

- 1 Calcium chloride, CaCl_2 , is an ionic solid.

The values of some energy changes are shown in Table 1.1.

Table 1.1

energy change	value / kJ mol^{-1}
lattice energy, $\Delta H_{\text{latt}}^{\ominus} \text{CaCl}_2(\text{s})$	–2237
standard enthalpy change of atomisation of calcium	+193
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1150
standard enthalpy change of atomisation of chlorine	+121
first electron affinity of chlorine	–364

- (a) Define lattice energy.

.....
 [1]

- (b) Use the data in Table 1.1 to calculate the standard enthalpy change of formation, $\Delta H_{\text{f}}^{\ominus}$, of calcium chloride. It may be helpful to draw an energy cycle. Show all your working.

$$\Delta H_{\text{f}}^{\ominus}(\text{CaCl}_2(\text{s})) = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

- (c) Three possible values for the first electron affinity of bromine are shown in Table 1.2. One of them is correct.

Place a tick by the correct value. Explain your choice.

Table 1.2

possible values	place one tick (✓) in this column
–342 kJ mol ^{–1}	
–364 kJ mol ^{–1}	
–386 kJ mol ^{–1}	

explanation

..... [1]

- (d) The enthalpy change of hydration of the chloride ion can be calculated using the lattice energy of calcium chloride and the data shown in Table 1.3.

Table 1.3

energy change	value / kJ mol ^{–1}
standard enthalpy change of solution of CaCl ₂ (s)	–83
standard enthalpy change of hydration of Ca ²⁺ (g)	–1650

- (i) Define the following terms.

enthalpy change of solution

.....

enthalpy change of hydration

.....

[2]

- (ii) Calculate the standard enthalpy change of hydration of the chloride ion, Cl[–](g). It may be helpful to draw an energy cycle. Show all your working.

$$\Delta H_{\text{hyd}}^{\circ}(\text{Cl}^{-}(\text{g})) = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

- (e)** Calcium fluoride, $\text{CaF}_2(\text{s})$, can be synthesised directly from its elements.

The value of $\Delta H_f^\circ(\text{CaF}_2(\text{s}))$ is $-1214 \text{ kJ mol}^{-1}$.

- (i)** Predict the sign of the entropy change, ΔS° , for this synthesis. Explain your answer.

The sign of the entropy change is

explanation

[1]

- (ii)** Use the value of $\Delta H_f^\circ(\text{CaF}_2(\text{s}))$ given in **(e)** and your answer to **(e)(i)** to predict how the feasibility for this synthesis will change with increasing temperature.

[2]

[Total: 11]

- 2 (a) Nitrogen monoxide, NO, reacts with ozone, O₃.



This reaction is first order with respect to both NO and O₃.
At 298 K, the rate constant $k = 11\,500 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

- (i) Complete the rate equation for this reaction.

rate = [1]

- (ii) A reaction is carried out in which the initial concentrations of NO and O₃ are both $1.20 \times 10^{-6} \text{ mol dm}^{-3}$.

Calculate the initial rate of the reaction. State its units.

rate of reaction = units = [2]

- (iii) The reaction described in (a)(ii) is monitored over a period of time.

Predict whether or not the graph of [NO] against time, under these conditions, shows that the reaction has a constant half-life. Explain your answer.

prediction

explanation

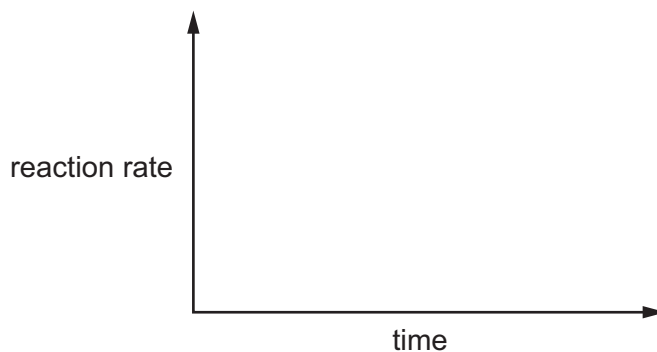
..... [1]

- (b) Nitrous oxide, N₂O, decomposes into its elements.

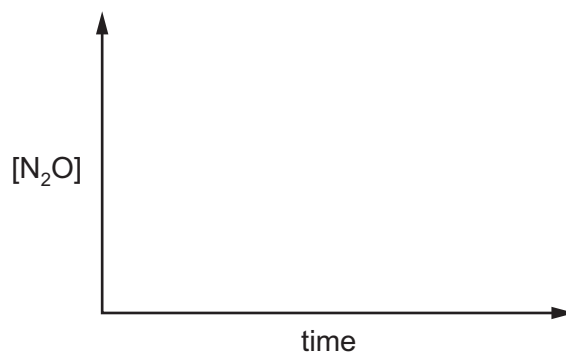


At a high temperature, a small amount of platinum wire is added to a large amount of nitrous oxide. The reaction follows zero order kinetics. The platinum wire behaves as a catalyst.

- (i) Sketch a graph, on the axes below, of reaction rate against time for the catalysed decomposition of N₂O under these conditions.



- (ii) Sketch a graph, on the axes below, of $[\text{N}_2\text{O}]$ against time for this reaction.



[1]

- (iii) Platinum behaves as a heterogeneous catalyst in this reaction.

Describe the mode of action of a heterogeneous catalyst.

.....

.....

.....

..... [3]

- (iv) Suggest a reason why this reaction has zero order kinetics when the amount of nitrous oxide is large and the amount of platinum is small.

.....

..... [1]

[Total: 10]

Question 3 starts on the next page.

- 3 Data should be selected from Table 3.1 in order to answer some parts of this question.

Table 3.1

electrode reaction	E°/V
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.38
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn}$	-1.18
$\text{Mn}^{3+} + \text{e}^- \rightleftharpoons \text{Mn}^{2+}$	+1.49
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_4^- + \text{e}^- \rightleftharpoons \text{MnO}_4^{2-}$	+0.56
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{MnO}_2 + 2\text{H}_2\text{O}$	+1.67
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.52

- (a) An electrochemical cell can be constructed from a Mg^{2+}/Mg half-cell and a $\text{MnO}_4^-/\text{Mn}^{2+}$ half-cell. The standard cell potential of this cell can be calculated using the standard electrode potentials of the two half-cells.

- (i) Define standard electrode potential. Include details of the standard conditions used.

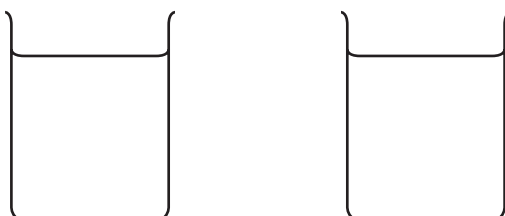
.....

.....

.....

..... [2]

- (ii) Complete the diagram below to show an electrochemical cell constructed from a Mg^{2+}/Mg half-cell and a $\text{MnO}_4^-/\text{Mn}^{2+}$ half-cell. Label your diagram.



[3]

- (iii) Use a positive (+) sign and a negative (-) sign to identify the polarity of each of the two electrodes in your diagram. Use an arrow and the symbol 'e' to show the direction of electron flow in the external circuit.

- (iv) Calculate the standard cell potential, $E_{\text{cell}}^{\ominus}$, of this cell.

$$E_{\text{cell}}^{\ominus} = \dots\dots\dots \text{V} \quad [1]$$

- (v) Construct an equation for the cell reaction.

..... [1]

- (vi) Predict how the cell reaction will change, if at all, when the solution in the Mg^{2+}/Mg half-cell is diluted by the addition of a large volume of water. Explain your answer.

.....

.....

..... [1]

- (b) A molten magnesium salt is electrolysed for 15.0 minutes by a constant current.

4.75×10^{22} magnesium atoms are produced at the cathode.

Calculate the value of the current used.

$$\text{current} = \dots\dots\dots \text{A} \quad [2]$$

[Total: 11]

- (iii) Calculate the pH of solution **X**. Show all your working.

pH = [2]

- (iv) A solution containing 2.00×10^{-3} mol of NaOH is added to solution **X**. A buffer solution is formed.

Calculate the pH of this buffer solution.

pH = [1]

[Total: 9]

5 Copper is a transition element. It forms a wide variety of compounds.

(a) Define transition element.

.....
 [1]

(b) An aqueous solution of copper(II) sulfate, CuSO_4 , contains $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ complex ions. If an excess of concentrated hydrochloric acid is added to this solution a ligand exchange reaction occurs and $[\text{CuCl}_4]^{2-}$ complex ions are formed.

(i) Complete Table 5.1 to state the geometry, the coordination number of copper, and one bond angle in each of the two complex ions.

Table 5.1

complex ion	geometry	coordination number	bond angle
$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$			
$[\text{CuCl}_4]^{2-}$			

[3]

(ii) In an isolated Cu^{2+} ion the d-orbitals are all degenerate. In a complex ion such as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ the d-orbitals are non-degenerate.

Define degenerate and non-degenerate in this context.

degenerate

non-degenerate

[1]

(iii) Explain why the solutions of the two complex ions in Table 5.1 are **different** colours.

.....
 [1]

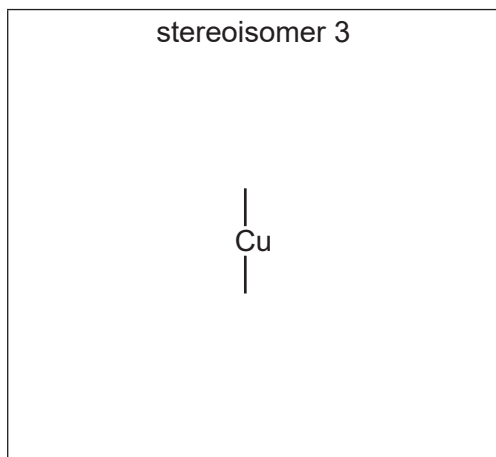
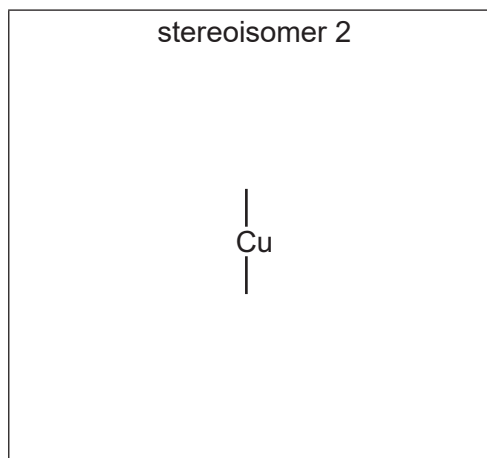
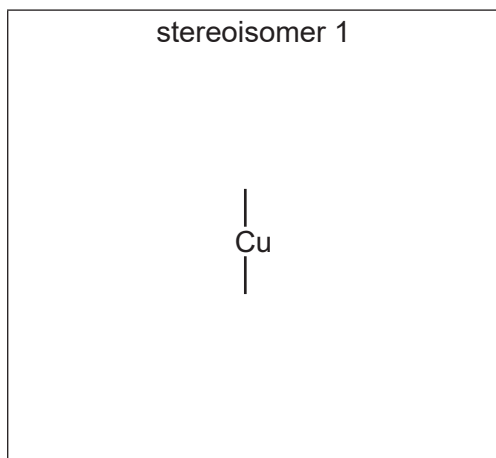
(c) Cu^{2+} forms a complex ion containing water molecules and ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, as ligands. The formula of the complex is $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$. The ethanedioate ion is a bidentate ligand.

(i) Explain what is meant by bidentate.

.....
 [1]

- (ii) There are three stereoisomers with the formula $[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^{2-}$.

Complete the three-dimensional diagrams to show these three stereoisomers.



[2]

- (iii) Use your answer to (c)(ii) to answer this question.

Stereoisomers 1, 2 and 3 show two different types of isomerism.

Name these two types of isomerism.

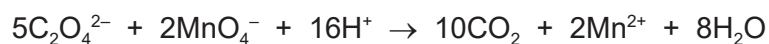
For each type of isomerism identify the pair of stereoisomers that demonstrate this isomerism.

type of isomerism	pair of stereoisomers
	and
	and

[2]

- (d) A solution contains 3.70 g of $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$ dissolved in 100 cm^3 of solution. A 25.0 cm^3 sample of this solution is warmed and then oxidised by $0.0100\text{ mol dm}^{-3}$ acidified potassium manganate(VII).

The equation for the redox reaction is shown.



Calculate the minimum volume of $0.0100\text{ mol dm}^{-3}$ acidified potassium manganate(VII) needed to oxidise all of the ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, in the 25.0 cm^3 sample. Show all your working.

$[M_r: \text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2], 321.5]$

minimum volume = cm^3 [3]

- (e) Copper(II) nitrate, $\text{Cu}(\text{NO}_3)_2$, and barium nitrate, $\text{Ba}(\text{NO}_3)_2$, both decompose when heated.

Copper(II) nitrate decomposes at a lower temperature than barium nitrate.

Suggest a reason for this difference. Explain your answer.

.....

 [2]

[Total: 16]

- 6 An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ complex ions.

- (a) (i) Complete Table 6.1 to describe what is observed when the named reagent is added to an aqueous solution of cobalt(II) chloride.

Table 6.1

reagent	colour of cobalt-containing product	state of cobalt-containing product
NaOH(aq)		
an excess of conc. HCl		

[2]

- (ii) Write an equation for the reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and NaOH(aq).

..... [1]

- (iii) Write an equation for the reaction between $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions and an excess of conc. HCl.

..... [1]

- (b) (i) Define stability constant.

.....
 [1]

- (ii) Write an expression for the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion.

$K_{\text{stab}} =$

[1]

- (iii) Give the units of the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion.

units = [1]

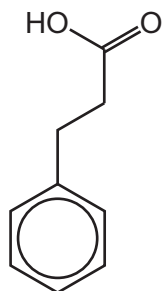
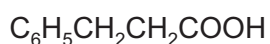
- (iv) The numerical value of the stability constant, K_{stab} , of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion is 7.7×10^4 .

In an aqueous solution the concentration of the $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex ion is $0.0740 \text{ mol dm}^{-3}$ and the concentration of NH_3 is $0.480 \text{ mol dm}^{-3}$ at equilibrium.

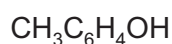
Calculate the concentration of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in this solution.

concentration = mol dm^{-3} [1]

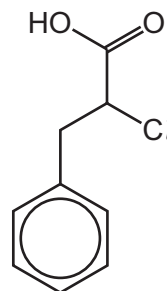
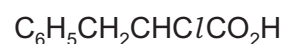
- 7 (a) The structural and displayed formulae of three aromatic compounds, **A**, **B** and **C**, are shown in Fig. 7.1.



A



B



C

Fig. 7.1

Compare the relative acidities of **A**, **B** and **C**.

..... > >

most acidic least acidic

Explain your answer.

..... [3]

- (b)** Methylbenzene, $\text{C}_6\text{H}_5\text{CH}_3$, can be made from benzene by an electrophilic substitution reaction.

- (i) Identify a compound that reacts with benzene to form methylbenzene. Identify the catalyst used.

compound

catalyst

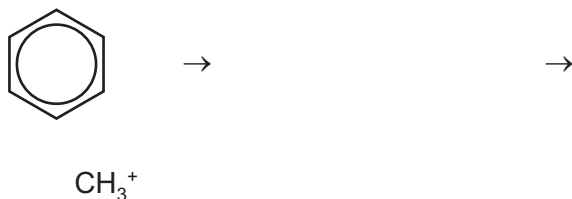
[1]

- (ii) The first step in the reaction is the generation of the CH_3^+ electrophile.

Write an equation for the reaction that generates this electrophile.

..... [1]

- (iii) Describe the mechanism for the reaction between benzene and the CH_3^+ electrophile. Include all relevant curly arrows and charges.



[3]

- (iv) Identify a suitable reagent to oxidise methylbenzene to benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$.

Write an equation for this reaction using [O] to represent one atom of oxygen from the oxidising agent.

reagent

equation

[2]

- (v) Methylbenzene and benzoic acid are both nitrated with a mixture of concentrated nitric acid and sulfuric acid to give mononitrated products. The structural formulae of these products are $\text{CH}_3\text{C}_6\text{H}_4\text{NO}_2$ and $\text{HOOC}\text{C}_6\text{H}_4\text{NO}_2$ respectively.

Draw the structures of these two products.

[1]

(c) A reaction scheme is shown in Fig. 7.2.

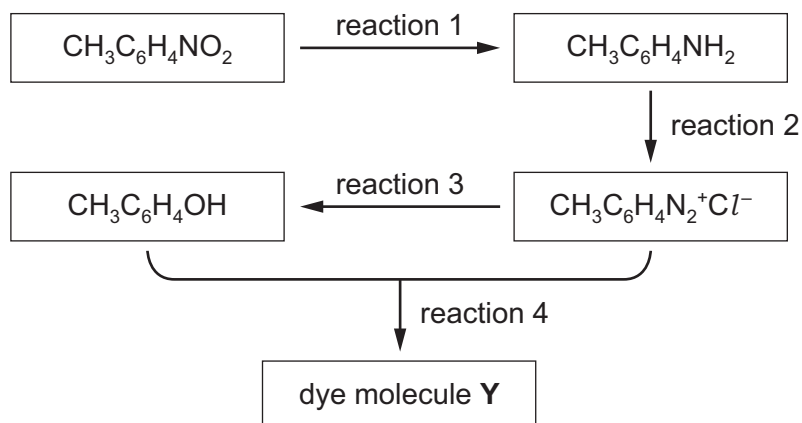


Fig. 7.2

- (i) Describe the reagents and conditions to produce $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ from $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ in reaction 2.

reagents

conditions

[1]

- (ii) Describe how $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ can be produced from $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ in reaction 3.

..... [1]

- (iii) Draw the structure of the dye molecule **Y** formed when $\text{CH}_3\text{C}_6\text{H}_4\text{N}_2^+\text{Cl}^-$ and $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ react together in reaction 4. Describe the conditions for this reaction.

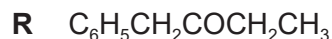
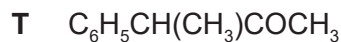
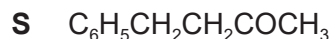
structure

conditions

[2]

[Total: 15]

- 8 When answering this question it should be assumed that together all the hydrogen atoms in a benzene ring result in a single unsplit peak at $\delta = 7.2$ in a proton (^1H) NMR spectrum. The structures of five isomeric ketones, **P**, **Q**, **R**, **S** and **T** are given.



- (a) Identify all the chiral carbon atoms on the structures above. Label each chiral carbon atom with an asterisk (*). [1]
- (b) The proton (^1H) NMR spectrum of one of the five isomers, **P**, **Q**, **R**, **S** or **T**, is shown in Fig. 8.1.

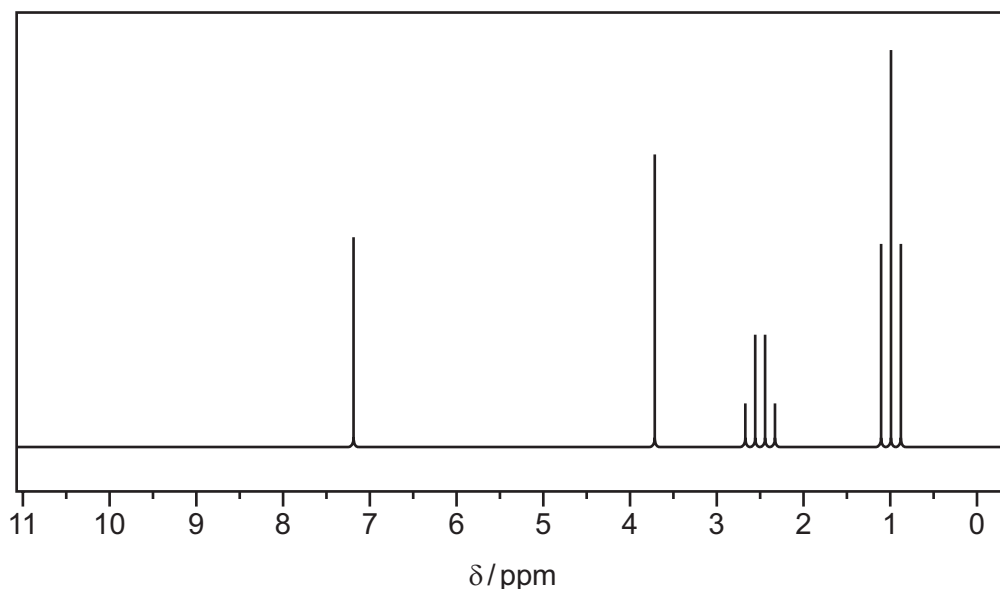
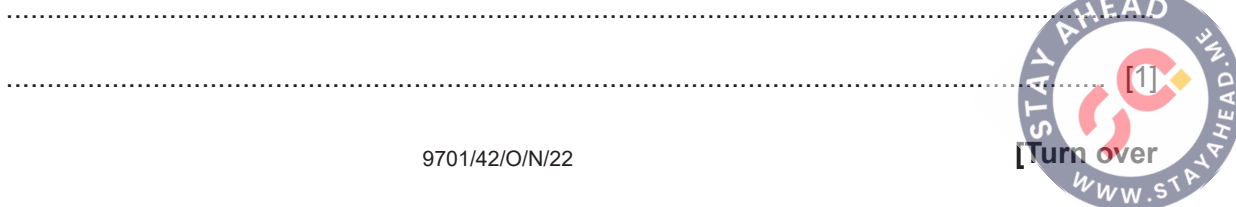


Fig. 8.1

- (i) Identify which of the compounds **P**, **Q**, **R**, **S** or **T** gives this spectrum. Draw the displayed formula of the compound you have identified. Identify the protons responsible for the peaks at $\delta = 3.7$, $\delta = 2.5$ and $\delta = 1.0$ on the structure you have drawn. [2]
- (ii) Name the splitting pattern of the peak at $\delta = 3.7$. Explain why it has this splitting pattern.



(c) Choose from the letters **P**, **Q**, **R**, **S** and **T** to identify:

(i) the **two** compounds that each have a doublet peak in the proton (^1H) NMR spectrum

..... [1]

(ii) the compound with only three peaks in its proton (^1H) NMR spectrum.

..... [1]

(d) Suggest a suitable solvent that should be used for obtaining the spectrum shown in Fig. 8.1.

..... [1]

(e) The proton (^1H) NMR spectrum of compound **T** is compared in the presence of D_2O and in the absence of D_2O .


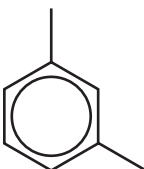
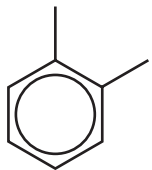

Describe any difference between the two spectra. Explain your answer.

.....

..... [1]

(f) Complete Table 8.1 below to give the number of peaks in the carbon-13 NMR spectrum of each compound.

Table 8.1

compound	number of peaks	compound	number of peaks
			
			

[2]

[Total: 10]

- 9 Tyrosine and lysine, shown in Fig. 9.1, are naturally occurring amino acids found in proteins.

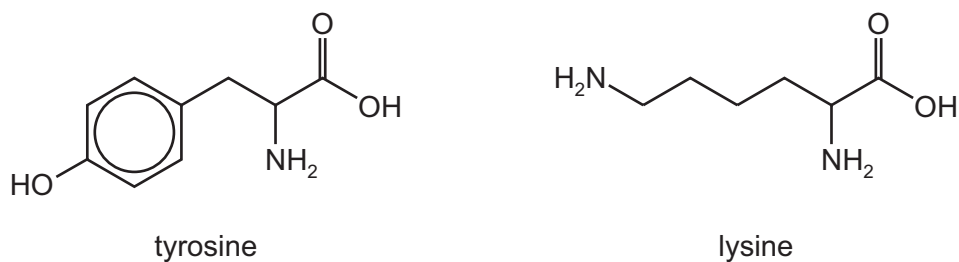


Fig. 9.1

- (a) The isoelectric point of lysine is 9.47.

Draw the structure of lysine at the stated pH in the boxes below.

lysine at pH 7.00



lysine at pH 9.47



lysine at pH 12.00



[2]

- (b) When ethanoic acid is treated with PCl_5 product **D** is formed.

When **D** is added to tyrosine two different isomeric products, **E** and **F**, are formed.

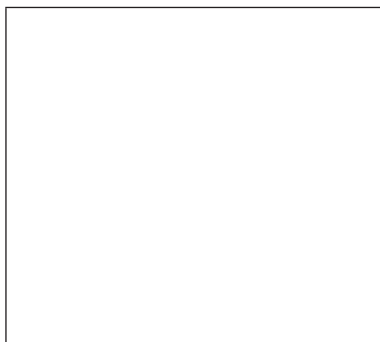
E has an ester linkage, **F** does not.

Draw the structures of **D**, **E** and **F** in the boxes below.

D



E



F



- (c) Complete Table 9.1 by drawing the structure of the organic product formed when tyrosine reacts with each named reagent.

Ignore the directing effect of the $-\text{CH}_2\text{CHNH}_2\text{COOH}$ substituent.

Table 9.1

reagent	structure
an excess of $\text{Br}_2(\text{aq})$	
an excess of $\text{NaOH}(\text{aq})$	
an excess of $\text{HNO}_3(\text{aq})$	

[3]

- (d) A mixture of tyrosine and lysine can be separated by thin-layer chromatography. Under certain conditions the R_f value of lysine is 0.14 and the R_f value of tyrosine is 0.45.

- (i) Explain what is meant by R_f value.

.....
 [1]

- (ii) Suggest an explanation for the difference in R_f values.

.....
 [1]

[Total: 10]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

The Periodic Table of Elements

Group																					
1	2													13	14	15	16	17	18		
														1 H hydrogen 1.0							