Instructions

- Use black ink or black ball-point pen.
- Fill in the boxes at the top of this page with your name, centre number and candidate number.
- Answer all questions.
- Answer the questions in the spaces provided – there may be more space than you need.

Information

- The total mark for this paper is 90.
- The marks for each question are shown in brackets – use this as a guide as to how much time to spend on each question.
- You may use a scientific calculator.
- For the question marked with an asterisk (*), marks will be awarded for your ability to structure your answer logically showing the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Try to answer every question.
- Check your answers if you have time at the end.
- Show all your working in calculations and include units where appropriate.
1. A phosphorus atom has mass number 31.

(a) How many of each sub-atomic particle are present in the phosphide ion, \( P^{3-} \)?

<table>
<thead>
<tr>
<th>Number of protons</th>
<th>Number of neutrons</th>
<th>Number of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ A</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>□ B</td>
<td>15</td>
<td>16</td>
</tr>
<tr>
<td>□ C</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>□ D</td>
<td>16</td>
<td>15</td>
</tr>
</tbody>
</table>

(b) Phosphorus(III) chloride molecules are pyramidal with a bond angle less than 109.5°.

(i) Explain why a phosphorus(III) chloride molecule has this shape and bond angle.
(ii) Which describes the polarity of the P—Cl bond and the polarity of the phosphorus(III) chloride molecule?

(1)

<table>
<thead>
<tr>
<th>Polarity of P—Cl bond</th>
<th>Polarity of molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ A non-polar</td>
<td>non-polar</td>
</tr>
<tr>
<td>□ B non-polar</td>
<td>polar</td>
</tr>
<tr>
<td>□ C polar</td>
<td>non-polar</td>
</tr>
<tr>
<td>□ D polar</td>
<td>polar</td>
</tr>
</tbody>
</table>

(c) Phosphorus has one naturally occurring isotope with mass number 31. Chlorine exists as two isotopes with mass numbers 35 and 37.

Give the formulae and mass/charge ratio of the ions responsible for the molecular ion peaks in the mass spectrum of phosphorus(III) chloride, PCl₃.

(2)

(Total for Question 1 = 6 marks)
2  Magnesium nitrate decomposes on heating as shown by the equation.

\[ 2\text{Mg(NO}_3\text{)}_2 \rightarrow 2\text{MgO} + 4\text{NO}_2 + \text{O}_2 \]

(a) Explain, in terms of all the relevant oxidation numbers, why this is a redox reaction. (3)

(b) Calcium nitrate decomposes in a similar way to magnesium nitrate, but requires a higher temperature for decomposition.

Explain this observation in terms of the charge and size of the cations. (3)

(Total for Question 2 = 6 marks)
This question is about halogens and redox reactions.

(a) The boiling temperatures of three halogens are shown in the table.

<table>
<thead>
<tr>
<th>Halogen</th>
<th>Boiling temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>chlorine</td>
<td>–35</td>
</tr>
<tr>
<td>bromine</td>
<td>59</td>
</tr>
<tr>
<td>iodine</td>
<td>184</td>
</tr>
</tbody>
</table>

Explain why the boiling temperatures increase from chlorine to iodine.

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(2)
(b) Potassium halides react with concentrated sulfuric acid to form potassium hydrogensulfate and the different products shown in the table.

<table>
<thead>
<tr>
<th>Potassium halide</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>potassium chloride</td>
<td>hydrogen chloride</td>
</tr>
<tr>
<td>potassium bromide</td>
<td>hydrogen bromide, bromine and sulfur dioxide</td>
</tr>
<tr>
<td>potassium iodide</td>
<td>hydrogen iodide, iodine, hydrogen sulfide and sulfur</td>
</tr>
</tbody>
</table>

By referring to any changes in oxidation numbers when these halides react with concentrated sulfuric acid, explain which halide is the strongest reducing agent.
(c) Use these electrode potentials to answer the following questions.

<table>
<thead>
<tr>
<th>Electrode reaction</th>
<th>$E^\circ / V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{I}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{I}^-(\text{aq})$</td>
<td>+0.54</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(\text{aq}) + e^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$</td>
<td>+0.77</td>
</tr>
<tr>
<td>$\text{Br}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$</td>
<td>+1.09</td>
</tr>
<tr>
<td>$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{Cl}_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$</td>
<td>+1.51</td>
</tr>
</tbody>
</table>

(i) Which species will oxidise $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$?

- [ ] A $\text{Br}_2(\text{aq})$
- [ ] B $\text{Cl}^-(\text{aq})$
- [ ] C $\text{I}_2(\text{aq})$
- [ ] D $\text{Mn}^{2+}(\text{aq})$

(ii) Write the ionic equation and calculate the $E^\circ_{\text{cell}}$ value for the reaction between $\text{MnO}_4^-$ ions and $\text{Br}^-$ ions in acidic solution. State symbols are not required.

(Total for Question 3 = 9 marks)
Iron and zinc are in the d-block of the Periodic Table.

(a) Which of these is the electronic configuration of an iron(II) ion, Fe\(^{2+}\)?

\[
\begin{array}{ccc}
3d & \quad 4s \\
\hline
A & \uparrow \downarrow & \uparrow \downarrow & \uparrow \downarrow & \text{[Ar]} & \uparrow \downarrow \\
B & \uparrow \downarrow & \uparrow & \uparrow & \uparrow & \uparrow & \text{[Ar]} & \text{[Ar]} \\
C & \uparrow \downarrow & \uparrow \downarrow & \text{[Ar]} & \uparrow \downarrow & \text{[Ar]} \\
D & \uparrow & \uparrow & \uparrow & \uparrow & \text{[Ar]} & \text{[Ar]} & \text{[Ar]} \\
\end{array}
\]

(b) Iron(II) ions, [Fe(H\(_2\)O)\(_6\)]\(^{2+}\), form a pale green solution but zinc ions, [Zn(H\(_2\)O)\(_6\)]\(^{2+}\), form a colourless solution. Explain why zinc ions are colourless.

(c) Hydrated iron(II) ions react with ethanedioate ions, C\(_2\)O\(_4\)\(^{2-}\), to form a complex ion.

\[
[\text{Fe(H}_2\text{O)}\(_6\)]\(^{2+}\) + 2C\(_2\)O\(_4\)\(^{2-}\) \rightleftharpoons [\text{Fe(C}_2\text{O}_4)_2\text{(H}_2\text{O)}\(_6\)]\(^{2-}\) + 4\text{H}_2\text{O}
\]

(i) Draw a structure of the [Fe(C\(_2\)O\(_4\))\(_2\)(H\(_2\)O)\(_6\)]\(^{2-}\) ion, showing all of the bonds.
(ii) Explain, in terms of entropy, why this reaction is feasible. (2)

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(d) Iodide ions, $I^-$, react with peroxodisulfate(VI) ions, $S_2O_8^{2-}$

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

This reaction is catalysed by iron(II) ions, $Fe^{2+}(aq)$. Write two ionic equations to show how iron(II) ions act as a catalyst in this reaction. State symbols are not required. (2)

(Total for Question 4 = 9 marks)
This question is about enthalpy changes and entropy changes.

(a) Which is the equation for the standard enthalpy change of formation, $\Delta H^\circ$, of aluminium oxide?

- **A** $4\text{Al}(s) + 3\text{O}_2(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$
- **B** $4\text{Al}(s) + 6\text{O}(g) \rightarrow 2\text{Al}_2\text{O}_3(s)$
- **C** $2\text{Al}(s) + 1\frac{1}{2}\text{O}_2(g) \rightarrow \text{Al}_2\text{O}_3(s)$
- **D** $2\text{Al}(s) + 3\text{O}(g) \rightarrow \text{Al}_2\text{O}_3(s)$

(b) Propan-1-ol is dehydrated to form propene.

\[
\begin{array}{c}
\text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{H} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{H} \quad \text{C} = \text{C} \\
\text{H} \quad \text{H} \\
\text{H} \\
\end{array} + \text{H}_2\text{O} \quad \Delta H^\circ = +42 \text{ kJ mol}^{-1}
\]

The relevant mean bond enthalpies are given in the table.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Mean bond enthalpy / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—C</td>
<td>347</td>
</tr>
<tr>
<td>C≡C</td>
<td>612</td>
</tr>
<tr>
<td>C—H</td>
<td>413</td>
</tr>
<tr>
<td>O—H</td>
<td>464</td>
</tr>
</tbody>
</table>

Calculate the C—O mean bond enthalpy, using the mean bond enthalpies given in the table and the enthalpy change of reaction.
(c) Which reaction has a negative value for $\Delta S_{\text{system}}$?

- A $2\text{Cu(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{CuO(s)}$
- B $2\text{H}_2\text{O}_2(\text{l}) \rightarrow 2\text{H}_2\text{O(l)} + \text{O}_2(\text{g})$
- C $\text{MgCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MgSO}_4(\text{aq}) + \text{H}_2\text{O(l)} + \text{CO}_2(\text{g})$
- D $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})$

(d) What is the expression for $\Delta S_{\text{total}}$?

- A $\Delta S_{\text{surroundings}} + \frac{\Delta H}{T}$
- B $\Delta S_{\text{surroundings}} - \frac{\Delta H}{T}$
- C $\Delta S_{\text{system}} + \frac{\Delta H}{T}$
- D $\Delta S_{\text{system}} - \frac{\Delta H}{T}$
(e) Calcium carbonate decomposes on heating.

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

\[ \Delta H = +178 \text{ kJ mol}^{-1} \]

\[ \Delta S_{\text{system}} = +165 \text{ J mol}^{-1} \text{ K}^{-1} \]

Show, by calculating the value for the free energy change, \( \Delta G \), that this decomposition is not feasible at 298 K, and then calculate the minimum temperature to which calcium carbonate must be heated to make it decompose.

(Total for Question 5 = 9 marks)
Magnesium bromide, MgBr$_2$, is an ionic compound.

(a) (i) Draw a dot-and-cross diagram to show the bonding in magnesium bromide. Only outer shell electrons are required.

(ii) State all the conditions under which magnesium bromide conducts electricity.
(b) The table shows the enthalpy changes needed to calculate the first electron affinity of bromine.

<table>
<thead>
<tr>
<th>Enthalpy change</th>
<th>Value / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>enthalpy change of atomisation of magnesium, $\Delta_{at}H^\theta[\text{Mg(s)}]$</td>
<td>+148</td>
</tr>
<tr>
<td>1ˢᵗ ionisation energy of magnesium, 1ˢᵗ IE[\text{Mg(g)}]</td>
<td>+738</td>
</tr>
<tr>
<td>2ⁿᵈ ionisation energy of magnesium, 2ⁿᵈ IE[\text{Mg⁺(g)}]</td>
<td>+1451</td>
</tr>
<tr>
<td>enthalpy change of atomisation of bromine, $\Delta_{at}H^\theta[\frac{1}{2}\text{Br}_2(l)]$</td>
<td>+112</td>
</tr>
<tr>
<td>lattice energy of magnesium bromide, LE[\text{MgBr}_2(s)]</td>
<td>-2440</td>
</tr>
<tr>
<td>enthalpy change of formation of magnesium bromide, $\Delta_fH^\theta[\text{MgBr}_2(s)]$</td>
<td>-524</td>
</tr>
</tbody>
</table>

(i) Complete the Born-Haber cycle for magnesium bromide with formulae, electrons and labelled arrows. The cycle is not drawn to scale.

```
Mg(g) + Br₂(l) → MgBr₂(s)  $\Delta_{at}H^\theta[\text{Mg(s)}]$
```

```
Mg(s) + Br₂(l) → MgBr₂(s)  $\Delta_fH^\theta[\text{MgBr}_2(s)]$
```
(ii) Calculate the first electron affinity of bromine, in kJ mol\(^{-1}\).

(c) (i) The first ionisation energy of sodium is 496 kJ mol\(^{-1}\).

Explain why the first ionisation energy of magnesium is higher than that of sodium.

(ii) Write the equation, including state symbols, to show the third ionisation energy of magnesium.

(Total for Question 6 = 11 marks)
In acid-base neutralisation reactions, there is a temperature change.

(a) The enthalpy change when hydrochloric acid reacts with aqueous ammonia is \(-53.4\, \text{kJ mol}^{-1}\).

\[
\text{HCl(aq)} + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4\text{Cl(aq)}
\]

Calculate the temperature change you would expect when 25.0 cm\(^3\) of 1.00 mol dm\(^{-3}\) hydrochloric acid is mixed with 25.0 cm\(^3\) of 1.00 mol dm\(^{-3}\) aqueous ammonia.

Give your answer to an appropriate number of significant figures.

Assume: the density of the solution is 1.00 g cm\(^{-3}\)

the specific heat capacity of the solution is 4.18 J g\(^{-1}\) °C\(^{-1}\)
*(b) The table shows the enthalpy changes of reaction when 1 mol of different acids are neutralised by sodium hydroxide solution, at 298 K.*

<table>
<thead>
<tr>
<th>Acid</th>
<th>Enthalpy change of reaction for 1 mol of acid / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrochloric acid, HCl</td>
<td>-58</td>
</tr>
<tr>
<td>nitric acid, HNO₃</td>
<td>-58</td>
</tr>
<tr>
<td>sulfuric acid, H₂SO₄</td>
<td>-115</td>
</tr>
<tr>
<td>ethanoic acid, CH₃COOH</td>
<td>-56</td>
</tr>
</tbody>
</table>

Comment on the relative enthalpy changes of reaction, using the data from the table and including any relevant equations.

(Total for Question 7 = 9 marks)
8 2-Hydroxyethanoic acid, also known as glycolic acid, CH$_2$OHCOOH, is an alpha hydroxy acid used in some skincare products. It has a $K_a$ value of $1.5 \times 10^{-4}$ mol dm$^{-3}$.

The structure of glycolic acid is

\[
\begin{array}{c}
\text{H} \\
\text{H-C-C-OH} \\
\text{OH}
\end{array}
\]

(a) A solution of glycolic acid of concentration 0.1 mol dm$^{-3}$ has a pH of 2.4

What is the approximate pH of the resulting solution after it has been diluted by a factor of 100?

\[
\begin{array}{c}
\text{A} \ 1.4 \\
\text{B} \ 2.4 \\
\text{C} \ 3.4 \\
\text{D} \ 4.4
\end{array}
\]

(b) Another solution of glycolic acid has a pH of 2.0

Calculate the concentration of this solution.
(c) The titration curve for adding glycolic acid to 25.0 cm³ of 0.100 mol dm⁻³ sodium hydroxide is shown.

(i) Use the information given in your Data Booklet to select a suitable indicator for this titration, including the colour change you would expect to see. Justify your selection. 

(ii) What is the concentration of this glycolic acid in mol dm⁻³?

- □ A 0.080
- □ B 0.100
- □ C 0.125
- □ D 0.250
(iii) The pH of the solution containing just sodium glycolate and water is

- A 2.8
- B 6.0
- C 8.3
- D 11.0

(d) Glycolic acid has an acid dissociation constant of $1.5 \times 10^{-4}$ mol dm$^{-3}$ compared with a value of $1.7 \times 10^{-5}$ mol dm$^{-3}$ for ethanoic acid.

(i) Give a possible explanation as to why the value of $K_a$ for glycolic acid is approximately ten times larger than that of ethanoic acid.

(ii) Complete the equation to show the conjugate acid-base pairs that would be produced when pure samples of glycolic acid and ethanoic acid are mixed.

\[
\text{CH}_2\text{OHCOOH} + \text{CH}_3\text{COOH} \rightarrow \text{__________________} + \text{__________________}
\]

(Total for Question 8 = 12 marks)
9  This question is about buffer solutions.

(a) A buffer solution is formed from disodium hydrogenphosphate, containing HPO$_4^{2-}$ ions, and sodium dihydrogenphosphate, containing H$_2$PO$_4^-$ ions.

Write the ionic equations involving HPO$_4^{2-}$ and H$_2$PO$_4^-$ ions to show how this solution acts as a buffer solution.

(b) Another buffer solution was formed by mixing 20.0 cm$^3$ of sodium hydroxide solution of concentration 0.100 mol dm$^{-3}$ with 25.0 cm$^3$ of ethanoic acid of concentration 0.150 mol dm$^{-3}$.

\[
\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

Calculate the pH of this buffer solution.

\[K_a\text{ for ethanoic acid} = 1.74 \times 10^{-5} \text{ mol dm}^{-3}\]

(Total for Question 9 = 7 marks)
10 Hydrogen is produced on a large scale by several different processes.

(a) One process for producing hydrogen involves reacting white-hot carbon with steam.

\[ C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g) \quad \Delta H = +131 \text{ kJ mol}^{-1} \]

The expression for the equilibrium constant, \( K_p \), is

\[ K_p = \frac{p(H_2) \cdot p(CO)}{p(H_2O)} \]

(i) Give a reason why the partial pressure of carbon is not included in the expression.

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(ii) Explain the effect of an increase in pressure on the equilibrium position of this reaction.

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(iii) Explain, by reference to any change in the value of \( K_p \), the effect of an increase in temperature on the equilibrium position of this reaction.

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(iv) At 1000 K and a total pressure of 2.0 atm, 1.00 mol of steam reacted with excess carbon.

At equilibrium, 0.81 mol of hydrogen was present.

Calculate the value of $K_p$ at 1000 K, stating any units.
(b) Carbon monoxide reacts with steam.

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)
\]

At 1100 K, \( K_c = 1.00 \)

In an experiment, 1 mol of carbon monoxide was mixed with 1 mol of steam, 2 mol of carbon dioxide and 2 mol of hydrogen.

Deduce, with reasons, the direction in which the reaction will shift to reach equilibrium. 

(Total for Question 10 = 12 marks)
### The Periodic Table of Elements

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>(1)</strong></td>
<td><strong>(2)</strong></td>
</tr>
<tr>
<td><strong>Relative atomic mass</strong></td>
<td><strong>Atomic symbol</strong></td>
</tr>
<tr>
<td><strong>Name</strong></td>
<td><strong>Atomic (proton) number</strong></td>
</tr>
</tbody>
</table>

#### Key
- relative atomic mass
- atomic symbol
- name
- atomic (proton) number

#### Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series
* Actinide series