles of Fe2+ (and hence Fe) in the original 250 cm3 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 3 is 9 marks)

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

(a) Standard electrode potentials: Mg2+/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 4 is 9 marks)

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5 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- ≤> 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 MnO4-(aq) + 8H+(aq) + 5e- ≤> Mn2+(aq) + 4H2O(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 5 is 6 marks)

6 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 6 is 9 marks)

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7 The standard electrode potentials predict that the reaction between acidified manganate(VII) ions and chloride ions, $MnO_4^-(aq) + 8H^+(aq) + 5e^- \leq> Mn^{2+}(aq) + 4H_2O(l)$ (E = +1.51 V) combined with $Cl_2(g) + 2e^- \leq> 2Cl^-(aq)$ (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 7 is 6 marks)

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8 This question analyses the measurement uncertainty in the redox titration described in Question 3.

(a) The 18.40 cm3 titre in Question 3 was obtained using a burette that can be read to ± 0.05 cm3 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 cm3 sample was measured using a pipette with an uncertainty of ± 0.06 cm3. 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 3 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 8 is 9 marks)

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

(a) Standard electrode potentials: Fe3+/Fe2+ = +0.77 V, Sn4+/Sn2+ = +0.15 V. Use these values to predict whether Sn2+ ions can reduce Fe3+ ions to Fe2+, writing an overall equation for any feasible reaction. **(3)**

(b) Standard electrode potential: I2/I- = +0.54 V. Use the electrode potentials to predict whether I- ions can reduce Sn4+ ions to Sn2+, 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 9 is 9 marks)

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10 This synoptic question links the EMF of the magnesium-silver cell from Question 4 to its Gibbs free energy change, and to the separate question of reaction rate.

(a) Using Ecell = +3.17 V from Question 4 (for Mg + 2Ag+ -> Mg2+ + 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)

Mark scheme · AC5D Redox and Electrochemistry: Depth and Exam Drill

Question 1

- (a) **B1** loss of electrons, oe
- **(a) Answer: Loss of electrons.**
- (b) **B1** a species that accepts electrons from another species (causing it to be oxidised) and is itself reduced, oe
- **(b) Answer: A species that accepts electrons from another species and is itself reduced.**
- (c) **B1** 298 K (25 degrees C), 100 kPa pressure for any gases, and 1 mol/dm3 concentration for solutions, oe
- (c) **B1** measured relative to a standard hydrogen electrode, oe
- **(c) Answer: 298 K, 100 kPa, 1 mol/dm3, measured against a standard hydrogen electrode.**

Question 2

- (a) **B1** correct atom balance: $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
- (a) **B1** correct electron balance: + 6e- on the left, giving matching charge (+6) on both sides
- **(a) Answer: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$**
- (b) **B1** $Fe^{2+} \rightarrow Fe^{3+} + e^-$
- **(b) Answer: $Fe^{2+} \rightarrow Fe^{3+} + e^-$**
- (c) **M1** multiply the Fe2+ half-equation by 6 so that 6 electrons are transferred in each half-equation
- (c) **A1** $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$
- **(c) Answer: $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$**
- (d) **B1** colour changes from orange (dichromate(VI)) to green (Cr3+), oe
- (d) **B1** oxidising agent = dichromate(VI) ions, $Cr_2O_7^{2-}$
- (d) **B1** reducing agent = Fe2+ ions
- **(d) Answer: Orange to green; oxidising agent $Cr_2O_7^{2-}$; reducing agent Fe^{2+}.**

Question 3

- (a) **M1** correct substitution: 0.0200 x (18.40/1000)
- (a) **A1** 3.68×10^{-4} mol, cao
- **(a) Answer: 3.68×10^{-4} mol**
- (b) **M1** use the mole ratio $Cr_2O_7^{2-}$: Fe^{2+} = 1 : 6, ft from (a)
- (b) **A1** 2.21×10^{-3} mol (accept $2.20\text{-}2.21 \times 10^{-3}$), ft
- **(b) Answer: 2.21×10^{-3} mol**
- (c) **M1** correct scale factor: 250/25.0 = 10, ft from (b)
- (c) **A1** 0.0221 mol (accept 0.0220-0.0221), ft
- **(c) Answer: 0.0221 mol**
- (d) **M1** mass of Fe = moles (from (c)) x 56.0, ft
- (d) **M1** percentage = (mass of Fe / 2.50) x 100
- (d) **A1** 49.5% (accept 49.4-49.6%), ft, cao
- **(d) Answer: 49.5%**

Question 4

- (a) **B1** Ag+/Ag is the positive terminal, since it has the more positive electrode potential (so it is reduced)
- (a) **B1** Mg2+/Mg is the negative terminal, since it has the more negative electrode potential (so it is oxidised)
- **(a) Answer: Ag+/Ag positive terminal; Mg2+/Mg negative terminal.**
- (b) **M1** correct method: Ecell = E(positive terminal) - E(negative terminal) = 0.80 - (-2.37)
- (b) **A1** +3.17 V, cao
- **(b) Answer: +3.17 V**
- (c) **M1** multiply the Ag+/Ag half-equation by 2 so both half-equations involve 2 electrons
- (c) **A1** Mg + 2Ag+ -> Mg2+ + 2Ag
- **(c) Answer: Mg + 2Ag+ -> Mg2+ + 2Ag**
- (d) **B1** two half-cells (a Mg rod in Mg2+(aq) solution; an Ag rod in Ag+(aq) solution), connected by a wire through a voltmeter, oe
- (d) **B1** a salt bridge (e.g. filter paper soaked in a saturated inert salt solution such as KNO3) completes the circuit by allowing ion flow between the half-cells without the two solutions mixing, oe
- (d) **B1** a high-resistance voltmeter is used so that negligible current flows, ensuring a true equilibrium (standard) potential is measured, oe
- **(d) Answer: Two half-cells joined by a wire (via a high-resistance voltmeter) and a salt bridge.**

Question 5

- (a) **B1** the electrode potential becomes less positive (decreases), oe
- (a) **B1** decreasing [Ag+(aq)] shifts the equilibrium Ag+ + e- ≤> Ag to the left, by Le Chatelier's principle, oe
- (a) **B1** this reduces the tendency of the half-cell to be reduced (to gain electrons), which is measured as a less positive electrode potential, oe
- **(a) Answer: The electrode potential becomes less positive.**
- (b) **B1** the electrode potential becomes more positive (increases), oe
- (b) **B1** increasing [H+(aq)] shifts the equilibrium to the right, by Le Chatelier's principle, oe
- (b) **B1** this increases the tendency of the half-cell to be reduced (to gain electrons), which is measured as a more positive electrode potential, oe
- **(b) Answer: The electrode potential becomes more positive.**

Question 6

- (a) **M1** convert time to seconds: 2.50 x 3600 = 9000 s, then use Q = It
- (a) **A1** 135000 C (1.35×10^5 C), cao
- **(a) Answer: 1.35×10^5 C**
- (b) **M1** correct substitution: 135000/96500, ft from (a)
- (b) **A1** 1.40 mol (accept 1.39-1.40), ft
- **(b) Answer: 1.40 mol**
- (c) **M1** moles of Cu = moles of electrons / 2, ft from (b)
- (c) **M1** mass = moles of Cu x 63.5
- (c) **A1** 44.4 g (accept 44.2-44.6 g), ft
- **(c) Answer: 44.4 g**
- (d) **B1** 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
- (d) **B1** this sludge can be collected and processed separately to recover the valuable metals, oe
- **(d) Answer: Less reactive impurities do not dissolve; they collect as anode sludge, which is processed separately.**

Question 7

- **Level 3** (5-6): 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.
- **Level 2** (3-4): 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.
- **Level 1** (1-2): 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.
- **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 8

- (a) **B1** absolute uncertainty = 0.05 + 0.05 = ± 0.10 cm3
- (a) **M1** correct substitution: (0.10/18.40) x 100
- (a) **A1** 0.54% (accept 0.5-0.55%)
- **(a) Answer: ± 0.10 cm3; 0.54%**
- (b) **M1** correct substitution: (0.06/25.0) x 100
- (b) **A1** 0.24%, cao
- **(b) Answer: 0.24%**
- (c) **M1** correct substitution: (0.005/2.50) x 100
- (c) **A1** 0.20%, cao
- **(c) Answer: 0.20%**
- (d) **M1** total percentage uncertainty = 0.54 + 0.24 + 0.20, ft
- (d) **B1** approximately 1.0% (accept 0.9-1.0%); the mass measurement (0.20%) contributes the least, oe
- **(d) Answer: Approximately 1.0%; the mass measurement contributes least.**

Question 9

- (a) **M1** identify that Fe3+/Fe2+ has the more positive electrode potential, so Fe3+ is reduced and Sn2+ is oxidised
- (a) **A1** Ecell = 0.77 - 0.15 = +0.62 V, which is positive, so the reaction is feasible
- (a) **B1** Sn2+ + 2Fe3+ -> Sn4+ + 2Fe2+
- **(a) Answer: Feasible; Sn2+ + 2Fe3+ -> Sn4+ + 2Fe2+ (Ecell = +0.62 V)**
- (b) **M1** correct method: Ecell = E(Sn4+/Sn2+) - E(I2/I-) = 0.15 - 0.54
- (b) **A1** Ecell = -0.39 V, which is negative, so the reaction is NOT thermodynamically feasible
- (b) **B1** I2/I- has a more positive electrode potential than Sn4+/Sn2+, so I- is too weak a reducing agent to reduce Sn4+ (equivalently, Sn4+ is not a strong enough oxidising agent to oxidise I-), oe
- **(b) Answer: Not feasible (Ecell = -0.39 V).**
- (c) **B1** 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
- (c) **B1** 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
- (c) **B1** a reaction is thermodynamically feasible only if Ecell (= E of the reduced half-cell minus E of the oxidised half-cell) is positive, oe
- **(c) Answer: The more positive half-cell is reduced (the oxidising agent); the more negative half-cell is oxidised (the reducing agent).**

Question 10

- (a) **M1** correct substitution: delta G = -2 x 96500 x 3.17, ft
- (a) **A1** -611800 J/mol (accept -611000 to -612000)
- (a) **B1** -612 kJ/mol (correct conversion to kJ/mol, appropriate sig figs)
- **(a) Answer: -612 kJ/mol**
- (b) **B1** delta G is large and negative, confirming that the reaction is thermodynamically feasible (spontaneous) under standard conditions, oe
- (b) **B1** this is consistent with the positive Ecell found in Question 4, since a positive Ecell always corresponds to a negative delta G, oe
- **(b) Answer: Confirms the reaction is thermodynamically feasible, consistent with the positive Ecell.**
- (c) **B1** 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
- (c) **B1** a large negative delta G only shows the reaction is thermodynamically favourable; it does not guarantee a fast rate, oe
- **(c) Answer: Reaction rate is determined by kinetic factors (activation energy), not by the size of delta G.**
- (d) **B1** the reaction involves simple electron transfer to/from the metal surface, oe
- (d) **B1** without requiring strong covalent bonds to be broken, unlike many organic reaction mechanisms, so a smaller activation energy is generally needed, oe
- **(d) Answer: Simple electron transfer at a metal surface needs no covalent bonds broken, so activation energy is typically low.**