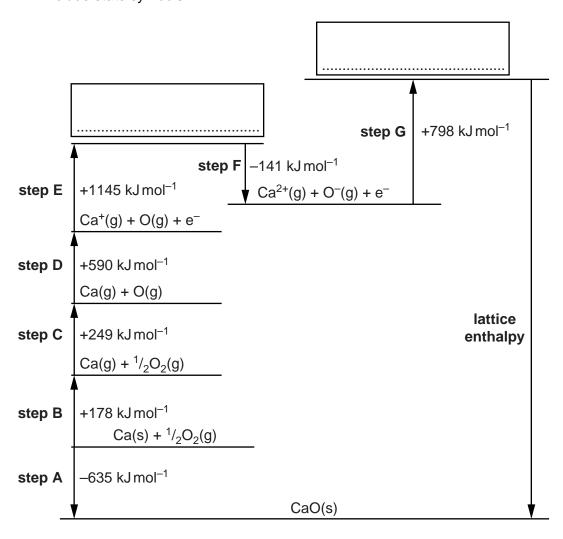
Answer all the questions.

- 1 Born–Haber cycles can be used to determine lattice enthalpies of ionic compounds.
 - (a) Define, in words, the term lattice enthalpy.

| |
|------|
| |
| |
| [2] |

- **(b)** The Born–Haber cycle below can be used to determine the lattice enthalpy of calcium oxide. The cycle includes the values for the enthalpy changes of the steps labelled **A–G**.
 - (i) Complete the Born–Haber cycle by adding the species present on the two dotted lines.

 Include state symbols.



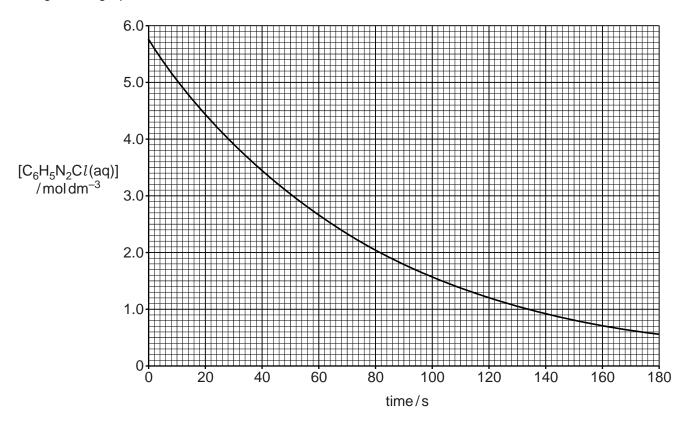
[2]

| | (ii) | Naı | me the enthalpy change | s for the fol | lowing steps | in the Born–I | Haber cycle. | |
|-----|-------|------|---------------------------|---------------|--------------|------------------|--------------|---------------------------------|
| | | • | step A | | | | | |
| | | • | step C | | | | | |
| | | • | step G | | | | | |
| | | | | | | | | [3] |
| | (iii) | Cal | culate the lattice enthal | oy of calciu | m oxide. | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | answer = | | | kJ mol ⁻¹ [2] |
| (c) | Des | crib | e and explain the factors | s that affect | the values o | of lattice entha | alpies. | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | [3] |
| | | | | | | | | [Total: 12] |

2 In aqueous solution, benzenediazonium chloride, C₆H₅N₂C*l*, decomposes above 10 °C.

$$\mathrm{C_6H_5N_2C}\mathit{l}(\mathrm{aq}) \ + \ \mathrm{H_2O(I)} \ \ \longrightarrow \ \ \mathrm{C_6H_5OH(aq)} \ + \ \mathrm{N_2(g)} \ + \ \mathrm{HC}\mathit{l}(\mathrm{aq})$$

A student investigates the rate of this reaction using an excess of water at 50 °C. The student takes measurements at intervals during the reaction and then plots his experimental results to give the graph shown below.



- (a) The student uses half-life to suggest the order of reaction with respect to C₆H₅N₂Cl.
 - (i) What is meant by the half-life of a reaction?

Show your working on the graph.

[1]

(ii) Confirm the order of reaction with respect to $C_6H_5N_2Cl$.

[2

| | (iii) | What would be the effect, if any, on the half-life of this reaction of doubling the initial concentration of $\rm C_6H_5N_2C\mathit{l}$? |
|-----|-------|---|
| | | [1] |
| (b) | The | student predicts that the rate equation is: rate = $k[C_6H_5N_2Cl]$. |
| | (i) | Using the graph and this rate equation, determine the rate of reaction after 40 s. |
| | | Show your working on the graph. |
| | | |
| | | |
| | | |
| | | |
| | | rate =units[3] |
| | (ii) | Calculate the rate constant, <i>k</i> , for this reaction and give its units. |
| | | |
| | | |
| | | |
| | | |
| | | k = units [2] |
| (c) | The | order of this reaction with respect to H ₂ O is effectively zero. |
| | Exp | lain why. |
| | | |
| | | |
| | | [1] |

Turn over

[Total: 10]

| 3 | Hydrogen | and iodine | react to | gether in a | a reversible | reaction: |
|---|--------------|------------|----------|--------------|------------------|-------------|
| • | i iyai ogoii | and loan o | TOUGH TO | gouioi iii i | 4 10 10 10 10 10 | i odolioii. |

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -9 \text{ kJ mol}^{-1}$$

A chemist mixes together 2.00 \times 10⁻³ mol H₂(g) and 4.00 \times 10⁻³ mol I₂(g) in a 1.00 dm³ container. The chemist seals the container.

The mixture is heated and left to reach equilibrium.

At equilibrium, the mixture contains 3.00 x 10^{-4} mol of H_2 .

(a) Calculate the equilibrium constant, $K_{\rm c}$, including units, if any, for this equilibrium.

Give your answer to three significant figures.

| K - | unite | Г | 51 |
|-----------|----------|---|----|
| $r_{C} =$ | umis | | ဎၟ |

- **(b)** The chemist repeats the experiment several times. In each experiment, the chemist makes one change.
 - (i) The chemist uses $3.00 \times 10^{-3} \text{ mol H}_2(g)$ instead of $2.00 \times 10^{-3} \text{ mol H}_2(g)$.

Predict whether the amounts of $H_2(g)$, $I_2(g)$ and HI(g) in the equilibrium mixture would be greater, smaller or the same as in the original experiment.

Answer by placing ticks in the appropriate boxes of the table below.

| | H ₂ (g) | I ₂ (g) | HI(g) |
|----------|--------------------|--------------------|-------|
| Greater | | | |
| Smaller | | | |
| The same | | | |

[2]

| (ii) | The chemist heats the mixture to a higher temperature at constant pressure. | |
|-------|---|------------|
| | Explain whether the value of $K_{\rm c}$ would be greater, smaller or the same. | |
| | | |
| | | |
| | | [1] |
| (iii) | The chemist increases the pressure of the mixture at constant temperature. | |
| | Explain whether the value of $K_{\rm c}$ would be greater, smaller or the same. | |
| | | |
| | | |
| | | [1] |
| | | [Total: 9] |

This question looks at pH values and reactions of acids, bases and buffers.

| (a) | $0.14\mathrm{moldm^{-3}}$ solutions of hydrochloric acid, HCl, and chloric(I) acid, HClO (p $K_{\mathrm{a}}=7.43$) have different pH values. |
|-----|---|
| | Explain why the pH values are different and calculate the pH of $0.14\mathrm{moldm^{-3}}$ solutions of HC l and HC l O to two decimal places . |
| | Show any working in calculations. |
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| | |
| | [5] |
| (b) | Aluminium powder is added to aqueous ethanoic acid, CH ₃ COOH. |
| () | Write full and ionic equations for the reaction that takes place. |
| | full equation |
| | ionic equation[2] |
| | |

(c) Calculate the pH of a $0.40\,\mathrm{mol\,dm^{-3}}$ solution of NaOH.

| | | [2] |
|-----|-----|--|
| (d) | | iochemistry, buffer solutions based on methanoic acid can be used in the analysis of urine oples. |
| | (i) | Explain what is meant by the term buffer solution. |
| | | Describe how a buffer solution based on methanoic acid can act as a buffer. |
| Ø | | In your answer you should explain how the equilibrium system allows the buffer solution to control the pH. |
| | | |
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| | | |
| | | [7] |
| | | |

| (ii) | A chemist prepares a buffer solution by mixing together the following: | | | | |
|------|---|--|--|--|--|
| | $200\rm cm^3$ of $3.20\rm moldm^{-3}$ HCOOH ($K_{\rm a}$ = $1.70\times10^{-4}\rm moldm^{-3})$ and $800\rm cm^3$ of $0.500\rm moldm^{-3}$ NaOH. | | | | |
| | The volume of the buffer solution is 1.00 dm ³ . | | | | |
| | • Explain why a buffer solution is formed when these two solutions are mixed together. | | | | |
| | Calculate the pH of this buffer solution. | | | | |
| | Give your answer to two decimal places. | | | | |
| | | | | | |
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| | | | | | |

5 Iron is heated with chlorine to form an orange–brown solid, **A**.

Solid **A** is dissolved in water to form an orange-brown solution, **X**, containing the complex ion $[Fe(H_2O)_6]^{3+}$.

Separate portions of solution **X** are reacted as shown in **Experiments 1–4** below.

Experiment 1

Aqueous sodium hydroxide is added to solution **X**. An orange–brown precipitate **B** forms.

Experiment 2

Excess zinc powder is added to solution X and the mixture is heated. The excess zinc is removed leaving a pale-green solution containing the complex ion C and aqueous Zn^{2+} ions.

Experiment 3

An excess of aqueous potassium cyanide, KCN(aq), is added to solution **X**. The solution turns a yellow colour and contains the complex ion **E**. **E** has a molar mass of 211.8 g mol⁻¹.

Experiment 4

An aqueous solution containing ethanedioate ions, $(COO^-)_2$, is added to solution **X**. A coloured solution forms containing a mixture of optical isomers **F** and **G**.

The structure of the ethanedioate ion is shown below.

| (a) | Writ | e an equation for the formation of solid A . | |
|-----|------|--|-----|
| | | | [1] |
| (b) | In E | xperiment 1, write an ionic equation for the formation of precipitate B. | |
| | | | [1] |
| (c) | In E | xperiment 2, | |
| | (i) | write an equation for the formation of complex ion C | |
| | | | [2] |
| | (ii) | state the type of reaction taking place. | |
| | | | [1] |

| (d) | In Experiment 3, | | | | | |
|-----|------------------|---|--|--|--|--|
| | (i) | write an equation for the formation of complex ion E | | | | |
| | | [2] | | | | |
| | (ii) | state the type of reaction taking place. | | | | |
| | | [1] | | | | |
| (e) | In E | Experiment 4, optical isomers F and G are formed. | | | | |
| | In y | ow the 3-D shapes of F and G . Four diagrams, show the ligand atoms that are bonded to the metal ions and any overall rges. | | | | |
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| | | | | | | |
| | | [3] | | | | |
| (f) | oxic | a separate experiment, iron metal is heated with potassium nitrate, KNO_3 , a strong dising agent. A reaction takes place and the resulting mixture is poured into water. A dark solution forms containing ferrate(VI) ions. The ferrate(VI) ion has a 2– charge. | | | | |
| | Sug | ggest a possible formula for the ferrate(VI) ion. | | | | |
| | | [1] | | | | |
| | | [Total: 12] | | | | |
| | | | | | | |

| 6 | The equation for the | reaction of CO | ₂ and H ₂ O t | o produce g | glucose, C ₆ l | H ₁₂ O ₆ , and | O ₂ is shown |
|---|----------------------|----------------|-------------------------------------|-------------|---------------------------|--------------------------------------|-------------------------|
| | below. | | | | _ | | |

$$6\text{CO}_2(g) \ + \ 6\text{H}_2\text{O}(I) \ \longrightarrow \ \text{C}_6\text{H}_{12}\text{O}_6(s) \ + \ 6\text{O}_2(g) \ \Delta H = +2879\,\text{kJ}\,\text{mol}^{-1}; \ \Delta S = -256\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

Standard entropies are given in the table below.

| Substance | CO ₂ (g) | H ₂ O(I) | O ₂ (g) |
|--|---------------------|---------------------|--------------------|
| S [⊕] / J K ⁻¹ mol ⁻¹ | 214 | 70 | 205 |

| | / _\ | \ /:\ | Coloulata tha | -444 | | of almono |
|---|-------------|-------|---------------|----------|--------|------------|
| (| (a) | , (i) | Calculate the | Stanuaru | еппору | oi giucose |

$$S^{\Theta} = JK^{-1} mol^{-1}$$
 [2]

(ii) Calculate ΔG , in kJ mol⁻¹, at 25 °C.

Show all your working.

$$\Delta G = \dots kJ \text{ mol}^{-1}$$
 [2]

(iii) Explain why this reaction is **not** feasible at **any** temperature.

| (b) | Although the reaction between CO2 and H2O to form C6H12O6 and O2 appears not to be |
|-----|--|
| | feasible, plants are able to make the reaction take place spontaneously by photosynthesis. |

Each year, $3.4 \times 10^{18} \, \text{kJ}$ of solar energy is taken in by all the plants on the Earth to make photosynthesis take place.

Calculate the mass of carbon dioxide that is removed each year from the atmosphere by photosynthesis on Earth.

| mass of CO ₂ = | | [2] |
|---------------------------|--|-----|
|---------------------------|--|-----|

[Total: 7]

7 Standard electrode potentials for seven redox systems are shown in **Table 7.1**. You may need to use this information in parts (a)–(d) of this question.

| Redox system | | | | E [⊕] /V |
|-----------------|---|----------------------|------------------------------------|-------------------|
| 1 | Mg ²⁺ (aq) + 2e ⁻ | \rightleftharpoons | Mg(s) | -2.37 |
| 2 | Cu ²⁺ (aq) + 2e ⁻ | | | +0.34 |
| 3 | A <i>l</i> ³⁺ (aq) + 3e ⁻ | | | -1.66 |
| 4 | Fe ³⁺ (aq) + e ⁻ | | Fe ²⁺ (aq) | +0.77 |
| 5 | I ₂ (aq) + 2e ⁻ | \rightleftharpoons | 2I ⁻ (aq) | +0.54 |
| 6 | $Cl_2(g) + 2e^-$ | \rightleftharpoons | 2C <i>l</i> ⁻ (aq) | +1.36 |
| 7 | ClO-(aq) + 2H+(aq) + e- | \rightleftharpoons | $\frac{1}{2}Cl_{2}(g) + H_{2}O(I)$ | +1.63 |

Table 7.1

| (a) | Define the term <i>standard electrode potential</i> . Include all standard conditions in your answer. |
|-----|--|
| | |
| | |
| | |
| | |
| | [2] |
| (b) | An electrochemical cell can be made based on redox systems 1 and 2. |
| | Write down the standard cell potential of this cell. |
| | |
| | |
| | standard cell potential =V [1] |
| (c) | Using redox systems 3 , 4 and 5 only in Table 7.1 , predict three reactions that might be feasible. |
| | (i) Write the overall equation for each predicted reaction. |
| | |
| | |
| | [3] |

| | (11) | actually take place. E° values may |
|-----|------|---|
| | | |
| | | |
| | | |
| | | [2] |
| (d) | In a | queous acid, $Cl^-(aq)$ ions react with $ClO^-(aq)$ ions to form chlorine gas, $Cl_2(g)$. queous alkali, chlorine gas, $Cl_2(g)$, reacts to form $Cl^-(aq)$ and $ClO^-(aq)$ ions. |
| | | lain this difference. Table 7.1 to help you with your answer. |
| | | |
| | | |
| | | |
| | | [4] |
| (e) | In a | cidic conditions, Sn ²⁺ ions react with IO ₃ ⁻ ions to produce iodine and Sn ⁴⁺ ions. |
| | | What is the oxidising agent in this reaction? Explain your answer. |
| | | |
| | | |
| | (ii) | Construct an equation for this reaction. |
| | | |
| | | |
| | | |
| | | |
| | | [2] |
| | | [Total: 15] |

8 Dimethylglyoxime, DMGH, can be used to analyse nickel(II) compounds.

An excess of a solution of DMGH is added to an acidic solution of a nickel(II) compound. Aqueous ammonia is added which precipitates out a nickel(II) complex, Ni(DMG)₂, as a red solid.

A sample of a hydrated nickel(II) salt is analysed using the procedure below.

Step 1

2.50~g of the hydrated nickel(II) salt is dissolved in dilute acid. An excess of an aqueous solution of DMGH is added.

Step 2

An excess of aqueous ammonia is added and the mixture is heated. A red precipitate of Ni(DMG)₂ forms.

An equation for the reaction is shown below.

$$Ni^{2+}(aq) + 2DMGH(aq) + 2NH_3(aq) \rightarrow Ni(DMG)_2(s) + 2NH_4^+(aq)$$

red precipitate

Step 3

The red precipitate is filtered, washed with water, dried and then weighed.

The precipitate of Ni(DMG)₂ has a mass of 2.57 g.

Assume that all Ni²⁺(aq) ions have been converted into Ni(DMG)₂(s).

 $M[Ni(DMG)_2] = 288.7 \,\mathrm{g}\,\mathrm{mol}^{-1}$.

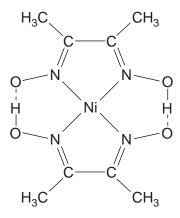
Step 4

A second 2.50 g sample of the hydrated nickel(II) salt is heated in a crucible to remove the water of crystallisation.

1.38 g of the anhydrous salt remains.

| (a) | Complete the electron configurations | s of nickel as the element and in the +2 oxidation state | €. |
|-----|--------------------------------------|--|----|
| | nickel as the element: | 1s ² 2s ² 2p ⁶ | |
| | nickel in the +2 oxidation state: | 1s ² 2s ² 2n ⁶ | [2 |

(b) The structure of $\operatorname{Ni}(\operatorname{DMG})_2$ is shown below.



| (i) | State and explain the role of ammonia in step 2 of this experiment. | |
|-------|--|-----------------|
| | | |
| | | |
| | | [1] |
| (ii) | State the coordination number of Ni in Ni(DMG) ₂ . | |
| | | [1] |
| (iii) | Why does the Ni(DMG) ₂ complex have no overall charge? | |
| | | |
| | | L4. |
| | | [1 _. |
| (iv) | Draw the structure of dimethylalyoxime DMGH | |

[1]

(c) Determine a possible formula of the hydrated nickel(II) salt.

Your answer **must** show relevant working.

[7]

[Total: 13]

END OF QUESTION PAPER