Q1 **(a) (i)** What is meant by the term *ligand* in the context of transition element chemistry?

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(ii) Decide which of the following species could be a ligand, and which could not be.
Place a tick (✓) in the appropriate column.

species	can be a ligand	cannot be a ligand
OH^-		
NH_4^+		
CH_3OH		
CH_3NH_2		

(b) Read the following description of some reactions of copper(II) sulfate, and answer the questions that follow.

When 0.1 mol of white anhydrous $CuSO_4$ is dissolved in liquid ammonia at –33 °C, a deep blue solution **C** results.
When 0.2 mol of solid NaOH is added to solution **C**, and the ammonia solvent allowed to evaporate, a solid residue is obtained.
Heating this residue to 200 °C produces a dark coloured mixture of two solids.
When water is added to this mixture, a black solid **D** and a colourless solution **E** are formed. Neither **D** nor **E** contains nitrogen.
Adding $BaCl_2(aq)$ to solution **E** produces a white precipitate **F**.
Solid **D** dissolves in $HNO_3(aq)$ on warming, without evolution of gas, to give a pale blue solution containing $Cu(NO_3)_2(aq)$.

(i) Suggest the formula of the compound contained in each of the following.

solution **C** .....

solid **D** .....

solution **E** .....

white precipitate **F** .....

(ii) Name the type of reaction that is occurring when **D** reacts with $HNO_3(aq)$.

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(c) (i) Describe what you would observe when a solid sample of anhydrous $Cu(NO_3)_2$ is strongly heated.

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(ii) Write an equation for this reaction.

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(Nov 2010 P42)

Q2 **(a)** Complete the following electronic configuration of the Cu^{2+} ion.

$1s^2\ 2s^2\ 2p^6$ .....

(b) In a free, gas-phase transition metal ion, the d-orbitals all have the same energy, but when the ion is in a complex the orbitals are split into two energy levels.

(i) Explain why this happens.

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(ii) How does this splitting help to explain why transition metal complexes are often coloured?

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(iii) Why does the colour of a transition metal complex depend on the nature of the ligands surrounding the transition metal ion?

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(c) Draw a fully-labelled diagram of the apparatus you could use to measure the E^{o} of a cell composed of the Fe^{3+}/Fe^{2+} electrode and the Cu^{2+}/Cu electrode.

(d) The E^{o} for Cu^{2+}/Cu is +0.34 V. When $NH_3(aq)$ is added to the electrode solution, the $E_{electrode}$ changes.

(i) Describe the type of reaction taking place between $Cu^{2+}(aq)$ and $NH_3(aq)$.

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(ii) Write an equation for the reaction.

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(iii) Describe the change in the colour of the solution.

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(iv) Predict and explain how the $E_{electrode}$ might change on the addition of $NH_3(aq)$.

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(e) Fehling's reagent is an alkaline solution of Cu^{2+} ions complexed with tartrate ions. It is used in organic chemistry to test for a particular functional group.
(i) Name the functional group involved.

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(ii) Describe the appearance of a positive result in this test.

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(iii) Write an equation for the reaction between Cu^{2+} and OH^- ions and a two-carbon compound containing the functional group you named in **(i)**.

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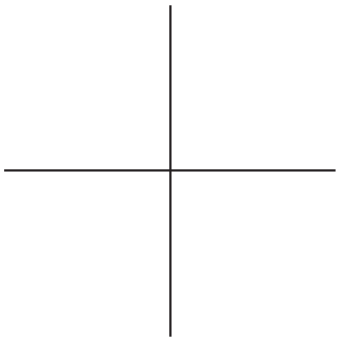
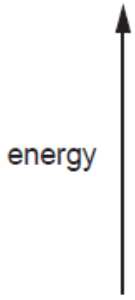
(f) A solution containing a mixture of tartaric acid and its sodium salt is used as a buffer in some pre-prepared food dishes.
Calculate the pH of a solution containing 0.50 mol dm^{-3} of tartaric acid and 0.80 mol dm^{-3} sodium tartrate.
[K_a(tartaric acid) = 9.3×10^{-4} mol dm^{-3}]

(Nov 2012 P43)

Q3 **(a)** On the following diagram draw a clear **labelled** sketch to describe the shape and symmetry of a typical d-orbital.



(b) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups.
(i) Draw an orbital energy diagram to show this, indicating the number of orbitals in each group.



(ii) Use your diagram as an aid in explaining the following.
• Transition element complexes are often coloured.

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• The colour of a complex of a given transition element often changes when the ligands around it are changed.

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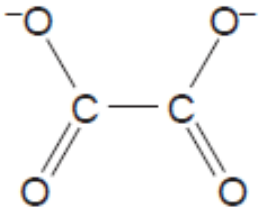
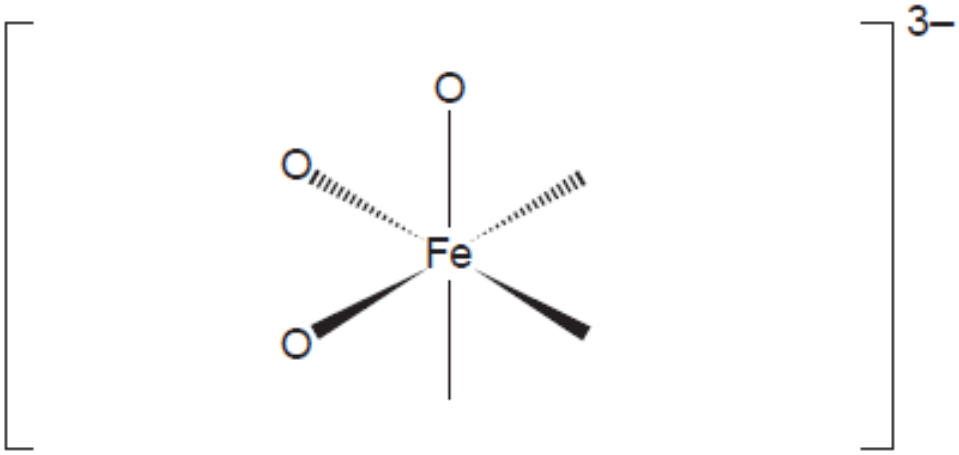
(c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$. The structure of the ethanedioate ion is as follows.



(i) Calculate the oxidation number of carbon in this ion. .....

(ii) Calculate the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$ .....
(iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Complete the following **displayed** formula of this ion.



(iv) In sunlight the complex decomposes into potassium ethanedioate, iron(II) ethanedioate and carbon dioxide. Use oxidation numbers to help you balance the following equation for this decomposition.

$$K_3Fe(C_2O_4)_3 \rightarrow \text{.....}K_2C_2O_4 + \text{.....}FeC_2O_4 + \text{.....}CO_2$$

(Nov 2011 P42)

Q4 **(a)** Explain why complexes of transition elements are often coloured.

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(b) When water is added to white anhydrous $CuSO_4$, the solid dissolves to give a blue solution. The solution changes to a yellow-green colour when concentrated NH_4Cl (aq) is added to it. Concentrating the solution produces green crystals of an ammonium salt with the empirical formula $CuN_2H_8Cl_4$. Explain these observations, showing your reasoning.

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(c) Copper can be recovered from low-grade ores by 'leaching' the ore with dilute H_2SO_4, which converts the copper compounds in the ore into $CuSO_4(aq)$. The concentration of copper in the leach solution can be estimated by adding an excess of aqueous potassium iodide, and titrating the iodine produced with standard $Na_2S_2O_3(aq)$.

$$2Cu^{2+} + 4I^- \longrightarrow 2CuI + I_2$$
$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

When an excess of KI(aq) was added to a 50.0 cm^3 sample of leach solution, and the resulting mixture titrated, 19.5 cm^3 of 0.0200 mol dm^{-3} $Na_2S_2O_3(aq)$ were required to discharge the iodine colour.
Calculate the $[Cu^{2+}(aq)]$, and hence the percentage by mass of copper, in the leach solution.

(Nov 2010 P43)

Q5 **(a)** Complete the electronic structures of the Cr^{3+} and Mn^{2+} ions.

Cr^{3+} $1s^2 2s^2 2p^6$ ..... Mn^{2+} $1s^2 2s^2 2p^6$ .....

(b) (i) Describe what observations you would make when dilute $KMnO_4(aq)$ is added slowly and with shaking to an acidified solution of $FeSO_4(aq)$ until the $KMnO_4$ is in a large excess.

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(ii) Construct an ionic equation for the reaction that occurs.

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(c) By selecting relevant E^o data from the *Data Booklet* explain why acidified solutions of $Fe^{2+}(aq)$ are relatively stable to oxidation by air, whereas a freshly prepared precipitate of $Fe(OH)_2$ is readily oxidised to $Fe(OH)_3$ under alkaline conditions.

- relevant E^o values and half equations

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- explanation

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(June 2010 P42)