2.12 Chemistry: Electrode Potentials and Transition Metals

Total Marks

AQA 7405 · Calculator allowed · about 140 minutes · Write-in edition

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question is about general properties of transition elements and a calculation on a hydrated transition metal salt.

(a) Explain, referring to the energies of the 3d and 4s orbitals, why transition metals commonly show variable oxidation states. **(2)**

(b) State two characteristic properties, other than variable oxidation states, that are shared by transition metals and/or their compounds. **(2)**

(c) A sample of hydrated cobalt(II) chloride, $CoCl_2.xH2O$, has a molar mass of 237.9 g mol-1. Given that the molar mass of anhydrous $CoCl_2$ is 129.9 g mol-1, calculate x, the number of moles of water of crystallisation per mole of $CoCl_2$. **(4)**

(Total for Question 1 is 8 marks)

2 This question is about precipitation reactions of transition metal ions with aqueous sodium hydroxide.

(a) State the colour of the precipitate formed, and identify the species present, when aqueous sodium hydroxide is added separately to solutions of $Fe^{2+}(aq)$, $Fe^{3+}(aq)$, and $Cu^{2+}(aq)$. **(3)**

(b) Chromium(III) hydroxide, $Cr(OH)_3$, is described as amphoteric. Using ionic equations, explain what this means with reference to its reactions with excess sodium hydroxide and with a strong acid. **(3)**

(c) The green precipitate of $Fe(OH)_2$ slowly turns to a rust-orange colour on standing in air. Explain this observation, giving an equation. **(2)**

(Total for Question 2 is 8 marks)

3 A colorimeter is calibrated using standard solutions of hydrated copper(II) sulfate, plotting absorbance against concentration to give a straight-line calibration graph through the origin, with gradient (calibration constant) k = 42.5 dm3 mol-1 (absorbance = k x concentration). An unknown copper(II) sulfate solution gives an absorbance of 0.638 using the same colorimeter and filter.

(a) Explain, in terms of the colour of the solution, why a red/orange filter (rather than a blue filter) should be selected for this colorimeter measurement. **(2)**

(b) Using the calibration data given, calculate the concentration, in mol dm-3, of Cu^{2+} in the unknown solution. **(3)**

(c) This solution was prepared by diluting 10.0 cm^3 of the original stock solution to a total of 250 cm^3 with distilled water before measuring its absorbance. Calculate the concentration, in mol dm-3, of Cu^{2+} in the original (undiluted) stock solution. **(2)**

(Total for Question 3 is 7 marks)

4 This question uses practical techniques from the required practical on titration. $EDTA^{4-}$ forms a 1:1 complex ion with Ca^{2+}, [Ca(EDTA)]2-, and this reaction is used to determine the total hardness of a water sample. A 100.0 cm^3 sample of tap water is titrated with 0.0100 mol dm-3 EDTA solution, using an indicator that changes colour once all the free Ca^{2+} (and Mg^{2+}) has been complexed. The mean titre required is 24.60 cm^3.

(a) State the coordination number of Ca^{2+} in the [Ca(EDTA)]2- complex ion, and explain why $EDTA^{4-}$ can form this complex with only one $EDTA^{4-}$ ion per Ca^{2+} ion. **(2)**

(b) Describe the colour change that would be observed at the end point of this titration, in general terms, given that the indicator used binds to free Ca^{2+} (giving one colour) but is a different colour when it is not bound to a metal ion. **(2)**

(c) Calculate the amount, in mol, of $EDTA^{4-}$ used in the titration, and hence the concentration, in mol dm-3, of Ca^{2+} in the water sample. **(4)**

(d) Express this hardness as a concentration in mg dm-3 of $CaCO_3$ equivalent (Mr of $CaCO_3$ = 100.1), and use the scale below to classify this water sample: soft, less than 60 mg dm-3; moderately hard, 60 to 120 mg dm-3; hard, 120 to 180 mg dm-3; very hard, greater than 180 mg dm-3 (all as $CaCO_3$). **(3)**

(Total for Question 4 is 11 marks)

5 This question uses techniques from the required practical on measuring the emf of an electrochemical cell. A student sets up a cell using a platinum electrode dipping into a solution containing both $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions, connected by a salt bridge to a second platinum electrode dipping into a solution containing both $Cr^{3+}(aq)$ and $Cr^{2+}(aq)$ ions, all under standard conditions. Standard electrode potentials: $E(Fe^{3+}/Fe^{2+}) = +0.77$ V; $E(Cr^{3+}/Cr^{2+}) = -0.41$ V.

(a) Explain why a platinum electrode, rather than a strip of metal, must be used for each of these two half-cells. **(2)**

(b) Calculate the standard emf of this cell. **(1)**

(c) State which half-cell forms the positive electrode of this cell, and explain your reasoning. **(2)**

(d) The student's measured emf for this cell was 1.16 V, slightly below the theoretical value. Suggest two reasons for this discrepancy that relate specifically to this cell using platinum electrodes with ion-ion redox couples in solution (rather than solid metal electrodes). **(3)**

(Total for Question 5 is 8 marks)

6 Standard electrode potentials: $E(MnO_4^-/Mn^{2+}$, acidic) = +1.51 V; $E(O_2/H_2O)$ = +1.23 V, for the half-equation $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$.

(a) Use these data to show, by calculation, that acidified potassium manganate(VII) solution is thermodynamically capable of oxidising water to oxygen gas. **(3)**

(b) Despite this, acidified $KMnO_4$(aq) solutions can be stored and used as titrants over the timescale of a normal titration without significant decomposition. Explain this observation in terms of reaction kinetics. **(3)**

(c) Suggest why $KMnO_4$(aq) solutions are typically stored in dark (brown glass) bottles, away from direct sunlight. **(2)**

(Total for Question 6 is 8 marks)

7 Explain why many transition metal ion complexes are coloured, but the corresponding complexes of calcium (Ca^{2+}) and zinc (Zn^{2+}) are colourless. Your answer should refer to d-orbitals, ligands and electronic transitions.

(Total for Question 7 is 6 marks)

8 Ammonium vanadate(V) solution (containing VO_2^+ ions, yellow) is reduced by an excess of zinc metal in dilute sulfuric acid. Standard electrode potentials: $VO_2^+ + 2H^+ + e^- \rightarrow VO_2^+ + H_2O$, E = +1.00 V; $VO_2^+ + 2H^+ + e^- \rightarrow V^{3+} + H_2O$, E = +0.34 V; $V^{3+} + e^- \rightarrow V^{2+}$, E = -0.26 V; $Zn^{2+} + 2e^- \rightarrow Zn$, E = -0.76 V.

(a) State the sequence of colour changes observed as reduction proceeds from vanadium(V) to vanadium(II), naming the oxidation state and colour present at each stage. **(4)**

(b) Using the standard electrode potentials given, show by calculation that zinc metal is able to reduce VO_2^+ all the way down to V^{2+}, i.e. that each of the three reduction steps is thermodynamically feasible. **(4)**

(c) Write the overall balanced ionic equation, including state symbols, for the direct reduction of VO_2^+ to V^{2+} by zinc metal in acidic solution. **(4)**

(Total for Question 8 is 12 marks)

9 Copper(I) ions are unstable in aqueous solution but can be stabilised as insoluble compounds or as complex ions. Standard electrode potentials: $E(Cu^{2+}/Cu^{+}) = +0.15$ V; $E(Cu^{+}/Cu) = +0.52$ V.

(a) Use an appropriate calculation to show that aqueous Cu^{+} ions disproportionate to form Cu^{2+} and Cu, and state which copper species is oxidised and which is reduced in this reaction. **(3)**

(b) Despite this, solid copper(I) oxide, Cu_2O, and copper(I) chloride, CuCl, are both stable compounds that do not spontaneously disproportionate. Suggest why Cu^{+} is stable in these solids but not in aqueous solution. **(3)**

(c) In the presence of excess copper metal and a source of ammonia, Cu^{+} can be stabilised in solution as the complex ion $[Cu(NH_3)_2]^{+}$, which does not readily disproportionate. Explain, in terms of the relative stabilisation of the Cu^{+} and Cu^{2+} oxidation states by ligands, how forming this complex ion helps to prevent disproportionation. **(4)**

(Total for Question 9 is 10 marks)

10 The standard electrode potential for $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ is +0.77 V. When cyanide ligands replace the water ligands, the standard electrode potential for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ falls to +0.36 V.

(a) State what this fall in E value indicates about the relative oxidising strength of $[Fe(CN)_6]^{3-}$ compared with $[Fe(H_2O)_6]^{3+}$. **(2)**

(b) Explain, in terms of the relative stabilisation of the Fe^{3+} and Fe^{2+} oxidation states by the CN^- ligand, why complexing with cyanide causes this decrease in electrode potential. **(3)**

(c) Given $E(I_2/I^-)$ = +0.54 V, use the E value of +0.36 V for $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ to determine whether $[Fe(CN)_6]^{3-}$ can oxidise iodide ions to iodine, and contrast this with the behaviour of $[Fe(H_2O)_6]^{3+}$. **(3)**

(Total for Question 10 is 8 marks)

11 This question is about catalysis by transition metals and their ions.

(a) Iron is used as a heterogeneous catalyst in the Haber process, and platinum, palladium and rhodium are used in catalytic converters. Explain, using the terms adsorption and active site, how a heterogeneous catalyst increases the rate of a reaction, and explain why catalytic converters use a fine mesh or honeycomb structure. **(4)**

(b) The reaction between $C_2O_4^{2-}(aq)$ and $MnO_4^-(aq)$ in acidic solution is autocatalysed by the Mn^{2+} ions produced. Explain what is meant by autocatalysis, why the initial rate of this reaction is slow, and describe the shape of a graph of $[MnO_4^-]$ against time that you would expect. **(4)**

(c) The reaction between peroxodisulfate ions, $S_2O_8^{2-}$, and iodide ions, I^-, is slow when the ions are mixed directly, but is catalysed homogeneously by Fe^{2+} ions. Standard electrode potentials: $E(S_2O_8^{2-}/SO_4^{2-}) = +2.01$ V; $E(Fe^{3+}/Fe^{2+}) = +0.77$ V; $E(I_2/I^-) = +0.54$ V. Show, using these E values, that Fe^{2+} can catalyse this reaction via two separate feasible steps, and explain why this two-step route avoids the main reason the direct, uncatalysed reaction is slow. **(5)**

(Total for Question 11 is 13 marks)

Mark scheme · 2.12 Chemistry: Electrode Potentials and Transition Metals

Question 1

(a) the 3d and 4s sub-shells are very close together in energy (oe) **M1**

(a) so successive ionisation energies (for removing electrons beyond the first two 4s electrons, from the 3d sub-shell) increase relatively gradually, without one very large jump, allowing a variable number of electrons to be lost to form ions of different, comparably-stable oxidation states (oe) **A1**

(a) Answer: The 3d and 4s orbitals are close in energy, so successive ionisation energies increase gradually rather than showing one large jump, allowing several oxidation states to be reasonably stable.

(b) forming coloured compounds/ions (in solution or as solids) **B1**

(b) acting as catalysts (as elements or as compounds/ions); allow forming complex ions with ligands as an alternative second property **B1**

(b) Answer: For example: forming coloured compounds/ions, and acting as catalysts (or forming complex ions with ligands).

(c) mass attributable to water = 237.9 - 129.9 = 108.0 **M1**

(c) x = 108.0 / 18.0 **M1**

(c) x = 6.00 cao **A1**

(c) so the formula is $CoCl_2.6H_2O$ **B1**

(c) Answer: x = 6; the formula is $CoCl_2.6H_2O$.

Question 2

(a) $Fe^{2+}(aq)$: green precipitate of $Fe(OH)_2$ **B1**

(a) $Fe^{3+}(aq)$: orange-brown (rust-coloured) precipitate of $Fe(OH)_3$ **B1**

(a) $Cu^{2+}(aq)$: pale blue precipitate of $Cu(OH)_2$ **B1**

(a) Answer: Fe^{2+}: green $Fe(OH)_2$. Fe^{3+}: orange-brown $Fe(OH)_3$. Cu^{2+}: pale blue $Cu(OH)_2$.

(b) amphoteric means $Cr(OH)_3$ can react with both a base and an acid (oe) **B1**

(b) with excess $OH^-(aq)$: $Cr(OH)_3(s) + 3OH^-(aq) \rightarrow [Cr(OH)_6]^{3-}(aq)$, the precipitate dissolves to give a (dark) green solution **B1**

(b) with a strong acid: $Cr(OH)_3(s) + 3H^+(aq) \rightarrow Cr^{3+}(aq) + 3H_2O(l)$, the precipitate dissolves to give a green Cr^{3+} solution **B1**

(b) Answer: Amphoteric means it reacts with both acids and bases. With excess OH^-: $Cr(OH)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-}$ (dissolves, green solution). With acid: $Cr(OH)_3 + 3H^+ \rightarrow Cr^{3+} + 3H_2O$ (dissolves, green solution).

(c) $Fe(OH)_2$ is oxidised by dissolved oxygen (and water) in the air to $Fe(OH)_3$, which is the rust-orange colour observed (oe) **B1**

(c) $4Fe(OH)_2(s) + O_2(g) + 2H_2O(l) \rightarrow 4Fe(OH)_3(s)$ **B1**

(c) Answer: $Fe(OH)_2$ is oxidised by atmospheric oxygen to $Fe(OH)_3$: $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$.

Question 3

(a) aqueous Cu^{2+} solutions ($[Cu(H_2O)_6]^{2+}$) are pale blue, meaning they strongly absorb light from the complementary (red/orange) part of the visible spectrum (oe) **B1**

(a) using a red/orange filter means the light passing through the solution is strongly absorbed, giving the largest, most sensitive change in absorbance reading with concentration (oe) **B1**

(a) Answer: The blue solution strongly absorbs red/orange light (its complementary colour); using a red/orange filter means absorbance changes most sensitively with concentration.

(b) concentration = absorbance / k = 0.638 / 42.5 **M1**

(b) 0.0150 mol dm-3 cao (awrt 0.0150) **A1**

(b) correct rearrangement of absorbance = k x concentration shown **B1**

(b) Answer: 0.0150 mol dm-3

(c) c1 = c2 x V2 / V1 = 0.0150 x 250 / 10.0 **M1**

(c) 0.375 mol dm-3 cao ft from (b) **A1**

(c) Answer: 0.375 mol dm-3

Question 4

(a) coordination number = 6 **B1**

(a) because $EDTA^{4-}$ is hexadentate, providing all six donor atoms (bonds) needed by Ca^{2+}, so only one $EDTA^{4-}$ ion is required per Ca^{2+} ion (oe) **B1**

(a) Answer: Coordination number = 6; since $EDTA^{4-}$ is hexadentate it alone can supply all six dative bonds to Ca^{2+}, so a 1:1 complex forms.

(b) before the end point, free Ca^{2+} ions are still present in solution, bound to the indicator, giving the indicator's 'metal-bound' colour **B1**

(b) at the end point, the last free Ca^{2+} ions are complexed by $EDTA^{4-}$ (which binds Ca^{2+} more strongly than the indicator does), releasing the indicator, which changes to its own (free/uncomplexed) colour (oe) **B1**

(b) Answer: While free Ca^{2+} remains, the indicator stays bound to it, showing its metal-bound colour; at the end point, $EDTA^{4-}$ (which binds Ca^{2+} more strongly) displaces the last of the indicator from Ca^{2+}, and the colour changes to the indicator's free (unbound) colour.

(c) $n(EDTA^{4-}) = 0.0100 \times (24.60/1000) = 2.460 \times 10^{-4}$ mol **M1**

(c) $n(Ca^{2+}) = n(EDTA^{4-}) = 2.460 \times 10^{-4}$ mol (1:1 ratio) **M1**

(c) concentration = n/V = 2.460e-4 / 0.1000 **M1**

(c) 2.46×10^{-3} mol dm-3 cao (awrt 2.46e-3) **A1**

(c) Answer: 2.46×10^{-3} mol dm-3

(d) mass of $CaCO_3$ equivalent per dm3 = $2.460 \times 10^{-3} \times 100.1$ **M1**

(d) 246 mg dm-3 cao (awrt 246) **A1**

(d) classified as very hard water (since 246 mg dm-3 is greater than 180 mg dm-3) ft **B1**

(d) Answer: 246 mg dm-3 as $CaCO_3$; this is classified as very hard water.

Question 5

(a) neither half-cell involves a solid metal in equilibrium with its own ion (both couples are between two different oxidation states of ions in solution), so there is no solid metal electrode available to use (oe) **M1**

(a) platinum is used because it is inert/unreactive: it does not itself take part in the reaction, but simply provides a conducting surface at which electrons can be transferred to or from the ions in solution (oe) **A1**

(a) Answer: Both couples involve only dissolved ions (no solid metal), so an inert platinum electrode is used to conduct electrons to/from the solution without itself reacting.

(b) +1.18 V cao (E cell = 0.77 - (-0.41)) **B1**

(b) Answer: +1.18 V

(c) the Fe^{3+}/Fe^{2+} half-cell is the positive electrode **B1**

(c) because it has the more positive (higher) standard electrode potential, so it is the couple that is reduced (accepts electrons) when the cell operates (oe) **B1**

(c) Answer: The Fe^{3+}/Fe^{2+} half-cell; it has the more positive E value, so it is reduced (accepts electrons from the Cr^{3+}/Cr^{2+} half-cell) when the cell operates.

(d) Cr^{2+} is a very strong reducing agent and is readily oxidised by dissolved oxygen in the air/solution before or during the measurement, reducing the effective concentration of Cr^{2+} (moving that half-cell away from standard conditions and altering its potential) (oe) **B1**

(d) surface contamination, incomplete platinisation, or slow electron-transfer kinetics at the inert platinum surface can mean true equilibrium (and hence the full theoretical potential) has not yet been established when the reading is taken (oe) **B1**

(d) small amounts of current drawn by the voltmeter (not perfectly infinite resistance) reduce the reading slightly below the true zero-current emf (oe); allow any two valid, distinct reasons specific to this system **B1**

(d) Answer: For example: Cr^{2+} is readily air-oxidised by dissolved oxygen, shifting that half-cell from standard conditions; and/or slow electron-transfer kinetics or surface contamination at the platinum electrodes mean equilibrium is not fully established when the reading is taken.

Question 6

(a) E cell = $E(MnO_4^-/Mn^{2+}) - E(O_2/H_2O)$ = 1.51 - 1.23 **M1**

(a) = +0.28 V cao **A1**

(a) positive E cell, so the reaction (MnO_4^- oxidising H_2O to O_2) is thermodynamically feasible **B1**

(a) Answer: E cell = +0.28 V, positive, so acidified $KMnO_4$ is thermodynamically capable of oxidising water to oxygen.

(b) a positive E cell value only shows that a reaction is thermodynamically feasible (energetically favourable); it gives no information about the rate at which the reaction occurs (oe) **M1**

(b) in the absence of a catalyst, this decomposition reaction has a high activation energy, so its rate at room temperature is extremely slow (oe) **M1**

(b) so, although $KMnO_4(aq)$ does very slowly decompose over long-term storage (which is why standard solutions are periodically re-standardised), this occurs far too slowly to have any measurable effect during the timescale of a single titration (oe) **A1**

(b) Answer: A positive E cell only shows the reaction is feasible, not that it is fast; with no catalyst present, the reaction has a high activation energy and is extremely slow at room temperature, so $KMnO_4(aq)$ remains usable as a titrant over the timescale of a titration, even though it very slowly decomposes over long-term storage.

(c) light (particularly UV/visible light) can provide energy that catalyses (accelerates) the decomposition reaction, e.g. by a photochemical pathway (oe) **M1**

(c) storing the solution in the dark minimises exposure to light, slowing this decomposition and keeping the concentration of the standard solution constant (accurate) for longer (oe) **A1**

(c) Answer: Light can catalyse (speed up) the decomposition of $KMnO_4(aq)$; storing it in the dark minimises this, keeping its concentration reliable for longer.

Question 7

Level 3 A coherent, logically structured explanation covering: the five d orbitals of a free/isolated metal ion are degenerate; ligands bonding to the metal ion cause the d orbitals to split into two groups of different energy; an electron can be promoted (absorbing energy) from the lower to the higher set of d orbitals (a d-d transition), and the energy absorbed corresponds to a frequency of visible light; the complementary colour (the light not absorbed) is seen; the size of the splitting (and hence the colour observed) depends on the ligand and the metal ion; Ca^{2+} and Zn^{2+} have either an empty (d0) or full (d10) d sub-shell, so no d-d transition is possible, hence they are colourless. **5-6**

Level 2 Some relevant chemistry given, e.g. describing d-orbital splitting by ligands and d-d electron transitions, but with incomplete or partly inaccurate linkage to why Ca^{2+}/Zn^{2+} complexes are specifically colourless. **3-4**

Level 1 Basic or isolated statement(s), e.g. 'transition metals have partly-filled d orbitals' or 'electrons absorb light', with little or no development of the mechanism. **1-2**

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

Indicative content:

- In a free (isolated, gaseous) transition metal ion, the five d orbitals are degenerate (all the same energy).
- When ligands bond to the central metal ion, they cause the d orbitals to split into two groups (sets) of different energy (e.g. a lower set of three and a higher set of two in an octahedral complex).
- An electron in the lower-energy set of d orbitals can absorb a specific quantity (quantum) of energy and be promoted into the higher-energy set; this is called a d-d transition.
- The energy absorbed corresponds to a particular frequency/wavelength of light, which for transition metal complexes typically falls within the visible region of the spectrum.
- The colour observed is the complementary colour to the light absorbed (the wavelengths not absorbed are transmitted or reflected, and this is what is seen).
- The size of the energy gap between the two sets of d orbitals (and therefore the frequency of light absorbed, and the colour seen) depends on the identity of both the ligand and the metal ion/its oxidation state.
- Ca^{2+} has an empty d sub-shell (d0), so there are no d electrons available to be promoted; Zn^{2+} has a full d sub-shell (d10), so there is no vacant d orbital for an electron to be promoted into.
- Because neither Ca^{2+} nor Zn^{2+} can undergo a d-d transition, no visible light is absorbed and their complexes are colourless.

Question 8

(a) vanadium(V), VO_2^+, yellow **B1**

(a) vanadium(IV), VO_2^+, blue **B1**

(a) vanadium(III), V^{3+}, green **B1**

(a) vanadium(II), V^{2+}, violet (lilac) **B1**

(a) Answer: Yellow VO_2^+ (V, +5) -> blue VO_2^+ (V, +4) -> green V^{3+} (V, +3) -> violet/lilac V^{2+} (V, +2).

(b) step 1: E cell = E(VO_2^+/VO_2^+) - E(Zn^{2+}/Zn) = 1.00 - (-0.76) = +1.76 V, positive so feasible **M1**

(b) step 2: E cell = E(VO_2^+/V^{3+}) - E(Zn^{2+}/Zn) = 0.34 - (-0.76) = +1.10 V, positive so feasible **M1**

(b) step 3: E cell = E(V^{3+}/V^{2+}) - E(Zn^{2+}/Zn) = -0.26 - (-0.76) = +0.50 V, positive so feasible **M1**

(b) since E(Zn^{2+}/Zn) = -0.76 V is more negative than all three vanadium E values, E cell is positive at every stage, so zinc can reduce V(+5) all the way to V(+2) cao **A1**

(b) Answer: E cell = +1.76 V, +1.10 V and +0.50 V for the three steps respectively; all positive, so zinc reduces VO_2^+ fully to V^{2+}.

(c) combined vanadium reduction half-equation: $VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$ **M1**

(c) zinc oxidation half-equation: $Zn \rightarrow Zn^{2+} + 2e^-$ **M1**

(c) half-equations correctly scaled to balance electrons transferred (vanadium x2, zinc x3, giving 6 electrons) **M1**

(c) $2VO_2^+(aq) + 8H^+(aq) + 3Zn(s) \rightarrow 2V^{2+}(aq) + 4H_2O(l) + 3Zn^{2+}(aq)$ fully balanced with state symbols cao **A1**

(c) Answer: $2VO_2^+(aq) + 8H^+(aq) + 3Zn(s) \rightarrow 2V^{2+}(aq) + 4H_2O(l) + 3Zn^{2+}(aq)$

Question 9

(a) E cell = E(Cu^+/Cu) - E(Cu^{2+}/Cu^+) = 0.52 - 0.15 = +0.37 V **M1**

(a) positive E cell, so $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ is thermodynamically feasible cao **A1**

(a) some Cu^+ is reduced to Cu (gains an electron) while the rest of the Cu^+ is oxidised to Cu^{2+} (loses an electron); i.e. Cu^+ acts as both the oxidising and reducing agent **B1**

(a) Answer: E cell = +0.37 V, positive, so $2Cu^+ \rightarrow Cu^{2+} + Cu$ is feasible; Cu^+ is simultaneously reduced (to Cu) and oxidised (to Cu^{2+}) - it disproportionates.

(b) in the solid state the Cu^+ ions are held in a fixed lattice, strongly bonded to the oxide/chloride ions (by ionic/some covalent-character bonding), rather than existing as free, mobile hydrated ions **M1**

(b) there is no mechanism for two neighbouring Cu^+ ions in a rigid solid lattice to come together and exchange an electron in the way that mobile $Cu^+(aq)$ ions can in solution (oe) **A1**

(b) so, although disproportionation may still be thermodynamically favourable overall, these solids are kinetically stable (do not disproportionate at a measurable rate) under normal conditions (oe) **A1**

(b) Answer: In Cu_2O and CuCl the Cu^+ ions are fixed in a rigid lattice rather than existing as free, mobile hydrated ions, so there is no route for neighbouring Cu^+ ions to exchange electrons; these solids are kinetically stable even though $Cu^+(aq)$ disproportionates readily.

(c) ammonia ligands form complexes with both Cu^+ and Cu^{2+}, but the two oxidation states are not stabilised to the same extent (oe) **M1**

(c) if ammonia complexation stabilises Cu^+ (lowers its energy/makes $[Cu(NH_3)_2]^+$ have a much larger stability constant) more than it stabilises Cu^{2+}, then converting Cu^+ to Cu^{2+} (as required for disproportionation) becomes energetically less favourable than in the uncomplexed aqua-ion system (oe) **M1**

(c) this effectively raises the relevant electrode potential for the Cu^{2+}/Cu^+ couple, reducing (or reversing the sign of) E cell for the disproportionation reaction, so it is no longer thermodynamically favourable, and free $Cu^+(aq)$ is removed from solution as the stable complex (oe) **A1**

(c) this implies that the stability constant of $[Cu(NH_3)_2]^+$ (the Cu^+ ammine complex) is much larger than that of the corresponding Cu^{2+} ammine complex, relative to their aqua ions (oe) **A1**

(c) Answer: Ammonia stabilises Cu^+ (as $[Cu(NH_3)_2]^+$) much more strongly than it stabilises Cu^{2+}, so oxidising Cu^+ to Cu^{2+} becomes less favourable once both are complexed; this effectively changes the relevant electrode potential enough that disproportionation is no longer feasible, implying the Cu^+ ammine complex has a disproportionately large stability constant compared with the Cu^{2+} ammine complex.

Question 10

(a) $[Fe(CN)_6]^{3-}$ is a weaker oxidising agent than $[Fe(H_2O)_6]^{3+}$ (oe) **B1**

(a) because it has a lower (less positive) tendency to be reduced/to gain an electron (oe) **B1**

(a) Answer: $[Fe(CN)_6]^{3-}$ is a weaker oxidising agent than $[Fe(H_2O)_6]^{3+}$, since its (less positive) E value shows a smaller tendency to be reduced.

(b) CN^- ligands stabilise the Fe^{3+} ion (with its higher charge density) more strongly than they stabilise the Fe^{2+} ion (oe) **M1**

(b) so complexation with CN^- lowers the energy of the Fe^{3+} complex, $[Fe(CN)_6]^{3-}$, by more than it lowers the energy of the Fe^{2+} complex, $[Fe(CN)_6]^{4-}$ (oe) **M1**

(b) this differential stabilisation makes the Fe^{3+} oxidation state relatively more stable (harder to reduce) within the cyanide complex than within the aqua complex, so the electrode potential for the couple decreases (oe) **A1**

(b) Answer: CN^- ligands stabilise Fe^{3+} more strongly than Fe^{2+} (because of its higher charge/greater polarising power), lowering the energy of $[Fe(CN)_6]^{3-}$ relatively more; this makes Fe^{3+} harder to reduce within the complex, so the electrode potential of the couple falls from +0.77 V to +0.36 V.

(c) for $[Fe(CN)_6]^{3-}$: E cell = 0.36 - 0.54 = -0.18 V, negative, so $[Fe(CN)_6]^{3-}$ cannot oxidise I^- to I_2 **M1**

(c) for $[Fe(H_2O)_6]^{3+}$: E cell = 0.77 - 0.54 = +0.23 V, positive, so $[Fe(H_2O)_6]^{3+}$ can oxidise I^- to I_2 **M1**

(c) so complexing Fe^{3+}/Fe^{2+} with cyanide changes the feasibility of this reaction: the aqua ion oxidises iodide but the cyanide complex does not cao **A1**

(c) Answer: $[Fe(CN)_6]^{3-}$: E cell = -0.18 V, not feasible. $[Fe(H_2O)_6]^{3+}$: E cell = +0.23 V, feasible. Complexation with cyanide therefore prevents the oxidation of iodide that the aqua ion can carry out.

Question 11

(a) reactant molecules are adsorbed onto active sites on the surface of the catalyst **B1**

(a) adsorption weakens the bonds within the reactant molecules (or holds them in a favourable orientation/proximity), providing an alternative reaction pathway of lower activation energy **B1**

(a) product molecules desorb from the surface, freeing the active site for further reactant molecules **B1**

(a) a fine mesh/honeycomb structure maximises the surface area (and so the number of exposed active sites) for a given mass of the expensive precious metal, increasing the rate of reaction while minimising cost **B1**

(a) Answer: Reactants adsorb onto active sites, weakening bonds and lowering activation energy via an alternative pathway; products desorb, freeing the site for reuse. A honeycomb/fine mesh structure maximises surface area (and active sites) per unit mass of catalyst, increasing rate while minimising the amount of costly metal needed.

(b) autocatalysis is where a reaction is catalysed by one of its own products (here, Mn^{2+}) (oe) **B1**

(b) at the very start of the reaction there is no Mn^{2+} present, so the reaction can only proceed by the slow, uncatalysed pathway (partly because $C_2O_4^{2-}$ and MnO_4^- are both negatively-charged ions, so electrostatic repulsion between them contributes to a high activation energy) (oe) **B1**

(b) as the reaction proceeds, Mn^{2+} is produced and catalyses further reaction, so the rate increases (the reaction accelerates) over the early part of the reaction (oe) **M1**

(b) the graph of $[MnO_4^-]$ against time starts with a shallow (slow) negative slope, becomes steeper (faster) as $[Mn^{2+}]$ builds up, then levels off towards zero as the reactants are used up towards completion (an S-shaped/sigmoidal decay curve) (oe) **A1**

(b) Answer: Autocatalysis is catalysis of a reaction by one of its own products; here Mn^{2+} catalyses the reaction. Initially, with no Mn^{2+} present and both reactants negatively charged, the rate is slow; as Mn^{2+} builds up the rate increases, giving a concentration-time graph for MnO_4^- that starts shallow, steepens, then levels off near zero (an S-shaped/sigmoidal curve).

(c) step 1: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$; E cell = 2.01 - 0.77 = +1.24 V, feasible **M1**

(c) step 2: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$; E cell = 0.77 - 0.54 = +0.23 V, feasible **M1**

(c) Fe^{2+} is regenerated in step 2, so it acts as a true catalyst overall (net equation: $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$) cao **A1**

(c) the direct, uncatalysed reaction between $S_2O_8^{2-}$ and I^- is slow mainly because both ions are negatively charged, so there is strong electrostatic repulsion between them, giving a high activation energy (oe) **M1**

(c) in each catalysed step, one of the two reacting species is a cation (Fe^{2+} or Fe^{3+}), so the anion-anion repulsion is avoided, lowering the activation energy of each step and increasing the overall rate (oe) **A1**

(c) Answer: Step 1: E cell = +1.24 V (feasible); Step 2: E cell = +0.23 V (feasible); Fe^{2+} is regenerated, so it is a true catalyst. The uncatalysed reaction is slow due to repulsion between the two anions; the catalysed route avoids this because each step involves a cation (Fe^{2+} or Fe^{3+}) reacting with an anion.