1. This question is about nickel compounds.

(a) Hydrated nickel(II) salts are green in colour. Give the electron configuration of a nickel(II) ion and hence state why the ion is coloured.

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(2)

(b) (i) Which is the only nickel compound, in Table 5.3 in the *Book of Data*, in which the nickel atom does **not** have an oxidation number of +2?

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(1)

(ii) What is the oxidation number of nickel in this compound?

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(1)

(c) Nickel(II) chloride solution contains the ion $Ni(H_2O)_6^{2+}(aq)$. On adding ammonia solution, the colour changes to blue or purple as different complexes are formed.

(i) Write the equation, including state symbols, for the displacement of **one** water molecule by an ammonia molecule.

(1)

(ii) Would you expect ΔS_{system} for this reaction to be positive, negative or close to zero? Justify your answer.

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(2)

(d) The complexes formed when ammonia solution is added to nickel(II) chloride solution have the formula $[Ni(H_2O)_x(NH_3)_{6-x}]Cl_2$. An experiment was carried out to determine the value of x in one of them.

A sample of 5.000 g of this complex was dissolved in water and reacted with excess silver nitrate. 6.133 g of silver chloride was produced.

(i) Write the ionic equation, including state symbols, for the formation of silver chloride.

(1)

(ii) Calculate the number of moles of silver chloride produced.

Each mole of the complex contains two moles of chloride ions. Calculate the number of moles of the complex present in the 5.000 g sample.

Hence calculate the mass of one mole of the complex.

(3)

(iii) Use your answer in (ii) to calculate the value of x and hence the formula of this complex ion.

(1)

(iv) Draw TWO possible structures for this complex ion.

(2)
(Total 14 marks)

2. This question is about the element chromium and its compounds.

(a) (i) State the full electronic configuration of a chromium atom in the ground state, using the s,p,d notation.

(1)

(ii) Apart from differing numbers of electrons, how does the ground state electronic configuration of chromium differ from those of the two adjacent elements in the Periodic Table, vanadium and manganese? Suggest the reason for this difference.

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(2)

(b) Compounds containing the chromium(II) ion, Cr^{2+}, are unstable in aqueous solution because they are readily oxidised by oxygen in the air.
State the appropriate electrode potentials and half-cells, and use them to explain why this oxidation takes place.

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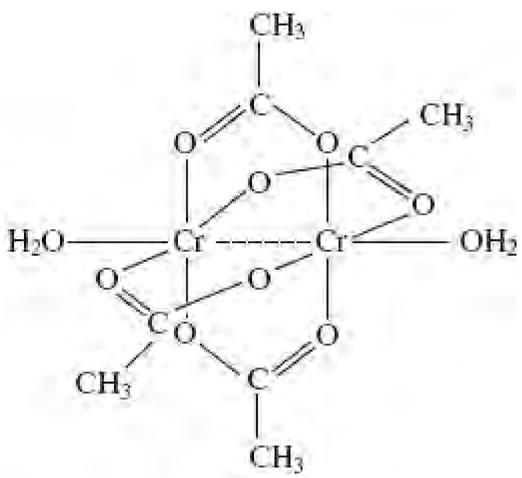
(3)

(c) A useful method of stabilising an unstable oxidation state is to form a complex. You may have prepared chromium(II) ethanoate, $Cr_2(CH_3CO_2)_4(H_2O)_2$, where the Cr^{2+} ion is stabilised in this way. [Details can be found on pages 464–465 of your *Students' Book*.]



(i) Explain how water acts as a monodentate ligand in this complex.

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(2)

(ii) What type of ligand is the ethanoate ion in this complex?

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(1)

(iii) Deduce the number of hydrogen peaks in the NMR spectrum of the complex from the structural formula $Cr_2(CH_3CO_2)_4(H_2O)_2$. Justify your answer.

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(2)

(iv) Suggest TWO characteristic absorptions in the infra-red spectrum of the complex.

You should state the bond associated with each absorption and give the corresponding absorption value in wavenumbers.

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(2)

(d) (i) When first introduced, breathalysers used acidified sodium dichromate(VI) crystals to detect ethanol on the breath. Using oxidation numbers, or otherwise, balance the equation for the reaction.

C_2H_6O + $Na_2Cr_2O_7$ + H_2SO_4 → C_2H_4O + $Cr_2(SO_4)_3$ + H_2O + Na_2SO_4

(2)

(ii) State the colour change you would expect to see if exhaled air containing an excessive amount of ethanol reacted with the breathalyser chemicals.

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(1)

(iii) What hazard is associated with the use of sodium dichromate(VI)?

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(1)
(Total 17 marks)

3. The element iodine can be produced from the mineral Chile saltpetre, which contains sodium iodate, $NaIO_3$. The iodate ions are converted to iodine in a two-step process.

Ionic equations for the reactions are shown below.

Step 1 $IO_3^-(aq) + 3HSO_3(aq) \rightarrow I^-(aq) + 3HSO_4^-(aq)$

Step 2 $IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$

(a) (i) Describe a test you could carry out to confirm the presence of iodide **ions** in a solution. Indicate the result of the test.

Test ....

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Result ....

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(2)

(ii) Identify the TWO elements in **Step 1** which show a change of oxidation number during the reaction.

Give their initial and final oxidation numbers.

First element .... Second element ....

Initial oxidation number .... Initial oxidation number ....

Final oxidation number .... Final oxidation number ....

(3)

(iii) The equation for **Step 1** shows that 1 mole of iodate ions, IO_3^-, reacts with 3 moles of hydrogensulphite ions, HSO_3. Show that your answers to (ii) agree with this ratio.

(1)

(b) An experiment was carried out to determine the concentration of the iodine prepared in **Step 2**

A 10.0 cm^3 portion of the iodine solution was titrated with sodium thiosulphate solution of concentration 0.0100 mol dm^{-3}. The volume of sodium thiosulphate solution added at the end-point was 24.0 cm^3.

The equation for the reaction is

$$I_2(aq) + 2Na_2S_2O_3(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$

(i) What piece of apparatus would you use to measure out the 10.0 cm^3 portion?

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(1)

(ii) Suggest a suitable indicator to show the end-point of this titration. State the colour change you would see.

Indicator ....

From ....to ....

(2)

(iii) Calculate the number of moles of sodium thiosulphate used in the titration.

(1)

(iv) Calculate the number of moles of iodine which reacted with the sodium thiosulphate solution.

(1)

(v) Calculate the concentration, in mol dm^{-3}, of the iodine solution.

(1)
(Total 12 marks)

4. Air is drawn through 10.0 cm^3 of an aqueous solution of vanadium(II) chloride of concentration 0.100 mol dm^{-3}. The colour of the solution slowly changes as oxidation takes place.

The air-oxidised solution is titrated with a solution of acidified potassium manganate(VII) of concentration 0.0200 mol dm^{-3}. The end point is found to be 20.0 cm^3.

(i) Draw a diagram of suitable apparatus for carrying out the air-oxidation of the vanadium(II) chloride solution.

(1)

(ii) Complete the half equation for acidified manganate(VII) ions acting as an oxidising agent.

$$MnO_4^-(aq) + \text{..............}H^+(aq) + 5e^-(aq) \rightarrow Mn^{2+}(aq) + \text{..............}H_2O(1)$$

(1)

(iii) Calculate the number of moles of manganate(VII) ions used in the titration, and hence the number of moles of electrons removed by the manganate(VII) ions.

Calculate the number of moles of vanadium(II) ions in the 10 cm^3 of solution used. Find the oxidation number of vanadium in the air-oxidised solution given that vanadium(V) ions are formed in the titration.

(4)

(iv) Suggest ONE reason why acidified potassium manganate(VII) is a useful oxidising agent in redox titrations.

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(1)
(Total 7 marks)

5. Brass is a widely-used alloy that contains copper and zinc. There are many varieties of brass with different compositions.

In the volumetric analysis of the composition of brass, the first step is to react a weighed sample of the alloy with nitric acid. This gives a greenish-blue solution.

(a) The following standard electrode potentials are needed for this question:

	$E^{\ominus}$/V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	– 0.76
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+ 0.34
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+ 0.81

(i) Use the **half equations given above** and the values of $E^{\ominus}$ to calculate the standard electrode potential for the reaction between zinc and nitric acid and derive the equation.

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(2)

(ii) Suggest why zinc does **not** produce hydrogen with nitric acid.

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(2)

(iii) If the greenish-blue solution is diluted with water it turns light blue and contains hydrated copper(II) ions.

Name the light blue complex ion and draw its structure so as to show its shape.

Name ....

Structure:

(2)

(iv) If concentrated hydrochloric acid is added to a portion of the light blue solution it turns green.

State the type of reaction that occurs and give an equation for the reaction.

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....

(2)

(b) The light blue solution from (a)(iii) is then neutralised, and reacted with an excess of potassium iodide solution.

The following standard electrode potentials are needed:

	$E^{\ominus}$/V
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+ 0.15
$I_2 + 2e^- \rightleftharpoons 2I^-$	+ 0.54

(i) Use these $E^{\ominus}$ values to explain why you would **not** expect the following reaction to occur.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

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(1)

(ii) Explain why, in practice, the reaction in (i) does occur and iodine is liberated.

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(2)

(iii) When the precipitate formed in the reaction in (i) is filtered off and then dissolved in concentrated aqueous ammonia, a colourless solution is produced.

Suggest the formula of the cation in this solution.

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(1)

(iv) If the colourless solution from (iii) is left to stand in air for some time, it turns blue.

State why this is so, naming the reactant responsible for the change.

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(2)

(c) In a determination of the composition of a sample of brass, 1.50 g of the alloy was treated to give 250 cm^3 of a neutral solution of copper(II) nitrate and zinc nitrate.

Excess potassium iodide solution was added to 25.0 cm^3 portions of this solution, and the liberated iodine titrated with 0.100 mol dm^{-3} sodium thiosulphate solution. The mean titre was 16.55 cm^3.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$
$$2S2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$$

(i) State which indicator you would use for the titration and the colour change seen at the end point.

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(2)

(ii) Explain why the indicator is **not** added until the reaction is nearly complete.

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(1)

(iii) Calculate the percentage of copper by mass in this brass.

(5)

(Total 22 marks)

6. (a) Give the electronic configuration of:

Cu : [Ar] ....

Cu^+: [Ar] ....

(1)

(b) (i) Explain why Cu^+ ions are colourless.

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(2)

(ii) Copper(I) ions disproportionate in aqueous solution. Give the equation for the reaction and use the standard electrode potentials given below to explain why the reaction occurs.

	$E^\ominus$/V
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+ 0.15
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+ 0.52

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(2)

(iii) Explain why your answer to (ii) does **not** rule out the existence of $Cu^+(aq)$ under standard conditions.

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(1)

(c) (i) When a **small** amount of dilute ammonia solution is added to a solution of copper(II) sulphate, a turquoise blue precipitate, **F**, is formed.

F has the composition Cu 49.4%, S 12.5%, O 37.4%, H 0.78% by mass. Calculate its empirical formula.

(2)

(ii) When **F** is dissolved in dilute hydrochloric acid, the resulting blue solution gives a white precipitate with barium chloride solution.

Suggest a formula for **F**, given that all the hydrogen is present in hydroxide ions.

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(2)

(iii) When excess concentrated ammonia is added to **F**, a deep blue solution is formed. Give the formula of the ion responsible for this colour.

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(1)

(iv) What **type** of reaction is occurring in (iii)?

....

(1)

(d) Copper metal can be used as a catalyst. When propan-1-ol vapour is passed over heated copper, the following reaction occurs:

$$CH_3CH_2CH_2OH \rightarrow CH_3CH_2CHO + H_2$$

(i) **Outline** how, by the use of 2,4-dinitrophenylhydrazine and suitable tables of data, you could show that the product is propanal.

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(4)

(ii) When propan-1-ol is oxidised with a solution of potassium dichromate(VI) in dilute sulphuric acid care must be taken to avoid further oxidation of the aldehyde product. How is this achieved?

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(1)

(iii) What is the further oxidation product of the aldehyde?

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(1)

(iv) Suggest why the oxidation of the alcohol by passing it over heated copper does **not** lead to further oxidation of the aldehyde.

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(1)

(v) There are a few places on the surface of the metal where catalysis can occur. These are called ‘active sites’.

Suggest why this leads to the rate of reaction being independent of the gas pressure unless this pressure is extremely low.

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(1)
(Total 20 marks)

7. (a) (i) Complete the electronic configurations of:

Cr: [Ar]…………………………….

Cu: [Ar]……………………………..

(1)

(ii) The electronic configurations of chromium and of copper are not readily predictable from a consideration of the elements on either side of them in the first transition series in the Periodic Table.

State how these electronic configurations differ from others in the first transition series and explain why this difference arises.

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(2)

(b) Chromium can form the ion $[Cr(H_2O)_6]^{3+}$ in aqueous solution.

(i) Draw the structure of this ion so as to clearly show its shape.

(1)

(ii) How are the bonds between the water ligands and the metal ion formed?

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(1)

(iii) Write an equation to show what happens initially when a solution containing hydroxide ions is added to a solution of $[Cr(H_2O)_6]^{3+}$ ions.

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(2)

(iv) State what you would **see** as dilute sodium hydroxide is gradually added to a solution of $[Cr(H_2O)_6]^{3+}$ until it is in excess.

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(2)

(v) What property of chromium(III) hydroxide is shown by the reaction in part (iv)?

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(1)

(c) (i) A 1.00 g sample of a metal alloy that contains chromium was converted into 250 cm^3 of an acidified solution of potassium dichromate(VI).

25.0 cm^3 of this solution was added to an excess of potassium iodide solution.

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

The iodine liberated was titrated with 0.100 mol dm^{-3} sodium thiosulphate solution.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

The mean (average) titre was 37.2 cm3.

Calculate the amount (moles) of iodine liberated and hence the percentage, by mass, of chromium in the alloy.

(5)

(ii) In titrations involving iodine, starch is usually added near the end-point to make the colour change clearer, although in many cases it is not really necessary.

Suggest why starch **is** necessary in the titration in (i).

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(1)
(Total 16 marks)

8. Methanol can be vigorously oxidised with an acidified solution containing dichromate(VI) ions, $Cr_2O_7^{2-}$, to form methanoic acid and chromic(III) ions.

(a) What are the oxidation numbers of **carbon** in methanol and methanoic acid?

	Methanol	Methanoic acid
A	–1	+1
B	–2	+2
C	+1	–1
D	+2	–2

(1)

(b) How many moles of methanol react with one mole of dichromate(VI) ion, $Cr_2O_7^{2-}$?

A 1

B ¾

C 1½

D 3

(1)
(Total 2 marks)

9. Which of the following will **not** act as a ligand in the formation of complexes?

A $C_6H_5NH_2$

B CH_3NH_2

C NH_4^+

D NH_3

(Total 1 mark)

10. Which of the following ground state electron configurations corresponds to an element most likely to form an oxide with catalytic properties?

A $1s^2\ 2s^2$

B $1s^2\ 2s^2\ 2p^6\ 3s^2$

C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$

D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$

(Total 1 mark)

11. Which chemical term best describes what happens, when butylamine is added to a solution of a copper(II) salt?

A precipitation

B redox

C proton transfer

D complex formation

(Total 1 mark)

12. (a) (i) Give the electron configuration of:

Fe [Ar] ....

Fe^{2+} [Ar] ....

(1)

(ii) Draw the structure of the hexaaquairon(II) ion, $[Fe(H_2O)_6]^{2+}$, clearly showing its shape.

(1)

(iii) Give the equation for the complete reaction of hydroxide ions with a solution of hexaaquairon(II) ions.

(1)

(iv) State what you would **see** if the product mixture in (iii) is left to stand in air.

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(1)

(b) Consider the equation for the half reaction

$$Fe^{2+} + 2e^{-} \rightleftharpoons Fe \qquad E^{\ominus} = -0.44\ V$$

(i) Define the term **standard electrode potential** with reference to this electrode.

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(3)

(ii) Explain why the value of $E^{\ominus}$ suggests that the iron will react with an aqueous solution of an acid to give Fe^{2+} ions and hydrogen gas.

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(2)

(iii) State why $E^{\ominus}$ values cannot predict that a reaction will occur, only that it is possible.

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(1)
(Total 10 marks)