2.12 Chemistry: Electrode Potentials and Transition Metals: Test Pack

AQA 7405 · Calculator allowed · about 45 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question is about the electron configurations of d-block elements and the definition of a transition element.

(a) Define, in terms of electron configuration, what is meant by the term transition element. **(2)**

(b) Chromium, Cr (Z = 24), has an anomalous ground-state electron configuration. Give the full electron configuration of a chromium atom, and explain why this differs from the configuration predicted by the simple aufbau filling order. **(2)**

(c) Iron, Fe, has atomic number 26. Give the electron configurations of the Fe^{2+} and Fe^{3+} ions. **(2)**

(d) Zinc, Zn (Z = 30), is a d-block element. Explain why zinc is not classified as a transition element. **(2)**

(Total for Question 1 is 8 marks)

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2 This question is about ligands, complex ions and the multidentate ligand $EDTA^{4-}$.

(a) Define the term ligand. **(1)**

(b) State the coordination number and name the shape of each of the following complex ions: $[Cu(H_2O)_6]^{2+}$, $[CuCl_4]^{2-}$, $[Ag(NH_3)_2]^{+}$. **(3)**

(c) Explain, in terms of bonding, how a ligand such as water bonds to the central metal ion in a complex ion such as $[Cu(H_2O)_6]^{2+}$. **(3)**

(d) $EDTA^{4-}$ is described as a hexadentate ligand. Explain what is meant by the term hexadentate, and state the coordination number of the complex ion formed between $EDTA^{4-}$ and a single Ca^{2+} ion. **(2)**

(e) Complexes formed with $EDTA^{4-}$ have a much larger stability constant than the equivalent complex formed with six monodentate ligands of similar donor strength (e.g. six water molecules). Explain this observation in terms of entropy. **(3)**

(Total for Question 2 is 12 marks)

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3 This question is about ligand substitution reactions of copper(II) complexes.

(a) Aqueous ammonia is added, a little at a time and then in excess, to a solution of aqueous copper(II) sulfate. Describe what would be observed, and give equations for the two stages of this reaction. **(4)**

(b) When excess concentrated hydrochloric acid is added instead to aqueous copper(II) sulfate, the solution turns from pale blue to yellow-green and the coordination number of copper changes from 6 to 4. Write an equation for this ligand substitution, and explain, in terms of ligand size, why the coordination number decreases. **(3)**

(c) The stability constant, Kstab, for the reaction $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ is Kstab = 2.0×10^{13} mol^{-4} dm12 at 298 K. Write the expression for Kstab, and state what this very large value indicates about the position of equilibrium and the relative stability of the two complexes. **(3)**

(Total for Question 3 is 10 marks)

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Mark scheme · 2.12 Chemistry: Electrode Potentials and Transition Metals: Test Pack

Question 1

(a) a d-block element (oe) **B1**

(a) that forms at least one stable ion with an incomplete (partially-filled) d sub-shell **B1**

(a) Answer: A transition element is a d-block element that forms at least one ion with an incomplete d sub-shell.

(b) 1s2 2s2 2p6 3s2 3p6 3d5 4s1 (oe, allow [Ar]3d5 4s1) **B1**

(b) a half-filled 3d sub-shell (3d5) with a single 4s electron is more stable/lower in energy than the predicted 3d4 4s2 arrangement (oe) **B1**

(b) Answer: 1s2 2s2 2p6 3s2 3p6 3d5 4s1 ([Ar]3d5 4s1); one electron moves from 4s into 3d to give the extra stability of a half-filled 3d sub-shell.

(c) Fe^{2+}: [Ar]3d6 (oe) **B1**

(c) Fe^{3+}: [Ar]3d5 (oe) **B1**

(c) Answer: Fe^{2+}: [Ar]3d6. Fe^{3+}: [Ar]3d5.

(d) zinc atoms, [Ar]3d10 4s2, only ever form Zn^{2+} ions, by loss of the two 4s electrons **M1**

(d) giving [Ar]3d10, a complete (full) d sub-shell, so zinc never forms an ion with an incomplete d sub-shell (oe) **A1**

(d) Answer: Zinc only ever forms Zn^{2+}, with configuration [Ar]3d10 - a full d sub-shell - so it does not meet the 'incomplete d sub-shell' requirement and is not classed as a transition element.

Question 2

(a) a molecule or ion that donates a lone pair of electrons to a (central) metal ion/atom, forming a dative covalent (coordinate) bond (oe) **B1**

(a) Answer: A ligand is a molecule or ion that can donate a lone pair of electrons to a central metal ion, forming a dative covalent bond.

(b) $[Cu(H_2O)_6]^{2+}$: coordination number 6, octahedral **B1**

(b) $[CuCl_4]^{2-}$: coordination number 4, tetrahedral **B1**

(b) $[Ag(NH_3)_2]^{+}$: coordination number 2, linear **B1**

(b) Answer: $[Cu(H_2O)_6]^{2+}$: 6, octahedral. $[CuCl_4]^{2-}$: 4, tetrahedral. $[Ag(NH_3)_2]^{+}$: 2, linear.

(c) each water ligand has a lone pair of electrons on the oxygen (donor) atom **M1**

(c) this lone pair is donated into an empty (vacant) orbital on the central Cu^{2+} ion, forming a dative covalent (coordinate) bond, in which both electrons of the shared pair originate from the ligand **A1**

(c) six such bonds form around the Cu^{2+} ion (matching the coordination number), arranged octahedrally in space, giving the shape of the complex ion **B1**

(c) Answer: Each water molecule donates a lone pair from its oxygen atom into an empty orbital on Cu^{2+}, forming a dative covalent bond; six such bonds arranged octahedrally give the $[Cu(H_2O)_6]^{2+}$ complex ion.

(d) hexadentate means the ligand has six donor atoms (lone pairs) and so can form six dative covalent bonds to the same central metal ion simultaneously (oe) **B1**

(d) coordination number of the Ca-EDTA complex = 6 **B1**

(d) Answer: Hexadentate means the ligand can form six dative bonds to one central ion at once (it has six donor atoms); the coordination number of [Ca(EDTA)]2- is 6.

(e) when $EDTA^{4-}$ replaces six monodentate H_2O ligands, the total number of free/independent particles in solution increases: 2 reactant particles (the hydrated ion and $EDTA^{4-}$) become 7 product particles (the new complex plus six released water molecules) (oe) **M1**

(e) this contrasts with monodentate ligand substitution, where the number of particles stays roughly the same (6 ligands replace 6 water molecules), giving little entropy change (oe) **M1**

(e) the large increase in the number of particles gives a large positive entropy change, making delta G more negative (via delta G = delta H - T delta S), so the chelate complex is thermodynamically more stable, giving a much larger stability constant (the chelate effect) (oe) **A1**

(e) Answer: Substituting one $EDTA^{4-}$ for six water ligands increases the total number of particles in solution (2 to 7), giving a large positive entropy change; this makes delta G more negative than for an equivalent monodentate substitution (where particle numbers barely change), so the chelate complex is much more stable (the chelate effect).

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Question 3

(a) with a small volume of aqueous ammonia, a pale blue precipitate forms **B1**

(a) $Cu^{2+}(aq) + 2NH_3(aq) + 2H_2O(l) \rightarrow Cu(OH)_2(s) + 2NH_4^+(aq)$ **B1**

(a) in excess ammonia the precipitate dissolves to give a deep (royal) blue solution **B1**

(a) $Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$ **B1**

(a) Answer: A pale blue precipitate of $Cu(OH)_2$ forms first ($Cu^{2+} + 2NH_3 + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+$); in excess ammonia this dissolves to give a deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ($Cu(OH)_2 + 4NH_3 + 2H_2O \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$).

(b) $[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$ **B1**

(b) chloride ions are larger (have a bigger ionic radius) than water molecules **M1**

(b) so fewer Cl^- ions than H_2O molecules can fit (pack) around the central Cu^{2+} ion, reducing the coordination number from 6 to 4 (oe) **A1**

(b) Answer: $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$; chloride ions are larger than water molecules, so fewer can pack around the Cu^{2+} ion, giving a lower coordination number (4 instead of 6).

(c) Kstab = $[Cu(NH_3)_4(H_2O)_2]^{2+} / ([Cu(H_2O)_6]^{2+} \times [NH_3]^4)$ **B1**

(c) a very large Kstab means the equilibrium position lies very far to the right (almost entirely towards the ammine complex) oe **M1**

(c) so the ammine complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is much more thermodynamically stable than the aqua complex, $[Cu(H_2O)_6]^{2+}$ oe **A1**

(c) Answer: Kstab = $[Cu(NH_3)_4(H_2O)_2]^{2+} / ([Cu(H_2O)_6]^{2+} \times [NH_3]^4)$; the very large value shows the equilibrium lies almost completely to the right, meaning the ammine complex is far more stable than the aqua complex.

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