SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 An electrochemical cell consists of a standard hydrogen electrode and a $Cu^{2+}(aq)|Cu(s)$ electrode which uses copper(II) sulfate solution. Which one of the following does **not** affect the e.m.f. of the cell?

☒ **A** The volume of the copper(II) sulfate solution.

☒ **B** The temperature.

☒ **C** The pressure of the hydrogen.

☒ **D** The concentration of the copper(II) sulfate solution.

(Total for Question 1 = 1 mark)

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2 Which answer corresponds to the correct value of $E^{\ominus}_{cell}$ for the oxidation of hydrogen peroxide by manganate(VII) ions? The half-reactions are

$$2H^+ + O_2 + 2e^- \rightleftharpoons H_2O_2 \qquad E^{\ominus} = +0.68\ V$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^{\ominus} = +1.51\ V$$

The overall equation is

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightleftharpoons 2Mn^{2+} + 8H_2O + 5O_2$$

☒ **A** $E^{\ominus}_{cell} = +2.19\ V$

☒ **B** $E^{\ominus}_{cell} = -0.83\ V$

☒ **C** $E^{\ominus}_{cell} = -0.38\ V$

☒ **D** $E^{\ominus}_{cell} = +0.83\ V$

(Total for Question 2 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

3 The transition metal complex $Pt(NH_3)_2Cl_2$ exists as two geometric isomers. This is because the complex

- ☒ **A** is square-planar.
- ☒ **B** is tetrahedral.
- ☒ **C** contains a double bond.
- ☒ **D** is octahedral.

(Total for Question 3 = 1 mark)

4 Hydrogen peroxide, H_2O_2, can be analysed by titration. The hydrogen peroxide solution is treated with acidified potassium iodide solution, and the liberated iodine is titrated with a standard solution of sodium thiosulfate, $Na_2S_2O_3$. The products are iodide ions and tetrathionate ions, $S_4O_6^{2-}$.

Which of the following applies to this reaction?

		Action of H_2O_2	Action of $S_2O_3^{2-}$
☒	**A**	oxidizing agent	oxidizing agent
☒	**B**	oxidizing agent	reducing agent
☒	**C**	reducing agent	oxidizing agent
☒	**D**	reducing agent	reducing agent

(Total for Question 4 = 1 mark)

5 A hydrated transition metal ion is colourless. Which of the following could be the electronic configuration of this ion?

- ☒ **A** [Ar] $3d^5 4s^2$
- ☒ **B** [Ar] $3d^8$
- ☒ **C** [Ar] $3d^{10} 4s^2$
- ☒ **D** [Ar] $3d^{10}$

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.

Question 6: N/A

7 When a solution containing 0.10 mol of chromium(III) chloride, $CrCl_3.6H_2O$, is treated with excess silver nitrate solution, 0.20 mol of silver chloride, AgCl, is immediately precipitated. The formula of the complex ion in the solution is

☒ **A** $[Cr(OH)_6]^{3-}$

☒ **B** $[Cr(H_2O)_6]^{3+}$

☒ **C** $[CrCl(H_2O)_5]^{2+}$

☒ **D** $[CrCl_2(H_2O)_4]^{+}$

(Total for Question 7 = 1 mark)

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8 Which of the following species is **not** able to act as a ligand in the formation of transition metal complexes?

☒ **A** $C_6H_5NH_2$

☒ **B** NH_3

☒ **C** $NH_2CH_2CH_2CH_2NH_2$

☒ **D** NH_4^+

(Total for Question 8 = 1 mark)

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9 The element zinc, with electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$, is **not** regarded as a transition element because

☒ **A** the oxide of zinc is amphoteric.

☒ **B** none of its ions has an unpaired electron in the *d*-subshell.

☒ **C** it does not readily form complex ions.

☒ **D** it has a boiling temperature low enough for it to be easily distilled.

(Total for Question 9 = 1 mark)

Question 10: N/A

Question 11: N/A

Question 12: N/A

Question 13: N/A

Question 14: N/A

15 Which sequence shows the bases in order of decreasing strength?

☒ **A** $C_6H_5NH_2 > CH_3NH_2 > NH_3$

☒ **B** $NH_3 > CH_3NH_2 > C_6H_5NH_2$

☒ **C** $CH_3NH_2 > NH_3 > C_6H_5NH_2$

☒ **D** $NH_3 > C_6H_5NH_2 > CH_3NH_2$

(Total for Question 15 = 1 mark)

Question 16: N/A

Question 17: N/A

Question 18: N/A

Question 19: N/A

20 Analysis suggests that a particular organic synthesis produces a medicine that contains trace impurities that may be hazardous. What is the best way for this discovery to be reported and evaluated?

- ☒ **A** In a scientific journal which subjects its articles to peer review.
- ☒ **B** On the Internet in an article on a website.
- ☒ **C** In a newspaper article in several broadsheet newspapers.
- ☒ **D** In a widely circulated magazine.

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS

SECTION B

Answer ALL the questions. Write your answers in the spaces provided.

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

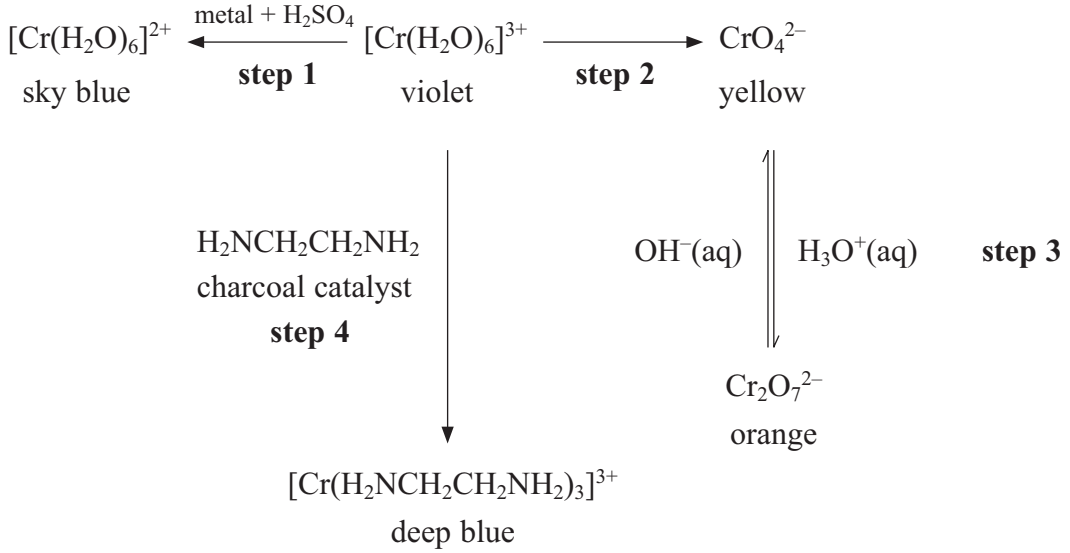
Complete the electronic configurations in *s,p,d* notation for vanadium and chromium.

(1)

Vanadium: [Ar] .....

Chromium: [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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(ii) Use $E^{\ominus}$ values from your data booklet to suggest a metal that could be used for **step 1**. Justify your answer by calculating $E^{\ominus}$ for your cell.

(2)

(iii) Explain, using oxidation numbers, whether or not the conversion in **step 3** is a redox reaction.

(2)

(iv) The organic compound $H_2NCH_2CH_2NH_2$ 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)

(v) Explain, in terms of its structure, how $H_2NCH_2CH_2NH_2$ can act as a bidentate ligand whereas H_2NNH_2 cannot.

(2)

(c) The half-equations relating the interconversion of the species $Cr^{2+}(aq)$, $Cr^{3+}(aq)$ and $Cr_2O_7^{2-}(aq)$ are given below.

Half-equation I: $Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$

Half-equation II: $Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

(i) Use your data booklet to find $E^{\ominus}$ for each of the above half-equations.

(1)

Half-equation I ..... Volts

Half-equation II ..... Volts

*(ii) Write the overall equation for the disproportionation of Cr^{3+} into Cr^{2+} and $Cr_2O_7^{2-}$.

Use the $E^{\ominus}$ values you have obtained in (c)(i) to show whether or not this disproportionation is feasible under standard conditions.

(4)

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(Total for Question 21 = 15 marks)

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box ☒. If you change your mind, put a line through the box ☒ and then mark your new answer with a cross ☒.

22 The following data are provided.

	$E^{\ominus}$ / V
$ClO^-(aq) + H_2O(l) + e^- \rightleftharpoons \frac{1}{2}Cl_2(aq) + 2OH^-(aq)$	+0.40
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

What is the value of $E^{\ominus}_{cell}$ in which the following disproportionation reaction occurs?

$$Cl_2(aq) + 2OH^-(aq) \rightarrow ClO^-(aq) + Cl^-(aq) + H_2O(l)$$

☒ **A** $+ \frac{1.36}{2} - 0.40$ V

☒ **B** $+ \frac{1.36}{2} + 0.40$ V

☒ **C** $+ 1.36 - 0.40$ V

☒ **D** $+ 1.36 + 0.40$ V

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23 Which of the following is always proportional to $E^{\ominus}_{cell}$ for a chemical reaction?

☒ **A** $\Delta H_{reaction}$

☒ **B** ΔS_{system}

☒ **C** $\Delta S_{surroundings}$

☒ **D** ΔS_{total}

Use this space for any rough working. Anything you write in this space will gain no credit.

24 The electrode system based on the half-equation below has the standard electrode potential +1.51 V.

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $\quad E^{\ominus} = +1.51\ V$

Which of the following statements about this electrode system is correct?

☒ **A** Changing the concentration of $Mn^{2+}(aq)$ would cause a change in the electrode potential.

☒ **B** $Mn^{2+}(aq)$ is acting as an oxidizing agent.

☒ **C** The electrode used is made of manganese.

☒ **D** When connected to a standard hydrogen electrode, the resulting cell voltage would be +0.51 V.

25 The hydrolysis of a transition metal cation can be represented by the following equation

$$[M(H_2O)_6]^{n+}(aq) + H_2O(l) \rightleftharpoons [M(H_2O)_5OH]^{(n-1)+}(aq) + H_3O^+(aq)$$

In this reaction

☒ **A** the solvent H_2O is acting as an acid by donating a proton to the metal cation.

☒ **B** the pH of the solution will be lower if the value of n is 2 instead of 3.

☒ **C** the equilibrium position lies further to the right if the value of n is 3 instead of 2.

☒ **D** the oxidation state of the metal in the cation has decreased from n to (n – 1).

Use this space for any rough working. Anything you write in this space will gain no credit.

26 In aqueous solution, manganate(VI) ions disproportionate into manganate(VII) ions and manganese(IV) oxide when carbon dioxide is bubbled through the solution. The ionic equation for the reaction is

$$3MnO_4^{2-}(aq) + 4H^+(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$$

The role of the carbon dioxide is to

- ☒ **A** lower the pH of the solution.
- ☒ **B** raise the pH of the solution.
- ☒ **C** oxidize the manganate(VI) ions.
- ☒ **D** reduce the manganate(VI) ions.

27 Consider the equation below.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$$

This reaction is best described as

☒ **A** acid-base.

☒ **B** redox.

☒ **C** addition.

☒ **D** ligand exchange.

28 The hydride ion, H^-, is a strong reducing agent, a good nucleophile and a strong base.

Which of the following changes could **not** be brought about by the hydride ion?

- ☒ **A** CH_3CHO to CH_3CH_2OH
- ☒ **B** C_2H_5Br to C_2H_6
- ☒ **C** $CH_2{=}CH_2$ to C_2H_6
- ☒ **D** CH_3COOH to CH_3COO^-

Answer ALL the questions. Write your answers in the spaces provided.

29 Hydrogen-oxygen fuel cells can operate in acidic or alkaline conditions.
One such commercial cell uses porous platinum electrodes in contact with concentrated aqueous potassium hydroxide solution, KOH(aq).

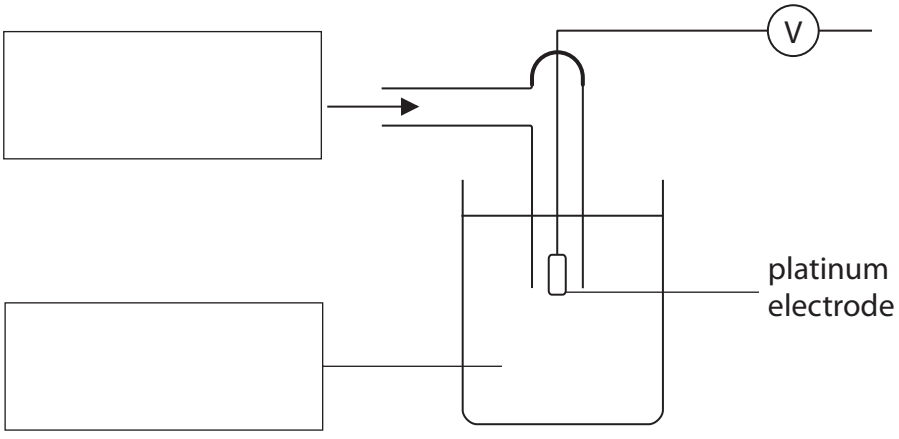
(a) Use relevant standard electrode potential values, on pages 15 and 17 of the Data Booklet, to complete the table below in which two $E^{\ominus}$ values are missing.

(2)

Half-equation	$E^{\ominus}$ / V
$2H_2O(l) + 2e^- \rightleftharpoons 2OH^-(aq) + H_2(g)$	−0.83
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	

(b) (i) Fill in the boxes to identify, by name or formula, the substances used in the **standard** hydrogen electrode.

(2)



(ii) State **three** conditions that are necessary for a standard hydrogen electrode.

(2)

1. .....

2. .....

3. .....

(c) Write appropriate half-equations and use them to derive an overall equation for the reaction which occurs when an **alkaline** hydrogen-oxygen fuel cell operates.

(2)

(d) Use the $E^{\ominus}$ values from the table in part (a) to calculate the $E^{\ominus}_{cell}$ for a hydrogen-oxygen fuel cell operating in alkaline conditions.

(1)

(e) Suggest why the $E^{\ominus}_{cell}$ for a hydrogen-oxygen fuel cell, operating in **acidic** conditions, is identical to that of an alkaline fuel cell.

(1)

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(f) Give **one** reason (other than cost implications) why the platinum electrodes are made by coating porous material with platinum rather than by using platinum rods.

(1)

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(g) Suggest **one** disadvantage of using a hydrogen-oxygen fuel cell compared with a rechargeable battery when providing electrical energy for a motor vehicle.

(1)

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= 12 marks)

SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

30

Titanium is the seventh most abundant metal in the Earth's crust and occurs principally as rutile (impure titanium(IV) oxide, 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 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 $[Ti(H_2O)_6]^{3+}(aq)$ 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, $TiCl_4$, is a colourless liquid with a boiling temperature of 136 °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, 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 $K_2Ti(OH)_6$.

(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)

.....

.....

.....

.....

(b) Complete the electronic configurations of

(2)

Ti [Ar] .....

Ti^{3+} [Ar] .....

Ti^{4+} [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, $[Ti(H_2O)_6]^{3+}$, is coloured.

(3)

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

(1)

*(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)

(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)

(iv) Titanium(IV) chloride is one of the catalysts used in the polymerization of propene to form poly(propene).

Give the displayed formula of the repeat unit of poly(propene).

(1)

(f) The concentration of a solution of titanium(III) chloride can be determined by titration with a solution of hydrogen peroxide, H_2O_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)

$H_2O_2 + 2H^+ +$ ..... $\rightarrow$ .....

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

In an experiment, 5.00 cm^3 of a sample of titanium(III) chloride solution was transferred to a volumetric flask and made up to 250 cm^3 of an aqueous solution. A 25.0 cm^3 portion of this diluted solution was acidified and titrated with a 0.0200 mol dm^{-3} solution of hydrogen peroxide, H_2O_2. The mean titre was 22.50 cm^3.

Calculate the concentration of the **original** titanium(III) chloride solution, in 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)

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= 23 marks)