Q1.

6 **(a)** Titanium is an important transition metal. The metal itself is a component of many high-strength low-weight alloys, and its oxide is used as an opaque agent in many paints and pigments.

(i) Write out the electronic configuration of the titanium atom.

.....

(ii) Titanium forms two chlorides. Suggest possible formulae for them.

.....

[2]

(b) Anhydrous copper sulphate, $CuSO_4(s)$, is a white powder that readily dissolves in water.

(i) Describe and explain what is seen when $CuSO_4(s)$ is stirred with water.

.....

.....

.....

(ii) Describe and explain the final colour change seen when an excess of $NH_3(aq)$ is added to $CuSO_4(aq)$.

.....

.....

.....

[4]

[Total : 6]

Q2.

4 **(a)** **(i)** State the electronic configuration of the iron atom.

.....

(ii) Apart from its electronic structure, state **two** properties of iron or its compounds that are characteristic of a transition element.

.....

.....

[3]

(b) Acidified solutions of iron(II) salts can be titrated using a dilute solution of potassium manganate(VII), $KMnO_4$.

(i) Use the *Data Booklet* to calculate the standard cell potential and to write a balanced ionic equation for the reaction that takes place during the titration.

.....

.....

.....

(ii) Explain why no indicator is required for this titration. What colour change would you see at the end point?

.....

.....

.....

[4]

(c) Use the reaction between Fe^{3+} ions and water molecules to explain the meanings of the terms *ligand* and *complex formation*.

.....

.....

.....

..... [2]

(d) An important biological molecule containing iron is haemoglobin.

(i) What is the role of haemoglobin in the body?

.....

(ii) Use your answer to **(i)** to explain why carbon monoxide is poisonous.

.....

.....

.....

[2]

(e) In a possible industrial synthesis of ethanol, the complex $Fe(CO)_5$ catalyses the reaction between carbon monoxide, hydrogen and methanol according to the following equation.

$$CH_3OH + 2CO + H_2 \xrightarrow[300\,atm]{200\,^{\circ}C} CH_3CH_2OH + CO_2$$

Describe a test (reagents and observations) that would distinguish ethanol from methanol.

reagents .....

observation with methanol .....

observation with ethanol ..... [2]

[Total: 13]

Q3.

3 **(a)** A transition element **X** has the electronic configuration [Ar] $4s^2\ 3d^3$.

(i) Predict its likely oxidation states.

.....

(ii) State the electronic configuration of the ion $\mathbf{X}^{3+}$.

.....

[2]

(b) Potassium manganate(VII), $KMnO_4$, is a useful oxidising agent in titrimetric analysis.

(i) Describe how you could use a 0.0200 mol dm^{-3} solution of $KMnO_4$ to determine accurately the $[Fe^{2+}]$ in a solution. Include in your description how you would recognise the end-point in the titration, and write an equation for the titration reaction.

.....

.....

.....

.....

.....

.....

(ii) A 2.00 g sample of iron ore was dissolved in dilute H_2SO_4 and all the iron in the salts produced was reduced to $Fe^{2+}(aq)$. The solution was made up to a total volume of 100 cm^3.

A 25.0 cm^3 portion of the solution required 14.0 cm^3 of 0.0200 mol dm^{-3} $KMnO_4$ to reach the end-point.

Calculate the percentage of iron in the ore.

.....

[8]

(c) High-strength low-alloy (HSLA) steels are used to fabricate TV masts and long span bridges. They contain very low amounts of phosphorus and sulphur, but about 1% copper, to improve resistance to atmospheric corrosion. When dissolved in nitric acid, a sample of this steel gives a pale blue solution.

(i) What species is responsible for the pale blue colour?

.....

(ii) Describe and explain what you would see when dilute aqueous ammonia is added to this solution.

.....

.....

.....

.....

[4]

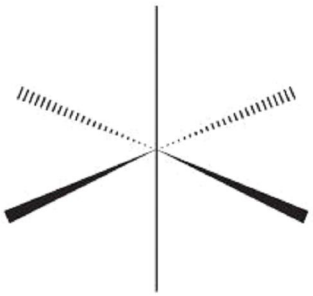
[Total: 14]

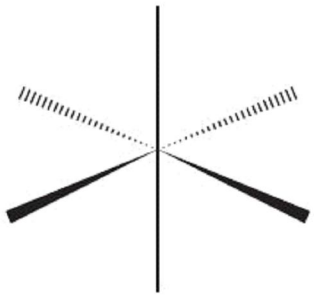
Q4.

4 The following passage is taken from an A level Chemistry text book.

"In an isolated atom, the five d-orbitals have the same energy. In an octahedral complex ion, however, the presence of the ligands splits the five orbitals into a group of three and a group of two. These two groups have slightly different energies."

(a) Use the following sets of axes to draw the shape of **one** d-orbital in **each** of the two groups mentioned above.





[2]

(b) Explain how the presence of the six ligands, ***L***, in $[Fe\boldsymbol{L}_6]^{3+}$ splits the 3d orbitals into two groups of different energy, and explain whether the two-orbital group or the three-orbital group has the higher energy.

.....

.....

.....

.....

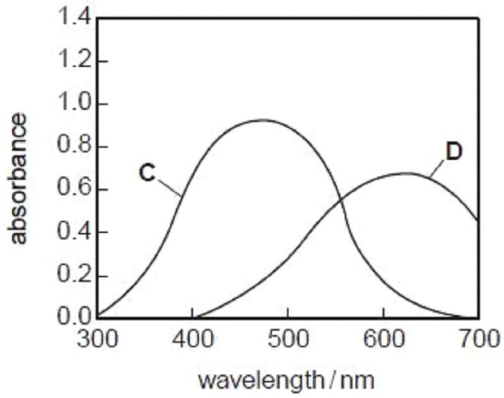
.....[3]

Use

(c) The following table lists the colours and energies of photons of light of certain wavelengths.

wavelength /nm	energy of photon	colour of photon
400	high	violet
450	↓	blue
500	lower	green
600	↓	yellow
650	low	red

The visible spectra of solutions of two transition metal complexes **C** and **D** are shown in the diagram below.



(i) A list of possible colours for these complexes is as follows.

yellow red green blue

Choose **one** of these words to describe the observed colour of each solution.

solution **C** ..... solution **D** .....

(ii) In which complex, **C** or **D**, will the energy gap between the two groups of orbitals be the larger? Explain your answer.

.....

.....

[3]

[Total: 8]

Q5.

3 **(a)** Explain what is meant by the term *transition element*.

For Examiner Use

.....

..... [1]

(b) Complete the electronic configuration of

(i) the vanadium atom, $1s^2 2s^2 2p^6$ .....

(ii) the Cu^{2+} ion. $1s^2 2s^2 2p^6$ .....

[2]

(c) List the **four** most likely oxidation states of vanadium.

..... [1]

(d) Describe what you would see, and explain what happens, when dilute aqueous ammonia is added to a solution containing Cu^{2+} ions, until the ammonia is in an excess.

.....

.....

.....

.....

.....

.....

..... [5]

(e) Copper powder dissolves in an acidified solution of sodium vanadate(V), $NaVO_3$, to produce a blue solution containing VO^{2+} and Cu^{2+} ions.
By using suitable half-equations from the *Data Booklet*, construct a balanced equation for this reaction.

..... [2]

[Total: 11]

Q6.

7 Metals play a vital part in biochemical systems. In this question you need to consider why some metals are essential to life, whilst others are toxic.

(a) For each of the metals, state where it might be found in a living organism, and what its chemical role is.

iron location in organism .....

role .....

.....

sodium location in organism .....

role .....

.....

zinc location in organism .....

role .....

.....

[6]

(b) Heavy metals such as mercury are toxic, and it is important that these do not enter the food chain.

(i) Give a possible source of mercury in the environment.

.....

(ii) Describe and explain **two** reasons why mercury is toxic, using diagrams and/or equations to help your explanation.

.....

.....

.....

[4]

[Total : 10]

Q7.

2 **(a)** Describe **three** characteristic chemical properties of transition elements that are not shown by Group II elements.

For Examiner's Use

.....

.....

.....[3]

(b) When $NH_3(aq)$ is added to a green solution containing $Ni^{2+}(aq)$ ions, a grey-green precipitate is formed. This precipitate dissolves in an excess of $NH_3(aq)$ to give a blue-violet solution.
Suggest an explanation for these observations, showing your reasoning and including equations for the reactions you describe.

.....

.....

.....

.....

.....

.....[4]

(c) Dimethylglyoxime, DMG, is a useful reagent for the quantitative estimation of nickel. It forms an insoluble salt with nickel ions according to the following equation.

$$Ni^{2+}(aq) + \underset{\text{DMG}}{C_4H_8N_2O_2} \longrightarrow \underset{\text{Ni-DMG}}{NiC_4H_6N_2O_2}(s) + 2H^+(aq)$$

A small coin of mass 3.40 g was dissolved in nitric acid and an excess of DMG was added. The precipitated Ni-DMG was filtered off, washed and dried. Its mass was 4.00 g.
Calculate the % of nickel in the coin.

percentage of nickel = ...% [3]

[Total: 10]

Q8.

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

For Examiner's Use

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

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

[2]

(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.

.....

.....

.....

.....

.....

.....

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

.....

[4]

(c) By selecting relevant $E^{\ominus}$ 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 $E^{\ominus}$ values and half equations

.....

.....

.....

.....

explanation

.....

.....

[4]

Q9.

(c) Many commercial copper and brass polishes contain ammonia. The tarnish that forms on the surface of copper is often copper sulfide, CuS. In the presence of O_2 from the air, NH_3 can combine with this copper sulfide to produce the soluble cuprammonium sulfate, $[Cu(NH_3)_4]SO_4$.

(i) Construct an equation for this reaction.

.....

(ii) State the colour of cuprammonium sulfate solution.

.....

(iii) Describe what you would see if a solution of cuprammonium sulfate was diluted with water. Explain your answer.

.....

.....

[3]

(d) When sulfuric acid is added to $Cu^{2+}(aq)$, no colour change occurs, but when concentrated hydrochloric acid is added to $Cu^{2+}(aq)$, the solution turns yellow-green. The solution reverts to its original colour when it is diluted with water.

Suggest the type of reaction occurring with $HCl(aq)$, suggest what is formed during the reaction, and write an equation for the change.

.....

.....

.....

.....[3]

Q10.

3 **(a)** **(i)** What is meant by the *density* of a substance?

.....

(ii) Use data from the *Data Booklet* to explain why the density of iron is greater than that of calcium.

.....

.....

.....

[3]

(b) In general, reactions of the compounds of transition elements can be classified under one or more of the following headings.

acid-base
ligand exchange
precipitation
redox

Choose the most suitable heading to describe each of the following reactions, by placing a tick (✓) in the appropriate column in the table below.
Only one tick should be placed against each reaction.

reaction	acid-base	ligand exchange	precipitation	redox
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$				
$[Cu(H_2O)_6]^{2+} + 4HCl \rightarrow [CuCl_4]^{2-} + 4H^+ + 6H_2O$				
$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$				
$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2 + 6H_2O$				
$2Fe(OH)_2 + ½O_2 + H_2O \rightarrow 2Fe(OH)_3$				
$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$				
$Cr(H_2O)_3(OH)_3 + OH^- \rightarrow [Cr(H_2O)_2(OH)_4]^- + H_2O$				
$[Cr(OH)_4]^- + 1½H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 4H_2O$				

[8]

(c) Alloys of aluminium, titanium and vanadium are used in aerospace and marine equipment, and in medicine.

When a powdered sample of one such alloy is heated with an excess of aqueous NaOH, only the aluminium reacts, according to the following equation.

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

Reacting 100 g of alloy in this way produced 8.0 dm^3 of hydrogen, measured under room conditions.

Calculate the percentage by mass of aluminium in the alloy.

percentage = ... %
[3]

[Total: 14]

Q11.

4 (a) (i) Suggest why transition elements show variable oxidation states in their compounds whereas s-block elements like calcium do not.

.....

.....

(ii) Calculate the oxidation number of the metal in each of the following ions.

VO_2^+ .....

CrF_6^{2-} .....

MnO_4^{2-} .....

[4]

(b) Explain why transition element complexes are often coloured whereas compounds of s-block elements such as calcium and sodium are not.

.....

.....

.....

.....

.....

.....

[4]

(c) SO_2 and MnO_4^- react together in acidic solution.

(i) Use the *Data Booklet* to construct a balanced equation for this reaction.

.....

(ii) Describe the colour change you would see when $SO_2(aq)$ is added to a sample of acidified $KMnO_4$ until the SO_2 is in excess.

from ..... to .....

[3]

(d) Describe the observations you would make when $NH_3(aq)$ is added gradually to a solution containing Cu^{2+} ions, until the NH_3 is in an excess.

.....

.....

.....

.....

[3]

[Total: 14]

Q12.

4 (a) The melting point and density of a typical transition element such as iron differ from those of a typical s-block element such as calcium. Describe and explain these differences.

Us

.....

.....

.....

.....[3]

(b) Suggest a reason why iron forms compounds containing Fe^{3+} ions as well as compounds containing Fe^{2+} ions, whereas calcium only forms compounds containing Ca^{2+} ions.

.....

.....[1]

(c) An important ore of iron is siderite, iron(II) carbonate. The first step in converting it into iron is to heat it in air. When heated in air, both calcium carbonate and iron(II) carbonate decompose, but in different ways.

(i) Write an equation to represent the thermal decomposition of calcium carbonate.

.....

(ii) When siderite is heated in air, carbon dioxide is evolved and iron(III) oxide, Fe_2O_3, is left.

Construct an equation for this reaction.

.....

(iii) Calculate how much iron(III) oxide can be obtained by heating 10 tonnes of siderite.

.....

.....

[4]

[Total: 8]

Q13.

Use

3 Potassium manganate(VII) and potassium dichromate(VI) are both used as oxidising agents in acidic solution.

(a) Using data from the *Data Booklet*, write *either* ionic *or* full equations for the reaction between

(i) $KMnO_4$ and $FeSO_4$ in dilute H_2SO_4,

(ii) $K_2Cr_2O_7$ and SO_2 in dilute H_2SO_4.

[3]

(b) $KMnO_4$ is often used in titrations to estimate reducing agents. It is added from a burette to a solution of the reducing agent.

(i) What colour is $KMnO_4$ solution?

.....

(ii) How is the end point in the titration recognised?

.....

(iii) A solution of 0.010 mol dm^{-3} $KMnO_4$ was used to estimate the amount of $FeSO_4$ in an iron dietary supplement tablet. The tablet was crushed under dilute H_2SO_4 and the $KMnO_4$ solution was added from the burette. It was found that 14.00 cm^3 were required.

Calculate the mass of $FeSO_4$ in the tablet.

.....

.....

.....

.....

[5]

Use

(c) Patients are prescribed iron dietary supplement tablets to cure anaemia, which is a deficiency of haemoglobin in the blood.

(i) Describe the function of haemoglobin, and how the iron atoms it contains carry out that function.

.....

.....

.....

(ii) Explain why even a **small** amount of carbon monoxide in the bloodstream is poisonous.

.....

.....

[3]

[Total : 11]

Q14.

Use

4 **(a)** Explain what is meant by the term *transition element*.

.....

..... [1]

(b) **(i)** How do the atomic radii of the transition elements vary from chromium to copper?

.....

(ii) Predict, with a reason, the variation in the densities of the transition elements from chromium to copper.

.....

..... [3]

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

$1s^2 2s^2 2p^6 3s^2 3p^6$ _____ [1]

(d) Copper ions in aqueous solution are pale blue, due to the formation of a complex ion.

(i) Explain what is meant by the term *complex ion*.

.....

.....

(ii) Draw the structure of the complex ion formed in a solution of $Cu^{2+}(aq)$.

[2]

(e) When dilute aqueous ammonia is added to a solution of $Cu^{2+}(aq)$, the colour changes as a new complex ion is formed.

(i) State the colour of the new complex .....

(ii) Write an equation showing the formation of the new complex.

..... [2]

(f) When concentrated hydrochloric acid is added to a solution of $Cu^{2+}(aq)$, the colour changes to yellow-green. On adding water, the colour returns to pale blue.

Suggest an explanation for these changes.

.....

.....

.....

.....

.....

.....

.....[3]

[Total: 12]

Q15.

10 Read the following article about the use of bacteria in mining, and then answer the questions that follow it.

The discovery that bacteria could 'mine' metals for us was made in Spain. The Rio Tinto mine, in the southwest corner of Spain, was originally mined for copper by the Romans some 2,000 years ago. In 1752, some mining engineers looked over the mine to see if it could possibly be re-opened. They noticed streams of a blue-green liquid running from spoil heaps of the processed rock that lay around the mine. When this blue-green liquid ran over iron, it coated the iron with a brown film. The brown film was metallic copper.

There was still some copper left in the spoil heaps. At the time, everybody thought that the copper was being dissolved in the liquid through a simple chemical reaction. But in 1947, US scientists discovered that the copper was being 'mined' by a bacterium called *Thiobacillus ferrooxidans*.

The bacterium *Thiobacillus ferrooxidans* lives off the chemical energy trapped in metal sulphides. In the ore, the copper exists as copper sulphide. The bacteria gain energy by converting the copper sulphide to copper sulphate, which is then excreted. At the same time, they absorb the difference in energy in the chemical bonds. These bacteria can also obtain energy in similar reactions with ores of zinc, lead and uranium.

(a) Use the *Data Booklet* to explain why the blue-green liquid coated the iron with copper. Write an equation for the reaction.

.....

.....

[2]

(b) Suggest **two** reasons why this method of extracting copper might be useful for ore containing only a small percentage of copper.

(i) .....

.....

(ii) .....

.....

[2]

(c) Suggest **one** disadvantage of using bacteria rather than traditional mining and smelting methods.

.....

.....[1]

(d) In conventional copper mining, the ore will typically contain 0.5 – 2.0% copper, which gives an idea of what a valuable resource copper is.

(i) The ore from a particular mine contains 0.75% copper, and 150 000 tonnes of ore are mined each year. From this ore about 60% of the copper is extracted, and the remainder is left in the 'spoil heaps' of processed ore.

What mass of copper is extracted each year?

(ii) If the use of bacteria can recover a further 17% of copper from the spoil heaps, what is the extra mass of copper produced?

[2]

(e) Suggest why bacteria are unlikely to be used in the extraction of aluminium.

.....

.....[1]

(f) Metals like copper and zinc from abandoned mines can contaminate ground-water. Suggest **one** way of removing these contaminants.

.....

.....[1]

[Total: 9]

Q16.

(b) Malachite is an ore of copper. It contains the following percentages by mass.

copper	57.7%
oxygen	36.2%
carbon	5.4%
hydrogen	0.9%

Malachite reacts with dilute H_2SO_4 producing a gas **B** that turns limewater milky and leaving a blue solution **C**.

When heated in the absence of air, malachite produces gas **B** and steam, and leaves a black solid **D**. **D** reacts with dilute H_2SO_4 to produce the same blue solution **C**.

Adding iron filings to **C** produces a pink solid **E** and a pale green solution **F**.

(i) Calculate the empirical formula of malachite.

.....

(ii) Suggest the formula of the ion responsible for the blue colour of solution **C**.

.....

(iii) Identify the black solid **D** and calculate the mass of **D** that could be obtained by heating 10 g of malachite.

.....

.....

.....

.....

(iv) Use data from the *Data Booklet* to identify the pink solid **E** and the solution **F**, and suggest an equation for the reaction producing them.

.....

.....

.....

(v) What type of reaction is the reaction that produces **E** and **F**?

.....

(vi) Describe and explain what you would see happen when dilute $NH_3(aq)$ is added slowly to the solution **C** until it is in an excess.

.....

.....

.....

.....

.....

[13]

[Total: 19]

Q17.

3 One major difference between the properties of compounds of the transition elements and those of other compounds is that the compounds of the transition elements are often coloured.

For Examiner's Use

(a) Explain in detail why many transition element compounds are coloured.

.....

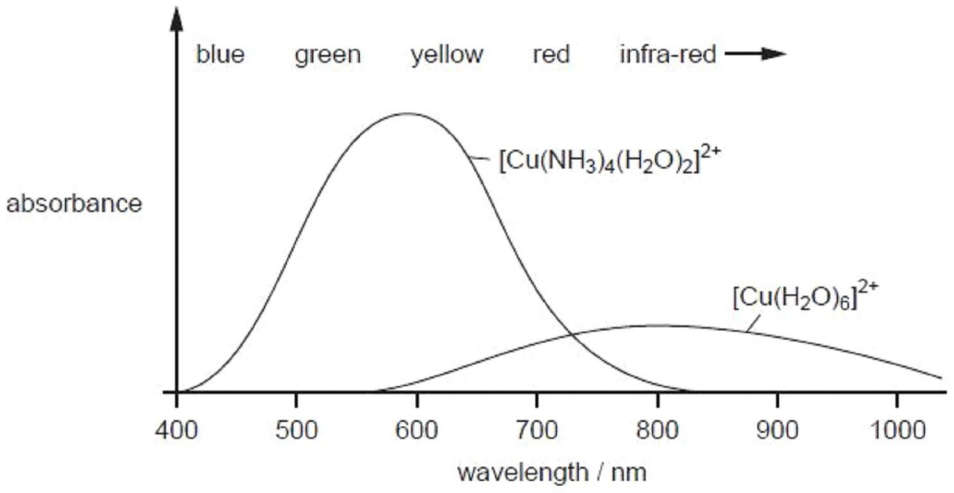
.....

.....

.....

..... [3]

(b) The following graph shows the absorption spectrum of two complexes containing copper.



(i) State the colours of the following complex ions.

$[Cu(H_2O)_6]^{2+}$ .....

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ .....

(ii) Using the spectra above give **two** reasons why the colour of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is deeper (more intense) than that of the $[Cu(H_2O)_6]^{2+}$ ion.

.....

.....

.....

(iii) Predict the absorption spectrum of the complex $[Cu(NH_3)_2(H_2O)_4]^{2+}$, and sketch this spectrum on the above graph. [6]

(c) Copper forms a complex with chlorine according to the following equilibrium.

$$Cu^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction, stating its units.

K_c = ... units .....

(ii) The numerical value of K_c is 4.2×10^5.
Calculate the $[[CuCl_4]^{2-}]/[Cu^{2+}]$ ratio when $[Cl^-] = 0.20\,mol\,dm^{-3}$.

.....

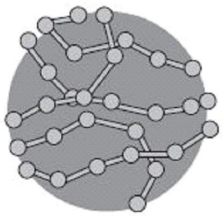
.....

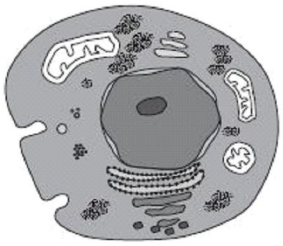
[3]

[Total: 12]

Q18.

9 **(a)** Put the following items in order of **increasing** size. Use the number 1 to indicate the smallest and 3 to indicate the largest.

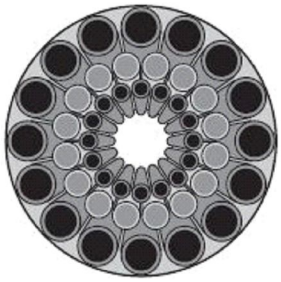




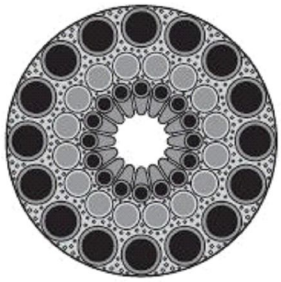
length of DNA molecule in a chromosome	nanosphere diameter	cell diameter

[2]

(b) Nanotechnology has an increasing range of uses across a number of fields including sport. For example, golf clubs are now being made using nanomaterials.



cross-section of normal golf club shaft



cross-section of golf club shaft with nanomaterial fill

Use the diagrams above and your knowledge of nanomaterials to suggest **two** properties of the new shafts. Explain your answers.

(i) .....

.....

.....

(ii) .....

.....

.....

[2]

(c) A mixture of nano-sized particles of tungsten and vanadium(IV) oxide can be applied to the surface of windows and reflects heat whilst letting all light in the visible range through.

For Examiner's Use

Suggest how this variable reflective property is possible using nano-sized particles.

.....

.....

.....[2]

(d) Although silver is well-known as a precious metal, its medicinal properties have been used for hundreds of years. In ancient Greece silver was used to purify water and until the development of antibiotics, silver was important in the treatment of large wounds.

(i) What property of silver makes it useful for jewellery?

.....

(ii) Suggest the property of silver that makes it useful in the treatment of large wounds.

.....

(iii) Suggest why nano-sized silver particles are more useful in treating wounds.

.....

.....

[3]

[Total: 9]

Q19.

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

For Examiner Use

.....

.....

(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		

[3]

(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 $HNO_3(aq)$.

.....

[5]

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

.....

.....

(ii) Write an equation for this reaction.

.....

[2]

[Total: 10]

Q20.

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

For Examiner's Use

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.....[3]

(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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.....[3]

(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.

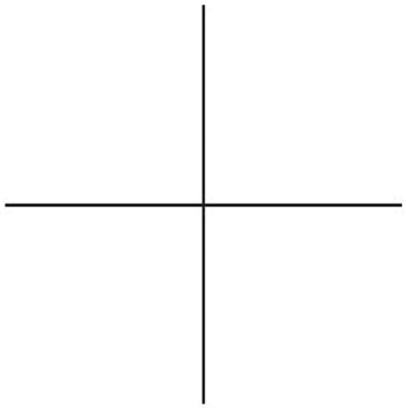
percentage of copper = ...% [3]

[Total: 9]

Q21.

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

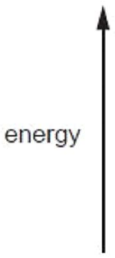
For Examiner's Use



[2]

(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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.....

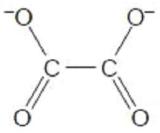
.....

[7]

(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 $[Fe(C_2O_4)_3]^{3-}$.

For Examiner's Use

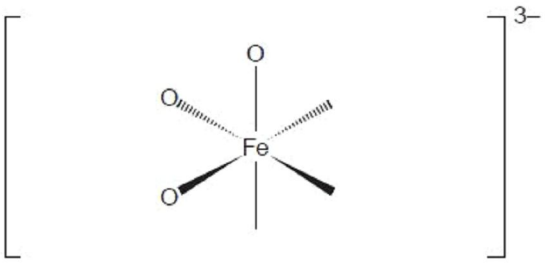
The structure of the ethanedioate ion is as follows.



(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.

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

[5]

[Total: 14]

Q22.

1 **(a)** Complete the electronic configurations of the following ions.

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

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

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

.....

.....

.....

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$

  from ..... to .....

- $K_2Cr_2O_7$

  from..... to .....

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

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(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

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.....

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess $Sn^{2+}(aq)$ ions are titrated with a standard solution of $KMnO_4$.

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

The equation for the reaction between $Sn^{2+}(aq)$ and $MnO_4^-(aq)$ is as follows.

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution.

.....

For Examiner's Use

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

- number of moles of Sn^{2+} this MnO_4^- reacted with

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

- mass of MnO_2 in 0.100 g pyrolusite

- percentage of MnO_2 in pyrolusite

percentage = ...%

[6]

Q23.

For Examiner's Use

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

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

(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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.....

[5]

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

[5]

(d) The $E^{\ominus}$ 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 $NH_3(aq)$.

.....

(ii) Write an equation for the reaction.

.....

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

.....

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

.....

.....

[4]

(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.

.....

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

.....

(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)**.

.....

[3]

(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}]

pH = ...
[2]

[Total: 20]