

## Transition Metals and Their Chemistry

### Past Year Topical Questions

June 2010

**23** More than half of the elements in the Periodic Table are transition elements. Vanadium, element 23, is a typical transition element.

- (a) (i) Give TWO properties shown by vanadium **compounds** that are characteristic of transition metal chemistry, other than variable oxidation state.

(2)

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- (ii) Vanadium(III) ions in aqueous solution exist as  $[\text{V}(\text{H}_2\text{O})_6]^{3+}$ .

Draw this ion so as to clearly show its shape. Name the type of bond between the ligand and the vanadium ion and state the feature of the ligand that enables this bond to be formed.

(3)

Jan 2011

**16** The leaves of the rhubarb plant contain ethanedioic acid,  $(\text{COOH})_2$ , a toxic white soluble solid. The acid is readily oxidized by potassium manganate(VII) under acidic conditions. A sample of 250 g of rhubarb leaves was finely chopped then soaked in warm water to release any ethanedioic acid present. The mixture was then filtered and made up to a volume of  $500 \text{ cm}^3$  using distilled water.  $10.0 \text{ cm}^3$  of the solution was then titrated with  $0.0100 \text{ mol dm}^{-3}$  acidified potassium manganate(VII) solution from a burette, requiring  $11.30 \text{ cm}^3$  to completely oxidize the sample.

- (a) (i) Write the half equation for the oxidation of ethanedioic acid to form carbon dioxide, and the half equation for the reduction of manganate(VII) ions,  $\text{MnO}_4^-$ , in acidic solution to form manganese(II) ions. State symbols are **not** required.

(2)

- (ii) Use your answers to (a)(i) to write the overall equation for the reaction, showing that the ratio of ethanedioic acid to manganate(VII) ions in the full equation is 5 : 2. State symbols are **not** required.

(1)

- \*(iii) Calculate the % by mass of the ethanedioic acid present in the leaves, giving your final answer to **two** decimal places.

(5)

- (iv) What is the level of accuracy of a burette in each reading? Use your answer to calculate the percentage error in the titre volume of  $11.30 \text{ cm}^3$ .

(2)

- (v) Suggest **two** reasons, other than the accuracy of the equipment used for measurements, why the results obtained in this experiment may be considered unreliable.

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- (vi) A student risk assessment for this experiment suggested wearing gloves, but a supervisor said that this was unnecessary. Why do you think this precaution was suggested by the student and why was it rejected by the supervisor?

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- (vii) An aqueous solution of  $\text{MnO}_4^-$  ions contained a small amount of chloride ions,  $\text{Cl}^-$ , as an impurity. Use this fact, and items 70 and 85 from page 16 of the data booklet, to suggest why this solution went cloudy after a time.

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- (b) An aqueous solution containing  $\text{Mn}^{2+}$  ions is pale pink in colour due to the presence of the complex ion  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ .

- (i) Complete the electronic configuration of the  $\text{Mn}^{2+}$  ion.

(1)

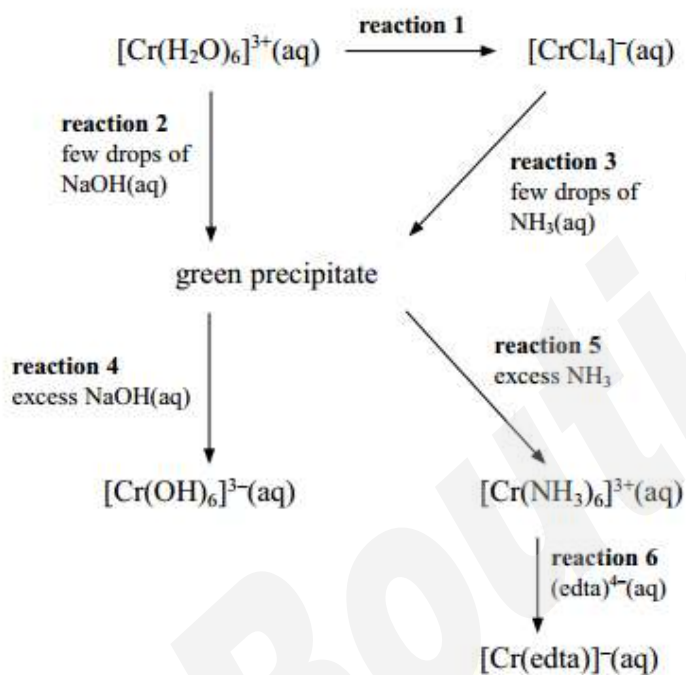
1s<sup>2</sup>

- (ii) What shape would you expect this complex ion to be?

(1)

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17 The reaction scheme below summarises some of the reactions of chromium ions in aqueous solution. Look carefully at the scheme and answer the questions that follow.





(a) (i) Explain why the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ion is coloured.

(3)

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(ii) Suggest what reagent is needed for **reaction 1** and identify the type of reaction.

(2)

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- (b) (i)  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ions react with water to form an acidic solution. Complete the equation for this reaction.

(2)



- (ii) The pH of an aqueous solution of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  is higher than that of an aqueous solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  of the same concentration. Suggest why this is so.

(2)

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- (c) Give the formula of the green precipitate formed in **reactions 2 and 3**.

(1)

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- (d) By considering the nature of the reactants in **reaction 4**, explain why the green precipitate reacts as shown in the scheme. Suggest how you could reverse **reaction 4**.

(3)

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- (e) Write the equation for **reaction 6** and use this to explain, in terms of the entropy change, why the complex  $[\text{Cr}(\text{edta})]^-$  is relatively more stable than  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ .

(2)

**Equation**

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June 2011

**16** This question is about the transition metal iron and some of its compounds.

- (a) Give the electronic configuration of the  $\text{Fe}^{3+}$  ion and use this to define what is meant by a transition element.

(2)

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- \*(b) Iron will act as a surface catalyst in some gaseous reactions. Outline the processes that take place during such catalysis and suggest two reasons to explain why the catalyst speeds up the reaction.

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- (c) One of the components of rust, found on objects made from iron, is iron(III) hydroxide,  $\text{Fe}(\text{OH})_3$ . Use items 17, 19 and 44 from the Standard Electrode Potential table in your data booklet to show how it is able to form in two steps, writing an equation for each step.

(4)

- (d) Haemoglobin is a complex containing iron(II) ions.

Describe how nitrogen atoms in the haemoglobin bond to the iron(II) ions.

(2)

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Jan 2012

- 21** (a) Chromium is a typical transition metal, although its electronic configuration does **not** fit the general trend found in the first transition series.

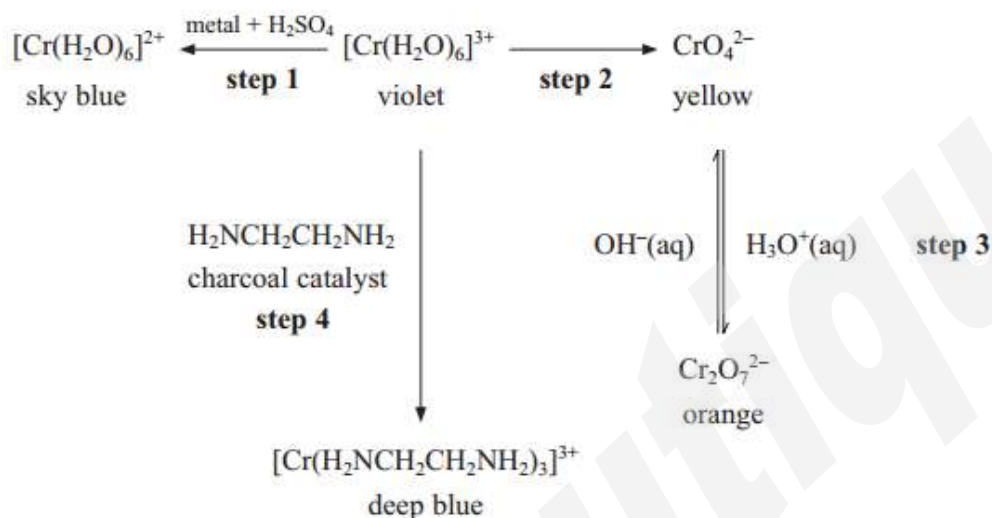
Complete the electronic configurations in *s, p, d* notation for vanadium and chromium.

(1)

Vanadium:  $[\text{Ar}]$  .....

Chromium:  $[\text{Ar}]$  .....

- (b) Some interconversions found in the chemistry of chromium are shown below. Use this information to answer the questions that follow.



- (i) State **two** typical properties of transition metals, other than the formation of coloured ions, which are shown in the diagram above.

(2)

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- (iv) The organic compound  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  that is used in **step 4** is 1,2-diaminoethane, often called ethylenediamine. It is a **bidentate ligand**. Explain the meaning of this term.

(1)

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- (v) Explain, in terms of its structure, how  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  can act as a bidentate ligand whereas  $\text{H}_2\text{NNH}_2$  cannot.

(2)

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June 2012

- (b) When an aqueous solution of nickel(II) ions is added to 1,2-diaminoethane, a complex ion forms.



- (i) Suggest the colour of this complex.

(1)

- (ii) Without using the data booklet, suggest why the complex formed is more stable than  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  by considering the appropriate entropy change.

(2)

- (iii) This complex can exist as two structures, which are non-superimposable mirror images.

Suggest the physical property that would enable you to distinguish between these two structures.

(1)

### Some unusual oxidation states

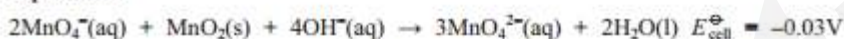
You will probably have seen manganese in its common oxidation states during your study of chemistry. Manganese(II) sulfate occurs as very pale pink crystals in the hydrated form. Manganese(IV) oxide is a black powder which is often used as a catalyst. Potassium manganate(VII) occurs as very dark purple crystals and forms a purple aqueous solution, which is a powerful oxidizing agent.

You are less likely to have seen compounds containing the other oxidation states of manganese, which are manganese(VI), manganese(V), manganese(III) and manganese(I). However, compounds containing each of these four oxidation states can be prepared.

### Manganese(VI)

Manganese(VI), in  $\text{MnO}_4^{2-}$ , can be prepared in a reverse disproportionation reaction, by reacting manganate(VII) ions with manganese(IV) oxide in alkali.

#### Equation 1



The reaction is not thermodynamically favourable under standard conditions. However, the  $E_{\text{cell}}$  value can be made positive by increasing the concentration of hydroxide ions so that green manganate(VI) ions form.

### Manganese(V)

Manganese(V) can be formed by adding a little potassium manganate(VII) to very concentrated ( $12 \text{ mol dm}^{-3}$ ) aqueous sodium hydroxide. The solution slowly becomes blue as manganate(V) ions,  $\text{MnO}_3^-(\text{aq})$ , form. The ionic half-equations are:

#### Equation 2



#### Equation 3



### Manganese(III)

A deep red solution containing manganese(III) ions is formed by the oxidation of manganese(II) hydroxide by potassium manganate(VII) in acid solution. The ionic equation for the reaction is:

#### Equation 4



### Manganese(I)

Manganese(I) ions are not stable in aqueous solution, but do form stable complex ions. They can be made by reducing hexacyanomanganate(II) ions,  $\text{Mn}(\text{CN})_6^{4-}$ , to hexacyanomanganate(I) ions,  $\text{Mn}(\text{CN})_6^{5-}$ .

(a) (i) Give the formula of manganese(IV) oxide.

(1)

(ii) How do catalysts speed up reactions?

(2)

(iii) Explain how transition metal ions can act as homogeneous catalysts.

(2)

(b) (i) Suggest why the preparation of manganate(VI) ions,  $\text{MnO}_4^{2-}$ , in **equation 1**, may be described as a reverse disproportionation reaction by considering the relevant oxidation states.

(2)



(d) Identify the reagents you would use to make manganese(II) hydroxide for the preparation of manganese(III) ions.

(2)

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(e) (i) Draw a dot and cross diagram to show the electron arrangement in the cyanide ion,  $\text{CN}^-$ .

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(ii) Explain how the cyanide ion acts as a ligand.

(2)

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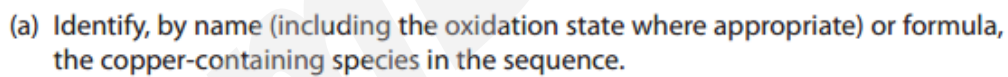
(iii) Suggest the name of the shape of the hexacyanomanganate(I) ion.

(1)

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**14** This question concerns the chemistry of copper. In the sequence below, **A**, **B**, **C**, **D**, **E** and **F** all contain copper in various oxidation states.



**A** \_\_\_\_\_

**B** \_\_\_\_\_

**C** \_\_\_\_\_

**D** \_\_\_\_\_

**E** \_\_\_\_\_

**F** \_\_\_\_\_



(b) Identify, by name or formula, the reagent that would be used to convert **B** into  $\text{CuSO}_4(\text{aq})$ .

(1)

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(c) (i) **C** and **F** are the same type of chemical species. Name this type.

(1)

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(ii) Explain why **C** is coloured but **F** is colourless.

(3)

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\*(iii) Explain why **F** changes into **C** on shaking.

(2)

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(d) The reaction of copper(I) iodide to form **D** and **E** is a disproportionation.

(i) Explain the term disproportionation.

(2)

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(ii) Write an ionic equation for this reaction. State symbols are **not** required.

(1)

(iii) Use the relevant standard reduction (electrode) potentials, from the table on page 17 of your data booklet, to calculate the  $E_{\text{cell}}^{\ominus}$  value for this reaction, giving your answer with the appropriate sign.

(2)

- \* (iv) If copper(I) iodide is treated with nitric acid, rather than sulfuric acid, a blue solution is still formed but no pink solid. Use the standard electrode potentials on page 15 of your data booklet to explain this. Quote any data that you use.

(4)

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June 2013

Titanium is the seventh most abundant metal in the Earth's crust and occurs principally as rutile (impure titanium(IV) oxide,  $\text{TiO}_2$ ).

Early attempts to extract the metal from its oxide by reduction with heated carbon failed because the compound titanium carbide is formed. In 1910, however, pure titanium was made by heating titanium(IV) chloride with sodium.

Titanium has a high melting temperature and a density of  $4.50 \text{ g cm}^{-3}$ . Titanium is as strong as steel, but is about 40% less dense and is therefore suitable for use in the aircraft industry. Titanium metal resists corrosion as it has an impervious coating of titanium(IV) oxide. The metal adheres well to bone, is not rejected by the body and is in demand for the manufacture of replacement joints.

Titanium has two common oxidation states, +3 and +4. Solutions containing the  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$  ion, such as titanium(III) chloride, are purple in colour and are readily oxidized by the oxygen in air to colourless titanium(IV) ions. An aqueous solution of titanium(III) chloride is a strong reducing agent. Titanium(IV) chloride,  $\text{TiCl}_4$ , is a colourless liquid with a boiling temperature of  $136^\circ\text{C}$ . This compound is used, in conjunction with organic compounds of aluminium, as a catalyst for the polymerization of propene to poly(propene). Titanium(IV) chloride is hydrolysed by water to give titanium(IV) oxide,  $\text{TiO}_2$  and hydrogen chloride gas.

Titanium(IV) oxide is a white, non-toxic solid at room temperature. It is used as a white pigment in paint, largely replacing toxic lead compounds which were used previously. Titanium(IV) oxide reacts with concentrated sulfuric acid to form a salt and water. Titanium(IV) oxide also reacts with aqueous potassium hydroxide solution, under suitable conditions, to form a compound with formula  $\text{K}_2\text{Ti}(\text{OH})_6$ .

- (a) (i) Write the equation for the reaction which occurs during the manufacture of titanium from titanium(IV) chloride as described in the article above. State symbols are not required.

(1)



- (ii) Explain, by stating the changes of oxidation numbers, why the reaction in (i) is classified as a redox reaction.

(2)

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- (b) Complete the electronic configurations of

(2)

**Ti** [Ar] .....

**Ti<sup>3+</sup>** [Ar] .....

**Ti<sup>4+</sup>** [Ar] .....

- (c) Use your answer to (b) to explain why titanium is

- (i) a *d*-block element

(1)

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- (ii) a transition element

(1)

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**\* (d) (i)** Explain why the hexaaquatitanium(III) ion,  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ , is coloured.

**(3)**

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**(ii)** Explain briefly why titanium(IV) compounds are colourless.

**(1)**

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**\* (e) (i)** Titanium(IV) oxide has a melting temperature of 1830 °C. Use this data, plus information in the article at the start of the question, to compare the structure and bonding in titanium(IV) oxide with that in titanium(IV) chloride. Hence explain why these two compounds change state at very different temperatures.

**(4)**

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- (ii) Give the term used to describe an oxide, such as titanium(IV) oxide, which can react with both acids and bases.

(1)

- (iii) Using information in the article, write the equation for the reaction between titanium(IV) oxide and aqueous potassium hydroxide solution. State symbols are not required.

(1)

- (f) The concentration of a solution of titanium(III) chloride can be determined by titration with a solution of hydrogen peroxide,  $\text{H}_2\text{O}_2$ , in acidic conditions. The end-point of the reaction is when the solution of titanium(III) chloride in the flask goes colourless.

- (i) Complete the ionic half-equation to show the reduction of hydrogen peroxide.

(1)



- \*(ii) One mole of hydrogen peroxide reacts with two moles of titanium(III) chloride.

In an experiment,  $5.00\text{ cm}^3$  of a sample of titanium(III) chloride solution was transferred to a volumetric flask and made up to  $250\text{ cm}^3$  of an aqueous solution. A  $25.0\text{ cm}^3$  portion of this diluted solution was acidified and titrated with a  $0.0200\text{ mol dm}^{-3}$  solution of hydrogen peroxide,  $\text{H}_2\text{O}_2$ . The mean titre was  $22.50\text{ cm}^3$ .

Calculate the concentration of the **original** titanium(III) chloride solution, in  $\text{mol dm}^{-3}$ .

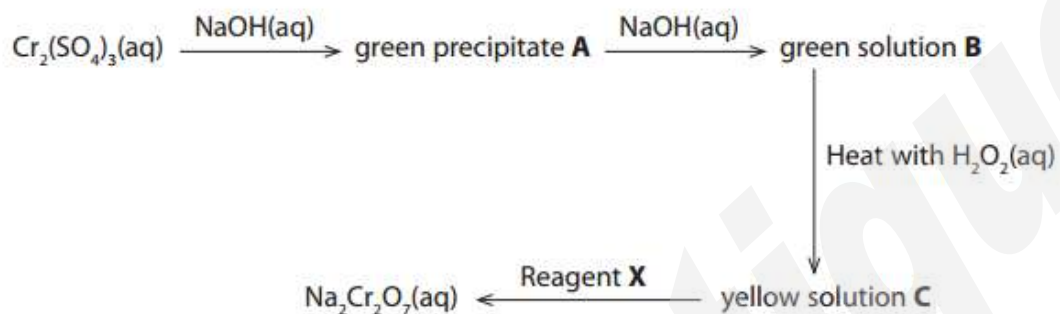
(3)

- (iii) Use information in the article to suggest why this titration gives a value that is lower than the true value for the concentration of titanium(III) chloride solutions.

(1)

June R 2013

- 20** Sodium dichromate(VI) may be prepared from chromium(III) sulfate using the sequence outlined below.



- (a) (i) Complete the table below, giving the **formula** of the chromium containing species.

(4)

Substance	Formula of chromium containing species
$\text{Cr}_2(\text{SO}_4)_3(\text{aq})$	
Green precipitate <b>A</b>	
Green solution <b>B</b>	
Yellow solution <b>C</b>	

(ii) Complete the half equation for the reduction of hydrogen peroxide,  $\text{H}_2\text{O}_2(\text{aq})$ .

(1)



(iii) Identify reagent **X**

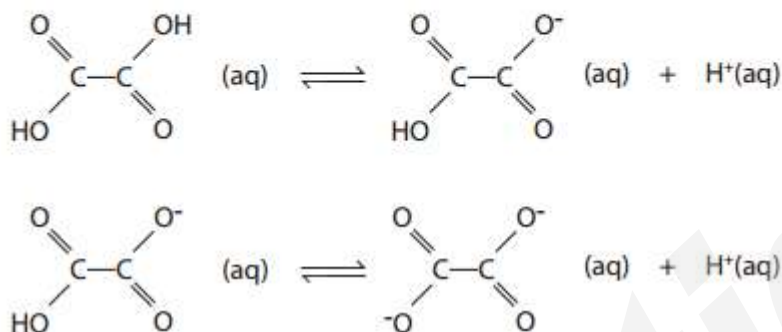
(1)

(iv) Write an **ionic** equation for the conversion of solution **C** to  $\text{Na}_2\text{Cr}_2\text{O}_7$ . State symbols are not required.

(1)



Ethanedioic acid (also known as oxalic acid) is a dicarboxylic acid. Like sulfuric acid, it has two replaceable hydrogen atoms so it dissociates in two stages which are shown below. Acids like these are called 'dibasic'.



As is always the case with dibasic acids, the first dissociation occurs to a far greater extent than the second. Ethanedioic acid is a carboxylic acid but, because there are two carboxyl groups, it is a much stronger acid than ethanoic acid.

Ethanedioic acid is toxic, mainly due to the precipitation of calcium ethanedioate in the kidneys. As it occurs in many plants, the toxicity of ethanedioic acid has caused a number of deaths notably during the First World War when people in England used rhubarb leaves, which contain significant concentrations of the compound, as a vegetable substitute. As it is a reducing agent, the concentration of ethanedioic acid is usually determined by titration with a solution of potassium manganate(VII) of known concentration.

The ethanedioate ion, which is formed when ethanedioic acid dissociates fully, is a bidentate ligand. The ethanedioate ion together with 1,2-diaminocyclohexane, another bidentate ligand, forms a complex with platinum(II) called oxaliplatin which has the same geometry as cisplatin. Oxaliplatin is an anti-cancer drug, which has been used to treat cancers that have become resistant to cisplatin.

Ethanedioic acid has numerous uses, from cleaning and rust removal to the purification of metals. Although it can be prepared from ethene in a two stage process, it is usually manufactured by the oxidation of carbohydrates or glucose using nitric acid, or air, in the presence of vanadium(V) oxide.



- (a) (i) Suggest why the presence of the second carboxylic acid group increases the extent of the **first** dissociation of ethanedioic acid compared with the dissociation of ethanoic acid.

(2)

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- (ii) Explain, by referring to the equilibria in the passage, why the second dissociation of a dibasic acid occurs to a lesser extent than the first.

(1)

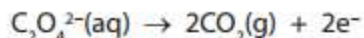
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- (b) In an experiment to determine the proportion of ethanedioic acid in rhubarb leaves, 250 g of leaves was crushed and boiled in a solution of sodium carbonate. The resulting mixture was filtered and the filtrate transferred, along with washings from the mixture, to a 250 cm<sup>3</sup> volumetric flask. The solution was acidified with sulfuric acid, made up to the mark and mixed thoroughly. 25.0 cm<sup>3</sup> portions of the solution were pipetted into a conical flask, about 25 cm<sup>3</sup> of sulfuric acid added and the mixture titrated against a solution of potassium manganate(VII) of concentration 0.0200 mol dm<sup>-3</sup>. The mean titre was 28.55 cm<sup>3</sup>. The relevant ionic half equations for the reaction are



- (i) State the colour change that occurs at the end-point of the titration.

(1)

- \*(ii) Calculate the percentage by mass of ethanedioic acid in rhubarb leaves.

(5)

(c) (i) Explain the term 'bidentate'.

(1)

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(ii) Draw a diagram of the oxaliplatin(II) complex, showing clearly the geometry and charge of the complex and how the ligands are attached to the central ion.

(3)

(d) (i) Suggest a two step **laboratory** synthesis of ethanedioic acid from ethene. Indicate the intermediate compound formed and the reagents required.

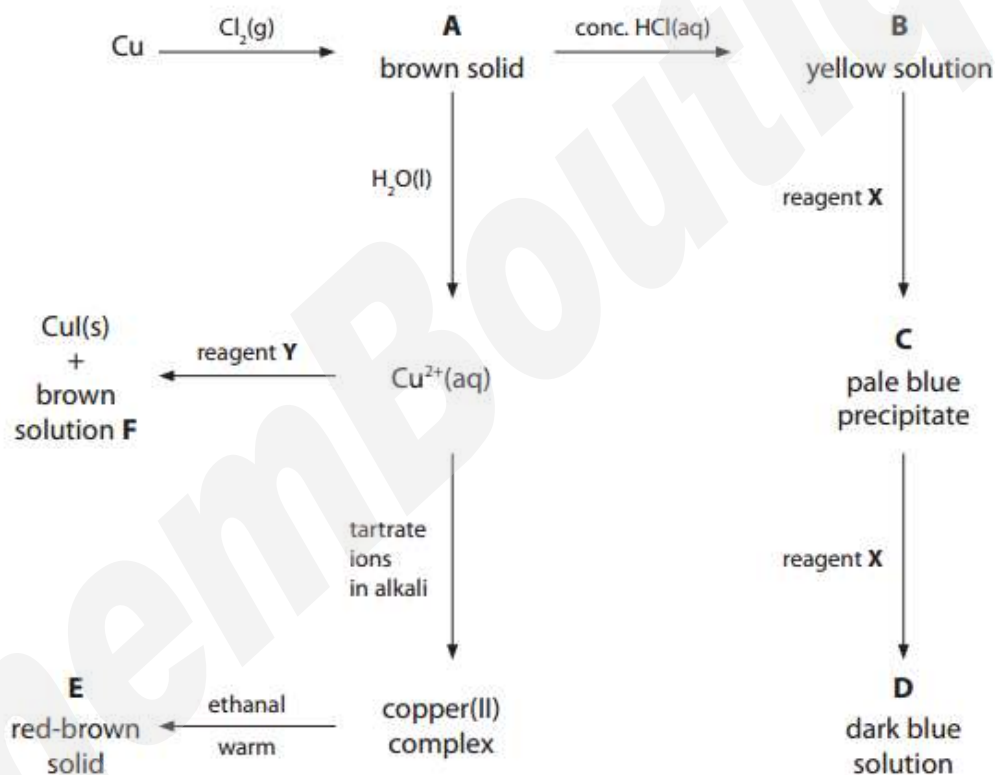
(3)

- (ii) Suggest why it is preferable from an environmental perspective that ethanedioic acid is manufactured from carbohydrates and glucose rather than from ethene.

(1)

Jan 2014

22 The scheme below summarises some reactions of copper and its compounds.





- (a) (i) Identify the copper containing species **A** to **E** either by name, including the oxidation number, or by formula. Also, identify the brown solution, **F**.

(6)

**A** .....

**B** .....

**C** .....

**D** .....

**E** .....

**F** .....

- (ii) Identify the reagents **X** and **Y**.

(2)

**X** .....

**Y** .....

- (iii) Identify the **organic** product of the reaction between the copper(II) complex and ethanal. Hence explain the role of ethanal in the reaction.

(2)

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- (iv) The reaction between  $\text{Cu}^{2+}(\text{aq})$  and reagent **Y** forms  $\text{CuI}(\text{s})$  and a brown solution, **F**. This reaction is the first stage in a method for the determination of the concentration of  $\text{Cu}^{2+}(\text{aq})$ .

Outline briefly how this method is used. Practical details are **not** required.

(1)

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\*(b) (i) Explain why **B** is coloured.

(4)

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(ii) Explain why **B** and **D** have different colours.

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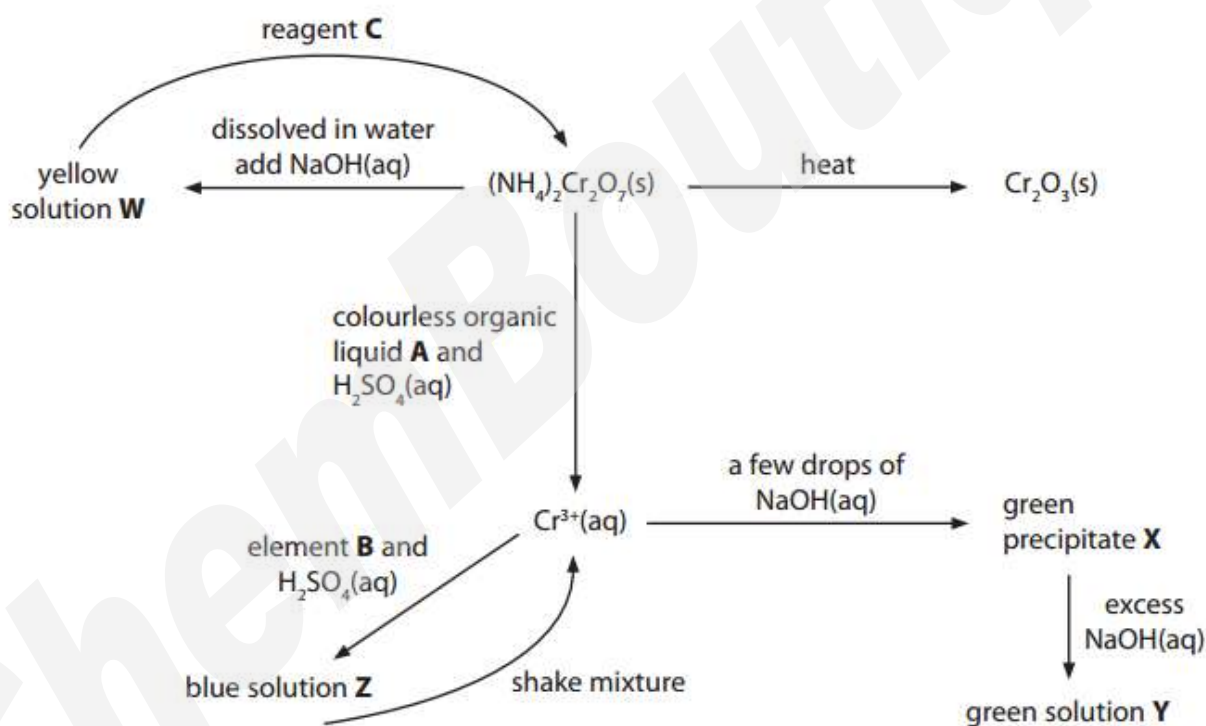
June R 2014

**21** Chromium is a typical transition metal: it forms complexes, coloured compounds and exists in a range of stable oxidation states. Chromium and some of its compounds also show catalytic properties.

(a) Define the term **transition metal**.

(1)

(b) The diagram below summarises some reactions of chromium compounds.



(i) Identify, by name (including the oxidation state where appropriate) or formula, the species containing **chromium** in the sequence.

(4)

W .....

X .....

Y .....

Z .....

(ii) Identify, by name or formula, suitable reagents for the sequence.

(3)

A .....

B .....

C .....

(iii) Write the ionic equation for the reaction between  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and NaOH to form the yellow solution. State symbols are not required.

(1)

(iv) When  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  is heated, steam and nitrogen are formed as well as  $\text{Cr}_2\text{O}_3$ . Write the equation for this reaction. State symbols are not required.

Explain why this is a redox reaction, stating any changes in oxidation numbers that occur.

(3)

Equation

Explanation

(v) Explain how shaking solution **Z** re-forms  $\text{Cr}^{3+}(\text{aq})$ .

(1)

(c) If excess aqueous ammonia is added to  $\text{Cr}^{3+}(\text{aq})$ , the ammonia acts as a ligand and the resulting green solution contains a chromium species which is different from the one found in **Y**.

(i) Explain the term 'ligand'.

(2)

(ii) Write an equation for the reaction that occurs, showing **all** the ligands involved for both the chromium species in the reaction. State symbols are not required.

(2)

Jan 2015

(d) Both copper and zinc are d-block elements, but only copper is a transition metal.

(i) Explain the term **d-block element**.

(1)

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(1)

(4)

(1)



June 2015

- 21** (a) The table below shows the first and second ionization energies of nickel, copper and zinc.

Element	1st ionization energy / kJ mol <sup>-1</sup>	2nd ionization energy / kJ mol <sup>-1</sup>
Ni	737	1753
Cu	746	1958
Zn	906	1733

- (i) Complete the electronic configurations for an atom of nickel and an atom of copper.  
(2)

Ni: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> .....

Cu: 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> .....

- \*(ii) The values for the first ionization energies of copper and nickel are similar, but the values of the second ionization energies are significantly different.

Explain how these data give evidence for the electronic configuration of a copper atom.

(2)

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- (iii) Suggest why you might expect the **third** ionization energies of the three elements to increase from nickel to zinc.

(1)

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- (b) (i)  $\text{Cu}^+(\text{aq})$  ions are not stable in solution and undergo a disproportionation reaction. Suggest an equation for this reaction, including state symbols.

(1)

- (ii) Suggest in what way the **appearance** of  $\text{CuI}$  is similar to that of  $\text{ZnI}_2$ . Give a reason for this similarity.

(2)

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- (c) Explain why zinc is **not** classified as a transition element.

(1)

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June IAL 2015

**22** Crystals of copper(II) sulfate dissolve in water to form a blue solution, **A**. When dilute aqueous ammonia is added to this solution, a pale blue precipitate, **B**, forms which dissolves in excess aqueous ammonia to form a dark blue solution, **C**.

- (a) (i) Give the **formula** of the copper species in **A**, **B** and **C**. You should include all of the ligands present in each species.

(3)

**A** .....

**B** .....

**C** .....

- (ii) Explain why solution **A** is coloured.

(4)

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- (iii) Explain why solution **A** is a different colour to solution **C**.

(2)

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- (b) A more concentrated solution of **C** may be prepared by using concentrated aqueous ammonia in place of dilute aqueous ammonia. The crystalline sulfate of **C** may be obtained by cooling the mixture in an ice bath and adding ethanol. The filtered crystals may be recrystallized using ethanol as the solvent.

The steps of the recrystallization are summarised below. In the spaces provided, explain the purpose of each step, referring particularly to any words in **bold** type.

(5)

Step 1 The solid was dissolved in the **minimum** amount of hot ethanol.

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Step 2 The **hot** solution was **filtered**.

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Step 3 The filtrate was cooled in an **ice bath**.

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Step 4 The mixture was **filtered** using **suction filtration**.

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Jan 2016

**21** This question is about the element chromium and some of its compounds.

- (a) (i) Complete the electronic configuration of the chromium atom, using the s, p, d notation.

(1)

[Ar] .....

- \*(ii) State how this electronic configuration of the chromium atom is unusual compared with most other transition metals.

Give **two** reasons why chromium has this electronic configuration.

(2)

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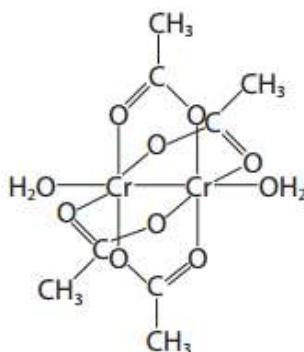
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- (c) Chromium(II) ions in aqueous solution are quickly oxidized by the oxygen in air. One method of stabilising chromium(II) ions is by adding a solution of sodium ethanoate, forming a complex,  $[\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2]$ . This complex may be represented by the structure below.



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

(1)

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- (ii) State the type of bonding which occurs between the ligands and the chromium(II) ions.

(1)

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- (iii) Suggest **two** unusual features in the structure and bonding of this complex.

(2)

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(iv) This complex is red.

Explain why the colour of chromium(II) ethanoate is different from that of  $\text{Cr}(\text{H}_2\text{O})_6^{2+}(\text{aq})$ .

(2)

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(v) Predict the number and relative areas of the peaks in the **low** resolution proton nmr spectrum of  $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$ .

Justify your answers.

(2)

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(d) An experiment is carried out to check the oxidation number of chromium in chromium(II) ethanoate  $\text{Cr}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2$ .

1.00 g ( $2.66 \times 10^{-3}$  mol) of chromium(II) ethanoate is dissolved in 25 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> sulfuric acid.

The solution is diluted with distilled water until the volume is 250 cm<sup>3</sup>.

25.0 cm<sup>3</sup> portions of the diluted solution are titrated with 0.00750 mol dm<sup>-3</sup> potassium manganate(VII).

Calculate the volume of potassium manganate(VII) needed to oxidize the chromium(II) ions present in each 25.0 cm<sup>3</sup> portion to the +6 oxidation state. The manganese is reduced to the +2 oxidation state.

Comment on your answer and suggest how the experiment could be improved to give a more suitable titre.

(5)

Comment .....

June 2016

**22** Copper and zinc are both in the d-block of the Periodic Table. Copper forms compounds that contain  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions but zinc only forms compounds that contain  $\text{Zn}^{2+}$  ions.

- (a) Complete the electronic configurations of the  $\text{Cu}^{2+}$  ions and  $\text{Zn}^{2+}$  ions and hence explain why copper is classified as a transition metal but zinc is not.

(2)

$\text{Cu}^{2+}$  [Ar] .....

$\text{Zn}^{2+}$  [Ar] .....

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- (b) Some photochromic glasses contain silver(I) and copper(I) chlorides.

Explain, with the aid of an equation, why these photochromic glasses go darker in sunlight.

(2)

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- (c) Copper forms a complex ion with the formula  $[\text{CuCl}_4]^{2-}$ . This has the same shape as  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .

Draw the shape of the  $[\text{CuCl}_4]^{2-}$  ion and state the type of bonding between the ligands and the metal ion.

(2)

Shape

Bonding

- (d) The  $[\text{CuCl}_2]^-$  ion is formed by boiling a solution of copper(II) chloride with copper turnings and concentrated hydrochloric acid.

(i) Write an equation for this reaction. State symbols are not required.

(1)

(ii) State the meaning of the term **disproportionation** and explain whether or not this reaction to form the  $[\text{CuCl}_2]^-$  ion is a disproportionation reaction.

(2)

(iii) Explain why the  $[\text{CuCl}_2]^-$  ions are colourless.

(2)

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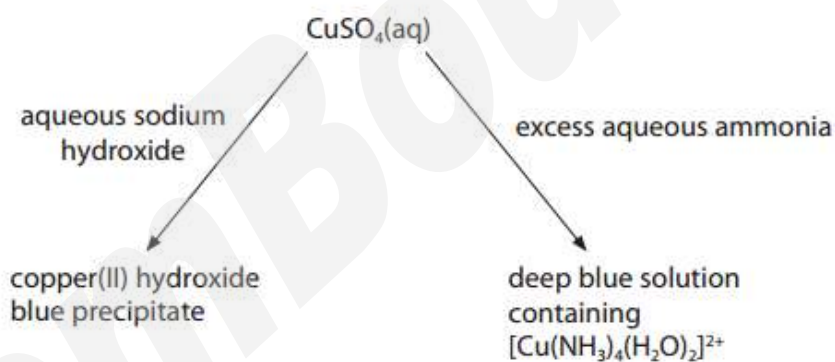
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(e) Copper(II) sulfate solution reacts with aqueous sodium hydroxide and with aqueous ammonia.



(i) Write the **ionic** equation for the reaction of copper(II) sulfate solution with aqueous sodium hydroxide. Include state symbols.

(1)

(ii) State the type of reaction occurring overall when excess aqueous ammonia is added to copper(II) sulfate solution.

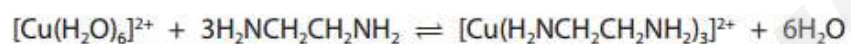
(1)

- (ii) State the type of reaction occurring overall when excess aqueous ammonia is added to copper(II) sulfate solution.

(1)

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- (f) 1,2-diaminoethane is a bidentate ligand. It reacts with copper(II) ions in aqueous solution.



- (i) State what is meant by the term **bidentate**.

(1)

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- (ii) Explain, in terms of entropy, why the reaction takes place.

(2)

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June IAL 2016

**21** Chromium is in the d-block of the Periodic Table and it is a transition metal.

(a) Scandium is also in the d-block of the Periodic Table but it is not a transition metal.

Explain, by giving any relevant electronic configurations, why scandium is **not** a transition metal.

(3)

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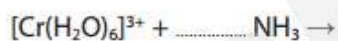
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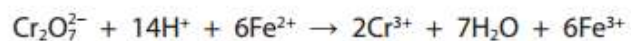
(b) When a few drops of aqueous ammonia are added to an aqueous solution of chromium(III) ions, a green precipitate of chromium(III) hydroxide is formed.

Complete the ionic equation for this reaction. State symbols are not required.

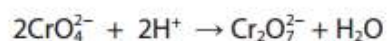
(2)



- (c) Explain, in terms of oxidation numbers of chromium, whether or not each of these two reactions are redox.



**Reaction 1**



**Reaction 2**

(2)

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- (d) Chromium(III) chloride can exist in aqueous solution as three possible complex ions with different numbers of free chloride ions.

	Complex ion	Free chloride ions
<b>X</b>	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	$3\text{Cl}^-$
<b>Y</b>	$[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$	$2\text{Cl}^-$
<b>Z</b>	$[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$	$\text{Cl}^-$

- (i) There are two possible structures for complex ion **Z**.

Complete the diagrams below to show the two possible structures for complex ion **Z**.

(2)



- (ii) Name the type of bond between the ligands and the chromium(III) ion and explain how it is formed.

(2)

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Jan 2017

**22** The elements from scandium to zinc belong to the d-block. Most of these elements are transition elements.

- (a) (i) Complete the electronic configurations of a scandium atom, a manganese(III) ion and an iron(II) ion.

(2)

		3d					4s
Sc [Ar]							
Mn <sup>3+</sup> [Ar]							
Fe <sup>2+</sup> [Ar]							

- (ii) Scandium, iron and manganese are **d-block elements**, but only iron and manganese are **transition elements**.

Explain the meaning of these terms.

(2)

d-block elements

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transition elements

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- (iii) Explain, in terms of electronic configurations, why  $\text{Fe}^{2+}$  ions are readily oxidised to  $\text{Fe}^{3+}$  ions but  $\text{Mn}^{2+}$  ions are not readily oxidised to  $\text{Mn}^{3+}$  ions.

(2)

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- (iv) Explain why the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions have **different** colours in aqueous solution.

A detailed explanation of why transition metal ions are coloured is **not** required.

(2)

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- (b) The concentration of a solution of potassium manganate(VII),  $\text{KMnO}_4$ , can be found by titration with arsenic(III) oxide,  $\text{As}_2\text{O}_3$ .

In this reaction, arsenic(III) oxide is oxidised to arsenic(V) oxide,  $\text{As}_2\text{O}_5$ , and the mole ratio of  $\text{As}_2\text{O}_3$  to  $\text{MnO}_4^-$  is 5:4.

Deduce the final oxidation number of the manganese. Explain your reasoning.

(3)

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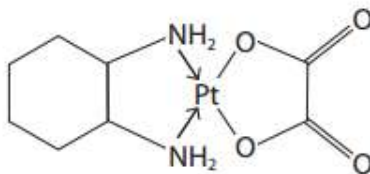
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- (c) Oxaliplatin is a drug used for the treatment of cancer. It consists of a platinum **ion** linked to two different bidentate ligands. The complex can be represented by the structure shown.



- (i) State the meaning of the term **bidentate ligand**.

(1)

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- (ii) Draw the structures of the two bidentate ligands in oxaliplatin.

(2)

- (iii) State the oxidation number of platinum in this complex.

(1)

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