1. Photochemical reactions can be initiated by visible or ultra-violet light. Calculate the frequency of radiation that would, in theory, start a reaction involving bromine (see page 9 of the Data Booklet).

SY/88

(4)

2. The emission spectrum of an element is seen as a series of bright coloured lines on a dark background.

Within a series the intervals between the frequencies of each line decrease until the lines are so close together that they converge to form a continuous spectrum or continuum as shown in the diagram. A graphical method can be used to find the start of the continuum. A plot of $\nu$ against $\Delta\nu$ can be extrapolated back to find where $\Delta\nu$ is 0. This is the start of the continuum.

(a) What causes a line in an emission spectrum?

(b) Why do the lines converge as they reach the continuum?

(c) (i) Calculate the energy, in kJ mol$^{-1}$, of the emission line at the start of the continuum if the curve $\Delta\nu$ intersects the $y$-axis ($\nu$) at $1.26 \times 10^{15}$ Hz.

(ii) What does this energy represent?

SY/99

(5)
3. Below is a simplified diagram of the Balmer series in the emission spectrum of atomic hydrogen.

Spectral lines arise as a result of electronic transitions in atoms. The Balmer series is produced by the transitions shown in the following diagram.

(a) What transition corresponds to a line A in the spectrum? Explain your answer.  
(b) Calculate the energy difference, in kJ mol\(^{-1}\), that gives rise to line A, with wavelength 656 nm.

4. The following technique is used to detect trace elements in steels and other alloys. The metal sample is sparked as shown in the diagram.

The output from one sample was as shown below.
(a) In which region of the spectrum do these lines lie?
(b) Calculate the energy, in kJ mol\(^{-1}\), of the line due to tin.
(c) Explain how this sparking procedure relates to the formation of the lines in the spectrum.
(d) Give one reason why elements are added in trace amounts to steels.

5. In the emission spectrum for hydrogen, there are several different series of ‘spectral lines’. These lines result from electrons emitting energy as they fall back from higher to lower energy levels. Each spectral line may be represented by the equation:

\[
\frac{1}{\lambda} = R_h \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)
\]

where \( \lambda \) = wavelength of the spectral line
\( R_h = \) a constant, \( 1.097 \times 10^7 \text{m}^{-1} \)
\( n_1 = \) energy level to which the electron falls
\( n_2 = \) energy level from which the electron falls.

The Balmer series occurs in the visible part of the electromagnetic spectrum, \( n_1 \) having a value of 2 for each line in the series. The first four spectral lines for this series are shown in the diagram.

(a) Use the equation to calculate the wavelength of the spectral line in the Balmer series that corresponds to the value \( n_2 = 4 \). State the colour of this spectral line.
(b) Lyman discovered a series of spectral lines for hydrogen in the ultra-violet region of the electromagnetic spectrum. What value must \( n_1 \) have for this series? Give a reason for your answer.
6. The electron configuration for nitrogen is:

\[
\begin{array}{cccc}
1s & 2s & 2p_x & 2p_y & 2p_z \\
\uparrow & \uparrow & \downarrow & \downarrow & \downarrow \\
\end{array}
\]

(a) What do the symbols \( \uparrow \) and \( \downarrow \) represent? 1
(b) What is the significance of \( x \), \( y \) and \( z \) in the 2p sublevel? 1
(c) (i) Describe the shape of the s and p orbitals. 2
   (ii) Describe the position of the p orbitals relative to each other. 1
(d) Why is the 2p\(_z\) electron for nitrogen not placed in the 2p\(_x\) or 2p\(_y\) orbital? 1
(e) Phosphorus is in the same group as nitrogen but has 15 electrons. A student wrote the following configuration for phosphorus:

\[
\begin{array}{cccc}
1s & 2s & 2p_x & 2p_y & 2p_z & 3s & 4p_x & 4p_y & 4p_z \\
\uparrow & \uparrow & \uparrow & \uparrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\
\end{array}
\]

Explain the two mistakes in the student’s answer. 2

7. The number of orbitals and the number of electrons in an energy level or sublevel is limited.

(a) Give the number of orbitals that make up:
   (i) the s sublevel 1
   (ii) the d sublevel. 1

(b) Give the number of electrons that are needed to completely fill:
   (i) the p sublevel 1
   (ii) the first energy level 1
   (iii) the third energy level. 1

(c) Give the sublevels in:
   (i) the first energy level 1
   (ii) the fourth energy level. 1
8. There are four statements that you have come across in your study of electrons and atomic orbitals. These statements are:

(1) The Aufbau principle  
(2) Heisenberg’s uncertainty principle  
(3) The Pauli exclusion principle  
(4) Hund’s rule of maximum multiplicity  

(a) The electronic configuration for boron is given by (i) and not (ii).

\[
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & 1 & \phantom{1} \\
\end{array}
\quad
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & 1 & 1 \\
\end{array}
\]

(ii)

Explain why (ii) is wrong and identify which of the above statements justifies your choice.  

(b) The electronic configuration for carbon is given by (iii) and not (iv).

\[
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & 1 & 1 \\
\end{array}
\quad
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & 1 & \phantom{1} \\
\end{array}
\]

(iv)

Explain why (iv) is wrong and identify which of the above statements justifies your choice.  

(c) The electronic configuration for nitrogen is given by (v) and not (vi).

\[
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & 1 & 1 \\
\end{array}
\quad
\begin{array}{c|c|c}
1s & 2s & 2p \\
\hline
1 & \phantom{1} & 1 \\
\end{array}
\]

(vi)

Explain why (vi) is wrong and identify which of the above statements justifies your choice.  

(6)
9. (a) Draw diagrams, including axes, to represent a 2s orbital and the three 2p orbitals.

(b) What does an orbital diagram represent?

(c) What is the significance of the number 2 in the terms 2s and 2p?

(d) The three 2p orbitals are often degenerate. What does the term ‘degenerate’ mean in this context?

(e) Draw an energy level box diagram to represent the relative energies of the 1s, 2s and 2p orbitals in an isolated atom.

SY/87
(7)

10. Copy the drawing below, which represents the Periodic Table (excluding hydrogen and helium), and mark on it ‘s’, ‘p’ and ‘d’ to show which type of orbital is being filled in each part of the table.

SY/95
(2)

11. The electron configuration of an atom of element Y in the ground state can be represented as:
(a) Identify element Y.  
(b) The electron configuration of an atom or ion may also be expressed in another form, e.g. 1s² 2s² 2p¹ for boron. Give the electron configuration for Y in this form.  
(c) Give the electron configuration of the ion Y³⁺.

12. The first 20 elements show many periodic properties, e.g. the variation in first ionisation energy (IE).

(a) Predict, from the graph, the first IE of rubidium.  
(b) Explain why the noble gases have the highest values of IE in each period.  
(c) (i) Explain why the Group 1 metals have the lowest value of IE.  
(ii) Explain why the values of IE decrease Li to Na to K.  
(d) Explain the general increase in value of IE from Li to Ne.  
(e) (i) Explain the drop in value of IE from Be to B.  
(ii) Explain the drop in value of IE from N to O.  

(SY/84)
13. When sodium vapour street lights are first switched on, they glow red before turning orange-yellow. This is because they contain some neon, which produces the red colour as the lamps warm up.

(a) Explain how the orange-yellow colour is produced by the sodium.

(b) How would the light coming from one of these street lights be analysed to prove the presence of both sodium and neon?

SY/92

(5)

14. The diagram below represents part of the emission spectrum of a metal.

![Emission Spectrum Diagram]

(a) Which line corresponds to the highest energy electron transition? Give a reason for your answer.

(b) In what way would an absorption spectrum of the metal differ in appearance from the above?

(c) Calculate the wavenumber, in cm\(^{-1}\), of the 620 nm line.

(d) What colour would be observed if a salt of this metal were placed in a bunsen flame?

SY/84

(6)

15. The concentration of calcium ions in a sample of tap water can be measured by atomic emission spectroscopy (flame photometry).

(a) How might the sample be energised?

(b) State the effect this has on the electrons of the calcium ions.

(c) (i) How then is energy emitted?

   (Answer in terms of the electrons.)

   (ii) What is detected by the spectrometer?

(d) How can the chemist operating the spectrometer be certain that the emission that is measured is caused only by the calcium ions?

(e) What property of this emission will be measured (and used to estimate the calcium ion concentration)?
16. The sodium salt of ethanoic acid is an ionic solid. It has the formula CH₃COO⁻Na⁺.

(a) Draw a Lewis electron dot diagram for the ethanoate ion. 1
(b) The bond lengths between the O atoms and the carbonyl C are found to be the same and are intermediate between a C–O and a C=O bond length.
(i) Draw **two** resonance structures to represent the ethanoate ion. 2
(ii) Draw a composite diagram for these two resonance hybrids. 1
(iii) Label the delocalised electrons and explain why the negative charge in (b) (ii) is not in exactly the same place as in (b) (i). 2

17. Methylamine, CH₃NH₂, is the simplest amine. Methylamine disturbs the ionic equilibrium in water and forms an alkaline solution in exactly the same way as ammonia. The equations for the reaction between ammonia and water are:

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

(a) Use equations to represent the reaction of methylamine with water. 1
(b) (i) Draw a Lewis electron dot diagram for methylamine. 1
(ii) Draw a Lewis electron dot diagram for the methylammonium ion formed in the above reaction.

18. The table below gives information about three compounds containing fluorine.

<table>
<thead>
<tr>
<th>Fluorine compound</th>
<th>Shape</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃(g)</td>
<td></td>
<td>120°</td>
</tr>
<tr>
<td>CF₄(g)</td>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>NF₃(g)</td>
<td>Pyramidal</td>
<td>107°</td>
</tr>
</tbody>
</table>

(a) What is the shape of the BF₃ molecule?  
(b) In terms of electron-pair repulsions, account for the difference in bond angle between CF₄ and NF₃.

19. (a) Sketch the shapes of NH₃ and BCl₃ molecules, showing clearly all the bond angles and their values. 
(b) Since both nitrogen and boron have three bonding electrons, why do NH₃ and BCl₃ not have the same molecular shape?

20. Chlorine and fluorine react to produce a compound of formula ClF₃. This molecule contains three chlorine–fluorine single bonds. Each fluorine atom contributes one electron to the bonding.

(a) How many electron pairs (both bonding and non-bonding) surround the central chlorine atom in the molecule?  
(b) What would be the three-dimensional arrangement of electron pairs (both bonding and non-bonding) around the chlorine atom?  
(c) The fluorine atoms may occupy different positions in this shape, giving rise to three possible shapes for the molecule. Draw two of these, showing the angles between the bonds.
21. Sodium chloride and caesium chloride have similar formulae but different crystal structures.

(a) Describe the sodium chloride structure. Include a sketch in your answer and label the ions.  
(b) Explain why two such similar compounds as sodium chloride and caesium chloride should differ so widely in their crystal structures.  
(c) Explain which of the two structures mentioned above is likely to be adopted by iron(II) oxide. (You may wish to consult your Data Booklet.)

22. The arrangement of ions in sodium chloride can be represented as shown below.

(a) Explain why the ions are said to have a 6:6 co-ordination.  
(b) Explain whether the lines joining the ions in the above sketch represent ionic bonding or ionic bonds.  
(c) Explain whether it is reasonable to talk about a molecule of sodium chloride.

23. A step in the processing of some semiconductors involves growing a single crystal of silicon on the surface of a polycrystalline wafer. This silicon is made by a gaseous reaction between hydrogen and trichlorosilane.

a) Show the gaseous reaction as a chemical equation.  
   (You can deduce the formula for silane by analogy with methane.)
(b) Name the dopant formed if the gaseous reaction mixture also contains:
   (i) diborane, $\text{B}_2\text{H}_6$  
   (ii) phosphine, $\text{PH}_3$.  
(c) What type of semiconductor would result in each case?  

24.  

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>B</td>
<td>Si</td>
<td>C graphite</td>
</tr>
<tr>
<td>E</td>
<td>F</td>
<td>G</td>
<td>H</td>
</tr>
<tr>
<td>Ge</td>
<td>P</td>
<td>As</td>
<td>C fullerene</td>
</tr>
</tbody>
</table>

In the diagram above:

(a) identify the **two** elements that are semiconductors  
(b) identify the **two** dopants used to make an n-type semiconductor  
(c) identify the dopant used to make a p-type semiconductor  
(d) identify the **two** metallic conductors.  

25.  

Silicon is a semiconductor. Alloying it with small quantities of phosphorus modifies its properties as a conductor.

(a) What name other than alloying is more often used for this process?  
(b) Copy and amend the above diagram to show the effect of an atom of phosphorus in a central position.  
(c) (i) Is this an n-type or a p-type semiconductor? Explain your answer.  
   (ii) Name an element that could be used in place of phosphorus to make the other type of semiconductor.
(d) State how n-type and p-type semiconductors conduct electricity.  
2
(e) (i) State how a p–n junction can be made.  
1
(ii) State how a p–n junction works in a solar cell.  
2

(10)

26. In the closing years of the twentieth century the search for superconductors intensified. As a result of this research the critical temperature \((T_c)\) of superconductors has steadily risen. An indication of the success achieved is shown below.

<table>
<thead>
<tr>
<th>Dates of discovery of superconductors and their critical temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature/°C</strong></td>
</tr>
<tr>
<td>-273</td>
</tr>
<tr>
<td>-250</td>
</tr>
<tr>
<td>-200</td>
</tr>
<tr>
<td>-150</td>
</tr>
</tbody>
</table>

(a) State what \(T_c\), the critical temperature, means when associated with superconductors.  
1
(b) Define the term ‘superconductor’ in terms of electrical resistance.  
1
(c) Why was liquid helium used to cool the first superconductors?  
1
(d) What breakthrough occurred in 1987 that was a major step forward in superconductor technology?  
1
(e) (i) State why a critical temperature of about 300K is being sought.  
1
(ii) State a possible use for superconductors at this temperature.  
1

(6)

27. Four different materials, A, B, C and D differ in their ability to conduct electricity:

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>semiconductor</td>
<td>superconductor</td>
</tr>
<tr>
<td>C</td>
<td>D</td>
</tr>
<tr>
<td>ionic conductor</td>
<td>metallic conductor</td>
</tr>
</tbody>
</table>
Identify the material(s):
(a) that provide loss-free energy transmission  
(b) that conduct better as solids at higher temperatures  
(c) that do not conduct at all when solid  
(d) that conduct better when exposed to light  
(e) whose conductivity decreases with increase in temperature.  

28.

The graphs above show how the resistance of certain materials varies with temperature. The graphs are not all drawn using the same scale.

(a) Which graph represents a superconductor?  
(b) Which graph represents a semiconductor?  
(c) Which graph represents a metallic conductor?  

(3)
29. Study the following data, which relates to the Periodic Table.

**Table 1**

<table>
<thead>
<tr>
<th>Element X</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p./°C</td>
<td>181</td>
<td>1278</td>
<td>2300</td>
<td>3550</td>
<td>-210</td>
<td>-218</td>
<td>-220</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Chloride</th>
<th>LiCl</th>
<th>BeCl₂</th>
<th>BCl₃</th>
<th>CCl₄</th>
<th>NCl₃</th>
<th>OCl₂</th>
<th>FCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p./°C</td>
<td>614</td>
<td>405</td>
<td>-107</td>
<td>-23</td>
<td>-27</td>
<td>-20</td>
<td>-154</td>
</tr>
<tr>
<td>b.p./°C</td>
<td>1350</td>
<td>487</td>
<td>12</td>
<td>77</td>
<td>71</td>
<td>4</td>
<td>-101</td>
</tr>
</tbody>
</table>

(a) Refer to Table 1. Explain the large change in melting point from carbon to nitrogen.

(b) Refer to Table 2.

(i) Which chloride is a gas at 0°C?

(ii) Which chloride is a typical ionic solid?

(iii) Which chloride is most likely to be a covalent solid at room temperature?

(iv) What happens to the polarity of the X–Cl bond as one progresses across the table from left to right? Why?

30. Explain why the ionic radius of the hydride ion (H⁻) is given in the Data Booklet rather than the ionic radius of the more common positive hydrogen ion (H⁺).

31. Dry chlorine is passed over hot aluminium to give anhydrous aluminium chloride. This sublimes at 183°C to give a vapour of relative molecular mass 267.

(a) From the above information suggest a formula for the vapour.

(b) What does the sublimation temperature suggest about the bonding in aluminium chloride?

(c) If the chlorine had not been dry, which compound of aluminium would have been formed? Explain your answer.
32. Consider the above arrangement, which is based on the Periodic Table.

(a) Give the ionic formula of one hydride of an element in section 1 and state its reaction with water.
(b) Write balanced equations to illustrate the amphoteric nature of an oxide of one of the elements in section 2.
(c) Write the formula of the chloride of an element in section 3 that undergoes hydrolysis. Describe what is observed in the reaction.
(d) Explain what is meant by hydrogen bonding and say how it affects the properties of a compound of one element in section 4.
(e) Going across the period from sodium to chlorine, what is the trend in the basic character of the oxides?

33. The 3d and 4s electronic structure for the nickel atom can be represented as follows:

\[ \begin{array}{c} \text{3d} \\ \text{4s} \end{array} \]

(a) Draw the corresponding diagrams for Fe\(^{2+}\) and Fe\(^{3+}\).
(b) How do these electron arrangements account for the relative stabilities of the two iron ions?

34. All three parts of the question below relate to the complex ion \([\text{Cu(CN)}_4]^{3-}\).

(a) What is the oxidation state of copper in the above ion?
(b) How many electrons occupy the 3d energy levels of copper in this complex ion?
35. Solutions of some complex ions are acidic. For example, an aqueous solution of iron(III) chloride can have a pH of 3.0. One of the processes occurring is:

\[ \text{[Fe(H}_2\text{O)}_6]^{3+} + 3\text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{[Fe(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}^+(\text{aq}) + 3\text{Cl}^-(\text{aq}) \]

(a) Name the two ligands in the complex structure on the right of the equation above and explain how they act as ligands.  
(b) Draw a diagram showing the shape of the complex ion on the right of the equation and name its shape.  
(c) It is more difficult to remove a proton from [Fe(H\text{H}_2\text{O)}_5\text{OH}]^{2+} than from [Fe(H\text{H}_2\text{O)}_6]^{3+}. Explain why this is so.

36. The electronic configuration of an atom of iron may be represented by:

\[ [\text{Ar}] \quad \begin{array}{cccccc} \text{é} & \text{ê} & \text{é} & \text{é} & \text{é} & \text{é} \end{array} \quad \text{3d} \]

(a) How does this arrangement for the 3d electrons follow Hund’s rule of maximum multiplicity?  
(b) Give a similar type of arrangement to represent the electronic configuration for an iron(III) ion.  
(c) In the complex ion hexacyanoferrate(III), two of the 3d orbitals are at a higher energy level than the other three. How many unpaired 3d electrons are there in the complex ion?

37. Three compounds can result from the reaction between copper(II) chloride and ammonia. These compounds were reacted with silver(I) nitrate solution and the number of moles of silver(I) chloride formed per mole of each compound was calculated.
**ELECTRONIC STRUCTURE AND THE PERIODIC TABLE**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Empirical formula</th>
<th>Moles of silver(I) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuCl₂₂NH₃</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>CuCl₂₃NH₃</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>CuCl₂₂NH₃</td>
<td>0</td>
</tr>
</tbody>
</table>

(a) Using the above table, give the formula of the complex ion present in each compound. State reasons for your answers.

(b) Suggest why these three compounds have different colours from aqueous copper(II) salts.

38. (a) The electron configuration of a neutral chromium atom is 1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹. Write down the electron configuration of chromium in the yellow chromate ion, CrO₄²⁻. Show how you arrived at your answer.

(b) What is the name of the theory that explains the origin of colour in ions like chromate?

(c) Chromate ions, which are yellow, change into orange dichromate ions, Cr₂O₇²⁻, on the addition of acid. Is this a redox reaction? Explain your answer.

39. Solutions of nickel(II) chloride and 1,2-diaminoethane, NH₂CH₂CH₂NH₂, of equal molarities were made up. From these a range of solutions of equal volume was prepared containing difference proportions of each. Each of the resulting solutions was then placed, in turn, in a colorimeter fitted with a filter that transmitted green light.
In this way the relative absorbance of each solution was determined and the following graph drawn.

(a) The formula of the complex may be represented by: 
\[ \text{[Ni}_x\text{\textsubscript{2} \text{CH}_2\text{CH}_2\text{NH}_2\text{]}}^2+ \]. Examine the graph. What are the likely values of \( x \) and \( y \)? Explain your reasoning briefly. 3

(b) Suggest why 1,2-diaminoethane molecules should complex with \( \text{Ni}^{2+} \) ions. 2

(c) Explain the use of the green-coloured filter in the colorimeter. 2

SY/80

(7)

40. Account for the green colour of an aqueous solution of \( \text{V}^{3+} \) ions. (Make reference to ligands, electrons and the visible spectrum in your answer.)

SY/85

(3)

41. In aqueous solution, \( \text{Fe}^{2+} \) forms a deep red complex with the colourless compound phenanthroline. The intensity of the colour for a particular concentration of \( \text{Fe}^{2+} \) is independent of pH in the range 2 to 9. With the aid of a single-beam colorimeter, an analysis of a series of solutions of \( \text{Fe}^{2+} \) with phenanthroline yielded the following results:
### ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

#### 42. The ability of a ligand to split the d orbitals when forming a complex ion is given in the spectrochemical series. Three ligands from this series and their relative ability to split the d orbitals are:

\[
\text{NH}_3 > \text{H}_2\text{O} > \text{Cl}^- 
\]

A study of part of the absorption spectrum for the complex ion, hexaaquanickel(II) shows a broad absorption band that peaks at around 410 nm.

(a) Explain the origin of the absorption band at this wavelength.  
(b) State towards which end of the visible spectrum the wavelength of the absorption band would move if the water ligands were replaced by chloride ions. Give an explanation for your answer.
43. The table below gives information about complex ions containing vanadium.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{V(H}_2\text{O)}_6])(^{2+})</td>
<td>Violet</td>
</tr>
<tr>
<td>([\text{V(H}_2\text{O)}_6])(^{3+})</td>
<td>Green</td>
</tr>
<tr>
<td>([\text{VO}]^{2+})</td>
<td>Blue</td>
</tr>
<tr>
<td>([\text{VO}_2]^+)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Determine the oxidation number of vanadium in the ions \([\text{VO}_2]^+\) and \([\text{V(H}_2\text{O)}_6]\)\(^{2+}\).
(b) Name and draw the shape of the green complex ion \([\text{V(H}_2\text{O)}_6]\)\(^{3+}\).
(c) (i) Give the electronic configuration for vanadium in the \([\text{VO}_2]^+\) ion.
(ii) Suggest why you would predict this ion to be colourless.
(d) Light of wavelength varying from 400 to 700 nm is passed through a solution containing \([\text{VO}]^{2+}\) ions. Copy the axes shown below and draw the absorption spectrum that you would expect to obtain. (Page 14 of your Data Booklet may be helpful.)

```
<table>
<thead>
<tr>
<th>% Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>0</td>
</tr>
</tbody>
</table>
```

SY/97
(7)
ELECTRONIC STRUCTURE AND THE PERIODIC TABLE

44. A green solution of nickel(II) chloride was added to a colourless solution of ammonium tetrafluoroborate, producing a pale lilac-coloured complex.

(a) Write down the electronic configuration for the Ni\(^{2+}\) ion. 1
(b) Give a brief explanation for the green colour of the nickel(II) chloride solution. 2
(c) Suggest a reason for the change in colour when the two solutions react together. 1

SY/99 (4)

45. (a) For the complex ion tetrachlorocuprate(II), give the formula of the ion, including its charge. 2
(b) Dilution of a solution containing tetrachlorocuprate(II) ions with water results in all of the chloro ligands being displaced by water ligands. An octahedral complex ion forms.
   (i) Name the octahedral complex ion. 1
   (ii) Draw its structure. 1

SY/92 (4)

46. (a) In aqueous solution, the complex ion [Ti(H\(_2\)O)\(_6\)]\(^{3+}\) has an available unoccupied energy level 239 kJ mol\(^{-1}\) above the highest occupied level. What wavelength of light will bring about the transition from the lower to the upper level? 3
(b) Using the spectral line data given on page 14 of the Data Booklet, state the colour to which the wavelength in (a) corresponds. Hence deduce the observed colour of the solution in daylight. 2

SY/89 (5)
47. The following are the absorption spectra of two coloured solutions containing complex cobalt(II) ions.

Spectrum of $[\text{CoCl}_4]^{2-}$

Spectrum of $[\text{Co(H}_2\text{O})_6]^{2+}$

(a) Predict the colour of the solution containing $[\text{CoCl}_4]^{2-}$ ions. 1
(b) Calculate the energy difference, in kJ mol$^{-1}$, corresponding to the absorbance peak at 540 nm for the solution containing $[\text{Co(H}_2\text{O})_6]^{2+}$ ions. 3

SY/95

(4)
48.  (a) In some textbooks, zinc is not regarded as a transition element. Explain in terms of electronic structure why this should be so.
(b) Mention two characteristics of transition elements that are not shown by zinc.
(c) Name three different transition elements that can act as catalysts, giving the reaction or process that each catalyses.
(d) What is thought to be a reason for so many catalysts being derived from transition elements?

49. Organic chemists now use a wide variety of catalysts when producing designer molecules. These include WC, Mo₂C, VC, W₂N and FeCl₃.

(a) Identify an area of the Periodic Table that is common to these compounds.
(b) Explain in terms of electron orbitals how catalysts of this kind can affect the activation energy of a reaction.
1. Brass is an alloy consisting mainly of copper and zinc. To determine the percentage of copper in a sample of brass, 2.63 g of the brass was dissolved in concentrated nitric acid and the solution diluted to 250 cm$^3$ in a standard flask. Excess potassium iodide was added to 25.0 cm$^3$ of this solution, iodine being produced according to the equation:

$$2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^- (\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$$

The iodine formed was titrated with 0.10 mol l$^{-1}$ sodium thiosulphate solution, $\text{Na}_2\text{S}_2\text{O}_3(\text{aq})$, the volume required for complete reaction being 24.8 cm$^3$.

$$\text{I}_2(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$$

colourless colourless

(a) Which species in the first equation is oxidised?  
(b) How could the end-point for the titration be made more obvious?  
(c) How many moles of sodium thiosulphate were required in the titration?  
(d) Calculate the percentage by mass of copper in the sample of brass.

2. 1.8 g of iron(II) ammonium sulphate, $\text{Fe(NH}_4\text{)}_2(\text{SO}_4)\_2\cdot6\text{H}_2\text{O}$, was dissolved in 35 cm$^3$ of distilled water. The solution was then diluted to 50 cm$^3$ using dilute sulphuric acid. The final solution was titrated against potassium permanganate solution and 40 cm$^3$ of the potassium permanganate solution was required to reach the end-point at which all the iron(II) had been converted to iron(III). Calculate the concentration of the potassium permanganate solution.

3. Before 1947, ‘silver’ coins were made from an alloy of silver, copper and nickel. To determine the metal composition, a coin weighing 10.00 g was dissolved in nitric acid and the resulting solution diluted to 1000 cm$^3$ in a standard flask. A 100 cm$^3$ portion
was treated in the following way. Hydrochloric acid (0.20 mol l\(^{-1}\)) was added to this solution until precipitation of silver(I) chloride was complete. The precipitate was recovered by filtration. It was washed and dried and found to weigh 0.60 g.

(a)  
(i) Calculate the percentage by mass of silver in the coin.  
(ii) How could you tell when precipitation was complete?

(b) The filtrate was treated to reduce the copper(II) ions to copper(I) ions. Ammonium thiocyanate solution was added to precipitate the copper as copper(I) thiocyanate:

\[
\text{Cu}^{+}(\text{aq}) + \text{CNS}^{-}(\text{aq}) \rightarrow \text{CuCNS(s)}
\]

After filtration, drying and weighing, the precipitate was found to weigh 0.31 g. Calculate the percentage by mass of copper in the coin.

4. An anhydrous salt is known to be a mixture of magnesium chloride and magnesium nitrate. To determine the composition of the mixture, the following procedure was carried out. 4.50 g of the salt was dissolved in water and the solution made up to 500 cm\(^3\) in a standard flask. A slight excess of silver(I) nitrate solution was then added to 100 cm\(^3\) of this solution and the resulting precipitate recovered by filtration. The precipitate was washed, dried and its mass found to be 2.01 g.

(a) How would you check that an excess of silver(I) nitrate had been added?  
(b) Calculate the percentage by mass of magnesium chloride in the mixture.  
(c) A variation of this method involved titrating the salt solution with standard silver(I) nitrate solution using a suitable indicator. What volume of 0.10 mol l\(^{-1}\) silver(I) nitrate solution would be required to react completely with 25 cm\(^3\) of the salt solution?

5. Crystals of hydrated sodium carbonate left exposed to the atmosphere gradually lose some of their water of crystallisation. The formula of the crystals may be given by Na\(_2\)CO\(_3\).\(x\)H\(_2\)O, where \(x\) has a numerical value between 0 and 10.
16.0 g of the crystals was dissolved in water and made up to 250 cm$^3$ of solution in a standard flask. To determine the value of $x$ in the formula, 25 cm$^3$ of the sodium carbonate solution was titrated with 1.0 mol l$^{-1}$ hydrochloric acid. 15.0 cm$^3$ of the acid was required for neutralisation.

(a) Calculate the mass of sodium carbonate (Na$_2$CO$_3$) in 16.0 g of the crystals.  
(b) Find the value of $x$ in the formula Na$_2$CO$_3$-$x$H$_2$O.

6. Anhydrous malonic acid has a relative formula mass of 104. 1.28 g of hydrated acid, CH$_2$(COOH)$_2$.nH$_2$O, was dissolved in water and made up to 250 cm$^3$ in a standard flask. 25.0 cm$^3$ of this acid was titrated with 0.1 mol l$^{-1}$ sodium hydroxide. 18.2 cm$^3$ of the alkali was required for complete neutralisation of the acid.

(a) Calculate the number of moles of acid that have been neutralised in the titration.  
(b) Calculate the mass of water in 1.28 g of the hydrated sample.  
(c) Find the value for $n$ in the formula CH$_2$(COOH)$_2$.nH$_2$O.

7. Sodium sulphite is a reducing agent that is oxidised to sodium sulphate by atmospheric oxygen. In order to determine its purity, a sample of sodium sulphite was analysed as follows.

5.02 g of the sample was dissolved in water and made up to 250 cm$^3$ in a standard flask. 50 cm$^3$ of the solution was pipetted into a beaker and treated with excess barium chloride solution to precipitate all the sulphite and sulphate ions as their barium salts, as shown in the equations below:

\[
\text{Na}_2\text{SO}_3(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow \text{BaSO}_3(\text{s}) + 2\text{NaCl}(\text{aq}) \\
\text{Na}_2\text{SO}_4(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})
\]

The mixed precipitate was then filtered off, washed with water and dried in an oven to constant mass. Excess dilute hydrochloric acid was added to the precipitate to dissolve the barium sulphite. The untreated barium sulphate was then filtered off, washed with water and dried in an oven to constant mass:
mass of mixed precipitate = 1.69 g
mass of barium sulphate = 0.60 g

(a) Calculate the number of moles of barium sulphite in the mixed precipitate.
(b) Calculate the percentage by mass of sodium sulphite in the sample.
(c) Analysis of sodium sulphite may also be carried out by a volumetric technique using acidified potassium permanganate solution. Give two reasons why acidified potassium permanganate would be a suitable reagent for this analysis.

SY/99
(7)

8. The value for the equilibrium constant, $K$, for a specific example of the following reaction is equal to 1:

$$\text{acid + alcohol} \rightleftharpoons \text{ester + water}$$

(a) (i) Predict the maximum yield of ester, given this value of $K$.
(ii) Give one reason why this yield might not be achieved in practice.
(b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion.
(c) Another pupil suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of $K$. Comment on this suggestion.

(6)

9. The balanced equation for the principle reaction in the contact process is:

$$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H = -\text{ve}$$

(a) (i) Write an expression for $K$, the equilibrium constant for this reaction, when the system has reached equilibrium.
(ii) State the units of $K$. 

(1)
(b) (i) State Le Chatelier's principle.  
(ii) Use this generalisation to predict how an increase in temperature would affect the position of equilibrium.  
(iii) Explain the effect this increase in temperature would have on the value of $K$.

10. Reaction A: \[ 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \]  
Reaction B: \[ \text{PCl}_5(s) \rightleftharpoons \text{PCl}_3(l) + \text{Cl}_2(g) \]  
Reaction C: \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]  
Reaction D: \[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \]  
Reaction E: \[ \text{C}_2\text{H}_5\text{OH}(l) + \text{C}_6\text{H}_5\text{COOH}(s) \rightleftharpoons \text{C}_6\text{H}_5\text{COOC}_2\text{H}_5(l) + \text{H}_2\text{O}(l) \]  

Each line on the graph below shows the effect of changing the pressure on the yield of products for each of the above reactions.

(a) Allocate a line on the graph (by number) to each reaction (by letter). Explain your choice in each case.  
(b) What effect would removing the catalyst have on the shape of line 1?
11. For the equilibrium:

\[ 2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \quad \Delta H^\circ = -115 \text{ kJ (left \rightarrow right)} \]

established in a closed vessel at a fixed temperature, the equilibrium constant reaction has a value of 15 l mol\(^{-1}\).

(a) Write an expression for the equilibrium constant \(K\).  

(b) What does the magnitude of \(K\) indicate?  

(c) What effect will increasing the temperature have on the value of the equilibrium constant \(K\)? Explain your answer.  

(d) Calculate the equilibrium concentration of \(\text{NO}_2\) when the equilibrium concentrations of \(\text{NO}\) and \(\text{O}_2\) are both 0.1 mol l\(^{-1}\).  

12. In the Data Booklet, the solubility of barium sulphate, shown by the equation:

\[ \text{BaSO}_4(s) + \text{water} \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \]

is given as less than 1 g l\(^{-1}\). In a more advanced textbook, it is noticed that an equilibrium constant, known as the solubility product \(K_{sp}\), can be written to represent the dissolving process. \(K_{sp}\) is equal to the product of the concentrations of the ions in the solution:

\[ K_{sp} = [\text{Ba}^{2+}] \times [\text{SO}_4^{2-}] \]

(a) At 298K, \(K_{sp}\) for barium sulphate is equal to \(1 \times 10^{-10}\) mol\(^2\) l\(^{-2}\). For a saturated solution of barium sulphate at 298K, calculate (i) the concentration of the barium ions dissolved in the solution (ii) the mass of barium sulphate dissolved in 1 litre of solution.  

(b) A small quantity of the very soluble sodium sulphate is now added to the saturated solution of barium sulphate. (i) What will happen to the value of \(K_{sp}\)? (ii) What will happen to the concentration of barium ions?
13. When a solute dissolves in each of two immiscible liquids the ratio of the concentrations of the solute, at equilibrium, in the two liquids is called the partition coefficient. The partition coefficient for an organic compound (X) between ether and water is 12.

Density of water = 1.0 g cm\(^{-3}\)  Density of ether = 0.714 g cm\(^{-3}\)

(a) State which solvent forms the upper layer in the separating funnel. Give a reason for your choice.  
(b) If 1.1 g of X is dissolved in 100 cm\(^3\) of water, how much of this compound will be extracted (after shaking for several minutes) with 100 cm\(^3\) of ether?  
(c) By calculation, show whether more or less solute will be extracted if the ether is used in two 50 cm\(^3\) extractions one after the other in the above experiment.  
(d) Explain why many organic compounds are more soluble in ether than in water.

14. Succinic acid (CH\(_2\)COOH)\(_2\), a dicarboxylic acid, can be partitioned between water and diethyl ether. In an experiment to find the partition coefficient, 2.36 g of succinic acid was dissolved in 100 cm\(^3\) of water in a separating funnel and 100 cm\(^3\) of ether was added. After shaking the mixture the aqueous layer was removed and titrated with 1.0 mol l\(^{-1}\) sodium hydroxide. It required 34.8 cm\(^3\) of the alkali to neutralise all the aqueous acid solution.

(a) Calculate the number of moles of acid in the aqueous layer before the addition of ether.  
(b) How many moles of the acid will be dissolved in the ether layer after shaking?
PRINCIPLES OF CHEMICAL REACTIONS

(c) What is the partition coefficient of the succinic acid between the ether and the water? 1

(d) How could the experiment be modified to reduce the concentration of acid in the aqueous layer while still using the same total volumes and ether and the same mass of succinic acid? 1

15. Paper chromatography is a good method for separating and identifying amino acids.

(a) From the sketch identify:
   (i) the mobile phase 1
   (ii) the stationary phase 1
   (iii) the minimum number of components in sample B 1
   (iv) one possible component of sample B (and explain why it is not possible to know which one with certainty) 2
   (v) the origin (or base line) 1
   (vi) the solvent front. 1
(b) Explain:

(i) the need for a lid
(ii) the use of $R_f$ values
(iii) why a pencil is often a better choice than an ink pen to draw the origin
(iv) why one component of sample A has not left the origin
(v) why the eluant is often a mixture of solvents and not a single solvent
(vi) whether more than one phase is involved in partition chromatography
(vii) why a developing agent is required in the above experiment.

16. A substance X was known to be a mixture of alkanes. To help identify the various alkanes in the mixture, gas chromatography was used. The chromatogram for the mixture is shown below.

![Chromatogram](image)

A sample, which was a mixture of known alkanes, was then run on the same machine. The following table lists the retention times found for these alkanes.

<table>
<thead>
<tr>
<th>Alkane</th>
<th>Retention time/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>4.1</td>
</tr>
<tr>
<td>Propane</td>
<td>6.2</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>7.3</td>
</tr>
<tr>
<td>Butane</td>
<td>8.1</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>9.3</td>
</tr>
<tr>
<td>Pentane</td>
<td>9.9</td>
</tr>
</tbody>
</table>
(a) (i) Name a suitable gas to use as the mobile phase (or carrier gas).  
(ii) Explain your choice.  
(b) The retention time for ethane is 4.1 minutes. What is meant by ‘the retention time’?  
(c) (i) Suggest a name for alkanes A, E and F.  
(ii) Explain your choice in each case.  

17. Write the formula for the conjugate base of each of the following acids:  
   (a) $\text{H}_3\text{O}^+$  
   (b) $\text{H}_2\text{O}$  
   (c) $\text{NH}_4^+$  

18. (a) According to the Brønsted–Lowry theory, the hydrogensulphite ion, $\text{HSO}_3^-$ (aq), is behaving as an acid in the following reaction:  

$\text{HSO}_3^-$ (aq) $\rightleftharpoons \text{H}^+$ (aq) + $\text{SO}_3^{2-}$ (aq)  

(i) Explain in terms of the Brønsted–Lowry theory how the equation shows $\text{HSO}_3^-$ acting as an acid.  
(ii) Write the formula for the conjugate base.  

(b) The theory states that the hydrogensulphite ion can also act as a base. Illustrate this statement with an equation.  

19. (a) Calculate the pH of a solution of ethanoic acid with a concentration of 0.01 mol l$^{-1}$.  
($K_a$ ethanoic acid = $1.7 \times 10^{-5}$)  

(b) A mixture of ethanoic acid and sodium ethanoate solution constitutes a buffer solution. Show how this buffer solution is able to resist a change in pH when small quantities of each of the following are added.  
(i) hydrochloric acid  
(ii) sodium hydroxide solution  
(Use of equations may be helpful.)
(c) The simplified equation for the pH of a buffer solution is:

\[ \text{pH} = \text{p}K_a - \log \frac{[\text{acid}]}{[\text{salt}]} \]

A buffer solution was prepared from ethanoic acid (0.25 mol l\(^{-1}\)) and sodium ethanoate solution (0.15 mol l\(^{-1}\)). Calculate the pH of the buffer solution.

2

SY/94

(9)

20. The ionic product for water (\(K_w\)) is usually taken to be \(10^{-14}\) mol\(^2\) l\(^{-2}\), but it varies with temperature. The following table shows this variation.

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>(K_w/\text{mol}^2 \text{l}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>(0.114 \times 10^{-14})</td>
</tr>
<tr>
<td>283</td>
<td>(0.293 \times 10^{-14})</td>
</tr>
<tr>
<td>298</td>
<td>(1.008 \times 10^{-14})</td>
</tr>
<tr>
<td>323</td>
<td>(5.476 \times 10^{-14})</td>
</tr>
<tr>
<td>373</td>
<td>(51.3 \times 10^{-14})</td>
</tr>
</tbody>
</table>

(a) What is meant by the term ‘ionic product of water’?

(b) Since \(K_w\) varies with temperature, the pH of pure water is not always 7. Calculate the pH of pure water at 373K.

(c) The ionisation of water is endothermic. Explain how the information in the table supports this statement.

1

SY/91

(5)

21. Phosphoric(V) acid, \(\text{H}_3\text{PO}_4\), is triprotic. When neutralised by sodium hydroxide solution, it can form three different salts.

(a) Give the formula for each of the three sodium salts of the acid.

(b) The first stage in the ionisation of phosphoric(V) acid has a dissociation constant of \(7.08 \times 10^{-3}\) mol l\(^{-1}\). Calculate the approximate pH of a 0.1 mol l\(^{-1}\) solution of phosphoric(V) acid. (You may assume that the other two stages in the ionisation do not significantly affect the hydrogen ion concentration.)

3

SY/91

(5)
22. At 298K the dissociation constant $K_w$ for water is $1 \times 10^{-14}$ mol² l⁻². The graph shows the variation of $K_w$ with temperature.

![Graph showing variation of $K_w$ with temperature.](image)

From the graph calculate the pH of water at 288K.

SY/96 (3)

23. Limewater is a saturated solution of calcium hydroxide. At 20°C, 100 cm³ of a limewater solution contained 0.126 g of calcium hydroxide.

(a) Calculate the concentration of hydroxide ions, in mol l⁻¹, in this solution.

(b) Using your answer to part (a), calculate the pH of the solution.

SY/99 (4)

24. Most indicators are weak acids of general formula HIn. Their dissociation in aqueous solution can be represented as:

$$\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$$

<table>
<thead>
<tr>
<th>Colour A</th>
<th>Colour B</th>
</tr>
</thead>
</table>

At the end point, $[\text{In}^-] = [\text{HIn}]$ and therefore $K_{\text{indicator}} = [\text{H}^+]$. 

**Additional Questions (AH Chemistry)**
Use the above and the information in the table below to answer the questions that follow.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>$K_{\text{indicator}}$/mol l$^{-1}$</th>
<th>Colour change (low pH → high pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl yellow</td>
<td>$5.1 \times 10^{-4}$</td>
<td>Red → yellow</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>$1.0 \times 10^{-7}$</td>
<td>Yellow → blue</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>$1.3 \times 10^{-9}$</td>
<td>Yellow → blue</td>
</tr>
</tbody>
</table>

(a) At what pH would the colour change be expected to take place in each of the indicators? 

(b) A student is asked to carry out a titration of ethanoic acid and sodium hydroxide. Which indicator in the table is most suitable for the titration? Give a reason for your choice.

The graph above shows the pH change when a solution of 0.1 mol l$^{-1}$ sodium hydroxide is added to 20 cm$^3$ of a solution of a monoprotic acid.

(a) What is the concentration of the acid?

(b) Is the acid weak or strong? Justify your answer.

(c) What factor must be considered when an indicator for a particular titration is selected?
PRINCIPLES OF CHEMICAL REACTIONS

(d) Sketch the graph into your book (no graph paper required) and show, by a dotted line starting from the pH axis, the curve you would expect if the alkali were replaced by 0.1 mol l⁻¹ ammonia solution.

(e) Comment on the use of an indicator for the titration in (d) above.

SY/90

(7)

26. 250 cm³ of sulphurous acid solution was prepared by dissolving 1.6 g of sulphur dioxide in water at 298K.

(a) Calculate the concentration of the acid solution in mol l⁻¹.

(b) Using your answer to (a) and page 12 of your Data Booklet, calculate the pH of the acid solution.

(c) Why is this acid solution unsuitable for use as a primary standard?

(d) If this acid solution is standardised using a strong alkali, what will be the approximate pH range of the indicator needed for the titration?

SY/98

(7)

27. Use the data on page 12 of the Data Booklet to calculate the pH of a solution of propanoic acid of concentration 10⁻¹ mol l⁻¹.

SY/93

(3)

28. Solid magnesium chloride exists in two forms: anhydrous(MgCl₂) and hydrated(MgCl₂.6H₂O).

(a) Calculate the enthalpy change for the process:
   \[ \text{MgCl}_2(s) \rightarrow \text{Mg}^{2+}(aq) + 2\text{Cl}^-(aq) \]

   Use the following data:
   \[ \text{Mg}^{2+}(g) \rightarrow \text{Mg}^{2+}(aq) \quad \Delta H = -1920 \text{ kJ mol}^{-1} \]
   \[ \text{Cl}^-(g) \rightarrow \text{Cl}^-(aq) \quad \Delta H = -364 \text{ kJ mol}^{-1} \]

   lattice enthalpy (anhdydrous magnesium chloride) = 2493 kJ mol⁻¹
(b) Calculate the enthalpy change for converting anhydrous magnesium chloride to hydrated magnesium chloride, given the following enthalpies of formation:

\[
\begin{align*}
\Delta H_f^\theta (\text{hydrated magnesium chloride}) & = -2500 \text{ kJ mol}^{-1} \\
\Delta H_f^\theta (\text{anhydrous magnesium chloride}) & = -642 \text{ kJ mol}^{-1} \\
\Delta H_f^\theta (\text{water}) & = -286 \text{ kJ mol}^{-1}
\end{align*}
\]

29. Consider the following data:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice-breaking enthalpy/kJ mol(^{-1})</th>
<th>Enthalpy of solution/kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KF</td>
<td>801</td>
<td>-17.7</td>
</tr>
<tr>
<td>KCl</td>
<td>701</td>
<td>+ 17.2</td>
</tr>
<tr>
<td>KBr</td>
<td>670</td>
<td>+ 20.0</td>
</tr>
</tbody>
</table>

(a) Why do the lattice-breaking enthalpies decrease down the series from KF to KBr?  
(b) Calculate the enthalpy associated with the hydration of the ions in KCl.  
(c) How would you expect the enthalpy associated with the hydration of the ions in calcium chloride to compare with that in potassium chloride? Explain your answer.

30. Water gas is prepared by passing steam over white hot coke. The equation for the reaction is:

\[
\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(g)
\]

The products of the reaction may be used to prepare methanol industrially, using chromium(III) oxide as a catalyst, a temperature of 300°C and a pressure of 300 atmospheres:

\[
\text{CO(g)} + 2\text{H}_2(g) \rightarrow \text{CH}_3\text{OH(l)}
\]

(a) The enthalpy change for the reaction to produce water gas is 130 kJ mol\(^{-1}\). Use this value, with information on page 9 of the Data Booklet, to calculate the bond enthalpy for the C–O bond in carbon monoxide.
(b) The mean bond enthalpy for C–O is 331 kJ mol⁻¹ and for C=O is 724 kJ mol⁻¹. Use this information and your answer to (a) to make a prediction about the nature of the bond in carbon monoxide.

(c) State two possible hazards associated with the industrial production of methanol.

31. (a) By referring to the Data Booklet write down the equation and the value for:
   (i) the enthalpy of formation of propane
   (ii) the enthalpy of combustion of carbon
   (iii) the enthalpy of combustion of hydrogen.

(b) Using the above data, calculate the enthalpy of combustion of propane.

32. (a) Name each of the changes shown by the equations (i) to (v) and beside each name write the value for the change as shown in the Data Booklet.
   (i) Na(s) → Na(g)
   (ii) ½O₂(g) → O(g)
   (iii) Na(g) → Na⁺(g)
   (iv) O(g) → O²⁻(g)
   (v) 2Na⁺(g) + O²⁻(g) → (Na⁺)₂O₂⁻(s)

(b) Write the equation for the enthalpy of formation of sodium oxide.

(c) (i) Construct a Born–Haber cycle using all the information in (a) and (b).
   (ii) Calculate the enthalpy of formation of sodium oxide.

33. 1,2-dichloroethane has been used as a solvent for lacquers and oils. One proposed method of production is the addition of hydrogen chloride to ethyne:

   \[ \text{C}_2\text{H}_2 + 2\text{HCl} \rightarrow \text{CH}_2\text{ClCH}_2\text{Cl} \]
34. Consider the following reactions and their values for $\Delta G^\circ$ and $\Delta H^\circ$ at 298K:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^\circ$/kJ mol$^{-1}$</th>
<th>$\Delta H^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$</td>
<td>$-95$</td>
<td>$-92$</td>
</tr>
<tr>
<td>(ii) $2Al(s) + \frac{1}{2}O_2(g) \rightarrow Al_2O_3(s)$</td>
<td>$-1576$</td>
<td>$-1669$</td>
</tr>
<tr>
<td>(iii) $\text{NH}_4\text{Cl}(s) \rightarrow \text{NH}_4^+(aq) + \text{Cl}^-(aq)$</td>
<td>$-7$</td>
<td>$+16$</td>
</tr>
</tbody>
</table>

(a) Reaction (ii) has the greatest difference in the values of $\Delta G^\circ$ and $\Delta H^\circ$. Suggest a reason for this difference. 1

(b) From the values given for reaction (iii), it can be concluded that ammonium chloride dissolves spontaneously in water under standard conditions with a drop in temperature. Why can we come to these two conclusions? 2

(c) Calculate the entropy change for reaction (i) at 298K. 2
35. In a catalytic reformer, straight-chain alkanes are converted to branched chains, cycloalkanes and aromatic hydrocarbons. Consider the sequence shown below.

Octane

```plaintext
A
```

2,3-dimethylhexane

```plaintext

B
```

1,2-dimethylcyclohexane + hydrogen

```plaintext

C
```

1,2-dimethylbenzene (o-xylene) + hydrogen

(a) Use the data in the table below to calculate $\Delta S^\circ$ for the conversion of octane to o-xylene and hydrogen at 298K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S^\circ$ J K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane</td>
<td>463</td>
</tr>
<tr>
<td>o-xylene</td>
<td>352</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>131</td>
</tr>
</tbody>
</table>

(b) Calculate the minimum temperature at which the conversion in (a) becomes thermodynamically feasible, given that $\Delta H^\circ = 227$ kJ mol$^{-1}$.

(c) Explain why the conversion in (a) can be achieved at or above the temperature calculated in (b), despite the fact that the equilibrium constant for reaction A is very much less than 1 at this temperature.
36. The apparatus shown in the diagram below can be used to find the decomposition temperature of sodium hydrogencarbonate.

![Diagram of the apparatus](image)

The equation for the decomposition is:

\[ 2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \quad \Delta H^\circ = +129 \text{ kJ mol}^{-1} \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( S^\circ /\text{J K}^{-1} \text{ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NaHCO}_3(s) )</td>
<td>102.1</td>
</tr>
<tr>
<td>( \text{Na}_2\text{CO}_3(s) )</td>
<td>136.0</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(g) )</td>
<td>188.7</td>
</tr>
<tr>
<td>( \text{CO}_2(g) )</td>
<td>213.6</td>
</tr>
</tbody>
</table>

(a) Calculate \( \Delta S^\circ \) for the reaction.

(b) Calculate the temperature at which the decomposition becomes thermodynamically feasible.

(c) As the temperature of the oil bath is increased, the volume of gas in the syringe increases. Sketch the shape of the graph you would expect to obtain if the volume of gas is plotted against temperature. Graph paper is not required. Start at room temperature and mark clearly the decomposition temperature on your graph.
37. The table below shows how the standard free energy change varies with temperature for the following reactions:

reaction A: \(2\text{Zn(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO(s)}\)
reaction B: \(2\text{C(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO(g)}\)

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>(\Delta G^\theta), reaction A/(\text{kJ mol}^{-1})</th>
<th>(\Delta G^\theta), reaction B/(\text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-615</td>
<td>-300</td>
</tr>
<tr>
<td>600</td>
<td>-595</td>
<td>-335</td>
</tr>
<tr>
<td>800</td>
<td>-555</td>
<td>-370</td>
</tr>
<tr>
<td>1000</td>
<td>-495</td>
<td>-405</td>
</tr>
<tr>
<td>1200</td>
<td>-425</td>
<td>-440</td>
</tr>
<tr>
<td>1400</td>
<td>-40</td>
<td>-475</td>
</tr>
<tr>
<td>1600</td>
<td>-260</td>
<td>-505</td>
</tr>
<tr>
<td>1800</td>
<td>-165</td>
<td>-540</td>
</tr>
</tbody>
</table>

(a) For each reaction, plot the graph of the standard free energy change against temperature.  
(b) Use your graph to:
   (i) determine the minimum temperature at which carbon can reduce zinc oxide  
   (ii) calculate the standard free energy change for this reaction at 1500K.  
(c) Give one advantage and one disadvantage of using carbon for this reduction on an industrial scale.

SY/ 92 (8)
38. Examine the Ellingham diagram below and answer the questions that follow.

(a) At what temperature does the thermal decomposition of zinc oxide become thermodynamically feasible? 1
(b) Write the balanced chemical equation for the reduction of zinc oxide using hydrogen. 1
(c) At what temperature does it become thermodynamically feasible to reduce zinc oxide using hydrogen? 1
(d) The melting point of zinc is approximately 700K. Explain, in terms of entropy, why the gradient of the graph changes at point A. 2
(e) From the graph, it is thermodynamically feasible to use hydrogen to reduce silver(I) oxide at all temperatures shown. Suggest why this reaction does not occur at room temperature. 1

SY/99

(6)
39. The diagram below shows the blast furnace for the extraction of iron from iron ore. An appropriate Ellingham diagram is also shown.

Iron ore (contains SiO₂ as impurity), limestone and coke

Waste gases (N₂, CO₂, CO)

Molten slag - contains mainly CaSiO₃

Molten iron

\[ \Delta G^\circ / \text{kJ mol}^{-1} \]

Temperature/K

\[ \begin{align*}
\text{Temperature/K} & \quad \text{Δ}G^\circ / \text{kJ mol}^{-1} \\
00              & \quad -600 \\
1000            & \quad -400 \\
1500            & \quad -200 \\
2000            & \quad 0 \\
\end{align*} \]
(a) Calculate the standard free energy change for the reduction of iron(II) oxide by carbon at 1900K.

(b) At what temperature will it be thermodynamically feasible for carbon monoxide to reduce iron(II) oxide?

(c) Explain why the reduction by carbon monoxide is more efficient than by carbon.

(d) Give a reason for adding limestone to the furnace.

(e) To achieve maximum economy, suggest a use for the waste gases.

---

The emf of the above cell operating under standard condition is 1.03 V.

(a) Calculate the standard reduction potential for the half-cell reaction:

\[ \text{M}^{2+}(aq) + 2e^- \rightarrow \text{M}(s) \]

(b) Calculate the free energy change for this cell operating under standard conditions.

(c) Why is a low resistance voltmeter not used to measure the emf of the cell?

(d) Name a solution which could be used in the salt bridge of the above cell.
41. When the above cell is operating under standard conditions, the reading on the voltmeter is 0.48 V.

a) Calculate the standard reduction potential for the half-reaction:

\[
\text{Co}^{2+}(aq) + 2e^- \rightarrow \text{Co(s)}
\]

b) Calculate the standard free energy change for this cell.

SY/98

(4)

42. Fuel cells are essentially devices for producing electricity from a combustion reaction. They consist of two electrodes and an electrolyte. Electrochemical reactions occur at the electrolyte/electrode interface, where chemical energy is converted directly into electrical energy. The electrodes catalyse the oxidation of the fuel and the reduction of the oxygen and they also function as interfaces between the reactants and the electrolyte.
Two types of fuel cell being developed for large-scale use, which use hydrogen and air as reactants, are described below.

1. The phosphoric acid fuel cell
The electrolyte is 95% phosphoric acid and the electrodes are carbon covered with platinum. The electrode half-reactions are:
$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \text{ and } H_2 \rightarrow 2H^+ + 2e^-$$

2. The alkaline fuel cell
The electrolyte is 30–70% potassium hydroxide and electrodes such as nickel, silver and platinum have been tried. The electrode half-reactions are:
$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \text{ and } H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$

A serious disadvantage of this cell is that the air must have carbon dioxide removed before use.

Fuel cells are clean (producing no toxic or corrosive substances) and silent, they contain no moving parts and are easily maintained. However, if fuel cells are to replace conventional power stations to generate electricity, these advantages must outweigh the two main disadvantages, namely:

(i) they are very expensive since the materials used in their manufacture must meet a high specifications
(ii) their efficiency is limited by the need to convert from direct to alternating current.

(a) Give a piece of information found in the passage above that suggests that fuel cell reactions are exothermic.

(b) Why must air have carbon dioxide removed from it before use as the oxidant in the alkaline fuel cell?

(c) The overall reaction is common to both cells. Show this by writing the appropriate equation.

(d) In the phosphoric acid fuel cell, the electrode is carbon covered with platinum. Give a reason for using this type of electrode.

(e) Fuel cells do not cause the pollution problems associated with conventional power generation. Give a specific example to justify this statement.
43. The reaction:
\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g}) \]

follows first-order kinetics with respect to both iodine and hydrogen. When this reaction was studied at different temperatures, the data shown in the table below were obtained. The data could be used to determine the activation energy for the forward reaction.

<table>
<thead>
<tr>
<th>Temperature/K</th>
<th>Rate constant/1 mol(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>556</td>
<td>(4.45 \times 10^{-5})</td>
</tr>
<tr>
<td>575</td>
<td>(1.37 \times 10^{-4})</td>
</tr>
<tr>
<td>629</td>
<td>(2.52 \times 10^{-3})</td>
</tr>
<tr>
<td>666</td>
<td>(1.41 \times 10^{-2})</td>
</tr>
<tr>
<td>700</td>
<td>(6.43 \times 10^{-2})</td>
</tr>
<tr>
<td>781</td>
<td>(1.34)</td>
</tr>
</tbody>
</table>

(a) Write the rate equation for the reaction.  
(b) Calculate the initial rate of reaction at 700K, if the initial concentrations of both iodine and hydrogen are 0.5 mol l\(^{-1}\).  
(c) The data shows that the rate constant increases with temperature. Explain this trend by sketching the distribution of kinetic energies among the reactant molecules at two different temperatures. Use the same set of axes for the two graphs and a single line to represent the energy of activation for the reaction.

44. The table below refers to the reaction between nitrogen monoxide and hydrogen at a temperature of:

\[ 1025K \text{2NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \]

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Initial concentration of NO/mol l(^{-1})</th>
<th>Initial concentration of H(_2)/mol l(^{-1})</th>
<th>Initial rate of formation of N(_2)/mol l(^{-1}) s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03</td>
<td>0.005</td>
<td>0.012</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>0.010</td>
<td>0.024</td>
</tr>
<tr>
<td>3</td>
<td>0.03</td>
<td>0.015</td>
<td>0.036</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.015</td>
<td>0.004</td>
</tr>
<tr>
<td>5</td>
<td>0.02</td>
<td>0.015</td>
<td>0.016</td>
</tr>
</tbody>
</table>
(a) Calculate the order of the reaction with respect to:
   (i) hydrogen
   (ii) nitrogen monoxide.
(b) Write the rate equation for the reaction.
(c) Calculate the rate constant, showing appropriate units.
(d) Copy the axes given (no graph paper required) and sketch a graph to show how the rate of the reaction varies with concentration of nitrogen monoxide (at constant concentration of H₂).

45. A set of experiments were carried out to investigate the reaction
    \[ A + B \rightarrow C. \]

The results are shown below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [A]/mol l⁻¹</th>
<th>Initial [B]/mol l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>
(a) Find the average rate of reaction for the first 2 minutes for each experiment.  

(b) Determine the order for A and B and deduce the rate equation for the reaction.  

(c) Calculate the rate constant for the reaction.  

---

46. Consider the reaction:  

\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \]

for which the rate equation has been shown by experiment to be:  

\[ \text{rate} = k[\text{NO}_2]^2 \]

The first stage of this two-stage reaction is the rate-determining step. The equation for this stage is:  

\[ \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g) \]

(a) Write the equation for the second stage, which completes the reaction.  

(b) The table gives kinetic data for the above reaction at constant temperature.  

<table>
<thead>
<tr>
<th>Relative [NO(_2)]</th>
<th>Relative [CO]</th>
<th>Relative rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>(x)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>(y)</td>
</tr>
</tbody>
</table>

Determine the values for \(x\) and \(y\) in the table.  

---

SY/96 (7)  

SY/98 (3)
47. Examine the reaction mechanism below.

\[
\begin{align*}
  & \text{fast} \quad \text{slow} \\
\text{A} + \text{B} & \rightarrow \text{C} \quad \text{step 1} \\
2\text{B} + \text{C} & \rightarrow \text{D} + \text{E} \quad \text{step 2} \\
\text{Overall:} & \quad \text{A} + 3\text{B} \rightarrow \text{D} + \text{E}
\end{align*}
\]

State how the rate of reaction depends on the concentrations of:

(a) \( A \)  
(b) \( B \).

SY/95  
(2)

48. Rate studies on the bromination of propanone in the presence of alkali give the rate equation:

\[
\text{rate} = k[\text{Br}_2]^1[\text{CH}_3\text{COCH}_3]^1[\text{OH}^-]^1
\]

(a) A mechanism proposed for this reaction is:

\[
\begin{align*}
\text{CH}_3\text{C} = \text{CH}_3 + \text{OH}^- & \rightleftharpoons \text{CH}_3\text{C} - \text{CH}_3 + \text{H}_2\text{O} \\
\text{Step 1} \\
\text{CH}_3\text{C} = \text{CH}_3 + \text{Br}_2 & \rightleftharpoons \text{CH}_3\text{C} - \text{CH}_3\text{Br} + \text{Br}^- \\
\text{Step 2}
\end{align*}
\]

Which of the two steps is likely to be the rate determining step? Explain your answer.

(b) Estimation of the bromine concentration was achieved by titration with sodium thiosulphate solution. The latter reacts with bromine, the colour of which gradually fades until it is pale yellow. At this point, a few drops of potassium iodide solution and starch are added. The titration is then completed.

(i) What would you observe on the addition of the potassium iodide and the starch? Explain your answer.

(ii) How would you know when the end-point of the titration was reached?

SY/92  
(5)
1. The reaction scheme shown below is an example of a chain reaction.

\[(i) \quad \text{Br}_2 \rightarrow 2\text{Br}^* \quad \text{initiation step}\]
\[(ii) \quad \text{C}_2\text{H}_6 + T \rightarrow \text{C}_2\text{H}_5^* + U\]
\[(iii) \quad V + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + W\]
\[(iv) \quad \text{Br}^* + \text{Br}^* \rightarrow X\]
\[(v) \quad \text{C}_2\text{H}_5^* + \text{C}_2\text{H}_5^* \rightarrow Y\]
\[(vi) \quad \text{C}_2\text{H}_5^* + Z \rightarrow \text{C}_2\text{H}_5\text{Br}\]

(a) Write down the species represented by the letters T to Z in the reaction scheme.

(b) In step (i), the initiation step, explain if the process is exothermic or endothermic.

(c) (i) What name is given to the process represented by steps (ii) and (iii)?
(ii) What name is given to the process represented by steps (iv) to (vi)?

(d) Why is the reaction shown referred to as a chain reaction?

2. The electronic arrangement for carbon is 1s²2s²2p².

(a) Based on this information alone, how many unpaired electrons will carbon have?

(b) Explain why carbon is able to form four bonds.

(c) The C–C bond strength is 346 kJ mol⁻¹ and the C=C bond strength is 602 kJ mol⁻¹. In terms of bonding types explain why the C=C bond is not twice as strong as the C–C bond.

(d) Draw a molecule of ethene showing all the overlapping atomic orbitals.
3. Haloalkanes are extremely versatile organic compounds and are widely used in syntheses and preparations, as indicated in the following flow diagram.

(a) Name the type of reaction involved in reactions • to „ .
(b) Why can haloalkanes take part in the type of reaction in (a)?
(c) How is the reagent OR– obtained from an alcohol?
(d) 1-bromopropane was used as the starting material for the preparation of carboxylic acids. Name the carboxylic acid formed:
   (i) via route „
   (ii) via route • .

4. Haloalkanes are suitable compounds from which to synthesise other compounds. The flow diagram below shows how different compounds can be prepared from 2-bromopropane.
(a) Draw the structural formula for 2-bromopropane.  

(b) Which single term is used to describe reagents X and Y?  

(c) The equation for the reaction that produces compound Q is:

\[
\text{\text{2C}_2\text{H}_5\text{OH}} \rightarrow \text{\text{H}—\text{C}—\text{O}—\text{C}—\text{H}} + \text{\text{H}_2\text{O}}
\]

To which class of organic compound does Q belong?  

(d) Draw the structural formula for an isomer of Q that belongs to a different homologous series.  

(e) Draw the structural formula for compound R.  

(f) Describe briefly how to distinguish between compounds Q and R.  

(g) Name the organic compound produced on oxidising compound P with acidified potassium dichromate solution.  

---

5. Consider the reaction sequence outlined below:

\[
\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{A}} \text{C}_2\text{H}_5\text{O} \quad \text{(I)} \\
\text{a secondary alcohol} \xrightarrow{\text{B}} \text{C}_3\text{H}_7\text{Cl} \quad \text{(II)}
\]

(a) Give the name of ion (I).  

(b) Name:  
   (i) reagent A  
   (ii) reagent B.  

(c) Draw the full structural formula for compound (II).  

---

SY/99 (7)  

SY/97 (4)
6. Study the organic reactions below.

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \quad \text{C}_2\text{H}_5\text{Br} \quad \text{CH}_2=\text{CH}_2 \\
\text{C}_2\text{H}_5\text{Br} & \quad \quad \downarrow \quad \quad \downarrow \\
\text{C}_2\text{H}_5\text{CN} & \quad \quad \downarrow \\
\text{C}_2\text{H}_5\text{COOH} & \quad \quad \downarrow \\
\text{C}_2\text{H}_5\text{COOCH}_3 & \quad \quad \downarrow \\
\text{C}_2\text{H}_5\text{COONH}_4 & \quad \quad \downarrow \\
\text{C}_2\text{H}_5\text{HO} &
\end{align*}
\]

The reagents necessary to bring about the conversions are numbered. Copy the numbers into your book and alongside each number put:

(a) the type of reaction occurring
(b) the appropriate reagent to bring about the conversion.

SY/90
(14)

7. Examine this organic reaction sequence:

\[
\begin{align*}
\text{C}_6\text{H}_5 & \xrightarrow{\text{concentrated nitric and sulphuric acids}} \text{C}_6\text{H}_4\text{O}_2\text{N} \quad \xrightarrow{\text{reduction}} \text{C}_6\text{H}_5\text{N}
\end{align*}
\]

(a) Give possible structural formulae for B and C.
(b) What type of reaction is involved in the conversion of A to B?

SY/91
(3)

8. A synthetic route to the analgesic compound D is shown below. The percentage yield for each step is given below each arrow.

\[
\begin{align*}
\text{A} \quad \text{B} \quad \text{C} \quad \text{D}
\end{align*}
\]

(a) The percentage yield for each step is given below each arrow.
(b) The type of reaction involved in each step.

SY/91
(3)
ORGANIC CHEMISTRY

(a) Name reactant A.  
(b) What nitrating mixture would be used to react with A in step 1?  
(c) Which type of reaction takes place in step 2?  
(d) Calculate the mass of analgesic that would be formed starting from 43.6 g of compound C.  
(e) Draw the structure of the organic compound formed when compound C is reacted with: 
   (i) dilute hydrochloric acid  
   (ii) sodium hydroxide solution.  

9. Benzene is one of the most important aromatic feedstocks in the chemical industry. It can be made during the catalytic reforming of the naphtha fraction from crude oil and separated from the mixture of products. The diagram below shows four of the industrially important synthetic routes from benzene.

(a) What do you understand by the term ‘catalytic reforming’?  
(b) The preparation of compound • can be achieved in a single step. Compounds , and † require more than one step in their preparation, but the first step involves the same type of reaction as that for the preparation of compound •. Name the type of reaction involved and name the type of organic compound used along with benzene.  
(c) Name the type of reaction involved in the conversion of benzene to compound ‡.  
(d) Compound • is used as a feedstock for making an important domestic product. Name the product.
(e) Compounds , and  are used in making plastics.
   (i) Draw the structure of part of a polymer made by
       linking three molecules of compound .  
       2
   (ii) Compound  reacts with methanal to form a plastic.
       Name the type of polymerisation involved.  
       1

SY/94  
(8)

10. Two aliphatic compounds A and B, which contain carbon, hydrogen
    and oxygen only, are isomers. They can both be oxidised as
    follows:

    \[
    \begin{align*}
    \text{A} & \xrightarrow{\text{oxidation}} \text{C} \\
    \text{B} & \xrightarrow{\text{oxidation}} \text{D}
    \end{align*}
    \]

    The table below shows the wavenumbers of the main absorptions in
    the infra-red spectra caused by the functional groups in
    compounds A to D between 1500 and 4000 cm\(^{-1}\) (absorptions
    caused by C–H bonds in alkyl components have been omitted).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Wavenumber(s)/cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3300</td>
</tr>
<tr>
<td>B</td>
<td>3350</td>
</tr>
<tr>
<td>C</td>
<td>2750, 1730</td>
</tr>
<tr>
<td>D</td>
<td>1700</td>
</tr>
</tbody>
</table>

In answering the following questions, you are advised to consult
the data on page 13 of the Data Booklet.

(a) Examine the table above and identify the functional groups
    present in:
    (i) A and B
    (ii) C
    (iii) D.  
    3

(b) Describe a chemical test you could use to provide support
    for your answers to (ii) and (iii) of (a).  
    3

(c) Compound C will undergo further oxidation to produce
    compound E. Estimate the wavenumbers of the main infra-
    red absorptions caused by the functional groups in
    compound E (only those between 1500 and 4000 cm\(^{-1}\)).  
    2

SY/93  
(8)
11. Compound X contains, by mass, 69.77% carbon, 11.63% hydrogen and 18.60% oxygen and has a relative molecular mass of 86.

Compound X is a neutral, colourless liquid that reacts slowly with sodium to produce hydrogen gas. X does not immediately decolourise bromine water but decolourises acidified potassium permanganate solution, producing compound Y.

Y reacts with 2,4-dinitrophenylhydrazine to produce a bright yellow solid. This yellow solid can be purified by recrystallisation from hot ethanol. The infra-red spectra of X and Y are shown below.

![Infra-red spectrum of compound X](image1)

![Infra-red spectrum of compound Y](image2)
(a) Calculate the empirical (simplest) formula for compound X. 2
(b) Which functional group is present in compound X? 1
(c) Write the molecular formula for compound X and give its systematic name. 2
(d) Which functional group, not present in X, is responsible for a major absorption peak in the infra-red spectrum of Y? 1
(e) Draw the structural formula for Y. 1
(f) Identify an impurity that may have been removed from the yellow solid by the process of recrystallisation. 1

12. Grignard reagents have the general formula RMgX, where R = an alkyl group and X = a halogen atom. Preparation involves reacting an alkyl halide with magnesium in dry ethoxyethane (an ether) to prevent hydrolysis occurring. The Grignard reagent methyl magnesium iodide, CH₃MgI, was reacted with carbon dioxide:

\[ \text{CH}_3\text{MgI} + \text{CO}_2 \rightarrow \text{CH}_3\text{COOMgI} \]

This was followed by hydrolysis with dilute sulphuric acid.

\[ \text{CH}_3\text{COOMgI} + \text{H}_2\text{O} \rightarrow \text{Y} + \text{Mg(OH)}\text{I} \]

The organic product Y dissolves in the ether and the magnesium compound dissolves in the dilute acid, giving two immiscible layers.

(a) Suggest how Y can be isolated. 1
(b) Give one advantage and one disadvantage of using an ether as a solvent for chemical reactions. 2
(c) The infra-red spectrum for a pure sample of Y shows a broad absorption band in the range 3500–2500 cm⁻¹ and at least one other characteristic absorption band, apart from those due to C–H bonds. Use the information above and on page 13 in the Data Booklet to:
   (i) identify Y 1
   (ii) suggest the wavenumber range of the other main absorption band. 1
(d) Explain why in a Grignard reagent the methyl group acts as a nucleophile, whereas in methyl iodide the methyl group acts as an electrophile.

SY98

13. Essential fatty acids are found in plant sources. They are always cis-isomers. Trans fatty acids tend to interfere with metabolic processes, since these are usually based on enzymes.

(a) (i) Name the structural feature in fatty acids that gives rise to these stereoisomers.
(ii) What name is given to this kind of stereoisomerism?
(b) (i) Using a suitable notation, show the structural arrangement of these two isomers.
(ii) Explain why the structural feature in (a) (i) leads to isomerism.
(c) Explain why trans fatty acids interfere with metabolic processes.

14. A simple test such as determining the melting point can help to distinguish between different isomers, e.g. between pentane and 2,2-dimethylpropane or between maleic acid and fumaric acid.

(a) (i) Draw the structural formulae for pentane and 2,2-dimethylpropane.
(ii) Use these structures to help explain which isomer will have the higher melting point.
(b) 

(i) What are the systematic names for maleic acid and fumaric acid?
(ii) By referring to their shapes explain which isomer has the higher melting point.
15. Glucose and fructose both contain six carbon atoms

(a) Only four of the carbon atoms in glucose are chiral. Identify the two carbon atoms that are achiral. 1

(b) How many carbon atoms in fructose are achiral? 1

16.

(a) (i) Name this molecule. 1
(ii) Name the straight-chain isomer. 1

(b) Does the molecule shown have an optically active carbon? Explain your answer. 2

(c) Draw the structural formula for a molecule that has one more carbon atom than the above molecules and also has a chiral carbon atom. 1

17. Lactic acid, \( \text{CH}_3\text{CH(OH)COOH} \), extracted from milk, was found to rotate the plane of polarised light, but another sample of lactic acid, which was synthesised in the laboratory, did not affect polarised light.

(a) Give a systematic name for lactic acid. 1

(b) (i) Draw the full structural formula for lactic acid. 1
(ii) Place an * on the carbon atom that is said to be asymmetric (i.e. the chiral centre).

(c) Explain why the sample synthesised in the laboratory was not optically active.

18. (a) Draw the structures of two isomers of butan-2-ol that are non-superimposable mirror images.
(b) In comparing these isomers what difference would you expect in:
   (i) physical properties (e.g. melting points)
   (ii) chemical properties (e.g. ease of oxidation)
(c) A solution of one of these isomers was found to rotate plane polarised light to the left by 10°.
   (i) What rotation would you expect for a solution of the same concentration of the other isomer in the same polarimeter tube?
   (ii) Suggest a reason why a bought sample of butan-2-ol was found to be optically inactive.

19. Stereoisomerism includes both geometric isomerism and optical isomerism.
(a) Which of the above types of isomer can be studied in a polarimeter?
(b) Give the essential structural requirements for a substance to exhibit:
   (i) geometric isomerism
   (ii) optical isomerism
(c) Identify a suitable substance from those given on the next page to illustrate:
   (i) geometric isomerism
   (ii) optical isomerism.
20. Ants release chemicals to send warnings to fellow members of the colony. Two of these chemicals are:

\[ \text{C}_2\text{H}_5\text{CH} = \text{CHCH}_2\text{CHO} \quad \text{and} \quad \text{C}_2\text{H}_5\text{CH(}\text{CH}_3\text{)COC}_2\text{H}_5 \]

(a) Describe two tests that could be used to distinguish molecule A from molecule B.

(b) Molecule A can exist in two structural isomers. Draw these two structures and name each one.

(c) (i) Explain, with the help of a structural formula, why molecule B is optically active.

(ii) Explain why the same chemical as molecule B made in the laboratory by oxidising the corresponding secondary alcohol would not be likely to be optically active.
21. (a) Provide words or formulae to correspond with (i) to (vi). 6
(b) Draw the structural isomer of 1,2-dichloroethane. 1
(c) Draw the geometric isomers of but-2-ene. 1
(d) Draw a structural formula for the lightest alkane molecule containing a chiral carbon atom. 1

22. 0.315 g of an organic compound containing C, H and O was completely burned in oxygen and was found to produce 0.630 g of carbon dioxide and 0.258 g of water. Calculate the empirical formula for this compound. 4
23. A sample of a compound was known to be a short-chain alkanol. The sample was treated as follows:

- sample burned in excess oxygen.
- the gases passed through a tube packed with CaCl₂
- remaining gases passed through concentrated KOH solution.

Experimental results:
(i) 0.508 g sample burned
(ii) CaCl₂ tube increased in mass by 0.610 g
(iii) Volume of gas reduced by 610 cm³ on passing through the KOH(aq).

The molar volume on the day of the experiment was 24.0 litres.

(a) Use the experimental results to identify the alkanol. 5
(b) State why this experiment is best carried out in duplicate. 1

24. The mass spectrum of a molecule of empirical formula \( \text{CH}_4\text{O} \) is shown below.

(a) Suggest a formula for an ion for each peak in the above spectrum. 2
(b) What is measured by the peak height in the above spectrum? 1
(c) Occasionally two electrons can be removed from each fragment produced. Where will these peaks appear in the mass spectrum? 1
25. When an organic compound is passed through a mass spectrometer some of its molecules are broken down into fragments. The simplified mass spectrum of an organic compound is shown below.

![Mass spectrum graph]

The molecule was known to be either:

(a) Suggest which fragments of the molecule could be responsible for each peak in the mass spectrum.  
(b) By referring to your answer in part (a) decide which of the molecules could have given rise to the spectrum. Explain your choice.

26. After chlorinating benzene a sample of the product was subjected to mass spectral analysis:

![Mass spectrum graph]
(a) Draw the structure of the product. Give a reason for your answer.  
(b) There is evidence for two isotopes of chlorine in the sample. Identify this evidence.  
(c) By reference to the above spectrum, state what is meant by a molecular ion.  
(d) The most intense fragment ion occurs at 77.  
   (i) What is a fragment ion?  
   (ii) What evidence is there that the ion at 77 contains no chlorine?  
   (iii) Suggest a formula for the ion at 77. 

27. If a very thin sample of an organic compound is subjected to energy from the infra-red region of the electromagnetic spectrum, specific frequencies of radiation are absorbed. 

   (a) What kind of movement is induced in the molecules when infra-red radiation is absorbed?  
   (b) What can be deduced about a molecule by examining its infra-red spectrum?  
   (c) How could infra-red be used to show that a sample produced after distillation was pure? 

28. (a) Nuclear magnetic resonance (NMR) spectroscopy is a non-destructive method of analysis. Explain what is meant by this statement.  
   (b) Name another non-destructive method of analysis.  
   (c) Can the technique of atomic absorption spectra be classified as non-destructive? Explain your answer. 

29. NMR, infra-red and colorimetry involve absorption of energy by samples. What part of the electromagnetic spectrum does each involve? 

30. The hydrogen atoms in a molecule spin about their axes.  

   (a) What property does this confer on these atoms that is useful in NMR analysis?
(b) If a magnetic field is applied to the molecule then these hydrogen atoms take up one of two orientations.
   (i) Describe these orientations.  
   (ii) Explain which of these is of lower energy.
(c) Electromagnetic energy (high frequency radio waves) is now applied and many of the hydrogen atoms ‘flip’.
   What is meant by ‘flip’?
(d) Since more atoms started in the lower energy state there is a net energy change. Explain whether this is absorption or an emission of energy.
(e) The immediate surroundings of the hydrogen atoms in the molecule will determine whether it flips or not at a certain radio frequency. The NMR spectrum of the molecule consists of a number of peaks.
   (i) What can be deduced from the positions of the peaks?
   (ii) What can be deduced from the areas of the peaks?

31. Tetramethylsilane (TMS) is used as a reference in proton NMR.
   (a) How many hydrogen atoms are there in TMS?
   (b) All the hydrogen atoms in TMS are said to be in the same chemical environment. Explain.
   (c) What is the numerical value of the chemical shift for the peak(s) produced by TMS?

32. The $^1$H NMR spectrum of ethanol (C$_2$H$_5$OH) is shown below.

![NMR Spectrum Diagram]
a) Which chemical produced the peak named TMS and what is its purpose?  

b) Give two reasons for the chemist deciding that peak C was due to the CH₃ group.  

c) Link peaks A and B to the hydrogen atoms in ethanol. (Give two reasons in each case.)

33. A hydrocarbon liquid, of empirical formula C₈H₁₀, was subjected to ¹H NMR analysis:

(a) What is peak D?  
(b) (i) What name is given to the line above each peak?  
     (ii) How do the values shown relate to the number of hydrogens in the molecule?  
(c) Suggest a structural formula for the molecule and justify your choice.

34. An alcohol has a molecular formula of C₃H₈O.

(a) Suggest two possible isomeric structures for this compound  
(b) The ¹H NMR spectrum for one isomer showed four peaks.  
     (i) Which isomer does this indicate?  
     (ii) How many peaks would the other isomer have?  
     (iii) Comment on the relative integrals (i.e. the areas under the peaks).
35. An $^1\text{H}$ NMR spectrum was recorded for each of these straight-chain hydrocarbons: $\text{CH}_4$, $\text{C}_2\text{H}_6$, $\text{C}_3\text{H}_8$ and $\text{C}_4\text{H}_{10}$.

(a) (i) Which of the compounds would show only one peak?  
(ii) Explain your choice by reference to all the structural formulae.

(b) How many peaks would you expect for both the isomers of $\text{C}_4\text{H}_{10}$?

(c) A compound of formula $\text{C}_4\text{H}_{12}$ also shows only one peak. Suggest a structural formula for this isomer.

36. The following electron density map was obtained from an aromatic compound with molecular formula $\text{C}_6\text{H}_3\text{Cl}_3\text{O}$.

(a) Explain why the hydrogen atoms do not show up clearly in the electron density map.

(b) Draw the full structural formula for this compound.

(c) Draw the electron density map that would be obtained for methanoic acid.
37. In the late 1950s and 1960s, Dorothy Hodgkin was the first person to unravel the structures of big molecules like vitamin B12 (still injected as a cure for pernicious anaemia) and insulin (a molecule with over 800 atoms).

(a) What technique did she pioneer in solving these structures?
(b) Suggest a reason why it was a breakthrough to know the structure of vitamin B12.
(c) (i) In what way would a carbon atom differ from a chlorine atom in an electron density map?
(ii) Explain why hydrogen atoms cannot be easily detected by this technique.
(d) The electron density map for an organic molecule is shown below.

(i) Suggest the structural formula for this molecule.
(ii) State where the nuclei of the carbon atoms are to be found in the above diagram.
(iii) Draw a similar diagram for the molecule monochlorobenzene.

38. Some medicines operate by binding to receptors. Such medicines can act as agonists or antagonists.

(a) What type of molecule is a receptor and where is it normally situated?
(b) What function does a receptor have?
(c) What effect does an agonist have when it binds to a receptor?
(d) What effect does an antagonist have when it binds to a receptor?
39. In 1997, aspirin (acetyl salicylate) was 100 years old. All the compounds shown below are related in structure to aspirin and have the ability to relieve pain.

Identify the pharmacophore that is responsible for the pain-killing effect.  

40. When designing a drug for a particular illness, chemists normally start from a molecule that is already pharmacologically active. This molecule can be modified to make derivatives, which are exhaustively tested.

(a) Explain the terms in bold type.  
(b) By comparing the derivatives that are pharmacologically active, the pharmacophore can be identified. Explain.  
(c) Suggest how these derivatives may be ‘exhaustively tested’.  

41. Drug discovery in the first half of the twentieth century owed much to good fortune and good observation. For example, sulphonamides were discovered when it was found that certain dyes had antibacterial activity. Penicillin was discovered when Alexander Fleming returned from holiday and noticed a fungal contaminant on an old petri dish had antibacterial activity. Since the Second World War, thousands of sulphonamide derivatives and penicillin derivatives have been made. Moreover, completely new antibacterial drugs have been discovered from a variety of sources.

(a) Suggest examples of the ‘variety of sources’ that have provided new antibacterial drugs.  
(b) (i) State what is meant by the term ‘pharmacophore’.  
(ii) Explain why it is possible to make thousands of sulphonamide derivatives all having antibacterial activity.
42. Thalidomide was marketed as a non-addictive sedative for pregnant women in the 1950s. It was banned in 1961 when it was discovered that one optical isomer of the drug led to severe deformities in the foetus.

(a) Identify the chiral center in the thalidomide molecule with an asterisk (you need copy only a small part of the molecule).

(b) Suggest an additional aspect to drug testing that has since been introduced.

43. Many drugs fit into complex receptor sites around the body, just like keys fitting into locks.

(a) What analytical technique is used to find the structural features in the receptor?

(b) (i) What name is given to the active part of the drug?
(ii) State why the shape of the drug molecule is important.

(c) Computers can reduce the time and hence the cost of finding suitable drugs. Suggest two facilities that computers possess that are helpful.

44. Enzymes are biological catalysts that are so specific that most organisms contain thousands of different enzymes.

(a) What is meant by ‘specific’ in this context?

(b) Enzymes are globular proteins, each of which has a characteristic notch or groove on its surface called the active site.

(i) Explain the significance of the surface shape of an enzyme on its ability to act as a catalyst.
(ii) Explain why an enzyme can continue to act as a catalyst time after time.
1. The diagram below represents a section of the line emission spectrum for hydrogen.

(a) If the spectrum of hydrogen is viewed through a spectroscope only one set of lines is seen.
   (i) Why is this? 1
   (ii) Which series is seen? 1

(b) Explain how any particular line in this spectrum is produced. 3

(c) The last line or convergence limit of the Lyman series has a wavenumber of approximately $11 \times 10^6$ m$^{-1}$. Using the data on page 19 of the Data Booklet, calculate the energy equivalent of this in kJ mol$^{-1}$. 3

(d) What does the energy referred to in (c) correspond to? 1

SY/82
(9)

2. (a) The ions Na$^+$, F$^-$, Mg$^{2+}$ and O$^{2-}$ are isoelectronic.
   (i) Write in full orbital notation the electron configuration of these ions. 1
   (ii) Identify another chemical species with this electron configuration. 1

(b) (i) State Hund’s rule of maximum multiplicity. 1
(ii) The first ionisation energies of carbon, nitrogen and oxygen are listed on page 10 of the Data Booklet. Explain how these provide evidence that Hund’s rule applies to the electron configuration of these elements. 2

SY/80
(5)
3. (a) State what is meant by:
   (i) the principle quantum number of an electron
   (ii) degenerate orbitals.

(b) The electron configurations of magnesium and phosphorus are:

Mg: \[1s^2 2s^2 2p^6 3s^2 3p^2\]

P: \[1s^2 2s^2 2p^6 3s^2 3p^3\]

In a magnesium atom the two electrons in the third level occupy the same orbital, whereas in a phosphorus atom the three electrons in the 3p orbitals occupy separate orbitals. Account for this difference.

4. (a) The electron configuration of an aluminium atom may be written:

\[1s^2 2s^2 2p^6 3s^2 3p^1\]

Write the corresponding electron configuration for the Ti\(^{3+}\) ion.

(b) The graphs below show the first four ionisation energies for aluminium and titanium.

Why is there a sharp increase in the graph for aluminium but only gradual increases in the graph for titanium?
5. Wafers of silicon are used to make semiconductors. Precise areas on the surface of a wafer have their electrical characteristics changed by bombarding the spot with ions. Give the type of semiconductor that would be created:
   (a) when gallium has been implanted 1
   (b) when antimony has been implanted. 1

6. At the present time only a tiny fraction of our energy use comes from solar cells. Two major sources of fuel for producing electrical energy are fossil fuels and nuclear fuels.

   (a) Give **one** disadvantage of each of the energy sources mentioned compared to solar cells. 2
   (b) Name **four** elements used in the manufacture of solar cells. 2
   (c) (i) Describe how these elements can be used to create a p–n junction. 3
   (ii) Describe the effect of sunlight on a p–n junction. 2
   (iii) What name is given to this effect? 1

7. Crystals of caesium chloride and sodium chloride have different structures. The unit cell for sodium chloride is shown below.

   (a) Draw a sketch of the unit cell of caesium chloride. 1
   (b) The sodium chloride structure is said to have a co-ordination of 6:6.
      (i) What is the co-ordination of caesium chloride? 1
      (ii) Explain how these numbers are derived. 1
(c) Why does caesium chloride not take up the same structure as sodium chloride?  
(d) Use suitable data from the Data Booklet to predict which of these two structures potassium fluoride is most likely to take up. Explain your choice.  

8. Consider the following data concerning the compounds aluminium chloride and magnesium chloride.

<table>
<thead>
<tr>
<th></th>
<th>Aluminium chloride</th>
<th>Magnesium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Action of heat</td>
<td>Sublimes at 453K</td>
<td>Melts at 1690K</td>
</tr>
<tr>
<td>Relative molecular  mass (vapour phase)</td>
<td>267</td>
<td>95</td>
</tr>
<tr>
<td>Action with water</td>
<td>Reacts (hydrolysed)</td>
<td>Dissolves</td>
</tr>
</tbody>
</table>

(a) Use the above data to deduce the type of bonding in  
  (i) aluminium chloride  
  (ii) magnesium chloride.  
(b) Give the formula for aluminium chloride in the vapour phase.  
(c) Write a balanced equation for the reaction between aluminium chloride and water.  

9. (a) Copy and complete the following table.

<table>
<thead>
<tr>
<th>Type of bonding</th>
<th>Lithium hydride</th>
<th>Hydrogen bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effect on moist pH paper</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(b) Write the ion–electron equation for the reaction at the positive electrode when each of the following is electrolysed:
(i) molten lithium hydride
(ii) a molar aqueous solution of hydrogen bromide.

10.

\[ \begin{array}{c}
2p \\
2s \\
1s
\end{array} \]

The electron configuration of an oxygen atom may be represented as shown above.
(a) Explain how this structural representation agrees with:
   (i) the Pauli exclusion principle
   (ii) Hund’s rule of maximum multiplicity.
(b) The 2p orbitals are degenerate.
   (i) What does this mean?
   (ii) How do the 2p orbitals differ from each other?
(c) The electron configuration of oxygen may also be represented as:
   \[ 1s^22s^22p^4 \]

Write the electron configuration of the Mn\(^{2+}\) ion in this way.

11. (a) The d orbitals in an isolated ion or atom of a transition metal are degenerate. As soon as an ion is surrounded by ligands, these orbitals are no longer degenerate but are split into two groups having different energies. In complex ions with an octahedral arrangement of ligands, \([MX_n]^n\)\(^-\), the relative energies of the d orbitals are as shown below (M = transition metal, X = ligand, \(n = \) charge on the complex ion).

The energy difference, \(\Delta\), between the two groups of d orbitals depends on the ligand X. The splitting ability of
some ligands has been observed to be as follows:

\[ \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- \]

The colour of many transition metal complex ions can be explained by electronic transitions between the two sets of d orbitals.

(i) Explain why \([\text{Fe(H}_2\text{O)}_6]^2+\) is green.

(ii) Predict the colour of \([\text{Fe(CN)}_6]^{4-}\), giving reasons for your answer.

(b) Substances that are weakly attracted by a magnetic field are called paramagnetic substances. Paramagnetism is caused by the presence of unpaired electrons, as there is a small magnetic field created by a single spinning electron. \(\text{Fe(II)}\), which is present in both \([\text{Fe(H}_2\text{O)}_6]^2+\) and \([\text{Fe(CN)}_6]^{4-}\), has six d electrons. Of these two complex ions, only \([\text{Fe(H}_2\text{O)}_6]^2+\) is paramagnetic. Using d orbital diagrams, similar to the one above, show the d electron arrangements of \(\text{Fe(II)}\) in each of these two complex ions and suggest why one complex ion is paramagnetic while the other is not.

12. Iodine can have a number of oxidation states in different compounds. Iodine monochloride, \(\text{ICl}\), can be obtained as a dark red oily liquid by passing dry chlorine gas over solid iodine:

\[ \text{I}_2(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{ICl(l)} \]  \hspace{1cm} (reaction A)

If excess chlorine gas is used, the iodine monochloride is converted into iodine trichloride, \(\text{ICl}_3\). This is formed as a yellow crystalline solid:

\[ \text{ICl(l)} + \text{Cl}_2(\text{g}) \rightarrow \text{ICl}_3(\text{s}) \]  \hspace{1cm} (reaction B)

The iodine trichloride reacts with water as shown in the equation:

\[ 2\text{ICl(s)} + 3\text{H}_2\text{O(l)} \rightarrow 5\text{HCl(g)} + \text{ICl(l)} + \text{HIO}_3(\text{aq}) \]  \hspace{1cm} (reaction C)

Iodine trichloride also reacts with anhydrous sodium chloride to form the compound \(\text{NaICl}_4\):

\[ \text{NaCl(s)} + \text{ICl}_3(\text{s}) \rightarrow \text{NaCl}_4(\text{s}) \]  \hspace{1cm} (reaction D)
EXTRA QUESTIONS

(a) Calculate the oxidation states of the iodine in:
   (i) $\text{ICl}_3$
   (ii) $\text{HIO}_3$.

(b) (i) Which one of the four reactions A, B, C, D is not a redox reaction?
   (ii) Give another name for the reaction between $\text{ICl}_3$ and water.

(c) The ion $\text{ICl}_4^-$ is formed in reaction D:
   (i) Name this ion.
   (ii) Draw the shape of this ion.

13. The following diagram shows the simplified visible spectra of two complex ions. The complex ions are in aqueous solutions of equal concentration.

The $[\text{CoCl}_4]^{2-}$ solution has an intense (deep) blue colour while the $[\text{Co(H}_2\text{O)}_6]^{2+}$ solution has a much less intense (pale) pink colour. The hexaaquacobalt(II) ion can be converted into $[\text{Co(NH}_3)_6]^{2+}$ by the addition of excess ammonia solution. A solution of this new ion has an intense (deep) red colour.

In answering the following questions, you are advised to consult the data on page 15 of the Data Booklet.

(a) Why can chloride ions, water and ammonia molecules act as ligands?

(b) Name the ions:
   (i) $[\text{CoCl}_4]^{2-}$
   (ii) $[\text{Co(NH}_3)_6]^{2+}$. 
14. A textbook has the following two short paragraphs as part of a description of the Haber process:

Molecules of H₂ and of N₂ stick to the surface of the iron catalyst. Here they split up into atoms (of H and N), which then recombine as NH₃.

The catalyst is made by reducing an oxide of iron with synthesis gas in such a way that the final product has a porous surface consisting of tiny crystals. Promoters are included before the reduction to prevent larger crystals of iron forming.

(a) Which word do chemists use to mean 'stick to the surface'?

(b) (i) What is the electronic configuration of iron?

(ii) With reference to a specific group of orbitals, explain the way iron works as a catalyst.

(c) (i) What advantage is gained by the catalyst having a porous surface?

(ii) Why would larger crystals of iron be a disadvantage?

15. Among simple compounds, the oxides probably show most regular trends as we move across a row in the Periodic Table. In what sense can aluminium oxide be said to be intermediate in properties between the oxides of sodium and sulphur?

16. Excess iron(III) nitrate was added to 40.0 cm³ of 0.10 mol l⁻¹ potassium iodide solution and the iodine formed was titrated with sodium thiosulphate solution. The volume required for complete reaction was 15.0 cm³. The reaction can be represented by the equation:

\[ 2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq) \]

(a) Write the redox equation for the reaction between iron(III) ions and iodide ions.
17. In an experiment to find the percentage of iron ore, 2.650 g of ore was dissolved in hydrochloric acid. A powerful oxidising agent was then added and the solution diluted to 250 cm$^3$ in a standard flask. 25.0 cm$^3$ of this solution was then transferred to a conical flask and when a few drops of ammonium thiocyanate solution were added, a red colour appeared. The solution was titrated with 0.10 mol l$^{-1}$ titanium(III) sulphate solution until the red colour just disappeared. The titration results were as follows.

<table>
<thead>
<tr>
<th>Titre/cm$^3$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>22.65</td>
</tr>
<tr>
<td>3</td>
<td>22.60</td>
</tr>
<tr>
<td>4</td>
<td>22.65</td>
</tr>
</tbody>
</table>

Note: titanium(III) is a powerful reducing agent, itself being oxidised to titanium(IV).

(a) In what oxidation state is the iron when the thiocyanate complex is red? 
(b) Write the ion–electron half-equations for the reactions that occur during the titration. 
(c) (i) What volume of titanium(III) sulphate solution should be used for any calculation? Explain your answer. 
(ii) Calculate the percentage of iron in the ore.

18. The Haber process is represented by the equation:

$$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H^\circ = -92 \text{ kJ mol}^{-1}$$

2.0 mol of each reactant were allowed to react and come to equilibrium in a 1 litre container at 400K. At equilibrium, 0.4 mol of ammonia was formed.
(a) Write the expression for the equilibrium constant, \( K \), for this reaction.  
(b) Calculate:  
(i) the equilibrium concentrations of both nitrogen and hydrogen  
(ii) the value of the equilibrium constant at this temperature.  
(c) Explain what will happen to the value of \( K \), if the temperature is now raised to 600K.

19. Consider the equilibrium:

\[
2\text{HI}(g) \rightleftharpoons \text{H}_2(g) + \text{I}_2(g) \quad \Delta H^\circ = +12.5 \text{ kJ (left → right)}
\]

When 1 mol of hydrogen iodide is put into a litre container at 713K, 0.78 mol of hydrogen iodide is present at equilibrium.

(a) Write an expression for the equilibrium constant, \( K \).  
(b) Calculate the value of the equilibrium constant at 713K.  
(c) State the effect on the value of the equilibrium constant of:  
(i) increasing the temperature at constant pressure  
(ii) increasing the pressure at constant temperature.  
(d) At the same temperature, the standard free energy change, \( \Delta G^\circ \), for the dissociation of hydrogen bromide is more positive than that for the dissociation of hydrogen iodide. What does this information allow you to say about the equilibrium constant at this temperature for the equilibrium below?

\[
2\text{HBr}(g) \rightleftharpoons \text{H}_2(g) + \text{Br}_2(g)
\]

20. (a) What is meant by the term ‘partition coefficient’?  
(b) Will a change in temperature alter this relative concentration?  
(c) The following results were obtained in an experiment to measure the partition coefficient of ammonia between water and cyclohexane.
EXTRA QUESTIONS

<table>
<thead>
<tr>
<th>NH₃(aq)/mol 1⁻¹</th>
<th>0.081</th>
<th>0.11</th>
<th>0.16</th>
<th>0.31</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃(cyclohexane)/mol 1⁻¹</td>
<td>0.00026</td>
<td>0.00035</td>
<td>0.00052</td>
<td>0.001</td>
</tr>
</tbody>
</table>

(i) Calculate the partition coefficient for the system.

(ii) Suggest how the experimental data could have been obtained.

(d) The partition coefficient for the distribution of ammonia between water and ether was found to be 29, i.e.:

$$K = \frac{[\text{NH}_3 \text{ (aq)}]}{[\text{NH}_3 \text{ (ether)}]} = 29$$

(i) Which of the two named solvents is the better solvent for ammonia?

(ii) In terms of structure and bond type explain your answer.

(c) What value will a partition coefficient have if a solute is equally soluble in both solvents?

(f) Explain why water and ethanol cannot have a partition coefficient quoted for sodium chloride, despite the fact that salt is soluble in water and slightly soluble in ethanol.
Two samples (duplicates) of the colouring from a soft drink were investigated using paper chromatography. The sketch shows the chromatogram produced. The colouring appears to be composed of two dyes.

(a) Why is pencil, rather than pen, a good choice for drawing the base line?
(b) Calculate the $R_f$ value of both the coloured species.
(c) State two changes the operator might apply, each of which might improve the separation of the component spots while still using the same type of paper.
(d) Can you be certain that the original sample only contains two dyes? Explain your answer.
(e) Suggest a reason why the spots from sample 2 are fainter than those from sample 1.
22. (a) Give a definition of a base, according to the Brønsted–Lowry theory.

(b) (i) Identify the base in the following reaction, according to the Brønsted–Lowry theory:

\[ \text{HNO}_3(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \leftrightharpoons \text{CH}_3\text{COOH}_2^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \]

(ii) Identify the conjugate base in the above reaction.

23. When a pH electrode and ammeter are used to follow the titration between solutions of sodium hydroxide and methanoic acid, the following pH graph is obtained.

(a) Which one of the letters A to F corresponds to the point where the alkali is completely neutralised?

(b) Which of the following indicators could be used to detect the neutral point?

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>3.0–4.4</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.2–6.3</td>
</tr>
<tr>
<td>Phenol red</td>
<td>6.8–8.4</td>
</tr>
<tr>
<td>Alizarin yellow</td>
<td>10.0–12.0</td>
</tr>
</tbody>
</table>

(c) If the titration is stopped between E and F, the resulting solution acts as a buffer.

(i) Why can this solution act as a buffer?

(ii) Explain how the pH of the buffer solution remains constant when a little more acid is added.
24. A technician read the following information on a bottle of concentrated ammonia.

Density = 0.88 g cm\(^{-3}\)
Percentage of pure ammonia by mass = 28

(a) Calculate the concentration of the ammonia solution, in mol l\(^{-1}\).

(b) Why is concentrated ammonia solution not suitable for use as a primary standard?

(c) The table below shows the pK\(_a\) values for some acid–alkali indicators.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pK(_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromocresol green</td>
<td>4.7</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>7.0</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Choose the indicator most suitable for use in the titration of hydrochloric acid against ammonia solution. Explain the reason for your choice.

SY/92
(6)

25. A 12 V car battery has six electrochemical cells, consisting of lead electrodes in sulphuric acid, connected in series. The reactions that occur at the electrodes in each cell are:

\[
Pb(s) \rightarrow Pb^{2+}(aq) + 2e^- \quad E^o = +0.13 \text{ V} \\
PbO_2 + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l) \quad E^o = +1.47 \text{ V}
\]

(a) When a cell is operating under standard conditions, determine:
   (i) the potential difference (emf) expected from the cell
   (ii) the standard free energy change for the cell reaction

(b) Suggest why, in practice, the potential difference (emf) obtained from each cell in the battery is different from your answer to (a)(i).

(c) If the battery is discharged for too long, a white precipitate forms around each electrode. Name the white precipitate.

SY/97
(6)
26. (a) Although magnesium ores are very abundant in the earth's crust, the very high reactivity of magnesium makes it difficult to extract. During the Second World War, magnesium was manufactured by reduction of its oxide by carbon:

\[
\text{MgO} + \text{C} \rightleftharpoons \text{CO} + \text{Mg}
\]

Examine the Ellingham diagram below and answer the questions that follow.

- **(i)** In what temperature range is the above process thermodynamically feasible?  
- **(ii)** Describe two problems that the operation of the process at this temperature would present.  
- **(iii)** Use the Ellingham diagram to calculate \(\Delta G^\circ\) for the production of magnesium in the following reaction:
  \[
  2\text{MgO} + \text{Si} \rightleftharpoons \text{SiO}_2 + 2\text{Mg} \text{ at 1500K}
  \]

(b) In industry, the extraction of magnesium from magnesium oxide using silicon involves two modifications:
- a mixture of calcium oxide and magnesium oxide is used, and the calcium oxide reacts with the silicon oxide produced.
  \[
  \text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 \quad (\Delta G^\circ = -92\text{kJ mol}^{-1} \text{ at 1500K})
  \]
- the gaseous magnesium formed is continually removed from the reaction mixture.
Use this information to answer the questions below.

i) Calculate $\Delta G^\circ$ for the reaction:
\[
\text{CaO + 2MgO + Si} \rightarrow \text{CaSiO}_3 + 2\text{Mg}
\]
at 1500K

ii) Explain why the removal of magnesium from the reaction mixture helps the process.

SY/95

(7)

27. The data shown in the table below apply at 298K.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_f/\text{kJ mol}^{-1}$</th>
<th>$S^\theta/\text{J K}^{-1}\text{mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$Cl(s)</td>
<td>$-315.0$</td>
<td>$94.6$</td>
</tr>
<tr>
<td>NH$_3$(g)</td>
<td>$-46.2$</td>
<td>$193.0$</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>$-92.3$</td>
<td>$187.0$</td>
</tr>
</tbody>
</table>

The thermal decomposition of ammonium chloride is represented by the equation:

\[
\text{NH}_4\text{Cl}(s) \rightleftharpoons \text{NH}_3(g) + \text{HCl}(g)
\]

Use the data to predict the minimum temperature at which this decomposition becomes thermodynamically feasible.

(4)

28. (a) The mechanism for the reaction:

\[
\text{RCI} + \text{F}^{-} \rightarrow \text{RF} + \text{Cl}^{-}
\]

is thought to be:

\[
\begin{align*}
\text{RCI} & \quad \text{slow} \rightarrow \text{R}^+ + \text{Cl}^- \\
\text{R}^+ + \text{F} & \quad \text{fast} \rightarrow \text{RF}
\end{align*}
\]

when $\text{R}^+$ is:

and the solvent is liquid sulphur dioxide. What is the overall initial rate expression for this reaction?

1
29. Mercury(II) chloride is reduced by oxalate ions \((C_2O_4^{2-})\) according to the equation:

\[
2\text{HgCl}_2(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2\text{Cl}^{-}(\text{aq}) + 2\text{CO}_2(\text{g}) + 2\text{HgCl}(\text{s})
\]

The following data were obtained in a series of four experiments at the same temperature. The rate is measured by the decrease in concentration of \(\text{HgCl}_2(\text{aq})\) per minute.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial concentration of (\text{HgCl}_2(\text{aq}))/mol l(^{-1})</th>
<th>Initial concentration of (\text{C}_2\text{O}_4^{2-}(\text{aq}))/mol l(^{-1})</th>
<th>Initial rate/(\text{mol l}^{-1}\min^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.128</td>
<td>0.304</td>
<td>(1.82 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.064</td>
<td>0.608</td>
<td>(3.66 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>0.128</td>
<td>0.608</td>
<td>(7.31 \times 10^{-4})</td>
</tr>
<tr>
<td>4</td>
<td>0.064</td>
<td>0.304</td>
<td>(0.90 \times 10^{-4})</td>
</tr>
</tbody>
</table>

(a) From the date given above, deduce the overall rate equation for the reaction.
EXTRA QUESTIONS

(b) Using the results for Experiment 1 and your answer to (a), calculate the rate constant at the given temperature, giving the correct units.

(c) Calculate the initial rate of the reaction when the initial concentration of each reactant is 0.1 mol l⁻¹.

(d) (i) Draw a graph, which need not be to scale, to show how the concentration of HgCl₂(aq) changes as the reaction proceeds (graph paper not required).

(ii) Draw a line on your graph to represent the initial rate of the reaction.

SY/94

30. All life forms on earth incorporate about 20 amino acids in a vast variety of protein structures. These amino acids can be represented by the formula H₂NCHRCOOH where R represents a hydrogen atom or an alkyl group or some other group of atoms.

(a) Draw the full structural formula for an amino acid that does not have a chiral centre. Explain your choice.

(b) (i) Draw an amino acid that does have a chiral centre and label the chiral carbon atom with a *.

(ii) What property will this molecule have as a result of having this chiral centre?

31. Oils from plant sources contain only cis-fatty acids. When the oil is hydrogenated for margarine production some of the unsaturated fatty acids are converted to saturated molecules, but unfortunately some rearrangement of the remaining double bonds also occurs and the (allegedly) less healthy structural isomer is formed.

(a) (i) State how margarine manufacturers partially hydrogenate natural oils.

(ii) Explain why they change the molecules in this way.

(b) Linoleic acid (octadec-9,12-dienoic acid) is present in some triglycerides. Its formula is CH₃(CH₂)₄(CHCHCH₂)(CH₂)₆COOH.

(i) Show this as a structural formula, showing clearly the structural arrangement at each double bond.
(ii) Assume the double bond on carbon 12 is lost during the hydrogenation reaction. Show the structural formula of the new fatty acid formed if ‘rearrangement’ occurs at the remaining double bond.

(iii) Give this molecule a name that distinguishes it from its isomer.

(iv) Explain whether or not linoleic acid is optically active.

32. A sample of an alkanoic acid (0.507 g) was roasted at a high temperature and was found to produce carbon dioxide (0.905 g) and water (0.369 g).

(a) Calculate the empirical formula for this acid.

(b) Assuming that the acid is monoprotic, what is the molecular formula for the acid?

33. Two isomeric alcohols (A and B), both having a molecular mass of 60, give the following peaks in the mass spectrum. (The values in brackets give an indication of the relative intensity of each peak.)

<table>
<thead>
<tr>
<th>Alcohol A</th>
<th>60 (5%)</th>
<th>45 (100%)</th>
<th>27 (12%)</th>
<th>15 (5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol B</td>
<td>60 (10%)</td>
<td>59 (15%)</td>
<td>31 (100%)</td>
<td>27 (10%)</td>
</tr>
</tbody>
</table>

(a) Suggest structures for isomers A and B.

(b) Give the structures of the eight ions found in the mass spectra of A and B.

(c) Which isomer is B? Explain your choice.
34. Two structural isomers of molecular formula $\text{C}_2\text{H}_6\text{O}$ were investigated using $^1\text{H}$ NMR spectroscopy. The spectrum of one of these isomers is shown below.

(a) Draw the two possible structural formulae for the isomers.

(b) (i) Which of these isomers gave the spectrum shown?
(ii) Explain why there are four peaks in the spectrum.

(c) (i) What is the name given to the lines A, B and C?
(ii) What information do these lines give?

(d) Sketch the NMR spectrum of the other isomer.

(8)

35. Suggest a structure for compound $G$, which has the empirical formula $\text{CH}_3\text{O}$, from the $^1\text{H}$ NMR spectrum shown below.

(a) Why does the peak for tetramethylsilane (TMS) always appear at 0.0 $\delta$?
(b) What can be concluded from the fact that there are only two peaks in the spectrum?  
1

(c) Suggest a structural formula for compound G, giving reasons for your choice.  
3

(d) What major peak would you expect to see in the infra-red spectrum of G?  
1

36. (a) Draw structural formulae for the four isomeric alcohols having the molecular formula C_4H_{10}O and name them.  
2

(b) How many peaks would you expect in the 1H NMR spectrum of each of these molecules? Explain your answer in each case.  
4

37. A structure for cyclohexane-1,4-diol is shown below.

(a) Draw a structure for cyclohexane.  
1

(b) (i) How many peaks would you expect in the 1H NMR spectrum of each of these molecules?  
2

(ii) Explain your answer in detail.  
3

38. The approximate values and integrals for the 1H NMR spectrum for one of the isomers of C_4H_{10}O is given in the table below.

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Group</th>
<th>Approximate δ value</th>
<th>Integral</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH_3CH_2CH_2OCH_3</td>
<td>CH_3</td>
<td>0.8–1.3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>CH_2</td>
<td>1.2–1.8</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>CH_3O</td>
<td>3.5–4.0</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>OCH_3</td>
<td>3.0–4.0</td>
<td>3</td>
</tr>
</tbody>
</table>
(a) Using the information in the table, draw the $^1$H NMR spectrum for this isomer.  
(b) Draw a structural formula for:
   (i) an alcohol with molecular formula $C_2H_6O$
   (ii) an ether with molecular formula $C_2H_6O$.
(c) Construct a table (as above) for each of the isomers in (b).
(d) Draw the $^1$H NMR spectrum for the ether.

39. An organic compound (X) was analysed and found to contain $C$ 70.59% and $H$ 5.88%. Mass spectral analysis indicated a molecular mass of 136. The infra-red spectrum of X showed a large peak (along with others) at 1710 cm$^{-1}$. The proton NMR spectrum consisted of a broad peak between 6 and 7$\delta$ (integral 5) and a sharp peak about 2$\delta$ (integral 3).

(a) Calculate the empirical formula for X.  
(b) Use the mass spectral data to suggest a molecular formula for X.  
(c) Use IR and NMR data to propose two possible structures for X and explain why one fits the data better than the other.

40. (a) Define:
   (i) an agonist
   (ii) an antagonist.
(b) Explain in terms of a car-key analogy the difference between an agonist and an antagonist.
(c) The structure of a penicillin is drawn and numbered below.

\[ \text{Indicate which, if any, of the numbered carbon atoms are chiral centres.} \]