HL Paper 2

Ozone, O₃, in the upper atmosphere prevents harmful UV radiation reaching the surface of the Earth.

b. State the shape of the ozone molecule and estimate the bond angle.  

Shape:

Bond angle:

c. State the hybridization of the central oxygen atom.  

d. In terms of σ and π bonds, describe the two oxygen-oxygen bonds in the Lewis structure.  

e. The two oxygen-oxygen bonds in ozone are in fact of equal length. Deduce why this is the case and how the length of these would compare to oxygen-oxygen bond lengths in hydrogen peroxide, H₂O₂, and in the oxygen molecule, O₂.

Two hydrides of nitrogen are ammonia and hydrazine, N₂H₄. One derivative of ammonia is methanamine whose molecular structure is shown below.

\[
\text{N}_2\text{H}_4(aq) + \text{O}_2(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)
\]

The concentration of dissolved oxygen in a sample of water is \(8.0 \times 10^{-3} \text{ g dm}^{-3}\).

a. Estimate the H–N–H bond angle in methanamine using VSEPR theory.  

b. State the electron domain geometry around the nitrogen atom and its hybridization in methanamine.

c. Ammonia reacts reversibly with water.

\[
\text{NH}_3(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)
\]

Explain the effect of adding \(\text{H}^+(aq)\) ions on the position of the equilibrium.
d.i. Hydrazine reacts with water in a similar way to ammonia. (The association of a molecule of hydrazine with a second H⁺ is so small it can be neglected.)

\[ \text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{N}_2\text{H}_5^+(\text{aq}) + \text{OH}^- (\text{aq}) \]

\[ \text{pK}_b \text{ (hydrazine)} = 5.77 \]

Calculate the pH of a 0.0100 \(\text{mol dm}^{-3}\) solution of hydrazine.

d.ii. Suggest a suitable indicator for the titration of hydrazine solution with dilute sulfuric acid using section 22 of the data booklet.

e. Outline, using an ionic equation, what is observed when magnesium powder is added to a solution of ammonium chloride.

f. Determine the enthalpy change of reaction, \(\Delta H\), in kJ, when 1.00 mol of gaseous hydrazine decomposes to its elements. Use bond enthalpy values in section 11 of the data booklet.

\[ \text{N}_2\text{H}_4(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) \]

g. The standard enthalpy of formation of \(\text{N}_2\text{H}_4(l)\) is +50.6 kJ \text{mol}^{-1}. Calculate the enthalpy of vaporization, \(\Delta H_{\text{vap}}\), of hydrazine in kJ \text{mol}^{-1}.

\[ \text{N}_2\text{H}_4(l) \rightarrow \text{N}_2\text{H}_4(\text{g}) \]

(If you did not get an answer to (f), use −85 kJ but this is not the correct answer.)

h.i. Calculate, showing your working, the mass of hydrazine needed to remove all the dissolved oxygen from 1000 \(\text{dm}^3\) of the sample.

h.ii. Calculate the volume, in \(\text{dm}^3\), of nitrogen formed under SATP conditions. (The volume of 1 \text{ mol of gas} = 24.8 \text{ dm}^3\) at SATP.)

An organic compound, \(\text{X}\), with a molar mass of approximately 88 \(\text{g mol}^{-1}\) contains 54.5\% carbon, 36.3\% oxygen and 9.2\% hydrogen by mass.

a. Predict and explain the bond lengths and bond strengths of the carbon-oxygen bonds in \(\text{CH}_3\text{CH}_2\text{COO}^-\).

b. (i) State the meaning of the term *hybridization*.

(ii) Describe the hybridization of the carbon atom in methane and explain how the concept of hybridization can be used to explain the shape of the methane molecule.

(iii) Identify the hybridization of the carbon atoms in diamond and graphite and explain why graphite is an electrical conductor.

c. i. Aluminium chloride, \(\text{Al}_2\text{Cl}_6\), does not conduct electricity when molten but aluminium oxide, \(\text{Al}_2\text{O}_3\), does. Explain this in terms of the structure and bonding of the two compounds.

\(\text{Al}_2\text{Cl}_6:\)

\(\text{Al}_2\text{O}_3:\)

Two groups of students (Group A and Group B) carried out a project* on the chemistry of some group 7 elements (the halogens) and their compounds.
In this project the students explored several aspects of the chemistry of the halogens. In the original preparation of ICl(l), they observed the yellow-green colour of chlorine gas, Cl₂(g), reacting with solid iodine, I₂(s).

e. When iodine reacts with excess chlorine, ICl₃ can form. Deduce the Lewis (electron dot) structure of ICl₃ and ICl₂⁻ and state the name of the shape of each species.

<table>
<thead>
<tr>
<th></th>
<th>ICl₃</th>
<th>ICl₂⁻</th>
</tr>
</thead>
</table>
| Lewis structure | \( \cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\·...
<table>
<thead>
<tr>
<th>Structure</th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>O atom labelled (1)</td>
<td>·············</td>
<td>·············</td>
</tr>
<tr>
<td>O atom labelled (2)</td>
<td>·············</td>
<td>·············</td>
</tr>
</tbody>
</table>

c.ii. Deduce, giving a reason, the more likely structure.  

d. Absorption of UV light in the ozone layer causes the dissociation of oxygen and ozone. 

Identify, in terms of bonding, the molecule that requires a longer wavelength to dissociate.  
e. Carbon and silicon are elements in group 14. 

Explain why CO₂ is a gas but SiO₂ is a solid at room temperature.

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Bonds can be formed in many ways.

Bonds can be formed in many ways.

The equilibrium for a mixture of NO₂ and N₂O₄ gases is represented as:

\[
2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)
\]

At 100°C, the equilibrium constant, \( K_c \), is 0.21.

b.i. Discuss the bonding in the resonance structures of ozone.  

b.ii. Deduce one resonance structure of ozone and the corresponding formal charges on each oxygen atom.  

c. The first six ionization energies, in kJ mol\(^{-1}\), of an element are given below.  

<table>
<thead>
<tr>
<th>IE₁</th>
<th>IE₂</th>
<th>IE₃</th>
<th>IE₄</th>
<th>IE₅</th>
<th>IE₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>578</td>
<td>1816</td>
<td>2744</td>
<td>11576</td>
<td>14829</td>
<td>18375</td>
</tr>
</tbody>
</table>

Explain the large increase in ionization energy from IE₃ to IE₄.

d.i. At a given time, the concentration of NO₂(g) and N₂O₄(g) were 0.52 and 0.10 mol dm\(^{-3}\) respectively.  

Deduce, showing your reasoning, if the forward or the reverse reaction is favoured at this time.  

d.ii. Comment on the value of \( \Delta G \) when the reaction quotient equals the equilibrium constant, \( Q = K \).  

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The element boron has two naturally occurring isotopes, \(^{10}\text{B}\) and \(^{11}\text{B}\).

Phosphorus forms two chlorides, PCl₃ and PCl₅.
c.i. Apply the Aufbau principle to state the full electron configuration for an atom of phosphorus.

c.ii. Deduce the Lewis structures for PCl₃ and PCl₅.

<table>
<thead>
<tr>
<th></th>
<th>PCl₃</th>
<th>PCl₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>........................................................</td>
<td>........................................................</td>
</tr>
<tr>
<td>Bond angles</td>
<td>........................................................</td>
<td>........................................................</td>
</tr>
</tbody>
</table>

c.iiiPredict the shapes and the bond angles in the two molecules.

c.iv Identify the type of hybridization present in PCl₃.

c.v Compare the melting points of PCl₃ and PCl₅ and explain the difference.

d.i Define an acid according to the Lewis theory.

d.ii State and explain the acid-base character of PCl₃ according to the Lewis theory.

e. Explain the delocalization of π electrons using the O₃ molecule as an example, including two facts that support the delocalization.

Draw the Lewis structures, state the shape and predict the bond angles for the following species.

Consider the following Born-Haber cycle:

\[
\begin{align*}
\text{K}(s) & \quad + \quad \frac{1}{2}\text{Br}_2(l) & \quad \xrightarrow{\Delta H_f^\circ} & \quad \text{KBr}(s) \\
\text{(a) } a &= 90.0 & \quad \text{(c) } c &= 112 \\
\text{K}(g) & \quad \downarrow & \quad \text{Br}(g) & \quad \downarrow \\
\text{(b) } b &= 418 & \quad \text{(d) } d &= 342 \\
\text{K}^+(g) & \quad + \quad \text{Br}^-(g) & \quad \downarrow \\
\text{(e) } e &= 670
\end{align*}
\]

The magnitudes for each of the enthalpy changes \((a\) to \(e)\) are given in \(\text{kJ mol}^{-1}\) but their signs (+ or −) have been omitted.

a.i PCl₃
a. ii. \( \text{NH}_2^- \)  

b. i. State the names for the enthalpy changes c and d. 

b. ii. Deduce which two of the enthalpy changes a to e have negative signs.  

b. iii. Determine the value for the enthalpy of formation of potassium bromide.  

b. iv. Explain why the quantitative value for the lattice enthalpy of calcium bromide is larger than the value for the lattice enthalpy of potassium bromide.  

c. i. Compare the formation of a sigma (\( \sigma \)) and a pi (\( \pi \)) bond between two carbon atoms in a molecule.  

c. ii. Identify how many sigma and pi bonds are present in propene, \( \text{C}_3\text{H}_6 \).  

c. iii. Deduce all the bond angles present in propene.  

c. iv. Explain how the concept of hybridization can be used to explain the bonding in the triple bond present in propyne.  

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a. i. Ethanol is a primary alcohol that can be oxidized by acidified potassium dichromate(VI). Distinguish between the reaction conditions needed to produce ethanol and ethanoic acid.  

Ethanol:  

Ethanoic acid:  

a. ii. Determine the oxidation number of carbon in ethanol and ethanal.  

Ethanol:  

Ethanal:  

a. iii. Deduce the half-equation for the oxidation of ethanol to ethanal.  

a. iv. Deduce the overall redox equation for the reaction of ethanol to ethanal with acidified potassium dichromate(VI).  

b. Ethanol can be made by reacting aqueous sodium hydroxide with bromoethane.  

Explain the mechanism for this reaction, using curly arrows to represent the movement of electron pairs.  

c. i. Determine the orders of reaction of the reactants and the overall rate expression for the reaction between 2-bromobutane and aqueous sodium hydroxide using the data in the table.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NaOH] / mol dm⁻³</th>
<th>[C₂H₂Br] / mol dm⁻³</th>
<th>Rate / mol dm⁻³ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>1.00</td>
<td>1.66 × 10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>1.00</td>
<td>8.31 × 10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>0.25</td>
<td>1.02 × 10⁻⁴</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
<td>0.50</td>
<td>8.29 × 10⁻⁴</td>
</tr>
</tbody>
</table>

c.ii Determine the rate constant, \( k \), with its units, using the data from experiment 3.

c.iii Identify the molecularity of the rate-determining step in this reaction.

d.i 2-bromobutane exists as optical isomers.

State the essential feature of optical isomers.

d.ii 2-bromobutane exists as optical isomers.

Outline how a polarimeter can distinguish between these isomers.

f. Describe the formation of \( \sigma \) and \( \pi \) bonds in an alkene.

g. The two most abundant isotopes of bromine have the mass numbers 79 and 81.

Calculate the relative abundance of \( ^{79}\text{Br} \) using table 5 of the data booklet, assuming the abundance of the other isotopes is negligible.

Carbon and silicon belong to the same group of the periodic table.

d. Describe the delocalization of \( \pi \) (\( \pi \)) electrons and explain how this can account for the structure and stability of the carbonate ion, \( \text{CO}_3^{2-} \).

e. Explain the meaning of the term hybridization. State the type of hybridization shown by the carbon atoms in carbon dioxide, diamond, graphite and the carbonate ion.

f.i. Explain the electrical conductivity of molten sodium oxide and liquid sulfur trioxide.

f.ii. Samples of sodium oxide and solid sulfur trioxide are added to separate beakers of water. Deduce the equation for each reaction and predict the electrical conductivity of each of the solutions formed.

A sample of magnesium contains three isotopes: magnesium-24, magnesium-25 and magnesium-26, with abundances of 77.44%, 10.00% and 12.56% respectively.

A graph of the successive ionization energies of magnesium is shown below.
The graph below shows pressure and volume data collected for a sample of carbon dioxide gas at 330 K.

![Graph showing pressure and volume data](image)

a. (i) Calculate the relative atomic mass of this sample of magnesium correct to two decimal places. [4]

(ii) Predict the relative atomic radii of the three magnesium isotopes, giving your reasons.

b. (i) Explain the increase in ionization energy values from the 3rd to the 8th electrons. [3]

(ii) Explain the sharp increase in ionization energy values between the 10th and 11th electrons.

c. (i) Magnesium reacts with oxygen to form an ionic compound, magnesium oxide. Describe how the ions are formed, and the structure and bonding in magnesium oxide. [4]
(ii) Carbon reacts with oxygen to form a covalent compound, carbon dioxide. Describe what is meant by a covalent bond.

(iii) State why magnesium and oxygen form an ionic compound while carbon and oxygen form a covalent compound.

d. (i) Predict the type of hybridization of the carbon and oxygen atoms in $\text{CO}_2$.

(ii) Sketch the orbitals of an oxygen atom in $\text{CO}_2$ on the energy level diagram provided, including the electrons that occupy each orbital.

(iii) Define the term electronegativity.

(iv) Explain why oxygen has a larger electronegativity than carbon.

e. (i) Draw a best-fit curve for the data on the graph.

(ii) Use the data point labelled X to determine the amount, in mol, of carbon dioxide gas in the sample.

f. (i) Most indicators are weak acids. Describe qualitatively how indicators work.

(ii) Identify a suitable indicator for a titration between a weak acid and a strong base, using Table 16 of the Data Booklet.

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Nitrogen and silicon belong to different groups in the periodic table.

Draw the Lewis structures, state the shapes and predict the bond angles for the following species.

Consider the molecule $\text{HCONH}_2$. 
a. i. Distinguish in terms of electronic structure, between the terms group and period.

b. i. \( \text{SiF}_2^2^- \)

b. ii. \( \text{NO}_2^+ \)

d. Explain, using diagrams, why \( \text{NO}_2 \) is a polar molecule but \( \text{CO}_2 \) is a non-polar molecule.

f. ii. Explain the term \( \text{hybridization} \).

f. iii. Describe how \( \sigma \) and \( \pi \) bonds form.

f. iv. State the type of hybridization of the carbon and nitrogen atoms in \( \text{HCNH}_2 \).

Two chemistry students wished to determine the enthalpy of hydration of anhydrous magnesium sulfate. They measured the initial and the highest temperature reached when anhydrous magnesium sulfate, \( \text{MgSO}_4(s) \), was dissolved in water. They presented their results in the table below.

| mass of anhydrous magnesium sulfate / g | 3.01 |
| volume of water / cm³ | 50.0 |
| initial temperature / °C | 17.0 |
| highest temperature / °C | 26.7 |

The students repeated the experiment using 6.16 g of solid hydrated magnesium sulfate, \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O}(s) \), and 50.0 cm³ of water. They found the enthalpy change, \( \Delta H_2^\circ \), to be \(+18 \text{ kJ mol}^{-1}\).

The enthalpy of hydration of solid anhydrous magnesium sulfate is difficult to determine experimentally, but can be determined using the diagram below.

\[
\text{MgSO}_4\cdot7\text{H}_2\text{O}(s) \xrightarrow{\Delta H_2^\circ \text{water}} \text{Mg}^{2+}(aq) + \text{SO}_4^{2-}(aq)
\]

\[
\Delta H \xrightarrow{\text{water}} \text{MgSO}_4(s) + 7\text{H}_2\text{O}(l)
\]

a. (i) Calculate the amount, in mol, of anhydrous magnesium sulfate.

(ii) Calculate the enthalpy change, \( \Delta H_1^\circ \), for anhydrous magnesium sulfate dissolving in water, in kJ mol\(^{-1}\). State your answer to the correct number of significant figures.

b. (i) Determine the enthalpy change, \( \Delta H \), in kJ mol\(^{-1}\), for the hydration of solid anhydrous magnesium sulfate, \( \text{MgSO}_4 \).
(ii) The literature value for the enthalpy of hydration of anhydrous magnesium sulfate is \(-103\, \text{kJ mol}^{-1}\). Calculate the percentage difference between the literature value and the value determined from experimental results, giving your answer to one decimal place. (If you did not obtain an answer for the experimental value in (b)(i) then use the value of \(-100\, \text{kJ mol}^{-1}\), but this is not the correct value.)

c. Another group of students experimentally determined an enthalpy of hydration of \(-95\, \text{kJ mol}^{-1}\). Outline two reasons which may explain the variation between the experimental and literature values.

d. Magnesium sulfate is one of the products formed when acid rain reacts with dolomitic limestone. This limestone is a mixture of magnesium carbonate and calcium carbonate.

(i) State the equation for the reaction of sulfuric acid with magnesium carbonate.

(ii) Deduce the Lewis (electron dot) structure of the carbonate ion, giving the shape and the oxygen-carbon-oxygen bond angle.

Lewis (electron dot) structure:

Shape:

Bond angle:

(iii) There are three possible Lewis structures that can be drawn for the carbonate ion, which lead to a resonance structure. Explain, with reference to the electrons, why all carbon-oxygen bonds have the same length.

(iv) Deduce the hybridization of the carbon atom in the carbonate ion.

Phosphoryl chloride, \(\text{POCl}_3\), is a dehydrating agent.

\(\text{POCl}_3\) (g) decomposes according to the following equation.

\[
2\text{POCl}_3(g) \rightarrow 2\text{PCl}_3(g) + \text{O}_2(g)
\]

\(\text{POCl}_3\) can be prepared by the reaction of phosphorus pentachloride, \(\text{PCl}_5\), with tetraphosphorus decaoxide, \(\text{P}_4\text{O}_{10}\).

\(\text{PCl}_3\) and \(\text{Cl}^-\) can act as ligands in transition metal complexes such as \(\text{Ni(POCl)}_2\) and \([\text{Cr(H}_2\text{O)}_3\text{Cl}_3]\).

a.i. Predict and explain the sign of the entropy change, \(\Delta S\), for this reaction.  

a.ii. Calculate the standard entropy change for the reaction, \(\Delta S^0\), in \(\text{JK}^{-1}\text{mol}^{-1}\), using the data below.
### Table 1: Standard Entropy (S°) Values

<table>
<thead>
<tr>
<th>Substance</th>
<th>S° / J K⁻¹ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCl₃(g)</td>
<td>325.0</td>
</tr>
<tr>
<td>PCl₅(g)</td>
<td>311.7</td>
</tr>
<tr>
<td>O₂(g)</td>
<td>205.0</td>
</tr>
</tbody>
</table>

### Question 1

<table>
<thead>
<tr>
<th>Substance</th>
<th>ΔH° / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>POCl₃(g)</td>
<td>-542.2</td>
</tr>
<tr>
<td>PCl₅(g)</td>
<td>-288.1</td>
</tr>
</tbody>
</table>

#### a.iii Define the term standard enthalpy of formation, ΔH°.

#### a.iv Calculate the standard enthalpy change for the reaction, ΔH°, in kJ mol⁻¹, using the data below.

#### a.v Determine the standard free energy change for the reaction, ΔG°, in kJ mol⁻¹, at 298 K.

#### a.vi Deduce the temperature, in K, at which the reaction becomes spontaneous.

#### a.iv Deduce the Lewis (electron dot) structure of POCl₃ (with P as the central element) and PCl₅ and predict the shape of each molecule, using the valence shell electron pair repulsion theory (VSEPR).

#### b.ii State and explain the Cl–P–Cl bond angle in PCl₅.

#### b.i Deduce the Lewis (electron dot) structure of PCl₅.

#### b.vi Predict the shape of this molecule, using the valence shell electron pair repulsion theory (VSEPR).

#### c.iii Identify all the different bond angles in PCl₅.

#### c.iv PCl₅Br₂ has the same molecular shape as PCl₅. Draw the three isomers of PCl₅Br₂ and deduce whether each isomer is polar or non-polar.

#### d.ii Define the term ligand.

#### d.iv Explain why the complex [Cr(H₂O)₃Cl₃] is coloured.

In acidic solution, ions containing titanium can react according to the half-equation below.

\[
\text{TiO}^{2+}(aq) + 2\text{H}^+(aq) + e^- \rightleftharpoons \text{Ti}^{3+}(aq) + \text{H}_2\text{O}(l) \quad E^\circ = -0.06 \text{ V}
\]

In the diagram below, A and B are inert electrodes and, in the aqueous solutions, all ions have a concentration of 1 mol dm⁻³.
Sodium, silicon and sulfur are elements in period 3 of the periodic table that all form oxides.

Although carbon and silicon both belong to group 4 of the periodic table, carbon dioxide and silicon dioxide are different in many ways.

a. Define the term *standard electrode potential*, $E^\theta$. [1]

b.i. State the initial and final oxidation numbers of titanium and hence deduce whether it is oxidized or reduced in this change. [2]

<table>
<thead>
<tr>
<th>Initial oxidation number</th>
<th>Final oxidation number</th>
<th>Oxidized / reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b.ii. Considering the above equilibrium, predict, giving a reason, how adding more acid would affect the strength of the TiO$^{2+}$ ion as an oxidizing agent. [2]

c. In the two experiments below, predict whether a reaction would occur and deduce an equation for any reaction that takes place. Refer to Table 14 of the Data Booklet if necessary. [3]

Kl(aq) is added to a solution containing Ti$^{3+}$(aq) ions:

Zn (s) is added to a solution containing TiO$^{2+}$(aq) and H$^+$(aq) ions:

d.i. Using Table 14 of the Data Booklet, state the balanced half-equation for the reaction that occurs at electrode A and whether it involves oxidation or reduction. [2]

d.ii. Calculate the cell potential in V. [1]

d.iii. On the diagram above label with an arrow

- the direction of electron flow in the wire
- the direction in which the positive ions flow in the salt bridge.

e.i. Compare the properties of the three oxides by completing the table below. [3]
Sulfur dioxide is a significant contributor to acid deposition. Identify a major, man-made source of this pollutant.

As well as the oxide above, sodium forms a peroxide that contains the peroxide ion, $O_2^{2-}$. Draw the Lewis (electron dot) structure of the peroxide ion.

Describe the differences in the hybridization of these group 4 elements and the precise nature of the bonds that they form with the oxygen atoms.

Xenon, although a noble gas, forms an oxide, $XeO_2$, that has a structure related to that of $SiO_2$. Compare the geometry around the silicon atoms in $SiO_2$ with the geometry around the xenon atoms in $XeO_2$, using the valence shell electron pair repulsion (VSEPR) theory.

Consider the structure and bonding in $MgCl_2$ and $PCl_3$.

Consider the molecules $PBr_3$ and $SF_4$.

The structure of cis-but-2-ene-1,4-dioic acid is shown below.
a. State and explain the electrical conductivities of these two chloride compounds in their liquid state.

\[ \text{MgCl}_2 \]

\[ \text{PCl}_3 \]

b. i. Identify the acid-base character of the oxides of each of the elements from sodium to chlorine in period 3.

b. ii. State the equations for the separate reactions of sodium oxide and phosphorus(V) oxide with water.

c. i. Deduce the Lewis (electron dot) structure of both molecules.

c. ii. Predict the shapes of the two molecules, giving the Br–P–Br bond angle in \( \text{PBr}_3 \) and the F–S–F bond angles in \( \text{SF}_4 \).

<table>
<thead>
<tr>
<th>( \text{PBr}_3 )</th>
<th>( \text{SF}_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape:</strong></td>
<td><strong>Shape:</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bond angle:</strong></td>
<td><strong>Bond angles:</strong></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

c. iii. Explain why both \( \text{PBr}_3 \) and \( \text{SF}_4 \) are polar.

d. i. Describe the covalent bond between carbon and hydrogen in the molecule above and how it is formed.

d. ii. Deduce the hybridization of the oxygen atoms labelled \( \alpha \) and \( \beta \).

\( \alpha \):

\( \beta \):

d. iii. Describe sigma (\( \sigma \)) and pi (\( \pi \)) bonds between atoms.

\( \sigma \) bond:

\( \pi \) bond:

d. iv. Identify the number of sigma (\( \sigma \)) and pi (\( \pi \)) bonds present in a molecule of \( \text{cis-but-2-ene-1,4-dioic acid} \).
There is concern about damage done to the ozone layer in the stratosphere by jet-propelled aircraft.

a. Formulate two equations to show how nitrogen(II) oxide, NO, catalyses the destruction of ozone. [2]

b. Suggest why the loss of ozone is an international environmental concern. [2]

draw the Lewis structures, predict the shape and deduce the bond angles for xenon tetrafluoride and the nitrate ion.

<table>
<thead>
<tr>
<th>Species</th>
<th>Lewis structure</th>
<th>Shape</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₄</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calcium carbide, CaC₂, is an ionic solid.

a. Describe the nature of ionic bonding. [1]

b. Describe how the relative atomic mass of a sample of calcium could be determined from its mass spectrum. [2]

c. When calcium compounds are introduced into a gas flame a red colour is seen; sodium compounds give a yellow flame. Outline the source of the colours and why they are different. [2]

d.i. Suggest two reasons why solid calcium has a greater density than solid potassium. [2]

d.ii. Outline why solid calcium is a good conductor of electricity. [1]
e. Sketch a graph of the first six ionization energies of calcium.

\[
\begin{array}{c}
\text{log (I.E.)} \\
\hline
1 & 2 & 3 & 4 & 5 & 6 \\
\end{array}
\]

Number of electron removed

f. Calcium carbide reacts with water to form ethyne and calcium hydroxide.

\[
\text{CaC}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_2\text{H}_2(\text{g}) + \text{Ca(OH)}_2(\text{aq})
\]

Estimate the pH of the resultant solution.

g.i. Describe how sigma (\(\sigma\)) and pi (\(\pi\)) bonds are formed.

\[
\begin{align*}
\text{sigma (}\sigma\text{)}: & \\
& \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
\text{pi (}\pi\text{)}: & \\
& \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots
\end{align*}
\]

g.ii. Deduce the number of \(\sigma\) and \(\pi\) bonds in a molecule of ethyne.

\[
\begin{align*}
\text{sigma (}\sigma\text{)}: & \\
& \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \\
\text{pi (}\pi\text{)}: & \\
& \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots
\end{align*}
\]

SF\(_2\), SF\(_4\) and SF\(_6\) have different shapes. Draw their Lewis structures and use the VSEPR theory to predict the name of the shape of each molecule.
Hydrazine, \( \text{N}_2\text{H}_4 \), is a valuable rocket fuel.

The equation for the reaction between hydrazine and oxygen is given below.

\[
\text{N}_2\text{H}_4(l) + \text{O}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)
\]

The reaction between \( \text{N}_2\text{H}_4(aq) \) and \( \text{HCl}(aq) \) can be represented by the following equation.

\[
\text{N}_2\text{H}_4(aq) + 2\text{HCl}(aq) \rightarrow \text{N}_2\text{H}_6^{2+}(aq) + 2\text{Cl}^-(aq)
\]

a. (i) Draw the Lewis (electron dot) structure for \( \text{N}_2\text{H}_4 \) showing all valence electrons.

(ii) State and explain the H–N–H bond angle in hydrazine.

b. Hydrazine and ethene, \( \text{C}_2\text{H}_4 \), are hydrides of adjacent elements in the periodic table. The boiling point of hydrazine is much higher than that of ethene. Explain this difference in terms of the intermolecular forces in each compound.

c. (i) The enthalpy change of formation, \( \Delta H_f^\circ \), of liquid hydrazine is 50.6 \( \text{kJ mol}^{-1} \). Use this value, together with data from Table 12 of the Data\[16\] Booklet, to calculate the enthalpy change for this reaction.

(ii) Use the bond enthalpy values from Table 10 of the Data Booklet to determine the enthalpy change for this reaction.

(iii) Identify the calculation that produces the most accurate value for the enthalpy change for the reaction given and explain your choice.

(iv) Calculate \( \Delta S^\circ \) for the reaction using the data below and comment on its magnitude.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( S^\circ / \text{J K}^{-1} \text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2(g) )</td>
<td>205</td>
</tr>
<tr>
<td>( \text{N}_2(g) )</td>
<td>191</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(l) )</td>
<td>69.9</td>
</tr>
<tr>
<td>( \text{N}_2\text{H}_4(l) )</td>
<td>121</td>
</tr>
</tbody>
</table>

(v) Calculate \( \Delta G^\circ \) for the reaction at 298 K.
d. The reaction between $\text{N}_2\text{H}_4(\text{aq})$ and $\text{HCl}(\text{aq})$ can be represented by the following equation.

$$\text{N}_2\text{H}_4(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow \text{N}_2\text{H}_5^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$$

(i) Identify the type of reaction that occurs.
(ii) Predict the value of the $\text{H}-\text{N}-\text{H}$ bond angle in $\text{N}_2\text{H}_5^{2+}$.
(iii) Suggest the type of hybridization shown by the nitrogen atoms in $\text{N}_2\text{H}_5^{2+}$.

Consider the structure and bonding in $\text{MgCl}_2$ and $\text{PCl}_5$.

For each of the species $\text{PBr}_3$ and $\text{SF}_6$:

b. i. State and explain the difference in the electrical conductivity in the liquid state of the two chlorides.

<table>
<thead>
<tr>
<th>$\text{PBr}_3$</th>
<th>$\text{SF}_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Lewis structure:</td>
<td>(i) Lewis structure:</td>
</tr>
<tr>
<td>(ii) Shape:</td>
<td>(ii) Shape:</td>
</tr>
<tr>
<td>Bond angle:</td>
<td>Bond angle:</td>
</tr>
<tr>
<td>(iii) Polarity:</td>
<td>(iii) Polarity:</td>
</tr>
<tr>
<td>Explanation:</td>
<td>Explanation:</td>
</tr>
</tbody>
</table>
d.i. Compare the formation of sigma (σ) and pi (π) bonds between the carbon atoms in a molecule of ethyne.

Geometrical isomerism and optical isomerism are two sub-groups of stereoisomerism in organic chemistry.

Compound P has the following three-dimensional structure. P also has geometrical isomers.

![Molecule P](image)

Menthol can be used in cough medicines. The compound contains C, H and O only.

a. Describe what is meant by the term stereoisomers. [1]

b. Geometrical isomers have different physical properties and many drugs, such as doxepin (which has antidepressant properties), have geometrical isomers. [1]

Example of a geometrical isomer of doxepin

For each of the carbon atoms labelled 1 and 2 in doxepin, deduce the type of hybridization involved (sp, sp² or sp³).

1:
c. Clomifene, a fertility drug, whose three-dimensional structure is represented below, also has geometrical isomers.

Identify the name of one functional group present in clomifene.

d.i. Draw any two other isomers of P.

d.ii. Apply IUPAC rules to state the names of all the straight-chain isomers of compounds of molecular formula C₈H₆ (including P).

d.iii. State the structural formula of the organic products, Q, R, S and T, formed in the following reactions.
\[
\text{CH}_2\text{CH} = \text{CHCH}_2 + \text{HBr (g)} \rightarrow \text{Q}
\]

Q:

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CHCH}_3 & \xrightarrow{(1) \text{ concentrated } \text{H}_2\text{SO}_4(\text{aq})} \text{R} \\
\text{R} & \xrightarrow{(2) \text{H}_2\text{O}(\ell)} \text{R}
\end{align*}
\]

\[
\text{CH}_2\text{CH} = \text{CHCH}_2 + \text{Br}_2(\text{aq}) \rightarrow \text{S}
\]

S:

\[
\text{Q} + \text{OH}^-(\text{aq}) \rightarrow \text{T}
\]

T:

\[d.\text{v} \text{State the structural formula of the organic product formed, U, when R is heated under reflux with acidified potassium dichromate(VI).} \quad [1]
\]

\[d.\text{vi} \text{Apply IUPAC rules to state the name of this product, U.} \quad [1]
\]

\[e.\text{i} \text{When a } 6.234 \times 10^{-2} \text{ g of the compound was combusted, } 1.755 \times 10^{-1} \text{ g of carbon dioxide and } 7.187 \times 10^{-2} \text{ g of water were produced.} \quad [4]
\]

\[\text{Determine the molecular formula of the compound showing your working, given that its molar mass is } M = 156.30 \text{ g mol}^{-1}. \quad [4]
\]

\[e.\text{ii} \text{Menthol occurs naturally and has several isomers. State the structural feature of menthol which is responsible for it having enantiomers.} \quad [1]
\]

\[e.\text{iii} \text{State the instrument used to distinguish between each of the two enantiomers, and how they could be distinguished using this instrument.} \quad [1]
\]

\[e.\text{iv} \text{Compare the physical and chemical properties of enantiomers.} \quad [2]
\]

Physical properties:
Chemical properties:

But-2-ene is a straight-chain alkene with formula $\text{C}_4\text{H}_8$. The molecule contains both $\sigma$ and $\pi$ bonds.

The polymerization of the alkenes is one of the most significant reactions of the twentieth century.

a. (i) Explain the formation of the $\pi$ bond.

(ii) For each of the carbon atoms, C(1) and C(2), identify the type of hybridization shown.

C(1):

C(2):

b. But-2-ene shows geometrical isomerism. Draw the structural formula and state the name of the other geometrical isomer.

c. Identify the structural formula of an isomer of but-2-ene which does not decolourize bromine water, $\text{Br}_2(\text{aq})$.

d. (i) Outline two reasons why the polymers of the alkenes are of economic importance.

(ii) State the type of polymerization reaction shown by the alkene in part (a).

(iii) Deduce the structure of the resulting polymer showing three repeating units.

(iv) Explain why monomers are often gases or volatile liquids, but polymers are solids.

Calcium nitrate contains both covalent and ionic bonds.

Nitrogen also forms oxides, which are atmospheric pollutants.

a.i. State the formula of both ions present and the nature of the force between these ions.

Ions:
Nature of force:

a.ii. State which atoms are covalently bonded.

b. Bonding in the nitrate ion involves electron delocalization. Explain the meaning of electron delocalization and how it affects the ion.

c.i. Outline the source of these oxides.

c.ii. State one product formed from their reaction with water.

c.iii. State one environmental problem caused by these atmospheric pollutants.

Ethanedioic acid is a diprotic acid. A student determined the value of x in the formula of hydrated ethanedioic acid, $\text{HOOC-COOH} \cdot x\text{H}_2\text{O}$, by titrating a known mass of the acid with a 0.100 mol dm$^{-3}$ solution of NaOH(aq).

0.795 g of ethanedioic acid was dissolved in distilled water and made up to a total volume of 250 cm$^3$ in a volumetric flask.

25 cm$^3$ of this ethanedioic acid solution was pipetted into a flask and titrated against aqueous sodium hydroxide using phenolphthalein as an indicator.

The titration was then repeated twice to obtain the results below.

<table>
<thead>
<tr>
<th>Volume of 0.100 mol dm$^{-3}$ NaOH / cm$^3$</th>
<th>Titration 1</th>
<th>Titration 2</th>
<th>Titration 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final burette reading (± 0.05)</td>
<td>13.00</td>
<td>26.70</td>
<td>38.20</td>
</tr>
<tr>
<td>Initial burette reading (± 0.05)</td>
<td>0.00</td>
<td>13.00</td>
<td>25.70</td>
</tr>
</tbody>
</table>

a. Calculate the average volume of NaOH added, in cm$^3$, in titrations 2 and 3, and then calculate the amount, in mol, of NaOH added.

b.i. The equation for the reaction taking place in the titration is:

$$\text{HOOC-COOH(aq)} + 2\text{NaOH(aq)} \rightarrow \text{NaOOC-COONa(aq)} + 2\text{H}_2\text{O(l)}$$

Determine the amount, in mol, of ethanedioic acid that reacts with the average volume of NaOH(aq).

b.ii. Determine the amount, in mol, of ethanedioic acid present in 250 cm$^3$ of the original solution.

b.iii. Determine the molar mass of hydrated ethanedioic acid.

b.iv. Determine the value of x in the formula $\text{HOOC-COOH} \cdot x\text{H}_2\text{O}$.

c. Identify the strongest intermolecular force in solid ethanedioic acid.

d. Deduce the Lewis (electron dot) structure of ethanedioic acid, HOOC-COOH.

e. Predict and explain the difference in carbon-oxygen bond lengths in ethanedioic acid and its conjugate base, $^$OOC-COO$.  

[1] [2] [3]
Propane and propene are members of different homologous series.

b. (i) Draw diagrams to show how sigma (σ) and pi (π) bonds are formed between atoms.  

\[
\begin{align*}
\text{Sigma (σ):} \\
\text{Pi (π):}
\end{align*}
\]

(ii) State the number of sigma (σ) and pi (π) bonds in propane and propene.

<table>
<thead>
<tr>
<th>Number of sigma (σ) bonds</th>
<th>Number of pi (π) bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Propane</strong></td>
<td></td>
</tr>
<tr>
<td>..................................</td>
<td></td>
</tr>
<tr>
<td><strong>Propene</strong></td>
<td></td>
</tr>
<tr>
<td>..................................</td>
<td></td>
</tr>
</tbody>
</table>

d. Construct the mechanism of the formation of 2-bromopropane from hydrogen bromide and propene using curly arrows to denote the movement of electrons.

Lewis (electron dot) structures are useful models.

a. Draw the Lewis (electron dot) structures of PF\textsubscript{3} and PF\textsubscript{5} and use the VSEPR theory to deduce the molecular geometry of each species including bond angles.
b. Predict whether the molecules PF₃ and PF₅ are polar or non-polar.

[1]

c. State the type of hybridization shown by the phosphorus atom in PF₃.

[1]

PCl₅(g) and Cl₂(g) were placed in a sealed flask and allowed to reach equilibrium at 200 °C. The enthalpy change, ΔH, for the decomposition of PCl₅(g) is positive.

Deduce the Lewis (electron dot) structure and molecular geometry and the bond angles of PCl₃.
Urea, (H₂N)₂CO, is excreted by mammals and can be used as a fertilizer.

Urea can also be made by the direct combination of ammonia and carbon dioxide gases.

\[ 2\text{NH}_3(g) + \text{CO}_2(g) \rightleftharpoons (\text{H}_2\text{N})_2\text{CO}(g) + \text{H}_2\text{O}(g) \quad \Delta H < 0 \]

a. Calculate the percentage by mass of nitrogen in urea to two decimal places using section 6 of the data booklet.  

b. Suggest how the percentage of nitrogen affects the cost of transport of fertilizers giving a reason.

c. The structural formula of urea is shown.

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{C} \\
\text{O} \\
\text{N} \\
\text{H} \\
\end{array}
\]

Predict the electron domain and molecular geometries at the nitrogen and carbon atoms, applying the VSEPR theory.

<table>
<thead>
<tr>
<th></th>
<th>Electron domain geometry</th>
<th>Molecular geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>..................................................</td>
<td>..................................................</td>
</tr>
<tr>
<td>Carbon</td>
<td>..................................................</td>
<td>trigonal planar</td>
</tr>
</tbody>
</table>

c. Urea can be made by reacting potassium cyanate, KNCO, with ammonium chloride, NH₄Cl.

\[
\text{KNCO(aq)} + \text{NH}_4\text{Cl(aq)} \rightarrow (\text{H}_2\text{N})_2\text{CO(aq)} + \text{KCl(aq)}
\]

Determine the maximum mass of urea that could be formed from 50.0 cm³ of 0.100 mol dm⁻³ potassium cyanate solution.
d.i. State the equilibrium constant expression, \( K_c \). [1]

d.ii. Predict, with a reason, the effect on the equilibrium constant, \( K_c \) when the temperature is increased. [1]

d.iii. Determine an approximate order of magnitude for \( K_c \), using sections 1 and 2 of the data booklet. Assume \( \Delta G^\circ \) for the forward reaction is approximately +50 kJ at 298 K. [2]

e.i. Suggest one reason why urea is a solid and ammonia a gas at room temperature. [1]

e.ii. Sketch two different hydrogen bonding interactions between ammonia and water. [2]

f. The combustion of urea produces water, carbon dioxide and nitrogen. [2]

Formulate a balanced equation for the reaction.

g. Calculate the maximum volume of CO\(_2\), in cm\(^3\), produced at STP by the combustion of 0.600 g of urea, using sections 2 and 6 of the data booklet. [1]

h. Describe the bond formation when urea acts as a ligand in a transition metal complex ion. [2]

i. The C–N bonds in urea are shorter than might be expected for a single C–N bond. Suggest, in terms of electrons, how this could occur. [1]

j. The mass spectrum of urea is shown below. [2]

Identify the species responsible for the peaks at m/z = 60 and 44.

---

![Mass Spectrum](http://sdb.isb.ist.go/p)

60:

44:
k. The IR spectrum of urea is shown below.

Identify the bonds causing the absorptions at 3450 cm\(^{-1}\) and 1700 cm\(^{-1}\) using section 26 of the data booklet.

i.i. Predict the number of signals in the \(^1\)H NMR spectrum of urea.

i.ii. Predict the splitting pattern of the \(^1\)H NMR spectrum of urea.

i.iii. Outline why TMS (tetramethylsilane) may be added to the sample to carry out \(^1\)H NMR spectroscopy and why it is particularly suited to this role.

Phosphine (IUPAC name phosphane) is a hydride of phosphorus, with the formula PH\(_3\).

a. (i) Draw a Lewis (electron dot) structure of phosphine.

(ii) State the hybridization of the phosphorus atom in phosphine.

(iii) Deduce, giving your reason, whether phosphine would act as a Lewis acid, a Lewis base, or neither.

(iv) Outline whether you expect the bonds in phosphine to be polar or non-polar, giving a brief reason.

(v) Phosphine has a much greater molar mass than ammonia. Explain why phosphine has a significantly lower boiling point than ammonia.

(vi) Ammonia acts as a weak Brønsted–Lowry base when dissolved in water.

\[
\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})
\]

Outline what is meant by the terms “weak” and “Brønsted–Lowry base”.

b. Phosphine is usually prepared by heating white phosphorus, one of the allotropes of phosphorus, with concentrated aqueous sodium hydroxide. The equation for the reaction is:

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

(i) The first reagent is written as $P_4$, not 4P. Describe the difference between $P_4$ and 4P.

(ii) The ion $H_2PO_2^-$ is amphiprotic. Outline what is meant by amphiprotic, giving the formulas of both species it is converted to when it behaves in this manner.

(iii) State the oxidation state of phosphorus in $P_4$ and $H_2PO_2^-$. 

$P_4$:

$H_2PO_2^-:

(iv) Oxidation is now defined in terms of change of oxidation number. Explore how earlier definitions of oxidation and reduction may have led to conflicting answers for the conversion of $P_4$ to $H_2PO_2^-$ and the way in which the use of oxidation numbers has resolved this.

c. 2.478 g of white phosphorus was used to make phosphine according to the equation:

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \rightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

(i) Calculate the amount, in mol, of white phosphorus used.

(ii) This phosphorus was reacted with 100.0 cm$^3$ of 5.00 mol dm$^{-3}$ aqueous sodium hydroxide. Deduce, showing your working, which was the limiting reagent.

(iii) Determine the excess amount, in mol, of the other reagent.

(iv) Determine the volume of phosphine, measured in cm$^3$ at standard temperature and pressure, that was produced.

d. Impurities cause phosphine to ignite spontaneously in air to form an oxide of phosphorus and water.

(i) 200.0 g of air was heated by the energy from the complete combustion of 1.00 mol phosphine. Calculate the temperature rise using section 1 of the data booklet and the data below.

Standard enthalpy of combustion of phosphine, \( \Delta H_c^{\Theta} = -750 \text{ kJ mol}^{-1} \)

Specific heat capacity of air = 1.00 Jg$^{-1}$K$^{-1}$ = 1.00 KJg$^{-1}$K$^{-1}$

(ii) The oxide formed in the reaction with air contains 43.6% phosphorus by mass. Determine the empirical formula of the oxide, showing your method.

(iii) The molar mass of the oxide is approximately 285 g mol$^{-1}$. Determine the molecular formula of the oxide.

(iv) State the equation for the reaction of this oxide of phosphorus with water.

(v) Suggest why oxides of phosphorus are not major contributors to acid deposition.

(vi) The levels of sulfur dioxide, a major contributor to acid deposition, can be minimized by either pre-combustion and post-combustion methods. Outline one technique of each method.

Pre-combustion:
Post-combustion:
A compound with a molecular formula C\textsubscript{7}H\textsubscript{14}O produced the following high resolution \textsuperscript{1}H NMR spectrum.

\[ \text{Chemical shift / ppm} \]

\begin{align*}
\text{Number of hydrogen environments:} & \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\
\text{Ratio of hydrogen environments:} & \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \\
\text{Splitting patterns:} & \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 
\end{align*}

a.i. Deduce what information can be obtained from the \textsuperscript{1}H NMR spectrum. [3]

\[ \text{Number of hydrogen environments:} \]

\[ \text{Ratio of hydrogen environments:} \]

\[ \text{Splitting patterns:} \]

a.ii. Identify the functional group that shows stretching at 1710 cm\textsuperscript{-1} in the infrared spectrum of this compound using section 26 of the data booklet and the \textsuperscript{1}H NMR. [1]

a.iii. Suggest the structural formula of this compound. [2]

b.i. Bromine was added to hexane, hex-1-ene and benzene. Identify the compound(s) which will react with bromine in a well-lit laboratory. [1]

b.ii. Deduce the structural formula of the main organic product when hex-1-ene reacts with hydrogen bromide. [1]

c.i. State the reagents and the name of the mechanism for the nitration of benzene. [2]

\[ \text{Reagents:} \]

\[ \text{Name of mechanism:} \]
c.ii. Outline, in terms of the bonding present, why the reaction conditions of halogenation are different for alkanes and benzene.

d. Below are two isomers, A and B, with the molecular formula \( \text{C}_2\text{H}_5\text{Br} \).

![Image showing isomers A and B with molecular structures]

- A
- B

Explain the mechanism of the nucleophilic substitution reaction with \( \text{NaOH(aq)} \) for the isomer that reacts almost exclusively by an \( \text{S}_\text{N2} \) mechanism using curly arrows to represent the movement of electron pairs.

---

The reaction between hydrogen and nitrogen monoxide is thought to proceed by the mechanism shown below.

\[
\begin{align*}
2\text{NO} (g) & \rightleftharpoons \text{N}_2\text{O}_2 (g) & \text{fast equilibrium} \\
\text{N}_2\text{O}_2 (g) + \text{H}_2 (g) & \rightarrow \text{N}_2\text{O} (g) + \text{H}_2\text{O} (g) & \text{slow reaction} \\
\text{N}_2\text{O} (g) + \text{H}_2 (g) & \rightarrow \text{N}_2 (g) + \text{H}_2\text{O} (g) & \text{fast reaction}
\end{align*}
\]

a. (i) State the equation for the overall reaction.  

(ii) Deduce the rate expression consistent with this mechanism.  

(iii) Explain how you would attempt to confirm this rate expression, giving the results you would expect.  

(iv) State, giving your reason, whether confirmation of the rate expression would prove that the mechanism given is correct.  

(v) Suggest how the rate of this reaction could be measured experimentally.

b. The enthalpy change for the reaction between nitrogen monoxide and hydrogen is \(-664 \text{ kJ}\) and its activation energy is \(63 \text{ kJ}\).  

(i) Sketch the potential energy profile for the overall reaction, using the axes given, indicating both the enthalpy of reaction and activation energy.

(ii) This reaction is normally carried out using a catalyst. Draw a dotted line labelled “Catalysed” on the diagram above to indicate the effect of the catalyst.

(iii) Sketch and label a second Maxwell–Boltzmann energy distribution curve representing the same system but at a higher temperature, $T_{\text{higher}}$.

(iv) Explain why an increase in temperature increases the rate of this reaction.

c. One of the intermediates in the reaction between nitrogen monoxide and hydrogen is dinitrogen monoxide, $\text{N}_2\text{O}$. This can be represented by the resonance structures below:

\[ \text{N≡N}^+ \cdot \cdot \cdot \text{O}^- \quad \text{↔} \quad \text{N}^+ \text{N}^- \cdot \cdot \cdot \text{O} \]

(i) Analyse the bonding in dinitrogen monoxide in terms of $\sigma$-bonds and $\Delta$-bonds.

(ii) State what is meant by resonance.