CAMBRIDGE INTERNATIONAL EXAMINATIONS

A LEVEL CHEMISTRY – 9701

PAPER 4 – STRUCTURED QUESTIONS – PART 1

Topical Past Papers · Question Papers & Marking Schemes

COURSE INSTRUCTOR

FAHAD HAMEED AHMAD

Cambridge Chemistry Specialist · Educator · Content Creator

+92 323 509 4443 ◈ **www.megalecture.com**

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- **15+ Years** teaching Chemistry across Pakistan, UAE, and Singapore
- **20 Million+** video lecture views on YouTube and Megalecture
- **Cambridge Specialist** for 9701, 0620, 0625 and IB DP Chemistry

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PART 1 · Topics 1 - 6

Energetics & Group 2 · Electrochemistry · Further Aspects of Equilibria
Reaction Kinetics · Entropy & Gibbs Free Energy · Transition Elements

Student Name: _____ **Class:** _____

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Energetics
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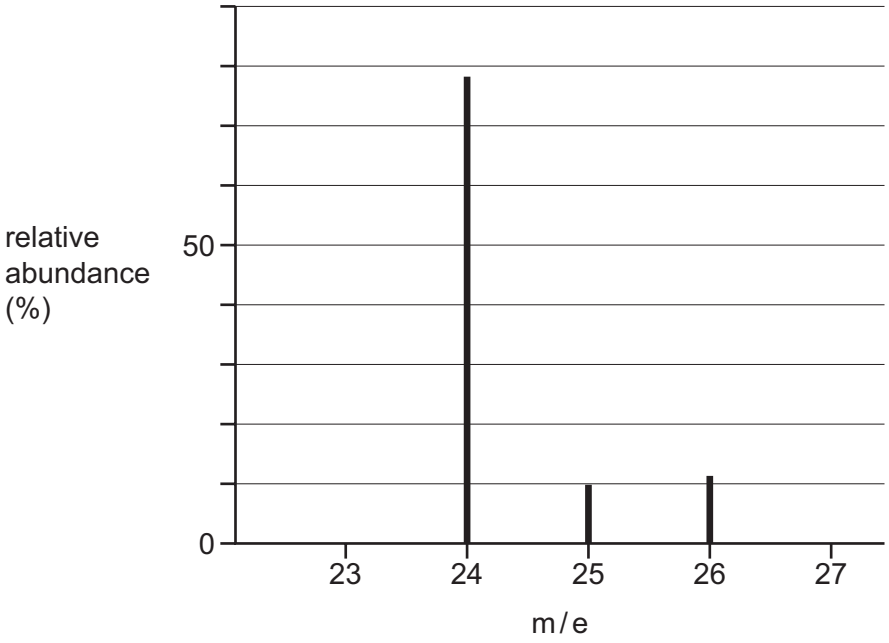

(i) From the mass spectrum, complete the table with the relative abundances of the three isotopes.

isotope	relative abundance
^{24}Mg	
^{25}Mg	
^{26}Mg	

[1]

(ii) Use your values in **(i)** to calculate the relative atomic mass, A_r, of magnesium to **two** decimal places.

A_r (Mg) = ... [1]

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.....

.....

.....

..... [3]

When lithium nitrate, $LiNO_3$, is heated, it readily decomposes giving off a brown gas. This reaction is similar to that which occurs when magnesium nitrate is heated, but it does not occur with other Group I nitrates.

(ii) Suggest an equation for the action of heat on $LiNO_3$.

..... [1]

(iii) Suggest why the Group I nitrates other than $LiNO_3$ do **not** decompose in this way when heated.

.....

..... [1]

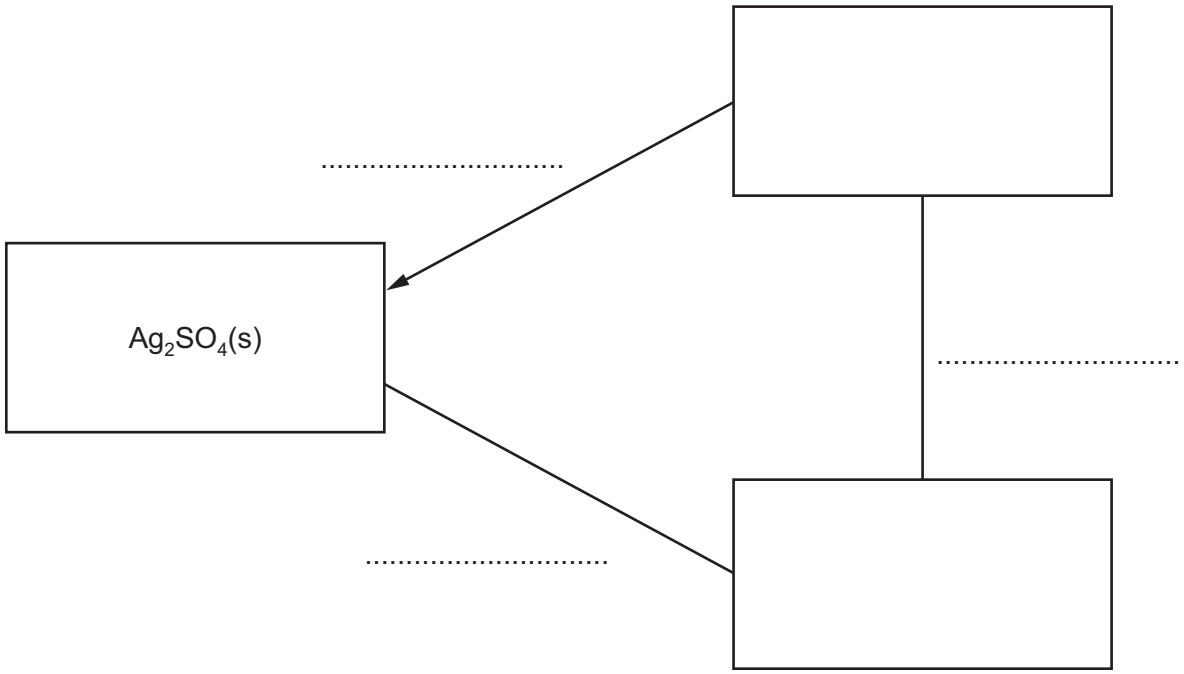
[Total: 7]

(2b) Using Ag_2SO_4 as an example, complete the following Hess' Law energy cycle relating the

- lattice energy, $\Delta H^{\ominus}_{latt}$,
- enthalpy change of solution, $\Delta H^{\ominus}_{sol}$, and
- enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$.

On your diagram:

- include the relevant species in the two empty boxes,
- label each enthalpy change with its appropriate symbol,
- complete the remaining two arrows showing the correct direction of enthalpy change.



[4]

P42/O/N/15/Q1

3 **(a)** Calcium has atomic number 20.

Complete the electronic structures for a

calcium atom, $1s^2 2s^2 2p^6$.....

calcium ion in the +2 oxidation state. $1s^2 2s^2 2p^6$.....

[1]

(b) Calcium nitrate, $Ca(NO_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

..... [1]

(c) **(i)** When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

.....

..... [1]

(ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

.....

.....

..... [2]

.....

.....

..... [2]

(ii) Use the following data to calculate the lattice energy, $\Delta H^{\ominus}_{latt}$, of calcium nitrate, $Ca(NO_3)_2(s)$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H^{\ominus}_{hyd}$ $(Ca^{2+}(g))$	$-1650\,kJ\,mol^{-1}$
$\Delta H^{\ominus}_{hyd}$ $(NO_3^-(g))$	$-314\,kJ\,mol^{-1}$
enthalpy change of solution for $Ca(NO_3)_2(s)$	$-19\,kJ\,mol^{-1}$

$\Delta H^{\ominus}_{latt}$ $Ca(NO_3)_2(s)$ = ... $kJ\,mol^{-1}$ [3]

(e) The standard enthalpy change of hydration for Ba^{2+}, $\Delta H^{\ominus}_{hyd}$ $(Ba^{2+}(g))$, is $-1305\,kJ\,mol^{-1}$.

Suggest an explanation for why the $\Delta H^{\ominus}_{hyd}$ of the Ba^{2+} ion is **less** exothermic than the $\Delta H^{\ominus}_{hyd}$ of the Ca^{2+} ion.

.....

.....

..... [2]

[Total: 12]

P43/O/N/15/Q1

4 **(a)** The dissolving of an ionic compound in water is accompanied by an energy change, the enthalpy change of solution, ΔH_{sol}.

$$MgCl_2(s) + aq \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

Describe, in terms of bond breaking and bond making, what happens to the solid ionic lattice when an ionic compound dissolves in water.

.....

.....

..... [2]

(b) **(i)** What is meant by the term *enthalpy change of solution*, ΔH_{sol}?

.....

..... [1]

(ii) Use the following data to calculate the standard enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, of chloride ions, $Cl^-(g)$.
You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H^{\ominus}_{hyd}$ ($Mg^{2+}(g)$)	–1925 kJ mol^{-1}
lattice energy of $MgCl_2(s)$	–2524 kJ mol^{-1}
enthalpy change of solution for $MgCl_2(s)$	–155 kJ mol^{-1}

Suggest an explanation for why the $\Delta H^{\ominus}_{hyd}$ of the Na^+ ion is **less** exothermic than the $\Delta H^{\ominus}_{hyd}$ of the Mg^{2+} ion.

.....

.....

..... [2]

(c) Describe and explain how the solubility of the Group II sulfates varies down the group.

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..... [4]

[Total: 11]

5 **(a)** Limewater is a saturated solution of $Ca(OH)_2$ in water. It is used to test for the presence of CO_2 in a gaseous mixture.

(i) Write an equation for the reaction between limewater and CO_2.

..... [1]

A saturated solution of $Ba(OH)_2$ can be used instead of $Ca(OH)_2$ to test for CO_2. A saturated solution of $Mg(OH)_2$ cannot be used for this test.

(ii) Explain why a saturated solution of $Ba(OH)_2$ **can** be used to test for CO_2.

.....

..... [1]

(iii) Explain why a saturated solution of $Mg(OH)_2$ **cannot** be used to test for CO_2.

.....

.....

..... [2]

(b) Describe and explain the trend in the thermal stabilities of the carbonates down Group 2.

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.....

..... [3]

(c) Nickel carbonate, $NiCO_3$, decomposes on heating.

Use the *Data Booklet* to explain whether $NiCO_3$ will decompose more or less readily than $CaCO_3$.

.....

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.....

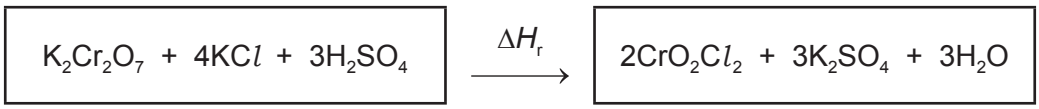
..... [2]

.

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

Use the following data to complete the Hess' Law cycle and calculate the enthalpy change of the reaction, ΔH_r.

compound	enthalpy change of formation, $\Delta H_f^{\ominus}$ / kJ mol^{-1}
$K_2Cr_2O_7$	–2061
KCl	–437
H_2SO_4	–814
CrO_2Cl_2	–580
K_2SO_4	–1438
H_2O	–286



ΔH_r = ... kJ mol^{-1} [2]

7 **(a)** Magnesium nitrate, $Mg(NO_3)_2$, is very soluble in water. When a hot saturated solution of magnesium nitrate is cooled, crystals of the hydrate, $Mg(NO_3)_2.6H_2O$, are formed.
In the crystals, six water molecules bond to each Mg^{2+} ion, and some of these water molecules are **also** bonded to the nitrate ions.

(i) Suggest the type of bonding that occurs between

H_2O and Mg^{2+}, ...

H_2O and NO_3^-. ..... [2]

(ii) Describe the arrangement of the water molecules around the Mg^{2+} ion.

..... [1]

(iii) Describe in detail what you would observe when crystals of $Mg(NO_3)_2.6H_2O$ are heated in a boiling tube, gently at first and then more strongly.
Write equations for any reactions that occur.

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..... [4]

(iv) Calculate the percentage **loss** in mass when $Mg(NO_3)_2.6H_2O$ is heated strongly to constant mass.

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..... [2]

(c) Magnesium nitrate and silver nitrate, $AgNO_3$, decompose on heating to produce the same gases. Silver nitrate also produces silver metal during decomposition.

Write an equation for the decomposition of $AgNO_3$.

..... [1]

[Total: 12]

.....

.....

.....

..... [3]

(b) Calcium reacts vigorously with HCl(aq) producing H_2(g).

$$Ca(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2(g)$$

(i) How would you expect the enthalpy change for this reaction to compare with the enthalpy change for the reaction where HNO_3(aq) is used in place of HCl but all other conditions are the same?
Explain your answer.

.....

..... [1]

$$Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g) \qquad \Delta H^\ominus = \mathbf{x}\ kJ\,mol^{-1}$$

Construct a **fully labelled** Hess' Law cycle to connect each side of this equation to the relevant gas phase ions.

Use your cycle, the following data, **and** data from the *Data Booklet*, to calculate a value for **x**.

standard enthalpy of atomisation of Ca(s), $\Delta H^\ominus_{at}(Ca)$	+178 kJ mol^{-1}
standard enthalpy of hydration of $Ca^{2+}(g)$, $\Delta H^\ominus_{hyd}(Ca^{2+})$	–1576 kJ mol^{-1}
standard enthalpy of hydration of $H^+(g)$, $\Delta H^\ominus_{hyd}(H^+)$	–1090 kJ mol^{-1}

x = ... kJ mol^{-1} [4]

(c) The standard enthalpy change for the reaction between Ca(s) and $CH_3CO_2H(aq)$ is **less negative** than **x** by 2 kJ mol^{-1}.

Suggest an explanation for this.

.....

..... [2]

Predict what would be observed when anhydrous copper(II) carbonate is heated.

.....

..... [1]

(b) Describe and explain how the thermal stability of the Group 2 carbonates varies down the group.

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.....

.....

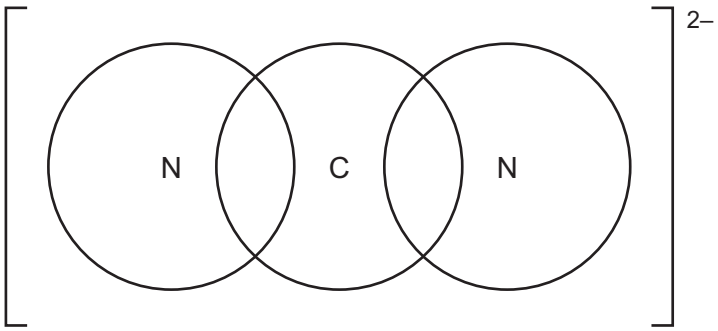
..... [3]

(c) Calcium cyanamide, $CaCN_2$, can be used as a fertiliser.

(i) Complete the 'dot-and-cross' diagram for the cyanamide ion, CN_2^{2-}.

Use the following key for the electrons.

- • electrons from carbon
- × electrons from nitrogen
- □ added electron(s) responsible for the overall negative charge



[2]

(ii) $CaCN_2$ decomposes readily on contact with water forming an insoluble white solid and ammonia only.

Suggest an equation for this reaction.

..... [2]

[Total: 8]

10 **(a)** Describe and explain the variation in the solubilities of the hydroxides of the Group 2 elements.

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..... [4]

The table lists the standard enthalpy changes of formation, $\Delta H_f^{\ominus}$, for some compounds and aqueous ions.

species	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$Ba^{2+}(aq)$	–538
$OH^-(aq)$	–230
$CO_2(g)$	–394
$BaCO_3(s)$	–1216
$H_2O(l)$	–286

(b) **(i)** Reaction 1 occurs when $CO_2(g)$ is bubbled through an aqueous solution of $Ba(OH)_2$.

Use the data in the table to calculate the standard enthalpy change for reaction 1, $\Delta H_{r1}^{\ominus}$.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l) \qquad \text{reaction 1}$$

$\Delta H_{r1}^{\ominus}$ = ... kJ mol^{-1} [2]

$$BaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ba(HCO_3)_2(aq) \qquad \text{reaction 2}$$

The standard enthalpy change for reaction 2, $\Delta H^{\ominus}_{r2}$, = –26 kJ mol^{-1}.

(ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the $HCO_3^-(aq)$ ion.

$\Delta H^{\ominus}_f$ $HCO_3^-(aq)$ = ... kJ mol^{-1} [2]

(iii) The overall process is shown by reaction 3.

Use your answer to **(ii)**, and the data given in the table, to calculate the standard enthalpy change for reaction 3, $\Delta H^{\ominus}_{r3}$.

$$Ba(OH)_2(aq) + 2CO_2(g) \rightarrow Ba(HCO_3)_2(aq) \qquad \text{reaction 3}$$

$\Delta H^{\ominus}_{r3}$ = ... kJ mol^{-1} [1]

(iv) How would the value of $\Delta H^{\ominus}_{r3}$ compare with the value of $\Delta H^{\ominus}_{r4}$ for the similar reaction with $Ca(OH)_2(aq)$ as shown in reaction 4?
Explain your answer.

$$Ca(OH)_2(aq) + 2CO_2(g) \rightarrow Ca(HCO_3)_2(aq) \qquad \text{reaction 4}$$

.....

.....

..... [2]

(c) The standard entropy change for reaction 1 is $\Delta S^{\ominus}_{r1}$.

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with $\Delta S^{\ominus}_{r1}$.

.....

.....

..... [2]

11 **(a)** **(i)** Describe and explain the variation in the thermal stabilities of the carbonates of the Group 2 elements.

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.....

..... [3]

(ii) Suggest and explain a reason why sodium carbonate is more stable to heat than magnesium carbonate.

.....

.....

..... [1]

(b) Sodium hydrogencarbonate, $NaHCO_3$, and potassium hydrogencarbonate, $KHCO_3$, decompose on heating to produce gases and the solid metal carbonate.

(i) Write an equation for the decomposition of $KHCO_3$.

..... [1]

(ii) Predict which of $NaHCO_3$ or $KHCO_3$ will decompose at the **lower** temperature. Explain your answer.

.....

..... [1]

energy change	value / kJ mol^{-1}
enthalpy change of atomisation of potassium, $\Delta H^{\ominus}_{at}$ K(s)	+89
electron affinity of O(g)	–141
electron affinity of O^-(g)	+798
enthalpy change of formation of potassium oxide, $\Delta H^{\ominus}_{f}$ K_2O(s)	–361

$\Delta H^{\ominus}_{latt}$ = ... kJ mol^{-1} [3]

(ii) State whether the lattice energy of Na_2O would be more negative, less negative or the same as that of K_2O. Give reasons for your answer.

.....

..... [1]

(12b) Magnesium(I) chloride, $MgCl$, is an unstable compound and readily decomposes as shown.

$$2MgCl(s) \rightarrow Mg(s) + MgCl_2(s)$$

Use the following data to calculate the enthalpy change of this reaction.

$\Delta H_f^{\ominus}$ $MgCl(s)$ = –106 kJ mol^{-1}
$\Delta H_f^{\ominus}$ $MgCl_2(s)$ = –642 kJ mol^{-1}

enthalpy change = ... kJ mol^{-1} [1]

(c) (i) The equation for which ΔH is the lattice energy for $MgCl$ is shown.

$$Mg^+(g) + Cl^-(g) \rightarrow MgCl(s)$$

Use the equation, the following data, and relevant data from the *Data Booklet* to calculate a value for the lattice energy of $MgCl$. You might find it helpful to construct an energy cycle.

electron affinity of $Cl(g)$ = –349 kJ mol^{-1}
enthalpy change of atomisation of Mg(s) = +147 kJ mol^{-1}
enthalpy change of formation of $MgCl(s)$ = –106 kJ mol^{-1}

(ii) Suggest how the lattice energies of $MgCl_2$ and $NaCl$ will compare to that of $MgCl$. Explain your answers.

$MgCl_2$ and $MgCl$ .....

.....

$NaCl$ and $MgCl$.....

.....
[3]

(d) Define the term *electron affinity*.

.....

..... [2]

13 Sodium oxide, Na_2O, is a white crystalline solid with a high melting point.

(a) Write an equation for the reaction of sodium with oxygen, forming sodium oxide. Include state symbols.

..... [2]

(b) Explain why sodium oxide has a high melting point.

.....

.....

.....

..... [2]

(c) When sodium oxide reacts with water an alkaline solution is obtained.

(i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

.....

.....

.....

..... [2]

(ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm^3 of water.

pH = ... [3]

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of sodium oxide, $\Delta H_f^{\ominus}$ $Na_2O(s)$	–416
standard enthalpy change of atomisation of sodium, $\Delta H_{at}^{\ominus}$ Na(s)	+109
electron affinity of O(g	–142
electron affinity of $^{-}$(g)	+844

$\Delta H_{latt}^{\ominus}$ $Na_2O(s)$ = ... kJ mol^{-1} [4]

(e) State how $\Delta H_{latt}^{\ominus}$ $Na_2S(s)$ differs from $\Delta H_{latt}^{\ominus}$ $Na_2O(s)$.
Indicate this by placing a tick (✓) in the appropriate box in the table.

$\Delta H_{latt}^{\ominus}$ $Na_2S(s)$ is more exothermic than $\Delta H_{latt}^{\ominus}$ $Na_2O(s)$	$\Delta H_{latt}^{\ominus}$ $Na_2S(s)$ is the same as $\Delta H_{latt}^{\ominus}$ $Na_2O(s)$	$\Delta H_{latt}^{\ominus}$ $Na_2S(s)$ is less exothermic than $\Delta H_{latt}^{\ominus}$ $Na_2O(s)$

Explain your answer.

.....

.....

.....

[2]

[Total: 15]

calcium .....

barium .....
[2]

(b) The decomposition temperatures of the Group 2 carbonates vary down the group.

State and explain the variation in the decomposition temperatures.

.....

.....

.....

.....

.....

..... [3]

(c) Magnesium carbonate was heated in an open test-tube. It was difficult to see whether a thermal decomposition reaction took place.

Explain why.

.....

.....

..... [2]

[Total: 7]

..... [2]

(ii) Describe what will be seen during this reaction.

.....

.....

..... [2]

(b) Describe and explain how the solubility of the Group 2 sulfates varies down the group.

.....

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..... [4]

[Total: 8]

P42/O/N/18/Q4abc

16 **(a)** Calcium nitride, Ca_3N_2, reacts readily with water to form a white precipitate suspended in an alkaline solution. The oxidation number of nitrogen does not change during the reaction.

Construct an equation for the reaction of Ca_3N_2 with water.

..... [2]

(b) The enthalpy changes of solution, $\Delta H^{\ominus}_{sol}$, of the hydroxides of the Group 2 elements become less endothermic down the group.

State and explain the trend in the solubilities of the Group 2 hydroxides.

.....

.....

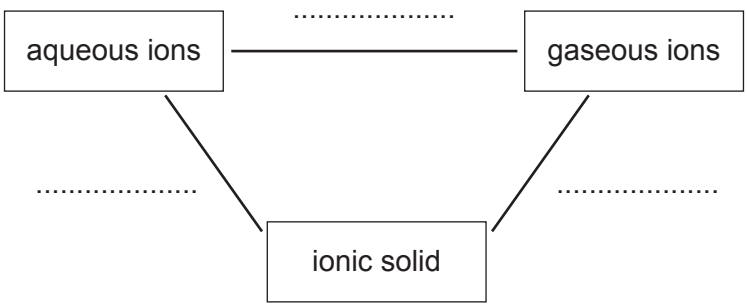
.....

..... [3]

(c) Complete the energy cycle to show the enthalpy changes that occur in the transformations between aqueous ions, gaseous ions and an ionic solid.

On your diagram label each enthalpy change with its appropriate symbol; lattice energy, $\Delta H^{\ominus}_{latt}$, enthalpy change of hydration, $\Delta H^{\ominus}_{hyd}$, or enthalpy change of solution, $\Delta H^{\ominus}_{sol}$.

Complete the three arrows showing the correct direction of each enthalpy change.



[3]

.....

.....

..... [2]

(b) Sodium nitrite, $NaNO_2$, is a decomposition product from heating sodium nitrate, $NaNO_3$.

A student analysed a sample of sodium nitrite by titration with aqueous cerium(IV) ions, $Ce^{4+}(aq)$. The equation for the titration reaction is shown.

$$NO_2^-(aq) + 2Ce^{4+}(aq) + H_2O(l) \rightarrow 2Ce^{3+}(aq) + NO_3^-(aq) + 2H^+(aq)$$

- 0.138 g of impure sodium nitrite was dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 25.0 cm^3 of this solution required 21.80 cm^3 of 0.0400 mol dm^{-3} $Ce^{4+}(aq)$ to reach the end-point.

You should assume the impurity does not react with $Ce^{4+}(aq)$.

Calculate the percentage purity of the sample of sodium nitrite.

..... % [3]

Write an equation for the decomposition of strontium nitrate.

..... [1]

(b) Describe and explain how the thermal stability of Group 2 nitrates changes with increasing atomic number.

.....

.....

.....

.....

..... [3]

(c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

(i) Suggest whether calcium amide, $Ca(NH_2)_2$, will decompose more or less readily than barium amide, $Ba(NH_2)_2$. Explain your answer.

.....

..... [1]

(ii) $Ba(NH_2)_2$ decomposes when heated to form barium nitride, Ba_3N_2, and ammonia as the only products.

Write an equation for this reaction.

..... [1]

(d) $Ba(NH_2)_2$ contains the NH_2^- ion.

Predict the bond angle of NH_2^-. Explain your answer using the qualitative model of electron-pair repulsion.

bond angle .....

explanation .....

.....

.....

[3]

[Total: 9]

energy change	always positive	always negative	either negative or positive
bond energy			
enthalpy change of formation			

[1]

(b) Explain what is meant by the term *enthalpy change of atomisation*.

.....

..... [1]

(c) The overall reaction for the atomisation of liquid bromine molecules, $Br_2(l)$, is shown.

$$Br_2(l) \rightarrow 2Br(g)$$

This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and relevant data from the *Data Booklet* to calculate the enthalpy change of vaporisation of $Br_2(l)$, $\Delta H^{\ominus}_{vap}$.
  The enthalpy change of atomisation of bromine, ΔH_{at}, = +112 kJ mol^{-1}.

$\Delta H^{\ominus}_{vap}$ = ... kJ mol^{-1} [3]

(d) Suggest how the $\Delta H^{\ominus}_{vap}$ of iodine, $I_2(l)$, would compare to that of bromine, $Br_2(l)$. Explain your answer.

.....

..... [1]

.....

..... [1]

(ii) Suggest why the enthalpy change of hydration of $Br^-(g)$ is **more** exothermic than that of $I^-(g)$.

.....

.....

..... [2]

[Total: 9]

Write an equation for the decomposition of the carbonate ion.

..... [1]

(b) Describe and explain how the thermal stability of the Group 2 carbonates changes with increasing atomic number.

.....

.....

.....

.....

..... [3]

(c) Lead(II) carbonate, $PbCO_3$, and zinc carbonate, $ZnCO_3$, decompose on heating in a similar way to calcium carbonate, $CaCO_3$.

State relevant data from the *Data Booklet* and use it to predict the order of thermal stability of these three carbonates.

data .....

.....

(most stable) ..... > ..... > ..... (least stable)
[2]

(d) Dolomite contains the double carbonate of calcium and magnesium, $CaMg(CO_3)_2$, and some impurities. When 0.642 g of a sample of dolomite reacts with an excess of hydrochloric acid, 125.0 cm^3 of CO_2 is formed under room conditions.

Calculate the percentage of $CaMg(CO_3)_2$ in the sample of dolomite. Show all your working.

Assume that none of the impurities react with HC*l*.

% of $CaMg(CO_3)_2$ in dolomite = ... %
[3]

[Total: 9]

energy change	always positive	always negative	either negative or positive
lattice energy			
enthalpy change of neutralisation			

[1]

(b) Define, in words, the term *enthalpy change of solution*.

.....

..... [1]

(c) The following enthalpy changes are given.

enthalpy change	value / kJ mol^{-1}
standard enthalpy change of formation, $\Delta H_f^{\ominus}$, for $K_3PO_4(s)$	–2035
standard enthalpy change, $\Delta H^{\ominus}$, for $P(s) + 2O_2(g) + 3e^- \rightarrow PO_4^{3-}(aq)$	–1284
standard enthalpy change, $\Delta H^{\ominus}$, for $K(s) \rightarrow K^+(aq) + e^-$	–251

Determine the standard enthalpy change of solution of potassium phosphate, $K_3PO_4(s)$. It may be helpful to draw a labelled energy cycle.

$\Delta H_{sol}^{\ominus}$ = ... kJ mol^{-1} [3]

compound	lattice energy value / kJ mol^{-1}
$CaBr_2(s)$	–2176
KBr(s)	–679

Suggest an explanation for why $\Delta H^{\ominus}_{latt}$ $CaBr_2$ is **more** exothermic than $\Delta H^{\ominus}_{latt}$ KBr.

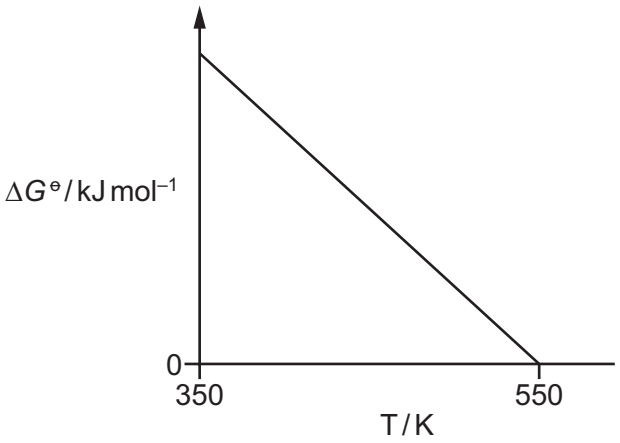
.....

.....

..... [2]

(e) For a particular gas phase reaction the variation in standard Gibbs free energy change, $\Delta G^{\ominus}$, with temperature is shown.

Assume standard enthalpy change, $\Delta H^{\ominus}$, and standard entropy change, $\Delta S^{\ominus}$, remain constant with temperature.



(i) Write the equation that relates $\Delta G^{\ominus}$ to $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$.

..... [1]

(ii) Use this equation to explain why $\Delta G^{\ominus}$ becomes **less** positive as temperature increases in this reaction.

.....

..... [1]

[Total: 9]

(a) (i) Write an equation for the change representing the first ionisation energy of magnesium. Include state symbols.

..... [1]

(ii) Write an equation for the reaction of strontium with cold water. Include state symbols.

..... [1]

(iii) Describe and explain the trend in reactivity observed in the reactions of these Group 2 metals with cold water.

.....

.....

..... [1]

(b) The Group 2 metal nitrates decompose when heated.

(i) Describe fully what is seen when anhydrous calcium nitrate is heated in a test-tube and decomposition occurs.

.....

..... [1]

(ii) Write an equation for the decomposition of calcium nitrate.

..... [1]

(iii) Describe and explain the variation in thermal stability of the Group 2 metal nitrates down the group.

.....

.....

..... [3]

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 12]

magnesium .....

strontium .....
[2]

(b) (i) Write an equation for each of the following processes. Include state symbols.

calcium is burned in air

.....

calcium carbonate is heated strongly

.....
[2]

(ii) Calcium hydroxide is formed when water is added to calcium oxide. Calcium hydroxide and calcium carbonate are both used in agriculture.

Describe the main benefit of adding calcium hydroxide or calcium carbonate to soil.

.....

..... [1]

(iii) Explain why the Group 2 hydroxides become more soluble down the group.

.....

.....

.....

..... [3]

(c) Describe the observations, if any, that you would make when:

- a few drops of NaOH(aq) are added to $BaCl_2$(aq)

.....

- a few drops of H_2SO_4(aq) are added to $BaCl_2$(aq).

.....
[2]

.....

.....

.....

.....

..... [3]

[Total: 13]

24 **(a)** An aqueous solution of cobalt(II) contains the $[Co(H_2O)_6]^{2+}$ complex ion.

(i) Define the term *complex ion*.

.....

..... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of $[Co(H_2O)_6]^{2+}$ with aqueous sodium hydroxide

  colour and state of the cobalt-containing species .....

  ionic equation .....

  type of reaction .....

- the reaction of $[Co(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

  colour and state of the cobalt-containing species .....

  ionic equation .....

  type of reaction .....

[6]

(b) When concentrated hydrochloric acid is added to a solution containing $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed and the following equilibrium is established.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$. Explain your answer.

.....

.....

..... [2]

Complete the three-dimensional diagrams to show the two isomers of $[Co(NH_3)_3Cl_3]$.

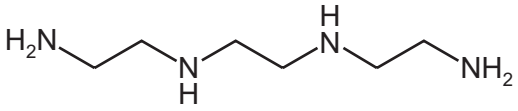
Suggest the type of stereoisomerism.

type of stereoisomerism .....

[2]

(d) Compound **X**, $C_6H_{18}N_4$, is a tetradentate ligand.

X



(i) Suggest why one molecule of **X** can form four dative bonds.

.....

.....

..... [1]

(ii) $C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion.

Construct an equation for this reaction.

..... [1]

[Total: 13]

.....

.....

.....

.....

.....

..... [4]

(b) The trend in the decomposition temperatures of Group 2 peroxides, MO_2, is similar to that of Group 2 carbonates.

Suggest which of barium peroxide, BaO_2, and calcium peroxide, CaO_2, will decompose at the **lower** temperature. Explain your answer.

.....

.....

..... [2]

(c) Magnesium iodate(V), $Mg(IO_3)_2$, decomposes when heated to form magnesium oxide, oxygen and iodine.

Construct an equation for this reaction.

..... [1]

.....

.....

..... [2]

(ii) Define the term *lattice energy*.

.....

.....

..... [2]

(b) Use the following data and relevant data from the *Data Booklet* to calculate a value for the enthalpy change of formation of zinc bromide, $ZnBr_2(s)$.

You might find it helpful to construct an energy cycle.

electron affinity of Br(g)	= –325 kJ mol^{-1}
enthalpy change of atomisation of Zn(s)	= +131 kJ mol^{-1}
enthalpy change of vaporisation of $Br_2(l)$	= +31 kJ mol^{-1}
lattice energy of $ZnBr_2(s)$	= –2678 kJ mol^{-1}

enthalpy change of formation of $ZnBr_2(s)$ = ... kJ mol^{-1} [4]

compound	lattice energy / kJ mol^{-1}
$ZnBr_2$	–2678
$ZnCl_2$	–2734
ZnO	–3971

(i) Explain why there is a difference between the lattice energies of $ZnBr_2$ and $ZnCl_2$.

.....

..... [1]

(ii) Explain why there is a difference between the lattice energies of $ZnCl_2$ and ZnO.

.....

..... [1]

[Total: 10]

compound	lattice energy / kJ mol^{-1}
LiF(s)	–1022
CaO(s)	–3513
SrO(s)	–3310

(i) Define the term *lattice energy*.

.....

.....

..... [2]

(ii) Explain why the lattice energy of CaO is more exothermic than the lattice energy of LiF.

.....

.....

..... [1]

(iii) Use the data in the table to estimate approximate values for the lattice energies of magnesium oxide and barium oxide.

ΔH_{latt}MgO(s) = ... kJ mol^{-1}

ΔH_{latt}BaO(s) = ... kJ mol^{-1}
[1]

(b) (i) Write an equation for the reaction between BaO and H_2O.
Include state symbols.

..... [1]

(ii) State and explain how the solubilities of the hydroxides of the Group 2 elements vary down the group.

.....

.....

.....

.....

.....

.....

You might find it helpful to construct an energy cycle.
Show your working.

electron affinity of F(g)	= –348 kJ mol^{-1}
enthalpy change of atomisation of Mg(s)	= +147 kJ mol^{-1}
enthalpy change of formation of MgF_2(s)	= –1102 kJ mol^{-1}

$\Delta H_{latt}MgF_2(s)$ = ... [3]

(d) (i) Define the term *electron affinity*.

.....

..... [2]

(ii) The electron affinity of carbon, C(g), is –120 kJ mol^{-1}.

Suggest an explanation for the difference between the electron affinity of fluorine and the electron affinity of carbon.

.....

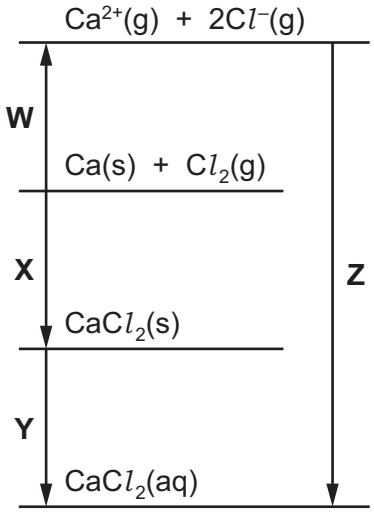
.....

.....

..... [1]

[Total: 15]

Each arrow indicates a transformation, **W**, **X**, **Y** and **Z**. Each transformation consists of one or more steps.



The following data and data from the *Data Booklet* should be used.

electron affinity of $Cl(g)$	$= -349\,kJ\,mol^{-1}$
enthalpy change of atomisation of Ca(s)	$= +193\,kJ\,mol^{-1}$
enthalpy change of formation of $CaCl_2(s)$	$= -795\,kJ\,mol^{-1}$
enthalpy change of solution of $CaCl_2(s)$	$= -83\,kJ\,mol^{-1}$
enthalpy change of hydration of $Cl^{-}(g)$	$= -364\,kJ\,mol^{-1}$

(i) Calculate the value of the enthalpy change corresponding to transformation **W**. Show your working.

enthalpy change **W** = ... $kJ\,mol^{-1}$ [2]

(ii) Use your answer to **(a)(i)** and other data to calculate the value of the enthalpy change corresponding to transformation **Z**.

enthalpy change **Z** = ... $kJ\,mol^{-1}$ [2]

enthalpy change of hydration of $Ca^{2+}(g)$ = ... kJ mol^{-1} [2]

(iv) Write an expression, in terms of **W**, **X**, **Y** and/or **Z**, to show how the enthalpy changes of **two** of the transformations can be used to calculate the lattice energy of $CaCl_2(s)$.

lattice energy of $CaCl_2(s)$ = ... [1]

(v) State whether the lattice energy of $CaCl_2(s)$ is more or less exothermic than the lattice energy of $MgF_2(s)$.

Explain your answer.

.....

.....

..... [1]

(b) The sulfates of the Group 2 elements vary in solubility down Group 2.

(i) Give the names of **two** solutions that could be mixed to form barium sulfate.

..... [1]

(ii) State and explain how the solubilities of the sulfates of the Group 2 elements vary down Group 2.

.....

.....

.....

.....

.....

.....

..... [4]

[Total: 13]

.....

.....

.....

.....

..... [3]

(b) (i) Lead(II) nitrate, $Pb(NO_3)_2$, decomposes on heating in a similar manner to the Group 2 nitrates.

Write an equation for the decomposition of lead(II) nitrate.

..... [1]

(ii) Suggest how the ease of decomposition of $Pb(NO_3)_2$ would compare to that of $Ba(NO_3)_2$. Explain your answer. You may find it useful to refer to the *Data Booklet*.

.....

..... [1]

(c) (i) Barium ethanedioate, BaC_2O_4, decomposes on heating to produce barium oxide and a mixture of two different gases.

Construct an equation for the decomposition of barium ethanedioate.

..... [1]

.....

.....

..... [2]

(ii) Use the following data to calculate a value for the enthalpy change of solution of copper(II) chloride, $CuCl_2(s)$. You might find it helpful to construct an energy cycle.

enthalpy change of hydration of Cl^- = –378 kJ mol^{-1}
enthalpy change of hydration of Cu^{2+} = –2099 kJ mol^{-1}
lattice energy of $CuCl_2(s)$ = –2824 kJ mol^{-1}

enthalpy change of solution of $CuCl_2(s)$ = ... kJ mol^{-1} [2]

(iii) The enthalpy change of hydration of Ca^{2+} is –1579 kJ mol^{-1}.

Use the *Data Booklet* to suggest why there is a big difference in the values of ΔH_{hyd} for Ca^{2+} and Cu^{2+}.

.....

.....

..... [2]

.....

..... [2]

(b) Write an equation for the process corresponding to the **second** ionisation energy of calcium. Include state symbols.

..... [1]

Some data relating to calcium and oxygen are listed. Select relevant data from this list for your answers to parts **(c)**, **(d)** and **(e)**.

process	value / kJ mol^{-1}
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	–142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$	+1933
lattice energy of CaO(s)	–3517

(c) Oxygen exists as O_2 molecules.

Use the data in this question to calculate a value for the bond energy of the O=O bond. Show all your working.

bond energy = ... kJ mol^{-1} [3]

.....

..... [1]

(ii) Suggest why the second electron affinity of oxygen is positive.

.....

..... [1]

(e) Calculate the enthalpy of formation of calcium oxide, CaO(s).

enthalpy of formation = ... $kJ\,mol^{-1}$ [2]

(f) The lattice energy of lithium fluoride, LiF(s), is $-1022\,kJ\,mol^{-1}$.

Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

.....

..... [2]

[Total: 12]

(a) State which of these two Group 2 carbonates requires the **higher** temperature before it begins to decompose. Explain your answer.

.....

.....

..... [2]

(b) After decomposition is complete, the 0.02 mol sample of calcium oxide is taken and added to 2.00 dm^3 of water. A solution is formed with no solid present. Dilute sulfuric acid is then added dropwise until a precipitate is seen.

The same procedure is repeated with the 0.02 mol sample of barium oxide, using the same concentration solution of dilute sulfuric acid.

Identify the sample to which **most** sulfuric acid must be added to cause a precipitate to appear.

Explain your answer. You should refer to the solubilities of the precipitates and relevant energy terms in your answer.

.....

.....

.....

..... [3]

(c) **(i)** Calculate the mass, in g, of CO_2 produced by the decomposition of 0.020 moles of calcium carbonate.

mass of CO_2 = ... g [1]

(ii) Calculate the minimum mass, in g, of propane that would, on complete combustion, produce the same mass of CO_2 calculated in **(c)(i)**.
Give your answer to three significant figures.

mass of propane = ... g [2]

[Total: 8]

33 Radium is a Group 2 element.

The predicted lattice energy, $\Delta H^{\ominus}_{latt}$, of radium sulfide, RaS, is –2612 kJ mol^{-1}.

(a) Define $\Delta H^{\ominus}_{latt}$.

.....

..... [2]

Some data relating to radium and sulfur are listed. Select relevant data from this list for use in your answers to parts **(b)** to **(e)**.

process	value / kJ mol^{-1}
enthalpy change for $Ra(s) \rightarrow Ra^{2+}(g) + 2e^-$	+1619
first ionisation energy of sulfur	+1000
second ionisation energy of sulfur	+2260
first electron affinity of sulfur	–200
second electron affinity of sulfur	+532
enthalpy change for $\frac{1}{8}S_8(s) + 2e^- \rightarrow S^{2-}(g)$	+555
lattice energy of RaS(s)	–2612

(b) Write an equation for the process corresponding to the **second** electron affinity of sulfur. Include state symbols.

..... [1]

(c) Sulfur exists as S_8 molecules in the solid state.

Use the data in this question to calculate the enthalpy change for the reaction $S_8(s) \rightarrow 8S(g)$.

enthalpy change = ... kJ mol^{-1} [3]

standard enthalpy change, $\Delta H_f^{\ominus}$ = ... kJ mol^{-1} [2]

(e) (i) State the **two** major factors that affect the numerical magnitude of a lattice energy.

.....

..... [2]

(ii) For **each** factor you have identified in **(e)(i)**, state whether it tends to make the lattice energy of radium sulfide more or less exothermic than that of sodium chloride.

Explain your answer.

.....

.....

.....

..... [2]

(iii) The lattice energies of sodium chloride, NaC*l*, and radium sulfide, RaS, are –771 kJ mol^{-1} and –2612 kJ mol^{-1}, respectively.

Identify the **dominant** factor in determining the relative numerical magnitudes of the lattice energies of radium sulfide and sodium chloride.

Explain your answer.

.....

..... [1]

[Total: 13]

(a) State which of these two Group 2 nitrates requires the **higher** temperature before it begins to decompose. Explain your answer.

.....

.....

.....

..... [2]

(b) After decomposition is complete the 0.01 mol sample of magnesium oxide is taken and increasing amounts of water are added to it, with stirring, until no solid remains.

This procedure is repeated with the 0.01 mol sample of strontium oxide.

Identify the sample to which most water must be added to cause all the solid to dissolve. Explain your answer by reference to the solubilities of the products formed when water is added to the oxides. You should refer to relevant energy terms in your answer.

.....

.....

.....

.....

..... [3]

(c) The nitrogen dioxide given off by the decomposition of 0.0100 mol of strontium nitrate is dissolved in water. The oxidising agent $H_2O_2(aq)$ is then added to give 150.0 cm^3 of a solution in which nitric acid, HNO_3, is the only nitrogen-containing product.

(i) Calculate the concentration, in mol dm^{-3}, of HNO_3 in the 150.0 cm^3 of solution.

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

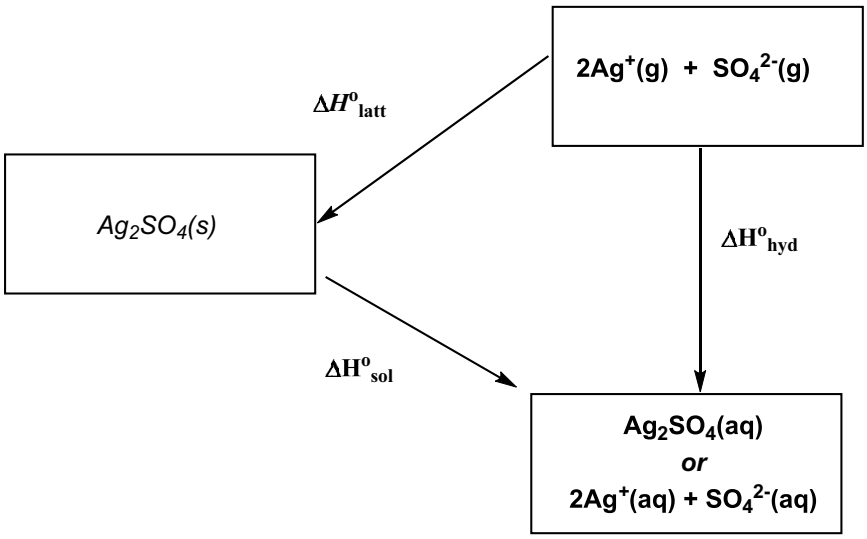
Calculate the minimum volume, in cm^3, of NaOH(aq) needed. Give your answer to three significant figures.

volume = ... cm^3 [1]

[Total: 7]

1 (a) (i)	<table><tr><th>isotope</th><th>relative abundance</th></tr><tr><td>^{24}Mg</td><td>**78–79**</td></tr><tr><td>^{25}Mg</td><td>**10**</td></tr><tr><td>^{26}Mg</td><td>**12–11**</td></tr></table> (**total must add up to 100 %**)	1
(ii)	e.g. 0.78x24 + 0.10x25 + 0.12x26 = **24.34**	1
(b) (i)	nitrates become more stable (down the group) as the ionic radius increases ***or*** charge density on cation/ion decreases decreasing its ability to distort/polarise the NO_3^-/nitrate ion	1 1 1
(ii)	$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$	1
(iii)	the **charge density** of the other cations are too small (to polarise the anion sufficiently so the anion is more stable)	1
		[Total: 7]

P41/M/J/15/Q4b

(2b)		1 1 1 1

Question	point	Marks
3 (a)	Ca $3s^2 3p^6 4s^2$ **and** Ca^{2+} $3s^2 3p^6$	1
(b)	$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$ **or** $CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$	1
(c) (i)	CaO **and** brown gas	1
(ii)	the (cat)ion size / radii increases decreasing its ability to polarise the nitrate ion / N-O bond	2
(d) (i)	(energy change when) 1 mole of ions **gaseous** (ions) dissolve in **water** (to form an infinitely dilute solution) *or* **gaseous** (ions) form an **aqueous** solution	2
(ii)	$\Delta H^{\ominus}_{latt} Ca(NO_3)_2 + \Delta H^{\ominus}_{sol} Ca(NO_3)_2 = \Delta H^{\ominus}_{hyd}\ Ca^{2+} + 2\Delta H^{\ominus}_{hyd}\ NO_3^-$ $\Delta H^{\ominus}_{latt} - 19 = -1650 + (2x\ -314)$ $-2259\ kJ\ mol^{-1}$	3
3	$Ca^{(2+)}$ is a smaller (ion) ***or*** $Ca^{(2+)}$ has a larger charge density $Ca^{(2+)}$ has a stronger attraction / bond to H_2O	2
		12

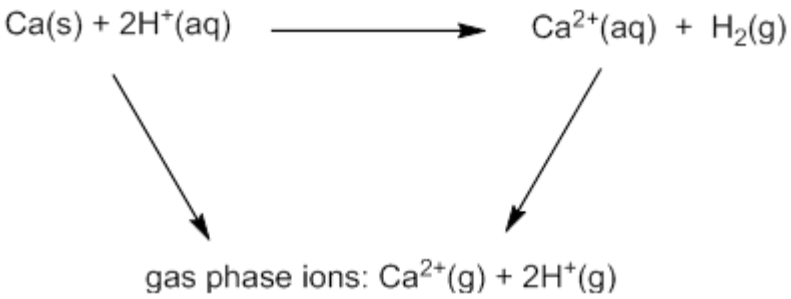
Question	Marking Point	Marks	Total Marks
4 (a)	ionic bonds break / bonds between Mg^{2+} and Cl^- break forces / bonds / attractions form between the ions and water	**2**	
(b) (i)	(the energy change) when 1 mole of a substance dissolves in water / becomes aq	**1**	
(ii)	$\Delta H^{\ominus}_{latt}\ MgCl_2 + \Delta H^{\ominus}_{sol}\ MgCl_2 = \Delta H^{\ominus}_{hyd}\ Mg^{2+} + 2\Delta H^{\ominus}_{lhyd}\ Cl^-$ $-2524 - 155 = -1925 + 2\Delta H^{\ominus}_{hyd}\ Cl^-$ $= -377\ kJ\,mol^{-1}$	**2**	
(iii)	magnesium / Mg is higher charge / sodium / Na is smaller charge magnesium / Mg is smaller / sodium / Na is larger Mg stronger attraction for water / Na weaker attraction for water any two	**2**	
(c)	• solubility decreases • lattice energy and hydration enthalpy decrease • hydration enthalpy decreases more rapidly / is dominant factor • so (enthalpy change of) solution becomes less exothermic / more endothermic	**4**	
			[Total: 11]

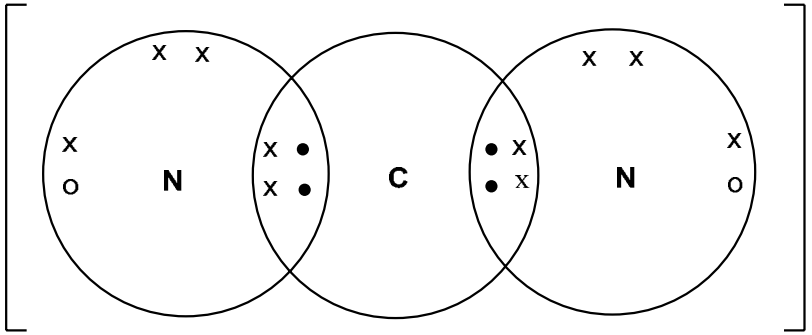
Question	Answer	Marks
5 (a) (i)	$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$	[1]
(ii)	$Ba(OH)_2$ is soluble, OR $BaCO_3$ is insoluble	[1]
(iii)	$Mg(OH)_2$ is insoluble / not very soluble will not form ppt. of $MgCO_3$	[1] [1]
(b)	carbonates are more stable down the group due to increase in cationic size / radius (causing) less polarisation of CO_3^{2-} ion	[1] [1] [1]
(c)	radius of Ni^{2+} = 0.070 nm; radius of Ca^{2+} = 0.099 nm so $NiCO_3$ decomposes more readily than $CaCO_3$	[1] [1]
		[Total: 9]

P41/M/J/16/Q8a

6 (a)	ΔH = [2(–580) + 3(–286) + 3(–1438)] – [–2061 + 4(–437) + 3(–814)] = **–**81 kJ mol^{-1}	[2]

Question	Answer	Marks
7 (a) (i)	dative (covalent) *or* coordinate Hydrogen / H (boding)	2
(ii)	octahedral	1
(iii)	$Mg(NO_3)_2.6H_2O \rightarrow Mg(NO_3)_2 + 6H_2O$ $Mg(NO_3)_2 \rightarrow MgO + 2NO_2 + \frac{1}{2}O_2$ *any three of* (solid) dissolves / turns to liquid condensation on tube white solid (forms / remains) brown fumes (evolved) gas formed that relights a glowing splint	4
(iv)	M_r values: $Mg(NO_3)_2.6H_2O$ = 256.3 MgO = 40.3 **or** (loss in molar mass = 256.3 – 40.3 =) 216 percentage loss = 100 × 216 / 256.3 = **84.3 / 84.4%**	2
(b)	(cat)-ionic radius / ion size **increases** (down the group) less polarisation / distortion of nitrate ion / NO_3^-	2
(c)	$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2$	1
		[Total: 12]

8	**(a)**	M1: solubility increases (down the group) M2: because lattice energy decreases faster than does $\Delta \boldsymbol{H}_{hyd}$ M3: ΔH_{sol} / enthalpy of solution becomes more exothermic / less endothermic	3
	(b) (i)	Should be the same / similar (enthalpy change), as (both acids) are fully ionised / strong acids	1
	(ii)	 $\boldsymbol{x} = \Delta H_{at}(Ca) + IE(1) + IE(2) - 2\Delta \mathbf{H}_{hyd}(H^+) + \Delta \mathbf{H}_{hyd}(Ca^{2+}) - 2IE(H) - E(H\text{-}H)$ $\boldsymbol{x} = 178 + 590 + 1150 + 2(1090) - 1576 - 2(1310) - 436$ $\boldsymbol{x} = \mathbf{-534}\ kJ\ mol^{-1}$	4
	(c)	CH_3CO_2H is incompletely ionised / weak acid / weaker acid enthalpy change of ionisation (of CH_3COOH) is $+2\ kJ\ mol^{-1}$ **or** energy needed to ionise / dissociate (CH_3COOH)	2
			[Total: 10]

Question	Answer	Mark
9(a)	solid remains	1 **1**
9(b)	stability increases (down the group) as size / radius of (metal) **ion** / $\mathbf{M^{2+}}$ increases so polarisation / distortion of anion / carbonate ion decreases	1 1 1 **3**
9(c)(i)		**2**
9(c)(ii)	$Ca(NO_3)_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$ $CaCO_3$ correct equation	1 1 **2**
	Total:	**8**

	ΔH_{latt} and ΔH_{hyd} both **decrease** **or** ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic	**1**
	ΔH_{latt} decreases / changes more (than ΔH_{hyd} as OH^- being smaller than M^{2+})	**1**
	ΔH_{sol} becomes more exothermic / more negative / less endothermic / less positive	**1**
10(b)(i)	ΔH_{r1} – (538 + 2x230 + 394) = –(1216 + 286) ΔH_{r1} – 1392 = –1502	**1**
	ΔH_{r1} = **–110**	**1**
10(b)(ii)	let $\Delta H_f(HCO_3^-(aq))$ = y 2y – 538 = –1216 – 394 – 286 – 26	**1**
	y = **–692**	**1**
10(b)(iii)	ΔH_{r3} –538 – 2(230 + 394) = –538 – 2(692) ΔH_{r3} = **–136**	**1**
10(b)(iv)	ΔH_{r3} will be identical to ΔH_{r4}, / unchanged	**1**
	as the reaction is the same, or: $2OH^-(aq) + 2CO_2(g) \longrightarrow 2HCO_3^-(aq)$ or metal ions stay in solution/metal ions are unchanged / are spectators	**1**
10(c)	more **gaseous moles** are being consumed (in reaction 3) **or** more **CO_2 moles** are being consumed (in reaction 3)	**1**
	ΔS is therefore expected to be **more negative/less positive** for reaction 3	**1**

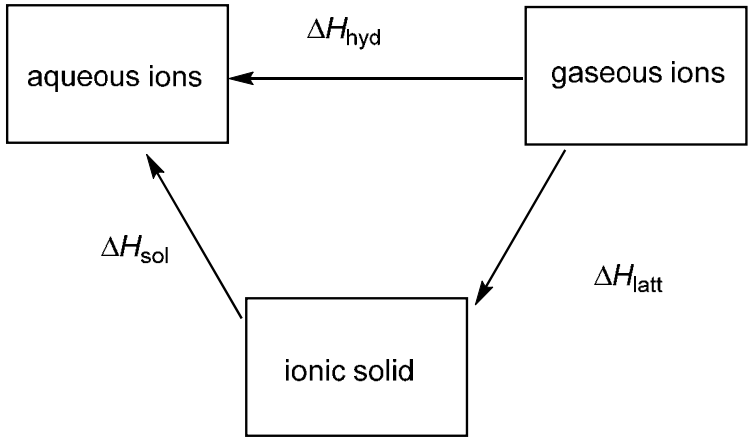
Question	Answer	Marks
11(a)(i)	increases down the group	**1**
	radius / size of (cat)ion/M^{2+} increases	**1**
	less polarisation / distortion of anion / carbonate **ion** / CO_3^{2-}	**1**
11(a)(ii)	Na^+ has smaller ionic charge **and** larger ionic radii OR the **charge density** of the **Na^+** is **lower**	**1**
11(b)(i)	$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$	**1**
11(b)(ii)	$NaHCO_3$ because Na^+ is **smaller** OR charge density Na^+ is **larger**	**1**
11(c)(i)	LE = $\Delta H_f - 2(\Delta H_{at} + IE) - ½(O=O) - (EA_1 + EA_2)$ = $-361 - 2(89)$ **–** $2(418) - 496/2 - (-141+798)$ = **–2280** (kJ mol^{-1}) correct answer scores [3]	**3** **1** **1** **1**
11(c)(ii)	LE of Na_2O will be **more negative** AND as $Na^{(+)}$ is smaller / larger charge density / smaller radii AND so greater attraction (between the ions) OR (ionic) bonds will be stronger	**1**
	Total:	**10**

12(b)	enthalpy change = (–642) – (2 × –106) = **–430**	**1**
12(c)(i)	–106 = 147 + 121 + 736 + (–349) + lattice energy lattice energy = –761	**3**
12(c)(ii)	$MgCl_2$ more exothermic / negative / bigger than $MgCl$ **and** $NaCl$ more exothermic / negative / bigger than $MgCl$	**1**
	(reason for $MgCl_2$) higher charge / lower radius of Mg^{2+} cation	**1**
	(reason for $NaCl$) smaller radius of Na^+ cation	**1**
12(d)	energy change when 1 mole of atoms / ions each gain an electron **or** energy change when 1 mole of atoms / ions gain 1 mole of electrons	**1**
	gaseous	**1**

13(a)	$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$	
	balanced with all formulae correct	**1**
	state symbols	**1**
13(b)	gi ionic	**1**
	strong bond / attraction between **AND** positive and negative ions / anions and cations / Na^+ and O^{2-} / oppositely charged ions	**1**
13(c)(i)	the reaction produces sodium hydroxide / hydroxide ions / OH^- ions	**1**
	the hydroxide ions can receive / accept H^+ ions / protons	**1**
13(c)(ii)	Calculation of Na_2O moles 3.10 g / 62 **OR** 0.05	**1**
	Calculation of $[OH^-]$ $0.05 \times (2 / 0.400) = 0.25$ mol dm^{-3}	**1**
	Calculation of pH –log 0.25 = 0.60 14 – 0.60 = 13.40	**1**
13(d)	use of (2×109) or 218 and (2×494) or 988	**1**
	use of (0.5×496) or 248	**1**
	use of 416, 142, 844	**1**
	evaluation of expression correctly $\Delta H_{lat} = -416 - (2 \times 109) - (0.5 \times 496) - (2 \times 494) - (-142 + 844) = -2572$	**1**
13(e)	the lattice energy of Na_2S is less exothermic	**1**
	the sulfide ion is larger than the oxide ion / S^{2-} larger than O^2 / ionic radii quoted 0.184 nm and 0.140 nm	**1**

Question	Answer	Marks
14(a)	calcium – red flame	**1**
	barium – green flame	**1**
14(b)	• the temperature increases down the group • ionic radius increases / charge density decreases down the group • decreasing distortion / polarisation **or** decreasing weakening of bonds • of the anion / the CO_3^{2-} ion 2 points = 1 mark 3 points = 2 marks 4 points = 3 marks	**3**
14(c)	the gas is colourless / looks like air / cannot be seen	**1**
	appearance of solid doesn't change / white solid becomes white solid	**1**

Question	Answer	Marks
15(a)(i)	$_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	**1**
	correct state symbols: (s), (s), (g), (g)	**1**
15(a)(ii)	**brown** gas / fumes / vapour	**1**
	white solid / residue (stays the same)	**1**
15(b)	solubility **decreases** (down the group)	**1**
	ΔH_{latt} and ΔH_{hyd} decrease / both become less exothermic / less negative	**1**
	ΔH_{latt} decreases / becomes less exothermic by a smaller extent **ora**	**1**
	ΔH_{sol} becomes less exothermic / less negative **ora**	**1**

Question	Answer	Marks
16(a)	$_3N_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2NH_3$ products are $Ca(OH)_2$ **and** NH_3 [1] rest of the equation, balanced [1]	**2**
16(b)	**M1**: solubility increases (down the Group) [1] **M2**: because lattice energy and hydration energy **decreases or** lattice energy and hydration energy become **less exothermic / (more) endothermic**[1] **M3**: because lattice energy decreases to a **greater extent** (than does ΔH_{hyd}) [1]	**3**
16(c)	 arrow label and direction correct [1] x 3	**3**

Question	Answer	Marks
17(a)	ionic radius / ion size **increases OR** charge density **decreases** (down the group) [1] less polarisation / distortion of anion / nitrate ion / NO_3^- / nitrate group **OR** N-O / N=O bond is less weakened / distorted / polarised **OR** more energy to break N-O / N=O bond [1]	**2**
17(b)	• moles of Ce^{4+} = 0.0400 × 21.8 / 1000 = 8.72×10^{-4} (moles of Ce^{4+}) • moles of NO_2^- = 8.72×10^{-4} / 2 = 4.36×10^{-4} in 25 cm^3 (use of 2:1 ratio correctly) • moles of NO_2^- = $4.36 \times 10^{-4} \times 4 = 1.74(4) \times 10^{-3}$ in 100 cm^3 (use of 4:1 ratio correctly) • mass $NaNO_2$ = $1.74(4) \times 10^{-3} \times (23.0 + 14.0 + 32.0) = 0.120$ g (use of M_r correctly) • % purity = 0.120 / 0.138 = 86.96% (use of 0.0138 correctly) two points = [1] four points = [2] all five points = [3]	**3**

Question	Answer	Marks
18(a)	S $_{3})_2$ → SrO + $2NO_2$ + ½O_2	**1**
18(b)	**M1** increases **M2** cationic radius / ion size **increases** (down the group) **M3** less polarisation/distortion of anion / nitrate ion / NO_3^- / nitrate group	**3**
18(c)(i)	readily **and** Ca^{2+} has a smaller ionic radius **or** more readily **and** Ca^{2+} has a greater charge density	**1**
18(c)(ii)	$3Ba(NH_2)_2 \rightarrow Ba_3N_2 + 4NH_3$	**1**
18(d)	**M1** bond angle 104–105° **M2** **explanation** two lone pairs and two bonding pairs **M3** lone pairs repel more	**3**

19(a)

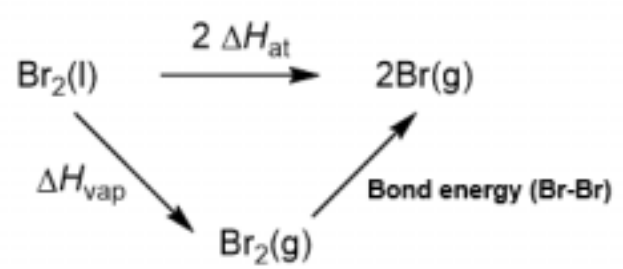
energy change	always positive	always negative	either negative or positive
bond energy	✓		
enthalpy of formation			✓

both ticks correct

1

19(b) (energy change) when **1 mole** of **gaseous atoms** are formed (from an element in its standard state) **1**

19(c)



M1: correct cycle: formulae and state symbols

M2: use of 1 × 193 **and** 2 × (112)

M3: for the correct sum and answer ecf from M2

$\Delta H^{\ominus}_{vap}$ (= (2 × 112) – (193)) = **+31** kJ mol^{-1} [scores M2 and M3]

3

19(d) more endothermic **and** greater Van der Waals / London / induced dipole-dipole forces **both** **1**

19(e)(i) (energy change) when **1 mole** of **gaseous ions** is dissolved in (an excess of) water **1**

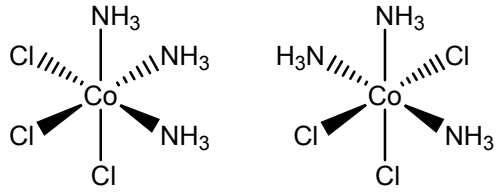
19(e)(ii) **M1**: Br^- has a smaller ionic radii **2**

Question	Answer	Marks
20(a)	$_3^{2-} \rightarrow O^{2-} + CO_2$ [1]	**1**
20(b)	Increases (with increasing atomic number / implied) [1] cationic radius / ion size **increases** (down the group) [1] less polarisation / distortion of anion/CO_3^{2-} [1]	**3**
20(c)	$^{2+}$) 0.120 nm; (Ca^{2+}) 0.099 nm; (Zn^{2+}) 0.075 nm [1] (most stable) $PbCO_3$ > $CaCO_3$ > $ZnCO_3$ (least stable) [1] **ECF** from atomic radii	**2**
20(d)	amount of CO_2 = 125 / 24000 = 5.21×10^{-3} mol [1] $CaMg(CO_3)_2$:CO_2 1:2 amount of carbonate = $2.60(4) \times 10^{-3}$ mol [1] ECF mass of carbonate = $184(.4) \times 2.60(4) \times 10^{-3}$ = 0.480 g % of $CaMg(CO_3)_2$ = $100 \times 0.480 / 0.642$ = **74.8** % [1] ECF	**3**

Question	Answer	Marks
21(a)	<table><tr><td>energy change</td><td>always positive</td><td>always negative</td><td>either negative or positive</td></tr><tr><td>lattice energy</td><td></td><td>✓</td><td></td></tr><tr><td>enthalpy of neutralisation</td><td></td><td>✓</td><td></td></tr></table> **both** [1]	**1**
21(b)	(energy change) when **1 mole** of solute is dissolved in an infinite amount of **water** to form a dilute solution	**1**
21(c)	calculation of $\Delta H^{\ominus}_{sol}$ with –251, –1284 and –2035 only and two correct signs [1] calculation of $\Delta H^{\ominus}_{sol}$ with –251, –1284 and –2035 only and correct signs **OR** calculation of $\Delta H^{\ominus}_{sol}$ with (–251 × 3), –1284 and –2035 only and two correct signs [2] $\Delta H^{\ominus}_{sol}$ = (3 × –251) + (–1284) – (–2035) = **–2** (kJ mol^{-1}) [3]	**3**
21(d)	$^{2+}$ have a higher charge / greater charge density [1] **ora** **stronger** electrostatic forces between Br^- and Ca^{2+} [1]	**2**
21(e)(i)	$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]	**1**
21(e)(ii)	TΔS is more positive **OR** –TΔS becomes more negative [1]	**1**

Question	Answer	Marks
22(a)(i)	$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$	**1**
22(a)(ii)	$Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$	**1**
22(a)(iii)	more reactive **and** easier to ionise down the group **OR** more reactive **and** ionisation energies decrease down the group	**1**
22(b)(i)	brown gas **and white** solid	**1**
22(b)(ii)	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	**1**
22(b)(iii)	**M1:** more stable (down the group) **M2:** cationic radius **increases /** charge density of M^{2+} decreases (down the group) **M3:** NO_3^- anion is less polarised / distorted	**3**
22(c)	**M1:** less soluble / decreases (down the group) **M2:** ΔH_{latt} and ΔH_{hyd} **both** decrease / less exothermic down the group **M3:** ΔH_{hyd} decreases by more (than ΔH_{latt}) **M4:** ΔH_{sol} becomes more endothermic / less exothermic	**4**

23(a)	**M1:** Mg – white **flame and** Sr – red **flame** **M2:** white solid product once	**2**
23(b)(i)	**M1:** $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$ $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ all substances, balanced **M2:** all state symbols	**2**
23(b)(ii)	neutralises acid / raises pH	**1**
23(b)(iii)	**M1:** ΔH_{lat} and ΔH_{hyd} decrease down group **M2:** ΔH_{lat} decreases / changes more **M3:** ΔH_{sol} becomes more exo / more –ve / less endo / less +ve	**3**
23(c)	• no change (for hydroxide) / colourless solution • white (for sulfate) • precipitate (for sulfate) Award 1 mark for two points, award 2 marks for all three points	**2**
23(d)	**M1:** stability increases / higher T needed for decompose **M2:** larger ionic radius **M3:** harder to distort / polarise anion / carbonate ion **or** harder to polarise / weaken C–O or C=O bond.	**3**

24(a)(ii)	M1: blue ppt/solid M2: $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ **OR** $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$ M3: precipitation/ acid-base M4: blue solution M5: $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ M6: **ligand** exchange/displacement/substitution/replacement	**6**
24(b)	• solution turns blue → pink • a white ppt. of AgC*l* forms • equilibrium shifts to the left / $[Cl^-]$ decreases Two correct responses = 1 mark Three correct responses = 2 marks	**2**
24(c)	 geometric **ALLOW** cis-trans Two correct responses = 1 mark Three correct responses = 2 marks	**2**
24(d)(i)	**each nitrogen** / the four nitrogen's has a **lone pair of electrons** (to the metal ion) Two correct responses = 1 mark	**1**
24(d)(ii)	$[Co(H_2O)_6]^{2+} + C_6H_{18}N_4 \rightarrow [Co(C_6H_{18}N_4)]^{2+} + 6H_2O$ **OR**	**1**

Question	Answer	Marks
25(a)	**M1** solubility decreases down the group **M2** ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic **M3** ΔH_{latt} changes less (than ΔH_{hyd} as SO_4^{2-} being larger than M^{2+}) **M4** ΔH_{sol} becomes less exothermic / less negative	**4**
25(b)	**M1** CaO_2 **and** Ca^{2+} has a smaller ionic radii/ Ca^{2+} has a higher charge density **M2** anion/O_2^{2-} becomes more polarised /distorted	**2**
25(c)	$Mg(IO_3)_2 \rightarrow MgO + 2.5O_2 + I_2$	**1**

Question	Answer	Marks
26(a)(i)	• energy change • when one electron is added • to each atom /ion in one mole of • gaseous atoms /ions Award one mark for two correct statements. Award two marks for four correct statements	**2**
26(a)(ii)	**M1** energy change when 1 mole of an ionic compound is formed **M2** from gas phase ions/ gaseous ions	**2**
26(b)	**M1** use of data (with no multipliers) 31, 131, -2678 **M2** extraction of data 908, 1730, 193 **M3** use of (2 x-325) **M4** evaluation of <u>their</u> expression correctly, as shown $\Delta H_f(ZnBr_2)$ = 131 + (908 +1730) + 193 + 31 + (2 x-325) + (-2678) = **-335** kJ mol^{-1} [4]	**4**
26(c)(i)	Br^- is a largest ion/larger ion than Cl^- so attraction between Br^- and Zn^{2+} is smaller	**1**
26(c)(ii)	O^{2-} is a smallest ion/smaller ion than Cl^- **AND** O^{2-} has the highest charge/ higher charge than Cl^- (so attraction between O^{2-} and Zn^{2+} is larger)	**1**

Question	Answer	Marks
27(a)(i)	**M1** energy released when 1 mole of an ionic compound is formed [1] **M2** from gaseous ions (under standard conditions) [1]	**2**
27(a)(ii)	Ca^{2+} & O^{2-} have a higher charge / charge density (than Li^+ and F^-) [1]	**1**
27(a)(iii)	MgO –3600 or more negative **AND** BaO –3200 or less negative **BOTH** [1]	**1**
27(b)(i)	$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(aq)$ [1]	**1**
27(b)(ii)	**M1** (solubility) increases (down the group) [1] **M2** both ΔH_{latt} and ΔH_{hyd} become less exothermic / less negative [1] **M3** ΔH_{latt} changes more / is dominant factor [1] **M4** ΔH_{sol} becomes more negative / more exothermic [1]	**4**
27(c)	**M1:** Use of $2 \times$ –348 (EA F) and +158 (bond energy of F_2) [1] **M2:** Use of +147 (at Mg) and +736 and +1450 (IEs of Mg) [1] **M3:** evaluation and calculation of their answer (–1102 – (147 + 158 + 736 + 1450 – 696)) = **–2897** ($kJ\ mol^{-1}$) [1] ecf	**3**
27(d)(i)	• (energy change) when an / one electron is added to • each atom / ion in one mole of • gaseous atoms / ions mark as • ✓ ✓ [2]	**2**
27(d)(ii)	F has greater nuclear charge / more protons	**1**

Question	Answer	Marks
28(a)(i)	(+193 + 242 + 590 + 1150 + (2 × –349)) [1] answer (+)1477 [1]	**2**
28(a)(ii)	(–795 – 83 – 1477) [1] –2355 [1]	**2**
28(a)(iii)	(–2355 –(2 × –364)) [1] –1627 [1]	**2**
28(a)(iv)	Z–Y or X–W [1]	**1**
28(a)(v)	less (exothermic) and both ions (in $CaCl_2$) are larger [1]	1
28(b)(i)	soluble barium salt **AND** soluble sulfate [1]	1
28(b)(ii)	less soluble (down the group) [1] ΔH_{lat} and ΔH_{hyd} both decrease down the group [1] ΔH_{hyd} decreases more / faster / is dominant factor [1] ΔH_{sol} gets less exo / more endo [1]	**4**

Question	Answer	Marks
29(a)	**M1:** increases down the group **M2:** radius / size of cation / M^{2+} increases **OR** charge density of cation / M^{2+} decreases **M3:** less polarisation / less distortion of anion / NO_3^- ion **OR** less weakening of NO bond	**3**
29(b)(i)	$_3)_2 \rightarrow PbO + 2NO_2 + ½O_2$	**1**
29(b)(ii)	lead nitrate / $Pb(NO_3)_2$ would decompose more / easier **AND** as Pb^{2+} is smaller / Pb^{2+} has larger charge density (so more polarising)	**1**
29(c)(i)	$_2O_4 \rightarrow BaO + CO_2 + CO$ **OR** $BaC_2O_4 \rightarrow BaO + 2CO + ½O_2$	**1**

P42/M/J/21/Q4a

Question	Answer	Marks
30(a)(i)	**M1:** energy change when 1 mole of a ionic compound is formed **M2:** from its gaseous ions under standard conditions	**2**
30(a)(ii)	$\Delta H_{sol} = (–2099) + (2\times – 378) – (–2824)$ $\Delta H_{sol} = –31$ kJ mol$^{–1}$ **M1:** use of $\times 2$ as only multiplier **M2:** correct signs and evaluation	**2**
30(a)(iii)	**M1:** Cu^{2+} is smaller **OR** Cu^{2+} has a higher charge density **M2:** Cu^{2+} attracts water molecules more / stronger **OR** (Cu^{2+}) forms stronger ion-dipole forces to water molecules	**2**

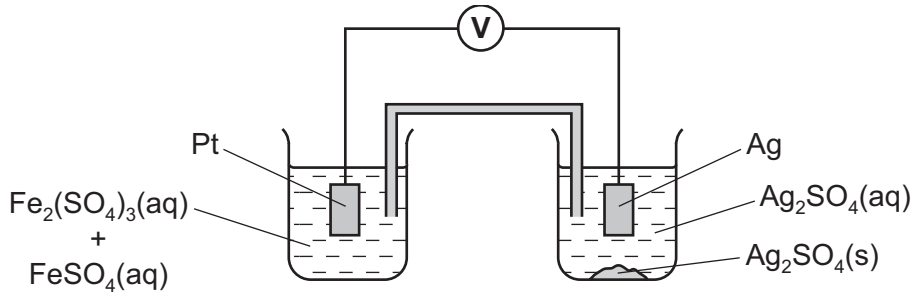
31(a)	• enthalpy/energy change • one mole of electrons gained • by one mole of atoms • gaseous (atoms)	**2**
31(b)	$^{+}(g) \rightarrow Ca^{2+}(g) + e^{-}$ [1]	**1**
31(c)	M1: selecting correct data 951, 844, 142 only M2: evaluation to give 249 (ΔH_{atom}) **OR** 2(951) = BE – 2(142) + 2(844) M3: evaluation to 498 (2×249) ecf M2 951 = ΔH_{atom} –142 + 844 ΔH_{atom} = 249 BE = **498** (kJ mol^{-1}) [3]	**3**
31(d)(i)	**attraction** between nucleus / protons / nuclear charge **and** electron [1]	**1**
31(d)(ii)	**repulsion** between 1– ion / electrons of O^{-} **and** electron [1]	**1**
31(e)	M1: selecting correct data 951, 1933, 3517 only (ignore signs) M2: evaluation to give –633 (ΔH_f) ecf ΔH_f = 951 + 1933 – 3517 = **–633** (kJ mol^{-1}) [2]	**2**
31(f)	io charge / charge density (of the ions) [1]	**2**

Question	Answer	Marks
32(a)	• barium carbonate / Ba / $BaCO_3$ • larger ionic radius **OR** smaller charge density of cation / M^{2+} [1] • anion / CO_3^{2-} / carbonate ion is less distorted / less polarised **OR** C-O / C=O less weakened [1]	**2**
32(b)	• calcium oxide / calcium hydroxide • Ca**SO_4 /** calcium **sulfate** is more soluble **OR** Ba**SO_4** is less soluble [1] • ΔH_{latt} and ΔH_{hyd} are less exothermic / more endothermic (for $BaSO_4$) [1] • ΔH_{hyd} is dominant factor / ΔH_{hyd} change is greater **OR** ΔH_{latt} changes less [1]	**3**
32(c)(i)	mass of CO_2 = 0.02×44 = **0.88** g [1]	**1**
32(c)(ii)	(writes correct equation, deduces 3 CO_2 per mole) moles of propane = 0.02 / 3 **OR** 0.00667 **OR** 1 / 150 [1] mass of propane = $0.02 / 3 \times 44$ = **0.293** g [1] ecf M1 $\times$ 44 3sf needed	**2**

33(a)	• enthalpy / energy change / given out / evolved / released • one mole is formed / made [1] • of compound / solid / lattice / crystal • (from) **gas**eous **ions** [1]	**2**
33(b)	$S^-(g) + e^- \rightarrow S^{2-}(g)$ [1]	**1**
33(c)	(555 + 200 – 532 = 223, 223 × 8 = 1784) M1 selecting correct data 555, 200, 532 **only**, (ignore signs and multipliers) [1] M2 evaluation to give +223 [1] M3 multiplying M2 by 8 and evaluation ans (+) 1784 [1]	**3**
33(d)	(1619 + 555 – 2612 = –438) M1 selecting correct data 1619 555 2612 only, (ignore signs and multipliers) [1] M2 evaluation to give –438 [1]	**2**
33(e)(i)	ionic radius / size / sum of ionic radii [1] ionic charge / product of ionic charges [1]	**2**
33(e)(ii)	M1 (size tends to make $\Delta H^{\ominus}_{latt}$ of radium sulfide) less exothermic since the ions are larger [1] M2 (charge tends to make $\Delta H^{\ominus}_{latt}$ of radium sulfide) less exothermic since the ions are more highly charged [1]	**2**
33(e)(iii)	(ionic) charge (since) **AND**	**1**

Question	Answer	Marks
34(a)	stront nitrate **AND** because of larger cationic radius [1] NO_3^- / nitrate **ion** / anion is less distorted / polarised **OR** N–O or N=O bond less weakened / distorted [1]	**2**
34(b)	M1 magnesium oxide requires more water to dissolve **AND** because $Sr(OH)_2$ is more soluble [1] M2 lattice and hydration energies less for $Sr(OH)_2$ [1] M3 lattice energy is dominant factor / change in lattice energy is greater [1]	**3**
34(c)(i)	0.13 [1]	**1**
34(c)(ii)	26.7 cm^3 **must be 3SF** [1]	**1**

Paper 4
Topic 2
Electrochemistry



(i) Use the *Data Booklet* to calculate the value of $E^{\ominus}_{cell}$ under standard conditions, stating which electrode is the positive one.

$E^{\ominus}_{cell}$ = ... positive electrode: ..... [1]

(ii) How would the actual E_{cell} of the above cell compare to the $E^{\ominus}_{cell}$ under standard conditions? Explain your answer.

.....

..... [1]

(iii) How would the E_{cell} of the above cell change, if at all, if a few cm^3 of concentrated $Na_2SO_4(aq)$ were added to

- the beaker containing $Fe^{3+}(aq) + Fe^{2+}(aq)$,

.....

- the beaker containing $Ag_2SO_4(aq)$?

.....
[2]

(iv) Explain any changes in E_{cell} you have stated in **(iii)**.

.....

..... [1]

(d) Solutions of iron(III) sulfate are acidic due to the following equilibrium.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad K_a = 8.9 \times 10^{-4}\,mol\,dm^{-3}$$

Calculate the pH of a $0.1\,mol\,dm^{-3}$ solution of iron(III) sulfate, $Fe_2(SO_4)_3$.

pH = ...
[2]

..... [1]

(ii) When a current of 1.2A was passed through dilute sulfuric acid for 30 minutes, it was found that 130 cm^3 of oxygen, measured at 25 °C and 1 atm, was collected at the anode.

The following reaction takes place.

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

Use these data and data from the *Data Booklet* to calculate a value for the Avogadro constant, *L*, by calculating

- the number of moles of oxygen produced,
- the number of moles of electrons needed for this,
- the number of coulombs passed,
- the number of electrons passed,
- the number of electrons in one mole of electrons (*L*).

L = ... mol^{-1}
[4]

(a) **(i)** Draw a fully labelled diagram to show how the standard electrode potential, $E^{\ominus}$, of $\mathbf{X}^{2+}(aq)/\mathbf{X}(s)$ could be measured.

[4]

(ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

..... [1]

(iii) State the charge carriers that transfer current through

the solutions, ... the wire. ..... [1]

(i) Write an equation for the reaction that would take place if the electrodes of this cell were connected by a wire.

..... [1]

When the current was allowed to pass for a period of time,

- the Ag electrode gained 1.30 g in mass,
- the electrode made of metal **X** lost 0.67 g in mass.

(ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
Show all your working. Use of the *Data Booklet* is relevant to this question.

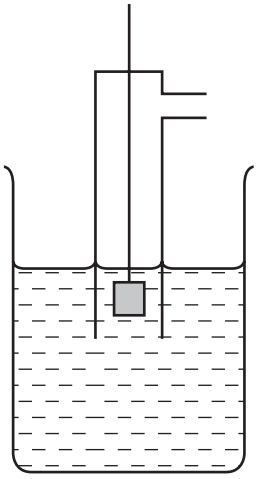
A_r = ...

X is .....
[4]

[Total: 11]

$$Cl_2(g) + 2Fe^{2+}(aq) \rightarrow 2Cl^-(aq) + 2Fe^{3+}(aq)$$

(a) (i) Complete and label the diagram to show how the standard cell potential, $E^{\ominus}_{cell}$, for the above reaction could be measured at standard conditions.



[4]

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this reaction.

[1]

(b) What colour change would you see when chlorine gas is bubbled through a solution containing $Fe^{2+}(aq)$ ions until the reaction is complete?

..... [1]

(c) Predict the effect, if any, of **decreasing** the concentration of $Cl^-(aq)$ on the magnitude of the cell potential in **(a)(ii)**. Explain your answer.

.....

.....

..... [2]

In the **alkaline** hydrogen-oxygen fuel cell, $H_2(g)$ and $O_2(g)$ are passed over two inert electrodes immersed in an alkaline solution.

Write the half-equations for the reactions taking place at each of these electrodes.

hydrogen electrode .....

oxygen electrode .....

[2]

(ii) Construct an equation for the overall reaction.

..... [1]

(iii) Suggest **one** possible advantage of using a hydrogen-oxygen fuel cell over a conventional 'simple cell' battery.

..... [1]

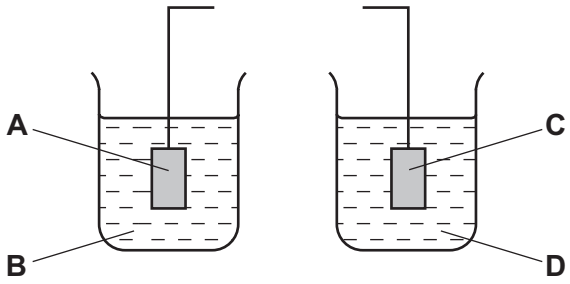
[Total: 12]

.....

.....

..... [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E^{\ominus}_{cell}$ for a cell composed of the Fe^{3+}/Fe^{2+} and Ag^{+}/Ag half-cells.



(ii) Complete the diagram, labelling the components you add. [1]

(iii) Identify the components **A**-**D**.

A .....

B .....

C .....

D .....

[3]

(b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in **(a)** are connected by a wire and the circuit is completed.

.....

..... [1]

(ii) Another electrochemical cell was set up using $0.31\,mol\,dm^{-3}$ $Ag^{+}(aq)$ instead of the standard Ag solution.

Use the Nernst equation, $E = E^{\ominus} + 0.059\log[Ag^{+}(aq)]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

Cu/Cu^{2+} electrode.

[4]

(ii) For the cell drawn in **(i)**, calculate the $E^{\ominus}_{cell}$ and state which electrode is positive.

$E^{\ominus}_{cell}$ = ... identity of the positive electrode .....
[1]

(d) A monobasic acid, **D**, has $K_a = 1.23 \times 10^{-5}\,mol\,dm^{-3}$.

(i) Calculate the pH of a $0.100\,mol\,dm^{-3}$ solution of **D**.

pH = ... [2]

(ii) An electrochemical cell similar to the one you have drawn in **(c)(i)** was set up using a $0.100\,mol\,dm^{-3}$ solution of **D** in the hydrogen electrode instead of the standard solution.

Use the data and the Nernst equation, $E = E^{\ominus} + 0.059 \log [H^+(aq)]$, to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

.....

.....

..... [2]

(b) (i) Draw a fully labelled diagram of the experimental set-up you could use to measure the standard electrode potential of the $Pb^{2+}(aq)/Pb(s)$ electrode. Include the necessary chemicals.

[4]

(ii) The $E^{\ominus}$ for a $Pb^{2+}(aq)/Pb(s)$ electrode is $-0.13\,V$.

Suggest how the E for this electrode would differ from its $E^{\ominus}$ value if the concentration of $Pb^{2+}(aq)$ ions is reduced. Indicate this by placing a tick (✓) in the appropriate box in the table.

more negative	no change	less negative

Explain your answer.

.....

.....

..... [2]

When a lead-acid cell is in use, Pb^{2+} ions are precipitated out as $PbSO_4(s)$ at the negative electrode.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

(i) Calculate the mass of Pb that is converted to $PbSO_4$ when a current of 0.40 A is delivered by the cell for 80 minutes.

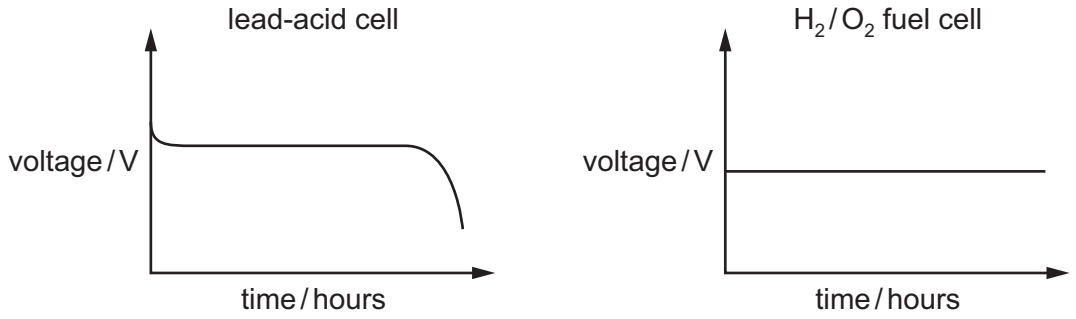
mass of Pb = ... g [2]

(ii) Complete the half-equation for the reaction taking place at the positive electrode.

$$PbO_2(s) + SO_4^{2-}(aq) + ... + ... \rightarrow PbSO_4(s) + ...$$

[1]

(d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.



Suggest a reason why

- the voltage of the lead-acid cell changes after several hours,

.....

.....

- the voltage of the fuel cell remains constant.

.....

.....

[2]

(a) (i) Use data from the *Data Booklet* to calculate a value for the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(ii) Write the ionic equation for the cell reaction.

..... [1]

(iii) Draw a fully labelled diagram of the apparatus you could use to measure the potential of this cell. Include the necessary chemicals.

[4]

calculate the $E^{\ominus}_{cell}$.

- $V^{2+}(aq)$ and $Sn^{4+}(aq)$

Does a reaction occur? .....

equation .....

$E^{\ominus}_{cell}$ .....

- $VO^{2+}(aq)$ and $Fe^{3+}(aq)$

Does a reaction occur? .....

equation .....

$E^{\ominus}_{cell}$ .....

[3]

[Total: 9]

electrolyte	substance liberated at the anode	substance liberated at the cathode
$AgNO_3(aq)$		
concentrated $NaCl(aq)$		
$CuSO_4(aq)$		

[3]

(b) Molten calcium iodide, CaI_2, is electrolysed in an inert atmosphere with inert electrodes.

(i) Write ionic equations for the reactions occurring at the electrodes.

- .....
- .....

[2]

(ii) The electrolysis of molten CaI_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced, explaining your answer by reference to oxidation numbers.

.....

.....

..... [2]

(iii) Describe **two** visual observations that would be made during this electrolysis.

1 .....

2 .....

[1]

(c) An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 hours using a current of 0.800 A. The electrolysis products are iron and oxygen. The mass of iron produced is 1.11 g.

Calculate the oxidation number of Fe in the oxide of iron. Show **all** your working.

oxidation number of Fe = ... [3]

electrolyte	substance liberated at the anode	substance liberated at the cathode
NaOH(aq)		
dilute $CuCl_2$(aq)		
concentrated $MgCl_2$(aq)		

[3]

(b) (i) The electrolysis of molten $ZnBr_2$ is a redox process.

Identify the ion that is oxidised and the ion that is reduced.

Use ionic half-equations to explain your answer.

.....

.....

.....

.....

..... [3]

(ii) Describe **one** visual observation that would be made during this electrolysis.

..... [1]

(c) Dilute sulfuric acid is electrolysed for 50.0 minutes using inert electrodes and a current of 1.20A. A different gas is collected above each electrode. The volumes of the two gases are measured under room conditions.

Calculate the maximum volume of gas that could be collected at the **cathode**.

volume = ... cm^3 [3]

[Total: 10]

The half-equation for the reaction at the methanol electrode is shown.

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- \qquad E^\ominus = -0.02\,V$$

(i) Use the *Data Booklet* to write an equation for the overall cell reaction.

.....

.....

..... [1]

(ii) Use $E^\ominus$ values to calculate the $E^\ominus_{cell}$ for this reaction.

$E^\ominus_{cell}$ = ... V [1]

[Total: 12]

(a) The reduction of chlorate(V) ions, ClO_3^-, with SO_2 forms chlorine dioxide, ClO_2, and sulfate ions, SO_4^{2-}, as the only products.

Construct an equation for this reaction.

..... [1]

(b) **(i)** Chlorine dioxide, ClO_2, disproportionates with hydroxide ions, $OH^-(aq)$, to form a mixture of ClO_2^- and ClO_3^- ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Explain, using this reaction as an example, what is meant by *disproportionation*.

.....

..... [1]

(ii) Deduce the ionic half-equations for the reaction in **(b)(i)**.

.....

..... [2]

(c) A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

(i) Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

- .....
- .....

overall equation .....
[2]

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$ for this cell.

$E^{\ominus}_{cell}$ = ... V [1]

Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

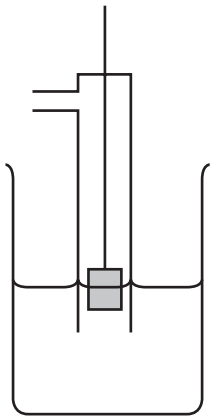
time = ... s [3]

.....

.....

..... [1]

(e) (i) Complete and **label** the diagram to show how the standard electrode potential, $E^{\ominus}$, of $Ag^{+}(aq)/Ag(s)$ could be measured under **standard conditions**.



[4]

(ii) Use the *Data Booklet* to label the diagram in **(e)(i)** to show

- which is the positive electrode,
- the direction of electron flow in the external circuit when a current flows.

[1]

[Total: 17]

14 An electrochemical cell is constructed using two half-cells.

- an Sn^{4+}/Sn^{2+} half-cell
- an Al^{3+}/Al half-cell

(a) State the material used for the electrode in each half-cell.

- Sn^{4+}/Sn^{2+} half-cell .....
- Al^{3+}/Al half-cell .....

[1]

(b) The cell is operated at 298 K.

The Al^{3+}/Al half-cell has standard concentrations.

The Sn^{4+}/Sn^{2+} half-cell has $[Sn^{4+}] = 0.300\ mol\ dm^{-3}$ and $[Sn^{2+}] = 0.150\ mol\ dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Sn^{4+}/Sn^{2+} half-cell under these conditions.

E = ... V [2]

(ii) Calculate the E_{cell} under these conditions.

E_{cell} = ... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

mass = ... units = ...
[4]

(d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

.....

.....

.....

..... [2]

[Total: 12]

15 An electrochemical cell is constructed using two half-cells.

- a Br_2/Br^- half-cell
- an Mn^{3+}/Mn^{2+} half-cell

(a) State the material used for the electrode in each half-cell.

Br_2/Br^- half-cell .....

Mn^{3+}/Mn^{2+} half-cell .....
[1]

(b) The cell is operated at 298 K.

The Br_2/Br^- half-cell has standard concentrations.

The Mn^{3+}/Mn^{2+} half-cell has $[Mn^{3+}] = 0.500\,mol\,dm^{-3}$ and $[Mn^{2+}] = 0.100\,mol\,dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Mn^{3+}/Mn^{2+} half-cell under these conditions.

E = ... V [2]

(ii) Calculate the E_{cell} under these conditions.

E_{cell} = ... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

..... [2]

The charge on one electron is -1.60×10^{-19} C.

The relative atomic mass of copper is 63.5.

Use these data to calculate an experimentally determined value for the Avogadro constant, *L*. Give your answer to **three** significant figures.

L = ... mol^{-1} [5]

(d) Explain why magnesium metal cannot be obtained by the electrolysis of dilute aqueous magnesium sulfate. Your answer should include data from the *Data Booklet*.

.....

.....

.....

..... [2]

[Total: 13]

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Water is oxidised in this process according to the following half-equation.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{half-equation 1}$$

(a) (i) Use these equations to deduce the half-equation for the reduction of carbon dioxide in this process.

[2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard electrode potential, $E^\ominus$, of $O_2(g)$ in half-equation 1 under standard conditions. Include all necessary chemicals.

[4]

(iii) For the cell drawn in **(a)(ii)**, use the *Data Booklet* to calculate the $E^\ominus_{cell}$ and deduce which electrode is positive.

$E^\ominus_{cell}$ = ... V

identity of the positive electrode = ...
[1]

.....

.....

..... [2]

An electrochemical cell is set up to measure the standard electrode potential of a cell, $E^{\ominus}_{cell}$, made of a Co^{3+}/Co^{2+} half-cell and a Cl_2/Cl^- half-cell.

(ii) Complete the table with the substance used to make the electrode in each of these half-cells.

half-cell	electrode
Co^{3+}/Co^{2+}	
Cl_2/Cl^-	

[1]

(iii) Use data from the *Data Booklet* to calculate the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(iv) Write the equation for the overall cell reaction.

..... [1]

(b) A fuel cell is an electrochemical cell that can be used to generate electrical energy.
A methanol-oxygen fuel cell can be used as an alternative to a hydrogen-oxygen fuel cell. When the cell operates, the carbon atoms in the methanol molecules are converted into carbon dioxide.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Calculate the volume of CO_2, in cm^3, formed when a current of 2.5A is delivered by the cell for 30 minutes. Assume the cell is operated at room conditions.

volume of CO_2 = ... cm^3 [2]

anode .....

cathode .....
[1]

(b) When molten sodium chloride is electrolysed, chlorine is liberated at the anode and sodium is liberated at the cathode.

A sample of molten sodium chloride is electrolysed for 1.50 hours using a current of 4.50A.

Calculate the volume of chlorine and the mass of sodium that are liberated under room conditions.

volume of chlorine = ... dm^3

mass of sodium = ... g
[4]

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\ominus = +1.52\,V$$

(i) Draw a diagram of the apparatus that would be used to measure the $E^\ominus$ value of this half-cell. Your diagram should be fully labelled to identify all apparatus, substances and conditions.

[4]

(ii) Use the *Data Booklet* to identify a substance that could be used to oxidise Mn^{2+} ions to MnO_4^- ions under standard conditions.

Write an equation for the reaction.

.....

.....

..... [2]

[Total: 11]

at the anode .....

at the cathode .....
[1]

(b) When dilute sulfuric acid is electrolysed, oxygen is liberated at the anode.

Dilute sulfuric acid is electrolysed for 15.0 minutes using a current of 0.750 A.

Calculate the volume of oxygen that is liberated under room conditions.

volume of oxygen = ... cm^3 [3]

(c) The halogens chlorine, bromine and iodine differ in their strengths as oxidising agents. These strengths are indicated by the $E^{\ominus}$ values for these halogens.

(i) Give the $E^{\ominus}$ values for chlorine, bromine and iodine acting as oxidising agents.

..... [1]

(ii) Deduce which of chlorine, bromine and iodine will react with a solution of $Sn^{2+}(aq)$ under standard conditions.

Explain your answer. Include a relevant equation in your explanation.

.....

.....

..... [3]

(iii) An excess of chlorine is added to a solution of acidified $Mn^{2+}(aq)$ under standard conditions.

Give the formula of the product of this reaction that contains manganese.

..... [1]

(i) Calculate the standard cell potential of this electrochemical cell.

$E^{\ominus}_{cell}$ = ... V [1]

(ii) State the material that should be used as the electrode in each half-cell.

in the Fe^{3+}/Fe^{2+} half-cell .....

in the $S_2O_8^{2-}/SO_4^{2-}$ half-cell .....
[1]

(iii) Describe **one** change to each half-cell that would **increase** the value of the cell potential. The temperature should remain at 298 K.

Fe^{3+}/Fe^{2+} half-cell .....

.....

$S_2O_8^{2-}/SO_4^{2-}$ half-cell .....

.....
[1]

[Total: 12]

.....

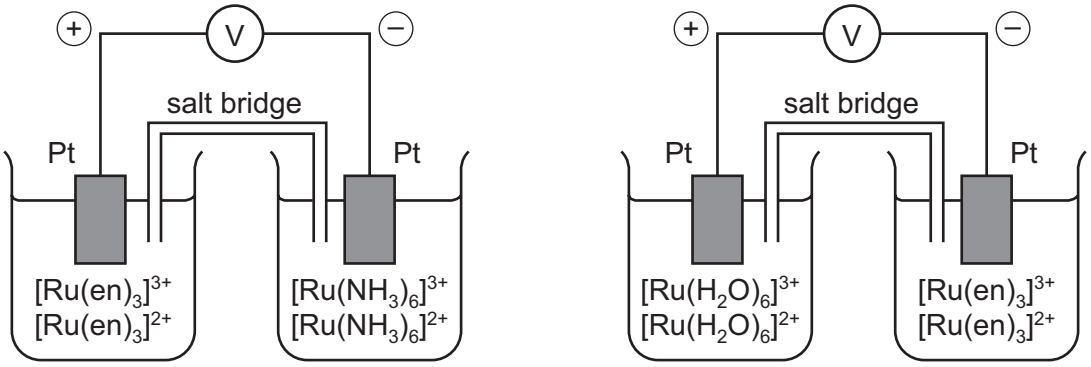
.....

..... [2]

Three redox systems, **A**, **B** and **C**, are shown. The ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is represented by en.

A	$[Ru(H_2O)_6]^{3+} + e^- \rightleftharpoons [Ru(H_2O)_6]^{2+}$
B	$[Ru(NH_3)_6]^{3+} + e^- \rightleftharpoons [Ru(NH_3)_6]^{2+}$
C	$[Ru(en)_3]^{3+} + e^- \rightleftharpoons [Ru(en)_3]^{2+}$

Two electrochemical cells are set up to compare the standard electrode potentials, $E^\ominus$, of three half-cells. The diagrams show the relative potential of each electrode.



(ii) Use this information to complete the table by adding the labels **A**, **B** and **C** to deduce the order of $E^\ominus$ for the three half-cells.

$E^\ominus$	redox system
most negative	
↑	
least negative	

[1]

P42/M/J/21/Q4b

(21b) (i) Identify the substances formed at the anode and at the cathode during the electrolysis of saturated $CaCl_2$(aq).

at the anode .....

at the cathode .....
[1]

(ii) Calcium can be produced by the electrolysis of molten calcium chloride, $CaCl_2$(l).

Calculate the mass, in g, of Ca formed when a current of 0.75A passes through $CaCl_2$(l) for 60 minutes.
[A_r: Ca, 40.1]

mass of Ca = ... g [2]

22 When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

A current of **x** A is passed through the solution for 14.0 minutes. 462 cm^3 of hydrogen are produced at the cathode, measured under room conditions.

(a) Calculate the number of hydrogen molecules produced during the electrolysis.

number of hydrogen molecules = ... [2]

(b) Calculate the total number of electrons transferred to produce this number of hydrogen molecules.

total number of electrons = ... [1]

(c) Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**.

quantity of charge = ... C [1]

(d) Calculate the current, **x**, passed during this experiment.

x = ... A [1]

$$HCl(g) + aq \rightarrow H^+(aq) + Cl^-(aq)$$

The overall change after electrolysis is that hydrogen chloride gas is converted into hydrogen and chlorine.

$$2HCl(g) \rightarrow H_2(g) + Cl_2(g)$$

When a current of 3.10A is passed through the solution for *Y* minutes, 351 cm^3 of chlorine are produced at the anode, measured under room conditions.

(a) Calculate the number of chlorine molecules produced during the electrolysis.

number of chlorine molecules = ... [2]

(b) Calculate the total number of electrons transferred to produce this number of chlorine molecules.

total number of electrons = ... [1]

(c) Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**.

quantity of charge = ... C [1]

(d) Calculate the time, *Y*, in minutes, for which the current flows.

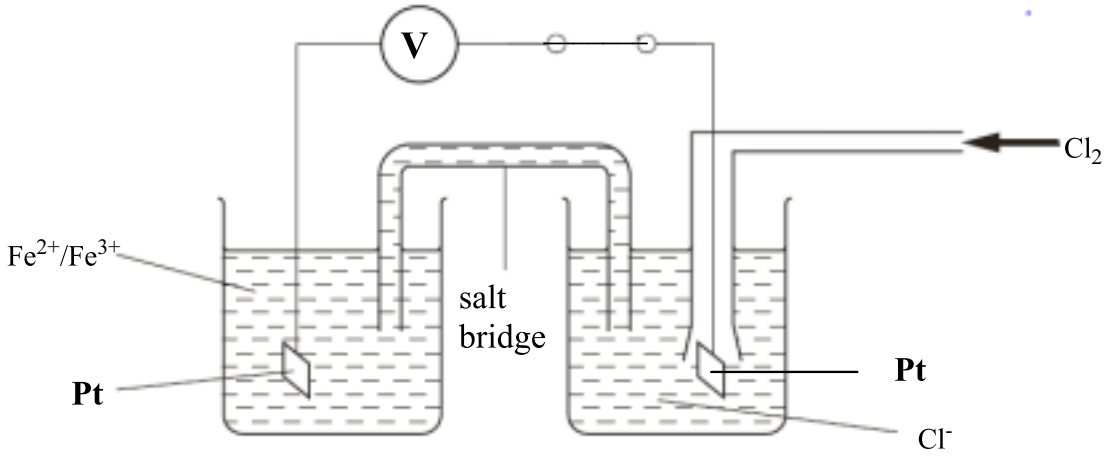
Y = ... minutes [1]

(1c) (i)	$E^{\ominus}_{cell}$ (= 0.80 – 0.77 =) (+)**0.03V and** Ag^+/Ag ***or*** Ag/silver ***or*** right	**1**
(ii)	E_{cell} would be less positive/more negative because the $[Ag^+(aq)]$ (in the Ag electrode) is less than 1.0 mol dm^{-3}	**1**
(iii)	• no change	**1**
	• more negative/less positive	**1**
(iv)	the $[Ag^+(aq)]$ will decrease $E_{electrode}$ becomes less positive ***or*** due to the common ion effect	 **1**
(d)	$[Fe^{3+}(aq)]$ = 0.2 mol dm^{-3} $[H^+] = \sqrt{(c.K_a)} = \sqrt{(0.2 \times 8.9 \times 10^{-4})}$ or 1.33×10^{-2} (mol dm^{-3}) pH = –log($[H^+]$) = **1.9** *(or 1.87–1.89)*	**1** **1**

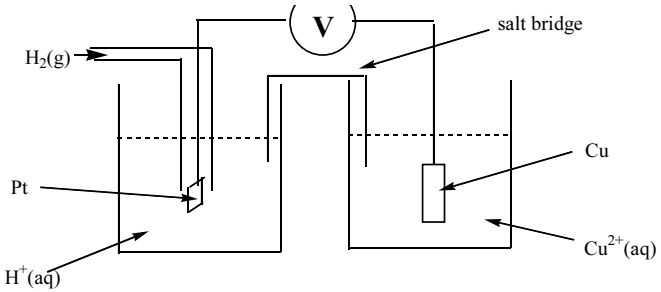
P41/M/J/15/Q5e

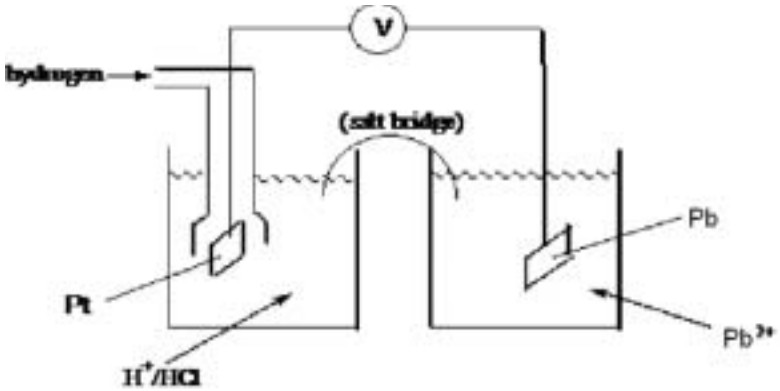
(2e) (i)	F = Le	**1**
(ii)	moles of $O_2(g)$ = 130/24000 = 5.417×10^{-3} mol moles of electrons needed = $4 \times 5.417 \times 10^{-3}$ ***or*** 2.17×10^{-2} mol no. of coulombs passed = 1.2 x 30 x 60 ***or*** 2160 C no. of electrons passed = $2160 / 1.6 \times 10^{-19}$ ***or*** 1.35×10^{22} no. of electrons per mole = $1.35 \times 10^{22} / 2.17 \times 10^{-2}$ = **6.2×10^{23}** (mol^{-1})	**1** **1** **1** **1**

Question	Marking point	Marks
3 (a) (i)	M1: salt bridge **and** voltmeter / M2: method of H_2 gas delivery M3: X **and** Pt electrode labelled M4: solution H^+ / HC*l*(aq) / H_2SO_4 **and** X^{2+} labelled	**4**
(ii)	25 °C / 298 K **and** 1 atm / 101 kPa pressure **and** 1 mol dm^{-3} (solution)	**1**
(iii)	solution – ions ***or*** H^+ and X^{2+} **and** wires – electrons / e^-	**1**
(b) (i)	$X + 2Ag^+ \rightarrow 2Ag + X^{2+}$	**1**
(ii)	moles Ag = 1.30 / 107.9 = 0.0120 1 moles of X react with 2 moles Ag^+ moles of X lost = 0.012 × 0.5 = 0.00602 A_r of X = 0.67/0.006 = 111–112 **and** X = Cd	**4**
		11

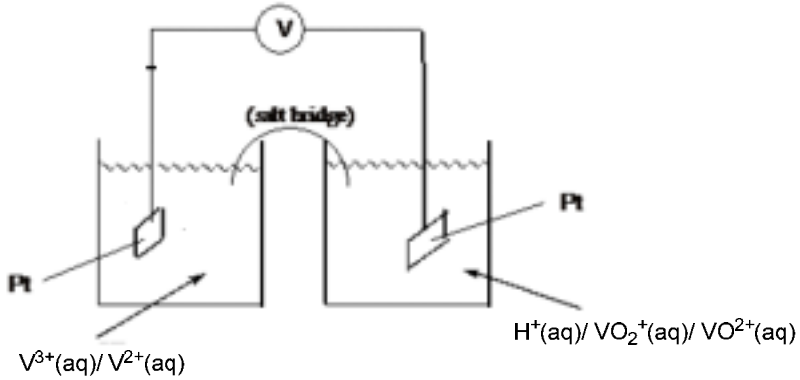
	• one sol^{n} 1 mol dm^{-3} • Cl^- (or suitable compound), • voltmeter, labelled or V • Cl_2, • 1 atm or 298K  	8 marking points = [4]		
(ii)	$E^{\ominus}_{cell}$ = 1.36 – 0.77 = 0.59 V		**1**	
(b)	yellow / orange / brown		**1**	
(c)	cell voltage increases or becomes more positive Cl_2/Cl^- electrode potential increases		**2**	
(d)	**(i)** $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$ O_2 $+ 2H_2O + 4e^- \rightarrow 4OH^-$		**2**	

Question		Marks
5 (a) (i)	SCP is the EMF / potential of a cell composed of two electrodes (OR half cells) under standard conditions (OR at 289 K OR 1 mol dm^{-3})	[1]
(ii)	voltmeter and salt bridge	[1]
(iii)	**A** is Ag **B** is $Ag^{+}(aq)$ or $AgNO_3(aq)$ **C** is Pt **D** is $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ (combination of **A** and **B** can be reversed with combination of **C** and **D**)	[3]
(b) (i)	$Ag^{+} + Fe^{2+} \longrightarrow Ag + Fe^{3+}$	[1]
(ii)	$E = E^{\ominus} + 0.059\log [Ag^{+}] = 0.80 - 0.03 = 0.77\,V$ so $E_{cell} = 0.77 - 0.77 = 0.0\,V$	[1] [1]
		[Total: 8]

6(c) (i)	 M1: voltmeter / V **and** salt bridge labelled M2: Cu **and** Cu^{2+} / $CuSO_4$ (any soluble Cu(II) salt) M3: H_2 (arrow **in**) and H^+ / HC*l* / H_2SO_4 / any mineral acid M4 Pt **and** one solution at 1 M / 1 mol dm^{-3} OR H_2 at 1 atm	4
(ii)	$E^{\ominus}_{cell}$ = 0.34 (V) **and** (Cu^{2+}) / Cu is the positive electrode	1
d (i)	$K_a = 1.23 \times 10^{-5}$ $[H^+] = \sqrt{(K_a.c)} = \sqrt{(1.23 \times 10^{-5} \times 0.1)} = 1.11 \times 10^{-3}$ mol dm^{-3} pH = **3.0 (2.96)** ecf from $[H^+]$	2
(ii)	$E = 0.0 + 0.059\log(1.11 \times 10^{-3})$ OR = –0.17(4)V so new E_{cell} = 0.34 + 0.17 = **0.51V** ecf from **(d)(i)**	2

7(a)	the potential **difference** between two half-cells / two electrodes (in a cell)	**1**
	under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol dm^{-3}	**1**
7(b)(i)	 8 marking points, any 2 points for each mark H_2 / hydrogen correct delivery system for H_2 Pb^{2+} (aq) Pb electrode Pt electrode H^+(aq) solution salt bridge voltmeter / V labelled	**4**
7(b)(ii)	more negative	**1**
	shifts Pb^{2+} (+ $2e^-$) ⇋ Pb equilibrium / reaction to the left	**1**

7(c)(i)	Q = 0.4 × 80 × 60 = **1920** C **and** use of 96500 / 193000 Moles of Pb = 1920 / 193000 = 9.95×10^{-3} Mass of Pb = $207.2 \times 9.95 \times 10^{-3}$ = **2.1 g** **OR** Q = 0.4 × 80 × 60 = **1920** C **and** use of 1.6×10^{-19} / 1.2×10^{22} atoms Pb = 6×10^{21}; moles of Pb = $6 \times 10^{21} / 6 \times 10^{23}$ = 0.01 Mass of Pb = 207.2 × 0.01 = **2.1 g**	**2**
7(c)(ii)	$PbO_2(s) + SO_4^{2-}(aq) + \mathbf{4H^+} + \mathbf{2e^-} \rightarrow PbSO_4(s) + \mathbf{2H_2O}$	**1**
7(d)	reagents / PbO_2 / H_2SO_4 **and** used up / concentration decreases	**1**
	as fuel / hydrogen is being continuously supplied / fuel has not run out	**1**

Question	Answer	Marks
8(a)(i)	$E^{\ominus}_{cell}$ = 1.00 – (–0.26) = (+)1.26 V	**1**
8(a)(ii)	$VO_2^+ + V^{2+} + 2H^+ \rightarrow VO^{2+} + V^{3+} + H_2O$	**1**
8(a)(iii)	 solutions labelled correctly in one half-cell [1] solutions labelled correctly in both half-cells [1] two graphite or platinum electrodes [1] salt bridge and voltmeter [1]	**4**
8(b)	• $V^{2+}(aq)$ and $Sn^{4+}(aq)$: yes and $E^{\ominus}_{cell}$ = +0.15 – (–0.26) = +0.41 V [1] $2V^{2+} + Sn^{4+} \rightarrow 2V^{3+} + Sn^{2+}$ [1] • $VO^{2+}(aq)$ and $Fe^{3+}(aq)$ no reaction [1]	**3**

<table>
<tr><td>9(a)</td><td>
<table>
<tr><td></td><td>anode</td><td>cathode</td></tr>
<tr><td>$AgNO_3$ (aq)</td><td>oxygen / O_2</td><td>silver / Ag</td></tr>
<tr><td>saturated NaCl (aq)</td><td>chlorine / Cl_2</td><td>hydrogen / H_2</td></tr>
<tr><td>$CuSO_4$ (aq)</td><td>oxygen / O_2</td><td>copper / Cu</td></tr>
</table>
</td><td>3</td></tr>
<tr><td>9(b)(i)</td><td>$2I^- \rightarrow I_2 + 2e^-$</td><td>1</td></tr>
<tr><td></td><td>$Ca^{2+} + 2e^- \rightarrow Ca$</td><td>1</td></tr>
<tr><td>9(b)(ii)</td><td>• Ca / Calcium reduced and I / iodine oxidised
• Oxidation number of calcium decreases from 2 to 0
• Oxidation number of iodine increases from –1 to 0

2 points = 1 mark
3 points = 2 marks</td><td>2</td></tr>
<tr><td>9(b)(iii)</td><td>• metal / grey / silvery
• purple AND vapour / gas / fumes
• amount of melt decreases

any 2 points for 1 mark</td><td>1</td></tr>
<tr><td>9(c)</td><td>$2 \times 60 \times 60 \times 0.8 = 5760$ C
AND
5760 / 96500 = 0.060 (0.0597) F</td><td>1</td></tr>
<tr><td></td><td>1.11 / 55.8 = 0.020 (0.0199) mol of Fe</td><td>1</td></tr>
<tr><td></td><td>0.06 / 0.02 = 3 ∴ Fe^{3+} or +3 or 3</td><td>1</td></tr>
</table>

10(a)	<table><tr><td></td><td>anode</td><td>cathode</td></tr><tr><td>NaOH (aq)</td><td>**oxygen / O_2**</td><td>**hydrogen / H_2**</td></tr><tr><td>dilute $CuCl_2$ (aq)</td><td>**oxygen / O_2**</td><td>**copper / Cu**</td></tr><tr><td>conc $MgCl_2$ (aq)</td><td>**chlorine / Cl_2**</td><td>**hydrogen / H_2**</td></tr></table>	**3**
10(b)(i)	$^-$ → Br_2 + $2e^-$ or $2Br^-$ – $2e^-$ → Br_2	**1**
	Zn^{2+} + $2e^-$ → Zn	**1**
	Zinc / Zn^{2+} reduced **and** Br^- / bromide oxidised	**1**
10(b)(ii)	liquid / molten metal ***or*** orange-**brown** / reddish **brown** vapour / gas (at anode) ***or*** amount of melt / electrolyte decreases	**1**
10(c)	• 50 × 60 × 1.2 **or** 3600 C (calculation of number of Coulombs) • 3600 / 96 500 **or** 0.0373 F (calculation of number of Faradays) • 0.0373 F / 2 **or** 0.01865 / 0.0187 mol H_2 (use of stoichiometry) • 0.01865 × 24 000 = **448–449** (Use of 24 000 & answer to 3sf) 2 points = 1 mark 3 points = 2 marks 4 points = 3 marks	**3**

Question	Answer	Marks
11(e)(i)	$2CH_3OH + 3O_2 \rightleftharpoons 2CO_2 + 4H_2O$ **OR** $2CH_3OH + 3O_2 \rightleftharpoons 2CO_2 + 4H^+ + 4OH^-$	**1**
11(e)(ii)	E^o_{cell} = 1.23 – 0.02 = **1.21** V	**1**

P41/M/J/19/Q3

Question	Answer	Marks
12(a)	$2Cl O_3^- + SO_2 \rightarrow 2Cl O_2 + SO_4^{2-}$	**1**
12(b)(i)	C*l* in ClO_2 gets both oxidised and reduced **or** C*l* goes from +4 → +5 and +4 → +3	**1**
12(b)(ii)	**M1** C $lO_2 + 2OH^- \rightarrow ClO_3^- + H_2O + e^-$ **M2** C $lO_2 + e^- \rightarrow ClO_2^-$	**2**
12(c)(i)	**M1** $Li \rightarrow Li^+ + e^-$ **and** $I_2 + 2e^- \rightarrow 2I^-$ **M2** $2Li + I_2 \rightarrow 2Li^+ + 2I^-$	**2**
12(c)(ii)	E^o_{cell} = 0.54 –(–3.04) = **+3.58 V** [1]	**1**
12(c)(iii)	**M1** amount of Li = 0.10 / 6.9 = 1.45×10^{-2} mol [1] **M2** Q needed = $96500 \times 1.45 \times 10^{-2}$ = **1399** (1398.55) C [1] ecf **M3** t = 1399 / (2.5×10^{-5}) = **5.6×10^7** s [1] ecf 2sf min	**3**

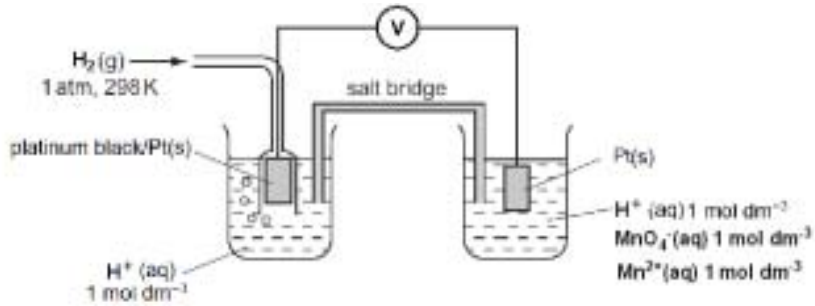
13(d)	The potential difference when a half-cell is connected to a (standard) hydrogen electrode under standard conditions [1] **OR** the potential difference / voltage / EMF between a hydrogen electrode and another half-cell under standard conditions [1]	**1**
13(e)(i)	bridge • voltmeter / V • Ag • Ag^+ (or soluble silver salt) • Pt • H_2 (and delivery correct) + H^+ (or named strong acid) • 1 atm. (pressure) • 1 mol dm^{-3} (and 298 K) • mark as • ✓ • ✓ • ✓ • ✓ [4]	**4**
13(e)(ii)	Ag electrode labelled **and** arrow (in the external circuit moving towards this electrode) [1]	**1**

14(a)	Platinum / Pt Aluminium / Al **BOTH**	**1**
14(b)(i)	**M1:** use of or quoting a valid Nernst equation $E = E^{\ominus} + 0.0590 / z \log [ox] / [red]$ ***OR*** $E = 0.15 + (0.0590 / 2)\log 2$ **M2:** E = (+)**0.16** (0.159) V minimum 2 sig. fig. correct answer scores 2 marks	**2**
14(b)(ii)	$E_{cell} = 0.16 - (-1.66) =$ **+1.82 V** minimum 3 sig. fig.	**1**
14(b)(iii)	$2Al + 3Sn^{4+} \rightarrow 2Al^{3+} + 3Sn^{2+}$ **M1:** species **M2:** balancing	**2**
14(c)	**M1:** number of C (= 300 000 × 60 × 60 × 24) = 2.59×10^{10} (C) **M2:** number of F(= $2.592 \times 10^{10} / 9.65 \times 10^{4}$) = 2.69×10^{5} (moles of electrons) **M3:** moles of Al (= $2.69 \times 10^{5} / 3$) = 8.95×10^{4} **M4:** mass of Al (= $8.95 \times 10^{4} \times 27$) = **2420 kg** correct answer scores 4 marks	**4**
14(d)	**M1:** ($Cr^{2+} + 2e^{-} \rightleftharpoons Cr$) $E^{\ominus} = -0.91$ **and** ($2H^{+} + 2e^{-} \rightleftharpoons H_2$) $E^{\ominus} = 0.00$ seen **M2:** hydrogen formed instead / hydrogen (ions) easier to reduce / hydrogen has more positive $E^{\ominus}$	**2**

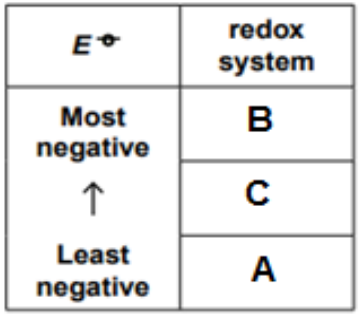
15(a)	Platinum **and** platinum	**1**
15(b)(i)	**M1:** Nernst quoted correctly $E = E^{\ominus} + 0.0590 / z \log [ox] / [red]$ or $E = 1.49 + 0.0590 \log 5$ **M2:** (+)1.53 V minimum 2 sig. fig. Correct answer scores 2 marks	**2**
15(b)(ii)	+ / – 0.46 minimum 2 sig. fig.	**1**
15(b)(iii)	**M1:** $Mn^{3+} + 2Br^- \rightarrow Mn^{2+} + Br_2$ **M2:** $2Mn^{3+} + 2Br^- \rightarrow Mn^{2+} + Br_2$	**2**
15(c)	**M1:** 16200 C **M2:** 1.0125×10^{23} electrons (use of 1.60×10^{-19}) **M3:** 0.0802 moles of copper (use of 5.09 and 63.5) **M4:** 0.1603 moles electrons **M5:** $L = 6.32 \times 10^{23}$ (correct answer [5] other approaches acceptable including: **M1:** 16200 C **M2:** 1.0125×10^{23} electrons (use of 1.60×10^{-19}) **M3:** 5.0625×10^{22} copper atoms **M4:** 0.0802 moles of copper (use of 5.09 and 63.5) **M5:** $L = 6.32 \times 10^{23}$ (correct answer [5])	**5**
15(d)	**M1:** $Mg^{2+} + 2e^- \rightleftharpoons Mg$ $E^{\ominus} = -2.38$ **and** $2H^+ + 2e^- \rightleftharpoons H_2$ $E^{\ominus} = 0.00$ **M2:** hydrogen produced instead / hydrogen easier to reduce / hydrogen preferentially reduced / hydrogen has more positive $E^{\ominus}$	**2**

Question	Answer	Marks
16(a)(i)	$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$ **ALLOW** $6CO_2 + 12H^+ + 12e^- \rightarrow C_6H_{12}O_6 + 3O_2$ for both marks **ALLOW** one mark for an unbalanced equation showing the correct species of either equation	**2**
16(a)(ii)	salt bridge (indicated) voltmeter / V labelled O_2 good delivery system H_2 good delivery system Pt electrode H^+ / HCl / H_2SO_4 solution labelled (at least once) 1 atm 1 mol dm^{-3} quoted Every two correct responses = 1 mark	**4**
16(a)(iii)	E^o_{cell} = (+) 1.23 V **AND** positive electrode = O_2 half-cell identified	**1**

Question	Answer	Marks
17(a)(i)	**M1** potential difference between two half-cells/two electrodes in a cell **M2** under conditions of 1 atm., 298 K, (all) solutions being 1 mol dm^{-3}	**2**
17(a)(ii)	**both** platinum	**1**
17(a)(iii)	E^{o}_{cell} = 1.82 – 1.36 = **(+)0.46 V**	**1**
17(a)(iv)	$2Co^{3+} + 2Cl^{-} \rightarrow Cl_2 + 2Co^{2+}$	**1**
17(b)	**M1** Q= 2.5 x 30 x 60 C = 4500 C **AND** 96500 **OR** 579000 seen moles of CO_2= 4500/579000 = 7.8 $x10^{-3}$ or 7.77 x 10^{-3} **M2** volume of CO_2 = 7.77 x 10^{-3} x 24000 = **187 cm^3**	**2**

18(b)	**M1:** Q = $1.5 \times 60 \times 60 \times 4.5$ = 24300 (C) [1] **M2:** no. of F / moles of e^- = 24300 / 96500 = 0.25(1813) [1] ecf **M3:** volume of Cl_2 = $24 \times 0.252 / 2$ = **3.02** dm^3 [1] ecf min 2sf **M4:** mass of Na = 0.252×23 = **5.79** (5.7917) g Na [1] ecf min 2sf	**4**
18(c)(i)	 • MnO_4^-, H^+, Mn^{2+} in same beaker **AND** H^+ in other beaker • both electrodes Pt(s) (**ALLOW** graphite) • one solute clearly identified as 1M / 1 mol dm^{-3} • 298 K **OR** 1 atm • voltmeter / potentiometer labelled (or circled V) • salt bridge labelled (must touch the solution) • a good delivery system for H_2(g) • H_2(g) mark as two correct points = 1 mark [4]	**4**
18(c)(ii)	F_2 **OR** $S_2O_8^{2-}$ **OR** H_2O_2 **OR** HOCl **OR** Co^{3+} **OR** Pb^{4+} [1] $2Mn^{2+} + 8H_2O + 5F_2 \rightarrow 2MnO_4^- + 16H^+ + 10F^-$[1] **OR** $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10SO_4^{2-}$ **OR** $Mn^{2+} + 4H_2O + 5Co^{3+} \rightarrow MnO_4^- + 8H^+ + 5Co^{2+}$ **OR** $2Mn^{2+} + 8H_2O + 5Pb^{4+} \rightarrow 2MnO_4^- + 16H^+ + 5Pb^{2+}$	**2**

19(a)	chlor **AND** hydrogen [1]	**1**
19(b)	15 × 60 × 0.75 = 675 C [1] 675 / 96 500 = 7.0×10^{-3} moles e^- [1] $7.0 \times 10^{-3} \times 0.25$ gives 1.75×10^{-3} moles O_2 $1.75 \times 10^{-3} \times 24000$ = 42 (41.969) cm^3 O_2 [1] **OR** 15 × 60 × 0.75 = 675 C [1] 675 / 1.60×10^{-19} = 4.22×10^{21} e^- = 7.01×10^{-3} moles e^- [1] gives 1.75×10^{-3} moles O_2 = 42 (42.047) cm^3 [1]	**3**
19(c)(i)	1.36 1.07 0.54 [1]	**1**
19(c)(ii)	all of them [1] (all $E^\ominus$ values) greater than 0.15 / $E^\ominus_{cell}$ greater than zero [1] e.g. $Sn^{2+} + X_2 \rightarrow Sn^{4+} + 2X$ [1]	**3**
19(c)(iii)	MnO_2 [1]	**1**
19(d)(i)	1.24 V [1]	**1**
19(d)(ii)	platinum, platinum [1]	**1**
19(d)(iii)	increase [Fe^{2+}] or decrease [Fe^{3+}] increase [$S_2O_8^{2-}$] or decrease [SO_4^{2-}] [1]	**1**

20(a)(i)	**M1:** voltage of an electrode / a half-cell compared to / connected to (standard) hydrogen electrode / half-cell **M2:** (at concentration of) 1 mol / dm^3 **AND** (pressure of) 1 atm / 101 kPa (or in Pa) **AND** 298 K / 25°C	**2**
20(a)(ii)		**1**

P42/M/J/21/Q4b

21(b)(i)	anode: chlorine / Cl_2 cathode: hydrogen / H_2	**1**
21(b)(ii)	**M1:** Q = 0.75 × 60 × 60 = 2700 C **AND** 96 500 or 193 000 used **M2:** [a] moles of Ca = 2700 / 193 000 = 0.0140 [b] mass = 0.0140 × 40.1 = 0.56 g	**2**

Question	Answer	Marks
22(a)	moles of H_2 = 462 / 24 000 = 0.01925[1] molecules of H_2 = $0.019 \times 6.02 \times 10^{23}$ = **1.16×10^{22}** (1.1×10^{22} / 1.2×10^{22}) [1] **min 2sf** ecf M1	**2**
22(b)	number of electrons = $1.16 \times 10^{22} \times 2$ = **2.32×10^{22}** [1] min 2sf ecf 1a	**1**
22(c)	Q = 2.32×10^{22} $\times 1.6 \times 10^{-19}$ = **3.71×10^{3}** [1] min 2sf ecf 1b	**1**
22(d)	x = $3.71 \times 10^{3} / (14 \times 60)$ = **4.4** (A) [1] min 2sf ecf 1c	**1**

P42/O/N/21/Q3abcd

Question	Answer	Marks
23(a)	0 / 24 = 0.015 (mol) [1] $0.015 \times 6.02 \times 10^{23} = 9.0 \times 10^{21} / 8.8 \times 10^{21}$ [1]	**2**
23(b)	$1.76 \times 10^{22} / 1.8 \times 10^{22}$ [1]	**1**
23(c)	/ 2816 / 2820 / 2800 C [1]	**1**
23(d)	/ 15.1 / 15.05 / 15.15 minutes [1]	**1**

Paper 4
Topic 3
Further Aspects of Equilibria

(i) Write an expression for the solubility product, K_{sp}, of Ag_2SO_4, and state its units.

K_{sp} = units: ..... [1]

(ii) Calculate the value for $K_{sp}(Ag_2SO_4)$ at 298 K.

K_{sp} = ... [1]

.....

..... [1]

(ii) The partition coefficient of a particular pesticide between hexane and water is 6.0.

A solution contains 0.0042 g of the pesticide dissolved in 25 cm^3 of water. The solution is shaken with 25 cm^3 of hexane.

Calculate the mass of pesticide that will be dissolved in the hexane layer at equilibrium

[2]

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

(a) Write the expression for K_p for this reaction, and state its units.

K_p =

units .....
[2]

(b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

$H_2S(g)$ 200 atm $CH_4(g)$ 100 atm

The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $CS_2(g)$ is 2 atm and that of the remaining $CH_4(g)$ is 98 atm.

(i) Calculate the equilibrium partial pressures of $H_2S(g)$ and $H_2(g)$.

$p(H_2S)$ = ... atm

$p(H_2)$ = ... atm
[2]

(ii) Calculate the value of K_p at this temperature.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\rightleftharpoons} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\rightleftharpoons} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

(a) The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a of ethanoic acid, CH_3CO_2H, is 4.76.

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

..... [1]

(ii) With reference to the table above, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,

.....

.....

.....

- become larger as n increases.

.....
[3]

(iii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid.

.....

..... [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

.....

..... [2]

(ii) Write two equations to show how monosodium butanedioate, $HO_2CCH_2CH_2CO_2Na$, acts as a buffer.

.....

..... [2]

(a) Explain what is meant by the term *weak* acid.

.....

..... [1]

(b) The pK_a values of four acids are listed below.

acid	structural formula	pK_a
1	CH_3CO_2H	4.8
2	$CH_3CH_2CO_2H$	4.9
3	$CH_3CHCl CO_2H$	2.8
4	$CH_2ClCH_2CO_2H$	4.0

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

..... [1]

(ii) With reference to acidity, explain the difference in pK_a values between

- acid 1 and acid 2,

.....

.....

- acid 2 and acid 3,

.....

.....

- acid 3 and acid 4.

.....

.....

[3]

- 10.0 cm^3 of a bleach solution was diluted to 250 cm^3 in a volumetric flask using distilled water.
- Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm^3 portion of this solution to liberate iodine.
- The resulting solution required 20.80 cm^3 of 0.100 mol dm^{-3} aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.

$$Cl^-O^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate the concentration, in mol dm^{-3}, of Cl^-O^- ions in the bleach solution.

concentration of Cl^-O^- = ... mol dm^{-3} [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

..... [1]

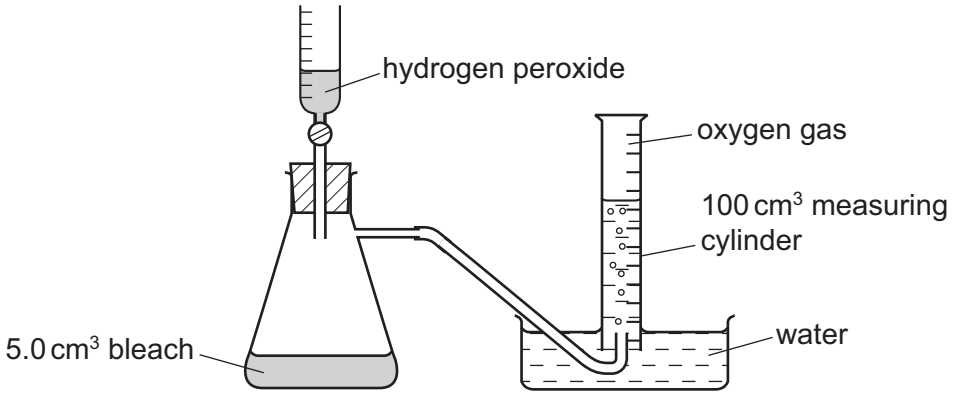
(ii) State the expected colour change you would observe at the end-point in this titration.

from ..... to ..... [1]

(iii) State when in the procedure you would add the indicator.

.....

$$H_2O_2 + NaClO \rightarrow NaCl + O_2 + H_2O$$



When an excess of aqueous hydrogen peroxide was added to 5.0 cm^3 of a different bleach solution, 82 cm^3 of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO^- ions in this bleach solution.

concentration of ClO^- = ... $mol\,dm^{-3}$ [2]

(d) Trichlorocyanuric acid, $C_3Cl_3N_3O_3$, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, $HClO$.

$$C_3Cl_3N_3O_3 + 3H_2O \rightleftharpoons C_3H_3N_3O_3 + 3HClO$$

(i) Write the expression for K_c for this equilibrium.

K_c =

[1]

(ii) In outdoor swimming pools, the $HClO$ is decomposed by sunlight. The decomposition of $HClO$ is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of $HClO$ on the equilibrium in **(d)**. State the effect on K_c.

.....

.....

effect on K_c .....

[2]

Suggest an equation for this reaction.

..... [1]

(e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3, and hydrogencarbonate ions, HCO_3^-. Healthy blood has a pH of 7.40.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_a = 7.94 \times 10^{-7}\,\text{mol}\,\text{dm}^{-3}$$

(i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

.....

.....

.....

..... [2]

(ii) A patient's blood has a $[HCO_3^-] : [H_2CO_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

pH = ... [2]

[Total: 16]

bonded in the order they are written.

(i) Draw 'dot-and-cross' diagrams of these two acids, showing outer shell electrons only.

HOCN, cyanic acid

HNCO, isocyanic acid

[3]

(ii) Suggest the values of the bond angles HNC and NCO in **isocyanic acid**.

HNC ..... NCO ..... [1]

(iii) Suggest which acid, cyanic or isocyanic, will have the **shorter** C–N bond length.
Explain your answer.

.....

..... [1]

(b) (i) Isocyanic acid is a weak acid.

$$HNCO \rightleftharpoons H^+ + NCO^- \qquad K_a = 1.2 \times 10^{-4}\,mol\,dm^{-3}$$

Calculate the pH of a 0.10 mol dm^{-3} solution of isocyanic acid.

pH = ... [2]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid.
Sodium cyanate is prepared commercially by reacting urea, $(NH_2)_2CO$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

isocyanic acid, the pH was measured.

(i) Calculate the $[OH^-]$ at the end of the addition.

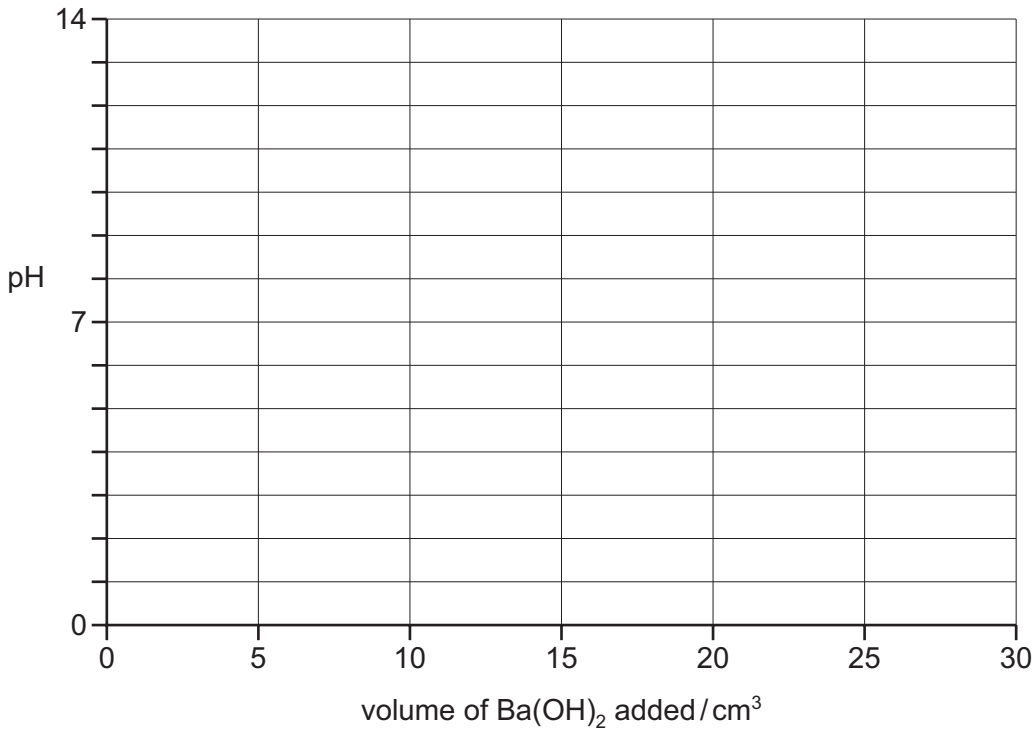
$[OH^-]$ = ... $mol\,dm^{-3}$ [2]

(ii) Use your value in **(i)** to calculate $[H^+]$ and the pH of the solution at the end of the addition.

final $[H^+]$ = ... $mol\,dm^{-3}$

final pH = ...
[2]

(iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm^3 of 0.100 $mol\,dm^{-3}$ $Ba(OH)_2$ to 20.0 cm^3 of 0.100 $mol\,dm^{-3}$ isocyanic acid.



(i) State what is meant by the terms

monodentate, ...

.....

ligand. .....

.....
[2]

Silver ions, Ag^+, react with cyanate ions to form a linear complex.

(ii) Suggest the formula of this complex, including its charge.

..... [2]

(e) When heated with HC*l*(aq), organic isocyanates, RNCO, are hydrolysed to the amine salt, RNH_3Cl, and CO_2.

$$RNCO + H_2O + HCl \rightarrow RNH_3Cl + CO_2$$

A 1.00 g sample of an organic isocyanate, RNCO, was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous $Ba(OH)_2$ according to the equation shown. The solid $BaCO_3$ precipitated weighed 1.66 g.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$$

(i) Calculate the number of moles of $BaCO_3$ produced.

moles of $BaCO_3$ = ... [1]

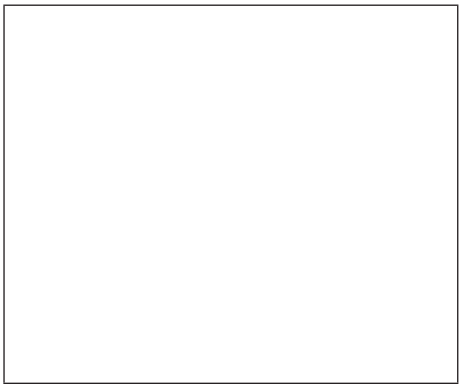
(ii) Hence calculate the M_r of the organic isocyanate RNCO.

M_r of RNCO = ... [1]

(iii) Use your M_r value calculated in **(ii)** to suggest the molecular formula of the organic isocyanate RNCO.

molecular formula of RNCO ..... [1]

(iv) Suggest a possible structure of the amine RNH_2, which forms the amine salt, RNH_3Cl.



[1]

[Total: 23]

acid	formula	pK_a
ethanoic acid	CH_3CO_2H	4.76
chloroethanoic acid	$C\ell CH_2CO_2H$	2.86
aminoethanoic acid (glycine)	$H_2NCH_2CO_2H$	9.87

(a) (i) State the relationship between pK_a and the strength of an acid.

..... [1]

(ii) State the mathematical relationship between pK_a and the acidity constant K_a.

..... [1]

(iii) Give reasons for why the pK_a value for chloroethanoic acid is **smaller** than that for ethanoic acid.

.....

.....

..... [2]

(b) (i) Use the zwitterionic structure for aminoethanoic acid (glycine) in aqueous solution to write an equation for its dissociation giving H^+(aq) ions.

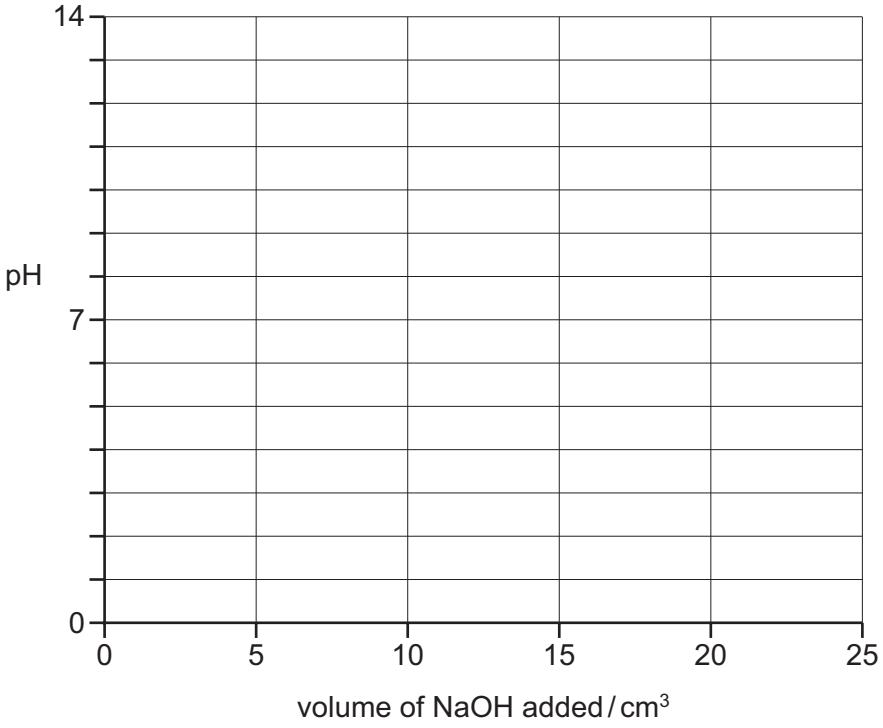
..... [1]

(ii) Calculate the pH of a 0.100 mol dm^{-3} solution of aminoethanoic acid.

pH = ... [2]

to be 12.5.

(iii) Using the following axes, sketch a graph showing how the pH changes during this titration.



[3]

[Total: 10]

- the iron atom, Fe $1s^2 2s^2 2p^6$ .....
- the iron(III) ion, Fe^{3+} $1s^2 2s^2 2p^6$ .....

[1]

(b) Solutions of iron(III) salts are acidic due to the equilibrium shown.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad K_a = 8.9 \times 10^{-4}\,\text{mol dm}^{-3}$$

Calculate the pH of a $0.25\,\text{mol dm}^{-3}$ $FeCl_3$ solution.

pH = ... [2]

(c) The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** H_2O molecule.

$$[M(H_2O)_6]^{n+}(aq) + L^-(aq) \rightleftharpoons [M(H_2O)_5L]^{(n-1)+}(aq) + H_2O(l)$$

metal ion, M	ligand, L	stability constant, K_{stab}
Fe^{3+}	F^-	1.0×10^6
Fe^{3+}	Cl^-	2.5×10^1
Fe^{3+}	SCN^-	9.0×10^2
Hg^{2+}	Cl^-	5.0×10^6

(i) What is meant by the term *stability constant,* K_{stab}?

.....

..... [1]

(ii) Use the data in the table to predict the formula of the complex formed in the greatest amount when

- a solution containing equal concentrations of both F^- and SCN^- ions is added to $Fe^{3+}(aq)$,

.....

- a solution containing equal concentrations of both Fe^{3+} and Hg^{2+} ions is added to $Cl^-(aq)$.

.....

(d) The complex $[Fe(ed)_2Cl_2]^{3-}$ can be formed according to the equation shown.

$$[Fe(H_2O)_4Cl_2]^{+}(aq) + 2ed^{2-}(aq) \rightleftharpoons [Fe(ed)_2Cl_2]^{3-}(aq) + 4H_2O(l)$$

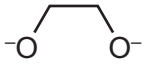
Write the expression for the equilibrium constant, K_{stab}, and state its units.

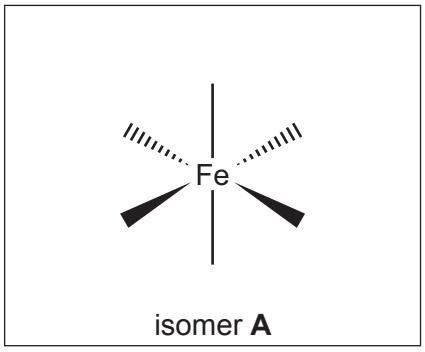
K_{stab} =

units .....
[2]

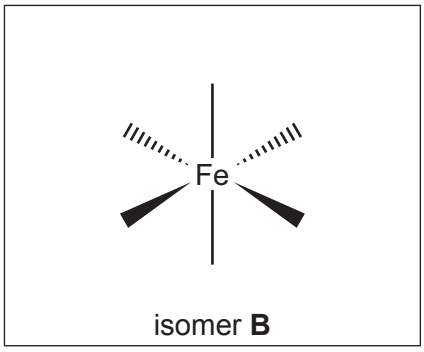
(e) $[Fe(ed)_2Cl_2]^{3-}$ shows geometrical and optical isomerism.

(i) Complete the three-dimensional diagrams to show the three stereoisomers of $[Fe(ed)_2Cl_2]^{3-}$.

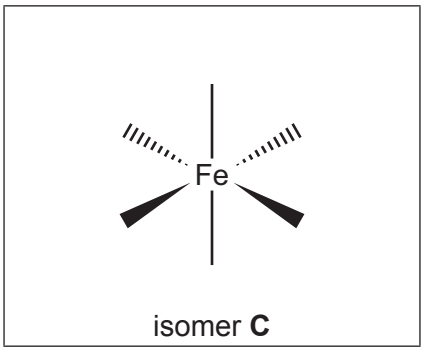
You may use  to represent ed^{2-}.



isomer **A**



isomer **B**



isomer **C**

[3]

(ii) Give the letters of two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which are geometrical isomers of each other.

..... [1]

(iii) Give the letters of the two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which show optical isomerism.

..... [1]

(iv) Give the letter of the isomer which has **no** dipole moment.

..... [1]

10 The compound chlorine dioxide, ClO_2, can be prepared by the reaction shown.

$$NaClO_2 + \tfrac{1}{2}Cl_2 \rightarrow ClO_2 + NaCl$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

.....

.....

..... [2]

(b) The central atom in the molecule of ClO_2 is chlorine.

Draw the 'dot-and-cross' diagram for ClO_2. Show outer electrons only.

[2]

(c) The reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

The rate of the reaction was measured at various concentrations of the two reactants and the following results were obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[F_2]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.010	0.060	2.20×10^{-3}
2	0.025	0.060	to be calculated
3	to be calculated	0.040	7.04×10^{-3}

The rate equation is rate = $k[ClO_2][F_2]$.

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

.....

..... [1]

rate constant, k = ... units ..... [2]

(iii) Use the data in the table to calculate

- the initial rate in experiment 2,

initial rate = ... $mol\,dm^{-3}\,s^{-1}$

- $[ClO_2]$ in experiment 3.

$[ClO_2]$ = ... $mol\,dm^{-3}$
[2]

(d) (i) What is meant by the term *rate-determining step*?

.....

..... [1]

(ii) The equation for the reaction between ClO_2 and F_2 is shown.

$$2ClO_2 + F_2 \rightarrow 2ClO_2F$$

$$\text{rate} = k[ClO_2][F_2]$$

The mechanism for this reaction has two steps.

Suggest equations for the **two** steps of this mechanism, stating which of the two steps is the rate-determining step.

step 1 .....

step 2 .....

rate-determining step = ...
[2]

(e) By considering the rate equation, explain why the rate increases with increasing temperature.

.....

..... [1]

7 (c) Magnesium hydroxide is sparingly soluble in water. The concentration of its saturated solution at 298 K is 1.7×10^{-4} mol dm^{-3}.

(i) Write an expression for the solubility product, K_{sp}, of $Mg(OH)_2$.

K_{sp} =

[1]

(ii) Calculate the value of K_{sp} for $Mg(OH)_2$ at 298 K and state its units.

K_{sp} = ... units ..... [2]

State and explain the trend in the solubility of the Group 2 sulfates down the group.

.....

.....

.....

.....

..... [3]

(b) (i) Write the expression for K_w, the ionic product of water.

K_w =

[1]

(ii) The numerical value of K_w increases with increasing temperature.

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[H^+] : [OH^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH			
ratio $[H^+] : [OH^-]$			

[2]

(c) An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

concentration = ... $mol\,dm^{-3}$ [2]

Write **two** equations to describe how hydrogencarbonate ions, HCO_3^-, and carbonic acid, H_2CO_3, control the pH of blood.

.....

..... [2]

(e) The K_a for ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 298 K.

(i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

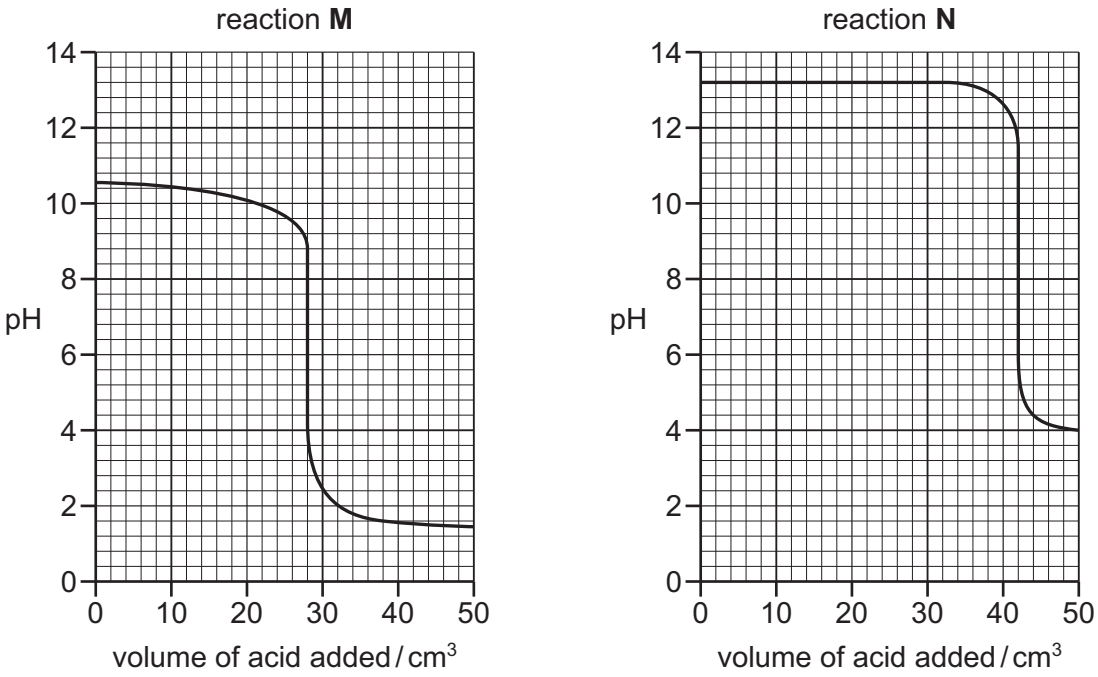
Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.

CH_3CO_2H + ... $\rightleftharpoons$ ..... + ...

[2]

(ii) A buffer solution was prepared by adding 30.0 cm^3 of 0.25 mol dm^{-3} ethanoic acid, an excess, to 20.0 cm^3 of 0.15 mol dm^{-3} sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. Give your answer to **one** decimal place.



(i) Use the titration curve for reaction **M** to deduce the volume of acid added at the end-point for this titration.

volume of acid added at the end-point = ... cm^3 [1]

(ii) The table shows some acid-base indicators.

name of indicator	pH range of colour change
malachite green	0.2–1.8
bromocresol green	3.8–5.4
bromothymol blue	6.0–7.6
thymolphthalein	9.3–10.6

Name a suitable indicator for each of the acid-base titrations **M** and **N**. Explain your answers.

reaction **M** ..... reaction **N** .....

explanation .....

.....

[2]

[Total: 19]

(i) Write an expression for the solubility product of CaF_2. Include its units.

K_{sp} =

units = ...
[2]

(ii) Calculate the solubility of CaF_2 at 298 K.

solubility = ... mol dm^{-3} [1]

[Total: 11]

(i) Explain the difference between a strong acid and a weak acid.

.....

..... [1]

(ii) Write the expression for the acid dissociation constant, K_a, for HNO_2.

K_a =

[1]

(iii) Calculate the pH of 0.15 mol dm^{-3} HNO_2.

pH = ... [2]

(iv) Calculate the percentage of HNO_2 molecules that are ionised in 0.15 mol dm^{-3} HNO_2.

% ionisation = ... [1]

(e) Solutions containing a mixture of HNO_2 and $NaNO_2$ are buffer solutions.

(i) Define what is meant by the term *buffer solution*.

.....

.....

..... [2]

(ii) Write **two** equations to show how a solution containing a mixture of HNO_2 and $NaNO_2$ acts as a buffer.

.....

..... [2]

(a) (i) Write an expression for the solubility product, K_{sp}, of $Ag_2S(s)$.

K_{sp} =

[1]

(ii) The solubility of $Ag_2S(s)$ in water at 298 K is 1.16×10^{-17} mol dm^{-3}.

Calculate the numerical value of the solubility product, K_{sp}, of $Ag_2S(s)$ at 298 K.

K_{sp} = ... [2]

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $Ag_2S(s)$ under standard conditions.

volume = ... dm^3 [2]

(i) Calculate the pH of 0.20 mol dm^{-3} HOBr(aq).

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH, are added to 20.0 cm^3 of 0.20 mol dm^{-3} HOBr(aq).

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

$$NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

(a) The ammonium ion is a weak acid. The pH of a 0.300 mol dm^{-3} solution of ammonium chloride is 4.89 under standard conditions.

(i) Calculate the $[H^+]$ in a 0.300 mol dm^{-3} solution of ammonium chloride.

$[H^+]$ = ... mol dm^{-3} [1]

(ii) Calculate the value of pK_a of the ammonium ion.

pK_a = ... [2]

(b) A buffer solution can be made by mixing ammonium chloride with ammonia solution.

(i) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong acid is added.

.....

..... [1]

(ii) Explain, with the aid of an equation, how this solution can behave as a buffer when a small amount of a strong base is added.

.....

..... [1]

Show your working.

$[H^+]$ = ... $mol\,dm^{-3}$ [1]

(ii) The pH of pure water at 50 °C is 6.64.

Calculate the numerical value of K_w at 50 °C.

K_w = ... [2]

[Total: 8]

(17b) **(i)** The numerical values of K_a for methanoic acid, HCO_2H, and pyruvic acid, CH_3COCO_2H, are given.

acid	K_a
HCO_2H	1.78×10^{-4}
CH_3COCO_2H	4.07×10^{-3}

An equilibrium mixture containing the two acid-base pairs is formed.

$$HCO_2^- + CH_3COCO_2H \rightleftharpoons HCO_2H + CH_3COCO_2^-$$

Use the K_a values to calculate the equilibrium constant, K_{eq}, for this equilibrium.

K_{eq} = ... [1]

(ii) Use your value of K_{eq} to predict the position of this equilibrium. Indicate this by placing a tick (✓) in the appropriate box in the table. Explain your answer.

equilibrium lies to the left	equilibrium lies in the middle	equilibrium lies to the right

.....

.....
[1]

(iii) Ethanedioic acid, HO_2CCO_2H, has two dissociation constants, K_{a1} and K_{a2}, whose pK_a values are 1.23 and 4.19.

Suggest equations to show the two dissociations that give rise to these pK_a values.

pK_{a1} 1.23 .....

pK_{a2} 4.19 .....
[2]

(iv) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

..... [1]

✓ = observed change
✗ = no observed reaction

test	reagent(s) and conditions	HCO_2H	CH_3COCO_2H	HO_2CCO_2H	observed change
1	....	✓	✗	✗	
2	....	✗	✓	✗	
3	....	✓	✗	✓	

Complete the table with the reagent(s) and conditions and the observed change for each test.
Assume these organic acids all have a similar acid strength. [5]

(g) The ionic product, K_w, for D_2O has a value of 1.35×10^{-15} mol^2 dm^{-6} at 298 K.

(i) Write the expression for the K_w of D_2O.

K_w =

[1]

(ii) Calculate the pH of pure, neutral D_2O at 298 K.
Assume $[D^+]$ is equivalent to $[H^+]$ for pH calculations.

pH = ... [2]

(i) Write an expression for the solubility product, K_{sp}, of Ag_2CO_3, and state its units.

K_{sp} =

units = ...
[2]

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CO_3 at 25 °C.

$[Ag^+]$ = ... mol dm^{-3} [1]

(iii) Solid Ag_2CO_3 is stirred at 25 °C with 0.050 mol dm^{-3} $AgNO_3$ until no more Ag_2CO_3 dissolves.

Calculate the concentration of carbonate ions, $[CO_3^{2-}]$, in this solution.

$[CO_3^{2-}]$ = ... mol dm^{-3} [1]

.....

.....

..... [2]

(b) (i) Write an expression for the acid dissociation constant, K_a, for ammonium ions, $NH_4^+(aq)$.

K_a =

[1]

(ii) Write **two** equations to describe how a solution containing ammonium ions, $NH_4^+(aq)$, and ammonia, $NH_3(aq)$, can act as a buffer.

.....

..... [2]

(iii) The numerical value of K_a for $NH_4^+(aq)$ is 5.6×10^{-10} at 298 K.
A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

Calculate the pH of the buffer solution formed at 298 K.

pH = ... [3]

[Total: 8]

(20d) Calcium iodate(V), $Ca(IO_3)_2$, is sparingly soluble in water.
The concentration of its saturated solution is 5.6×10^{-3} mol dm^{-3} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of $Ca(IO_3)_2$, and state its units.

K_{sp} =

units = ... [2]

(ii) Calculate the numerical value for K_{sp} $Ca(IO_3)_2$ at 298 K.

K_{sp} = ... [1]

(iii) When a few cm^3 of concentrated $Ca(NO_3)_2$(aq) is added to a saturated solution of $Ca(IO_3)_2$ a white precipitate forms.

Identify the white precipitate and give an explanation for this observation.

.....

.....

..... [2]

(e) Iodised salt is sodium chloride mixed with a small amount of sodium iodate(V), $NaIO_3$.

- 50.00 g of iodised salt is dissolved in distilled water and the solution made up to 250 cm^3 in a volumetric flask with distilled water.
- 50.0 cm^3 of this solution is pipetted into an excess of aqueous acidified potassium iodide.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

Calculate the mass of sodium iodate(V) present in 50.00 g of iodised salt.

mass of $NaIO_3$ = ... g [3]

(f) The half-equation for the reduction of iodate(V) ions is shown.

$$IO_3^- + 6H^+ + 5e^- \rightarrow \tfrac{1}{2}I_2 + 3H_2O \qquad E^\ominus = +1.19\,V$$

Use data from the *Data Booklet* to predict whether a reaction is feasible when aqueous solutions of acidified iodate(V) ions and bromide ions are mixed. Explain your answer.

.....

..... [1]

$$HIn \rightleftharpoons H^+ + In^-$$

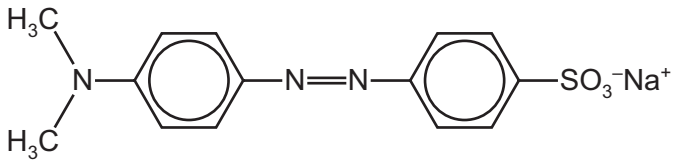
The K_a value for phenolphthalein is 5.0×10^{-10} mol dm^{-3} at 298 K. This indicator changes colour at a pH of approximately 8.8.

Calculate the ratio $\frac{[In^-]}{[HIn]}$ at pH 8.8.

ratio $\frac{[In^-]}{[HIn]}$ = ... [2]

(f) Methyl orange is another acid-base indicator. Its structure in aqueous solution at pH 4.4 is shown.

methyl orange



(i) On the structure of methyl orange, **circle** the bond or bonds that make this compound a dye. [1]

The colour of this indicator changes between pH 3.2 and pH 4.4.

(ii) Suggest the structure of methyl orange at pH 3.0. Assume the $-SO_3^-Na^+$ group is unreactive.

[1]

.....

.....

..... [2]

(b) K_{pc} of benzoic acid between octan-1-ol and water is 79.4.

(i) A solution of 0.400 g of benzoic acid in 25.0 cm^3 octan-1-ol is shaken with 125 cm^3 of water.

Calculate the mass of benzoic acid extracted into the water layer.

mass of benzoic acid extracted = ... g [2]

(ii) K_{pc} of benzophenone, $C_6H_5COC_6H_5$, between octan-1-ol and water is different from the value of K_{pc} of benzoic acid given in **(b)(i)**.

Explain why.

.....

.....

..... [1]

pH = ...

K_w = ...
[2]

(ii) Calculate the pH of 0.027 mol dm^{-3} NaOH(aq).

pH = ... [1]

(b) The K_a value of chloric(I) acid, HClO, is 3.72×10^{-8} mol dm^{-3}.

Calculate the pH of 0.010 mol dm^{-3} HClO(aq).

pH = ... [1]

(c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00 g of ethanamide is added to 50.0 cm^3 of water and this is then shaken with 50.0 cm^3 of octan-1-ol, it is found that the water layer contains 0.935 g of ethanamide at equilibrium.

(i) Calculate the partition coefficient, K_{pc}, for ethanamide in water and octan-1-ol.

K_{pc} = ... [1]

(ii) The 50.0 cm^3 of water containing 0.935 g of ethanamide is then shaken with 100.0 cm^3 of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm^3 of octan-1-ol at equilibrium.

mass of ethanamide = ... g
[2]

K_a =

[1]

(b) The hydroxylammonium ion, $HONH_3^+$, is a weak acid. A 1.00×10^{-3} mol dm^{-3} solution of hydroxylammonium ions has a pH of 4.41.

(i) Calculate the K_a of $HONH_3^+$.

K_a = ... [2]

(ii) Calculate the pK_a of $HONH_3^+$.

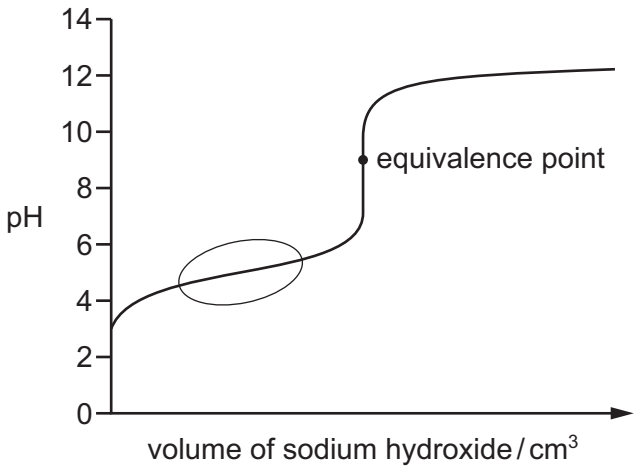
pK_a = ... [1]

(c) The solubility product of manganese(II) hydroxide, $Mn(OH)_2$, in water is 1.1×10^{-11} mol^3 dm^{-9} at 298 K.

Calculate the solubility of $Mn(OH)_2$ in water at 298 K.

solubility = ... mol dm^{-3} [2]

[Total: 6]



(i) In the region circled on the graph, identify the **two** organic species that are present in the solution. Explain why the pH of the mixture only changes slowly and gradually in this region when sodium hydroxide is being added.

two species present ....

.....

.....

.....

..... [3]

(ii) The equivalence point in this acid-base titration is where the two solutions have been mixed in exactly equal molar proportion.

Suggest why the pH is greater than 7 at the equivalence point in this titration.

.....

.....

.....

..... [1]

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.

$$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$$

When the resulting solution is titrated, 20.10 cm^3 of 0.0250 mol dm^{-3} acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Calculate the percentage by mass of NH_4VO_3 in the 0.150 g impure sample of NH_4VO_3.

Give your answer to **three** significant figures.

[M_r: NH_4VO_3, 116.9]

percentage by mass of NH_4VO_3 = ... % [3]

[Total: 7]

The resulting solution, containing unreacted acidified MnO_4^-, is titrated with 0.0500 mol dm^{-3} $Fe^{2+}(aq)$.

The end-point is reached when 30.40 cm^3 of 0.0500 mol dm^{-3} $Fe^{2+}(aq)$ has been added.

$$C_2O_4^{2-} \rightleftharpoons 2CO_2 + 2e^-$$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

Calculate the percentage by mass of BaC_2O_4 in the 0.500 g impure sample. Show your working.
[M_r: BaC_2O_4, 225.3]

percentage by mass of BaC_2O_4 = ... [4]

(d) Barium hydroxide, $Ba(OH)_2$, is completely dissociated in aqueous solution.

Calculate the pH of 0.120 mol dm^{-3} $Ba(OH)_2(aq)$ at 298 K.

pH = ... [2]

(a) (i) Write an expression for the K_a of $Cl(CH_2)_3CO_2H(aq)$.

K_a =

[1]

(ii) Write a mathematical expression to describe the relationship between K_a and pK_a.

..... [1]

(iii) Calculate $[H^+]$ in solutions **Y** and **Z**.

$[H^+]$ = ... $mol\,dm^{-3}$ [1]

(iv) Calculate the ratio $\frac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}}$.

$$\frac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}} = \text{.....}$$ [2]

(b) A buffer solution of pH 5.00 is produced by adding sodium propanoate to 5.00 g of propanoic acid in 100 cm^3 of distilled water.

Calculate the mass of sodium propanoate that must be used to produce this buffer solution. The K_a of propanoic acid is $1.35 \times 10^{-5}\,mol\,dm^{-3}$.

[M_r: propanoic acid, 74.0; sodium propanoate, 96.0]

mass of sodium propanoate = ... g [3]

Explain this observation.

.....

.....

.....

..... [2]

[Total: 10]

given. Water and octan-1-ol are immiscible.

$$K_{pc} = \frac{\text{concentration of } C_2H_5OC_2H_5 \text{ in octan-1-ol}}{\text{concentration of } C_2H_5OC_2H_5 \text{ in water}} = 6.760 \text{ at } 20\,°C$$

(a) In an experiment, octan-1-ol at 20 °C is added to a solution of ethoxyethane in water at 20 °C. The mixture is analysed immediately and a value of K_{pc} is calculated.

The calculation is performed correctly; the value calculated is 5.625.

Explain why the value calculated is **less** than 6.760.

.....

..... [2]

(b) A second experiment is performed and the value of K_{pc} is found to be 6.760. The concentration of ethoxyethane in the octan-1-ol layer is 7.62 g dm^{-3}.

(i) Calculate the concentration, in g dm^{-3}, of ethoxyethane in the aqueous layer.

..... g dm^{-3} [1]

(ii) 100 cm^3 of the octan-1-ol layer is taken and shaken with 100 cm^3 of water.

Calculate the maximum amount, in mol, of ethoxyethane that can be extracted into the water.

..... mol [3]

The concentration of Pb^{2+} in solution **X** is 5.68×10^{-3} mol dm^{-3}.

The concentration of I^- in solution **X** is 4.20×10^{-4} mol dm^{-3}.

(i) Use these data to calculate a value for the solubility product, K_{sp}, of lead(II) iodide.

State the units of K_{sp}.

K_{sp} = ...

units = ...
[2]

(ii) Potassium iodide is very soluble in water.

Describe and explain what is seen if a few drops of saturated potassium iodide solution are added to a portion of solution **X**.

.....

.....

..... [2]

[Total: 10]

1	**(a) (i)**	$K_{sp} = [Ag^+(aq)]^2[SO_4^{2-}(aq)]$ **and** units: mol^3dm^{-9}	**1**
	(ii)	$K_{sp} = (2 \times 0.025)^2 \times (0.025) =$ **6.25×10^{-5}**	**1**

P41/M/J/15/Q9c

(2c)(i)	equilibrium constant (for the solution) of a solute between two (immiscible) solvents ***or*** ratio of the concentration of the solute in (each of the) two solvents ***or*** ratio of the solubility of the solute in (each of the) two solvents	**1**
(ii)	$\frac{x/(25/1000)}{(0.0042-x)/(25/1000)}$ $x = 0.0252 - 6x$ $x =$ **0.0036g**	**1** **1**

3	**(a)**	$K_p = \{p(CS_2) \times (p(H_2))^4\} / \{(p(H_2S))^2 \times p(CH_4)\}$ units: atm^2 OR Pa^2	[1] [1]
	(b) (i)	$p(H_2S)$ = 196 atm $p(H_2)$ = 8 atm	[1] [1]
	(ii)	$K_p = (2 \times 8^4) / (196^2 \times 98) = 2.176 \times 10^{-3}$	[1]

P41/M/J/16/Q5

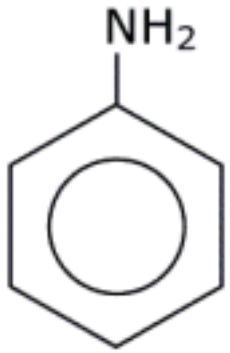
4	**(a) (i)**	$pK_a = -\log K_a$	[1]
	(ii)	diacids are more acidic than CH_3CO_2H HO_2C- group is electron-withdrawing, stabilising the monoanion OR HO_2C- group is electron-withdrawing, weakening the O–H bond OR monoanion is stabilised by H–bonding as n increases, the electron–withdrawing group is further away from the ionising CO_2H group OR the (intervening) alkyl groups destabilise the anion	[1] [1] [1]
	(iii)	removing H^+ from an anion is not electrostatically favourable	[1]
	(b) (i)	a solution which *resists* changes in pH when *small* amounts of H^+ or OH^- are added	[1] [1]
	(ii)	$HO_2CCH_2CH_2CO_2Na + H_+ \rightarrow HO_2CCH_2CH_2CO_2H + Na_+$ $HO_2CCH_2CH_2CO_2Na + NaOH \rightarrow NaO_2CCH_2CH_2CO_2Na + H_2O$	[1] [1]

5	**(a) (i)**	(an acid that is) partially / incompletely ionised / dissociated	
	(b) (i)	$pK_a = -\log K_a$ or $K_a = 10^{-pKa}$	1
	(ii)	ethanoic acid (1) is **more acidic** than propanoic acid (2) due to smaller electron-donating (R / alkyl) group / less electron-donating (R / alkyl) group(s) 2-chloropropanoic acid (3) is **more acidic** than propanoic acid (2) due to electron-withdrawing / electronegative (C*l* / chlorine) atom 2-chloropropanoic acid (3) is more acidic than 3¬-chloropropanoic acid (4) since the C*l* / chlorine / electronegative atom is closer to the CO_2^- / acid	3

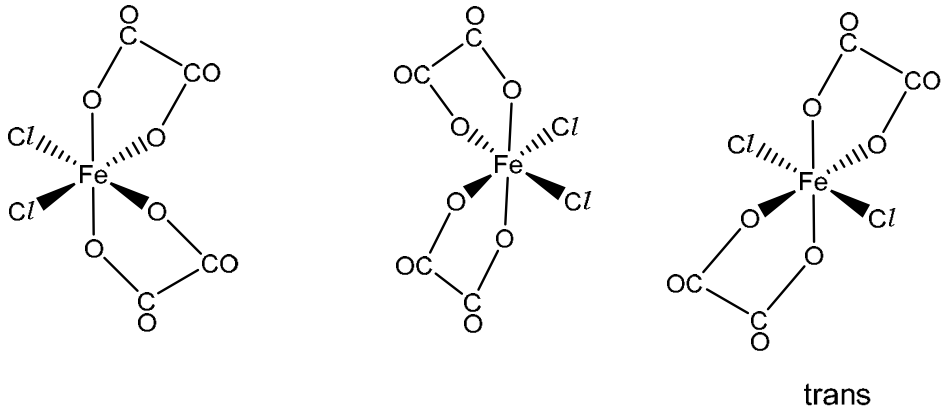
Question	Answer	Mark
6(a)	moles of thiosulfate = $0.1 \times 20.8 / 1000 = \mathbf{2.08 \times 10^{-3}}$ moles of $C\mathit{l}O^-$ in 25 cm^3 portion = $2.08 \times 10^{-3} / 2 = \mathbf{1.04 \times 10^{-3}}$ (moles of $C\mathit{l}O^-$ in 250 cm^3 = 1.04×10^{-2}) concentration of $C\mathit{l}O^- = 1.04 \times 10^{-2} / (10 / 1000) = \mathbf{1.04}$ (mol dm^{-3})	1 1 1 **3**
6(b)(i)		1 **1**
6(b)(ii)	**OR** black to colourless	1 **1**
6(b)(iii)	towards / close to the end-point of the titration / when the solution goes yellow	1 **1**
6(c)	moles of $O_2 = 82 / 24\,000 = 3.42 \times 10^{-3}$ = moles $C\mathit{l}O^-$ ions concentration of $C\mathit{l}O^- = 3.42 \times 10^{-3} / (5 / 1000) = \mathbf{0.68 / 0.683 / 0.684}$ (mol dm^{-3})	1 1 **2**
6(d)(i)	$K_c = \frac{[C_3H_3N_3O_3][HC\mathit{l}O_3]^3}{[C_3C\mathit{l}_3N_3O_3][H_20]^3}$	1 **1**
6(d)(ii)	(position of eqm) moves to the right / forward reaction predominates / more $HC\mathit{l}O$ made (as [$HC\mathit{l}O$] decreases) no effect on K	1 1

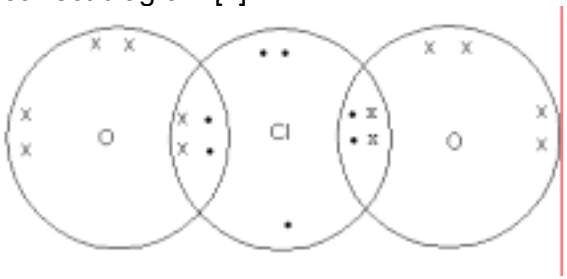
Question	Answer	Mark
6(d)(iii)	$2HClO \rightarrow 2HCl + O_2$ **OR** $2HClO \rightarrow H_2 + Cl_2 + O_2$	1 **1**
6(e)(i)	addition of acid: $H^+ + HCO_3^- \rightarrow H_2CO_3$ **OR** $H^+ + HCO_3^- \rightarrow H_2O + CO_2$ addition of base: $OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$ **OR** $H^+ + OH^- \rightarrow H_2O$ **and** position of eqm moves to the right **OR** $OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$	1 1 **2**
6(e)(ii)	$K_a = ([H^+][HCO_3^-] / [H_2CO_3])$ $[H^+] = (7.94 \times 10^{-7}) \times 1 / 9.5 = 8.36 \times 10^{-8}$ $pH = -\log[H^+] =$ **7.08**	 1 1 **2**
	Total:	**16**

Question	Answer	Marks
7(a)(i)		**1 + 1**
	16 electrons on each diagram	**1**
7(a)(ii)	HNC = 115–125° AND NCO = 180°	**1**
7(a)(iii)	cyanic acid, because it's a stronger / higher bond enthalpy / triple / C≡N / more electrons involved bond	**1**
7(b)(i)	$[H^+] = \sqrt{([HNCO]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})}$ or 3.46×10^{-3}	**1**
	pH = log $[H^+]$ = **2.5** (2.46)	**1**
7(b)(ii)	$Na_2CO_3 + 2(NH_2)_2CO \longrightarrow 2NaNCO + CO_2 + 2NH_3 + H_2O$	**1**
7(c)(i)	($n(OH^-)$ at start = $(2 \times 0.1 \times 30) / 1000 = 6 \times 10^{-3}$ mol) ($n(OH^-)$ reacted = $(0.1 \times 20) / 1000 = 2 \times 10^{-3}$ mol) $n(OH^-)$ remaining = $(6–2) \times 10^{-3} = 4 \times 10^{-3}$ mol, (in 50 cm^3)	**1**
	so $[OH^-]_{end} = (4 \times 10^{-3} \times 1000) / 50$ = **0.08 mol dm^{-3}**	**1**
7(c)(ii)	$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13}$ mol dm^{-3}	**1**
	so pH = $–\log(1.25 \times 10^{-13})$ = **12.9**	**1**
7(c)(iii)	curve starts at 2.46 / 2.5	**1**
	vertical portion (end point) at vol added = 10.0 cm^3	**1**

	ligand: a species that uses a lone pair of electrons to form a dative covalent bond to a metal atom/ metal ion	1
7(d)(ii)	$[Ag(NCO)_2]^-$ or $[Ag(OCN)_2]^-$ correct formula	**1**
	correct charge	**1**
7(e)(i)	$n(BaCO_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3}$ mol	**1**
7(e)(ii)	$n(RNCO) = 8.41 \times 10^{-3}$ mol, so $M_r = 1 / (8.41 \times 10^{-3})$ = **119**	**1**
7(e)(iii)	molecular formula = C_7H_5NO	**1**
7(e)(iv)		**1**
	Total:	**23**

Question	Answer	Marks
8(a)(i)	the lower / smaller the pK_a, the stronger the acid	**1**
8(a)(ii)	pK_a = –log(K_a) or pK_a = –lg(K_a) or $K_a = 10^{-pka}$	**1**
8(a)(iii)	(stronger than ethanoic acid because) C*l* is electron-withdrawing	**1**
	and so stabilises the RCO_2^- anion / conjugate base **or** weakens O-H bond (so H^+ is more easily released)	**1**
8(b)(i)	$NH_3^+CH_2CO_2^- \longrightarrow NH_2CH_2CO_2^- + H^+$ OR $NH_3^+CH_2CO_2^- + H_2O \longrightarrow NH_2CH_2CO_2^- + H_3O^+$	**1**
8(b)(ii)	$K_a = 10^{-9.87} = 1.35 \times 10^{-10}$ $[H^+] = \sqrt{(K_a.c)} = 3.67 \times 10^{-6}$	**1**
	pH = **5.4** (5.43–5.44) min 2sf	**1**
8(b)(iii)	curve starts at 5.4 and continuous	**1**
	vertical portion (end point) at vol added = 10.0 cm^3	**1**
	finishes at pH = 12.5 **at 20 cm^3** (and does not increase in pH)	**1**
	Total:	**10**

9(a)	Fe atom= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^6 4s^2$ Fe^{3+} ion= $(1s^2 2s^2 2p^6) 3s^2 3p^6 3d^5$	**1**
9(b)	$([H^+]^2 = 8.9 \times 10^{-4} \times 0.25$ ***or*** $2.225 \times 10^{-4})$ $[H^+] = 0.0149$	**1**
	pH = –log(0.0149) = **1.83**	**1**
9(c)(i)	K_{stab} is) the **equilibrium constant** for the formation of a complex (ion) (in a solvent from its constituent ions / molecules)	**1**
9(c)(ii)	$[Fe(H_2O)_5F]^{2+}$ **and** $[Hg(H_2O)_5Cl]^+$	**1**
9(d)	$K_{stab} = \dfrac{[Fe(ed)_2Cl_2^{3-}]}{[Fe(H_2O)_4Cl_2^+][ed]^2}$	**1**
	$mol^{-2}\,dm^6$	**1**
9(e)(i)	 trans	**3**
9(e)(ii)	any cis isomer **and** the trans isomer identified	**1**
9(e)(iii)	**both** correct cis isomers identified	**1**

10(a)	C*l* +3 to +4 (and oxidised)	**1**
	C*l* 0 to –1 (and reduced)	**1**
10(b)	19 electrons total [1] correct diagram [1] 	**2**
10(c)(i)	the exponent / power to which a concentration is raised in the rate equation	**1**
10(c)(ii)	(0.0022 k= (0.01) × (0.06)) k = 3.7 (3.67)	**1**
	$mol^{-1}\ dm^3\ s^{-1}$	**1**
10(c)(iii)	initial rate = 5.50×10^{-3}	**1**
	[ClO_2] = 0.048	**1**
10(d)(i)	slowest step (in a multi-step reaction)	**1**
10(d)(ii)	1 mole of F_2 and 1 mole ClO_2 reacting in the rate-determining step	**1**
	1st step is rate-determining step **and** a balanced mechanism consistent with overall equation e.g. $ClO_2 + F_2 \rightarrow ClO_2F_2$ $\quad$ $ClO_2 + ClO_2F_2 \rightarrow 2ClO_2F$ **or** $ClO_2 + F_2 \rightarrow ClO_2F + F$ $\quad$ $ClO_2 + F \rightarrow ClO_2F$	**1**
10(e)	k increases (as rate increases)	**1**

11(c)(i)	$K_{sp} = [Mg^{2+}] [OH^{-}]^2$	**1**
11(c)(ii)	$K_{sp} = (1.7 \text{ x } 10^{-4}) \times (2 \times 1.7 \times 10^{-4})^2 = 2.0 \times 10^{-11}$ (1.97×10^{-11})	**1**

	M2 because lattice energy and hydration energy **decreases** **OR** lattice energy and hydration energy become **less exothermic / more endothermic** [1] **M3** because hydration energy decreases to a **greater extent** (than does ΔH_{Latt}) [1]	
12(b)(i)	(K_w =) $[H^+][OH^-]$	**1**
12(b)(ii)	[1] or each correct tick effect of increasing temperature / decreases / stay the same / increase pH / ✓ / / / ratio of $[H^+]$:$[OH^-]$ / / ✓ / /	**2**
12(c)	$[H^+] = 10^{-13.25} = 5.62 \times 10^{-14}$ [1] $[OH^-] = K_w/[H^+] = 1.0 \times 10^{-14}/5.62 \times 10^{-14}$ $[OH^-]$ = **0.18** (0.178) (mol dm^{-3}) [1] ecf correct answer scores [2]	**2**
12(d)	$HCO_3^- + H^+ \rightarrow H_2CO_3$ **OR** $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ [1] $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ [1]	**2**
12(e)(i)	***CH_3COOH*** + $H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ [1] acid + base ⇌ base + acid [1]	**2**
12(e)(ii)	**M1** moles NaOH = 0.15 × 20/1000 = **0.0030** **AND** initial moles CH_3COOH = 0.25 × 30/1000 **OR 0.0075** [1] **M2** equilibrium moles CH_3COOH = **0.0045 AND** equilibrium moles CH_3COONa = **0.0030** [1] **M3** $[CH_3COOH]$ = 0.0045/0.05 = **0.090** AND $[CH_3COONa]$ = 0.003/0.05 = **0.060** $[H^+] = K_a \times [CH_3COOH]/[CH_3COONa]$ = **2.625×10^{-5}** [1] **M4** pH = $-\log[H^+]$ = **4.6** [1] correct answer scores [4]	**4**
12(f)(i)	end point = 28 cm^3	**1**

	K_{sp} = [illegible] units = $mol^3\ dm^{-9}$ [1]	
13(d)(ii)	$K_{sp} = 4x^3 = 3.45 \times 10^{-11}$ x= **2.05×10^{-4}** ($mol\ dm^{-3}$)	**1**

P42/O/N/18/Q5de

14(d)(i)	weak acid is partly ionised **and** strong acid is completely ionised	**1**
14(d)(ii)	$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$	**1**
14(d)(iii)	$K_a = [H^+]^2 / [HNO_2]$ $[H^+] = \sqrt{0.00069 \times 0.15} = 1.02 \times 10^{-2}$ [1] pH = $-\log[H^+]$ = **2.0 (1.99)** [1] minimum 2 sigificant figures	**2**
14(d)(iv)	% ionisation = $100 \times 1.02 \times 10^{-2} / 0.15$ = **6.7–6.8 %**	**1**
14(e)(i)	**M1** A solution that resists changes in pH [1] **M2** when small amounts of acid or alkali are added to it [1]	**2**
14(e)(ii)	**M1** $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$ [1] **M2** $NO_2^- + H^+ \rightarrow HNO_2$ [1]	**2**

15(a)(i)	$K_{sp} = [Ag^+]^2[S^{2-}]$	**1**
15(a)(ii)	• $[S^{2-}] = 1.16 \times 10^{-17}$ • $[Ag^+] = 2.32 \times 10^{-17}$ • $K_{sp} = \mathbf{6.2(4) \times 10^{-51}}$ minimum 2 sig. fig. correct answer scores 2 marks Award 1 mark for two points, award 2 marks for three points	**2**
15(a)(iii)	**M1**: moles $Ag_2S = 1 / 247.9 = 0.00403$ moles [1] 2sf min **M2**: $1.16 \times 10^{-17} = 0.0040 / V$ so $V = \mathbf{3.5 \times 10^{14}}$ (dm^3) [1] 2sf min ecf on M1 correct answer scores 2 marks	**2**
15(b)(i)	**M1:** $[H^+] = \sqrt{2.0 \times 10^{-9} \times 0.20}$ $[H^+] = 2.0 \times 10^{-5}$ (1.9976×10^{-5}) **M2:** pH = **4.7** (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	**2**
15(b)(ii)	**M1: Both** equilibria correctly stated moles KOH = $0.005 \times 0.2 = 1 \times 10^{-3}$ moles HOBr(initial) = $0.020 \times 0.2 = 4 \times 10^{-3}$ moles HOBr(eqm) = $4 \times 10^{-3} - 1 \times 10^{-3} = \mathbf{3 \times 10^{-3}}$ moles BrO^-(eqm) = $\mathbf{1 \times 10^{-3}}$ **M2:** ratio $[OBr^-]/[HOBr] = 1/3$ $[H^+] = 3 \times 2.0 \times 10^{-9} = 6 \times 10^{-9}$ pH = **8.2(2)** correct answer scores 2 marks	**2**

Question	Answer	Marks
16(a)(i)	1.3×10^{-5}	**1**
16(a)(ii)	**M1:** K_a expression used correctly **and** $K_a = 5.5(3) \times 10^{-10}$ **M2:** $pK_a = 9.26$ Award 2 marks for correct answer	**2**
16(b)(i)	$NH_3 + H^+ \rightarrow NH_4^+$	**1**
16(b)(ii)	$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ **or** $H^+ + OH^- \rightarrow H_2O$ **and** reference to expression in Q shifting R	**1**
16(c)(i)	quotes $K_w = 1 \times 10^{-14}$ or 1×10^{-1} $[H^+][OH^-]$ $[H^+] = 1 \times 10^{-7}$	**1**
16(c)(ii)	**M1:** $[H^+] = 2.3 \times 10^{-7}$ (calculator value 2.290867×10^{-7}) **and** $K_w = [2.3 \times 10^{-7}]^2$ **M2:** $K_w = 5.2 \times 10^{-14}$ calculator 5.248074×10^{-14} Award 2 marks for correct answer	**2**

<table>
<tr><td>17(b)(i)</td><td>K_{eq} = 4.07x10^{-3}/1.78x10^{-4} = 22.9</td><td>1</td></tr>
<tr><td>17(b)(ii)</td><td>3rd box ticked [to the right] AND as the K_{eq} is greater than one ecf on K_{eq}</td><td>1</td></tr>
<tr><td>17(b)(iii)</td><td>pK_a 1.23 $HO_2CCO_2H + H_2O \rightleftharpoons HO_2CCO_2^- + H_3O^+$
OR $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$

pK_a 4.19 $HO_2CCO_2^- + H_2O \rightleftharpoons {}^-O_2CCO_2^- + H_3O^+$
OR $HO_2CCO_2^- \rightleftharpoons {}^-O_2CCO_2^- + H^+$</td><td>2</td></tr>
<tr><td>17(b)(iv)</td><td>pK_a = – logK_a</td><td>1</td></tr>
<tr><td>17(c)</td><td><table>
<tr><th></th><th>reagents and conditions</th><th>observed change</th></tr>
<tr><td>test 1</td><td>M1 Tollen’s reagent, warm
OR
Fehling’s solution, warm</td><td>silver mirror

(brick)-red ppt.</td></tr>
<tr><td>test 2</td><td>M2 aqueous alkaline iodine
OR
2,4-DNPH</td><td>yellow ppt.

orange ppt.</td></tr>
<tr><td>test 3</td><td>M3 acidified MnO_4^- , warm</td><td>decolourises (and bubbles)</td></tr>
</table>
Two correct observations = 1 mark
Three correct observations = 2 marks</td><td>5</td></tr>
<tr><td>17(g)(i)</td><td>K_w = $[D^+][DO^-]$</td><td>1</td></tr>
<tr><td>17(g)(ii)</td><td>M1 $[D^+] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8}$

M2 pH = -log $[D^+]$ = 7.4(3) min 2sf</td><td>2</td></tr>
</table>

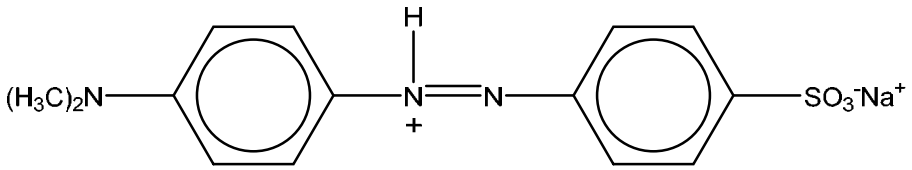
18(a)(i)	**M1** $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ **M2** units = $mol^3\ dm^{-9}$	**2**
18(a)(ii)	$x = \sqrt[3]{6.3 \times 10^{-12}/4} = 1.16 \times 10^{-4}$ (mol dm^{-3}) $[Ag^+] = 1.16 \times 10^{-4} \times 2 =$ **2.33×10^{-4}** (mol dm^{-3}) min 2sf	**1**
18(a)(iii)	$6.3 \times 10^{-12} = [0.05]^2[CO_3^{2-}]$ $[CO_3^{2-}] =$ **2.52×10^{-9}** (mol dm^{-3}) min 2sf	**1**

P41/M/J/20/Q8

Question	Answer	Marks
19(a)	**M1** a solution that resists changes in pH **M2** when small amounts of acid and alkali are added to it	**2**
19(b)(i)	$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$	**1**
19(b)(ii)	**M1** $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ **M2** $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	**2**
19(b)(iii)	**M1** moles NH_3(initial) = 0.25 x 0.80 = 0.200 **AND** moles HCl = 0.20 x 0.20 = 0.040 (= moles $NH_4^+{}_{eqm}$) **M2** moles $NH_{3(eqm)}$ = 0.20 – 0.04 = 0.160 $[H^+] = (5.6 \times 10^{-10} \times 0.04)/(0.16) = 1.4 \times 10^{-10}$ (mol dm^{-3}) ecf on M1 **M3** $pH = -\log(1.4 \times 10^{-10}) =$ **9.85** ecf on M2 min 2sf	**3**

20(d)(ii)	$K_{sp} = 4 \times (5.6 \times 10^{-3})^3$ K_{sp} = **7.03×10^{-7}** 2sf min	**1**
20(d)(iii)	**M1** $Ca(IO_3)_2$ **AND** as solubility of $Ca(IO_3)_2$ decreases **M2** due to common ion effect	**2**
20(e)	**M1** moles $S_2O_3^{2-}$ = 0.002 x 12.4/1000 = 2.48×10^{-5} moles of I_2 = 1.24×10^{-5} **M2** moles of IO_3^- = 4.13×10^{-6} in 50 cm^3 moles of IO_3^- = 2.07×10^{-5} in 250 cm^3 mass of $NaIO_3$ = 2.07×10^{-5} x 197.9 **M3** mass of $NaIO_3$ = **0.0041**	**3**
20(f)	It is feasible as the E_{cell} will be positive/+0.12 V	**1**

P42/M/J/20/Q4ef

Question	Answer	Marks
21(e)	**M1** $[H^+] = 10^{-8.8} = 1.585 \times 10^{-9}$ **M2** $[In^-]/[HIn] = 5.0 \times 10^{-10}/1.585 \times 10^{-9} = 0.315$	**2**
21(f)(i)	bond circled between the two Ns, or N=N or –N=N–	**1**
21(f)(ii)	 **or** H	**1**

22(a)	**M1** ratio of the concentration of a solute in the two immiscible solvents /liquids **M2** at equilibrium	**2**
22(b)(i)	**M1** 79.4 = (0.4-x/25)/(x/125) **M2** x = **0.0237** g [2] min 2sf	**2**
22(b)(ii)	(higher as) benzophenone is more non-polar/more soluble in octan-1-ol **ora**	**1**

Question	Answer	Marks
23(a)(i)	(pH =) –log[H^+] OR –lg[H^+] [1] (K_w =) [H^+][OH^-] [1]	**2**
23(a)(ii)	[H^+] = $1 \times 10^{-14} / 0.027 = 3.7037 \times 10^{-13}$ pH = –log(3.7037×10^{-13})= **12.4** [1] min 3sf	**1**
23(b)	[H^+] = $\sqrt{3.72 \times 10^{-8} \times 0.010} = 1.9287 \times 10^{-5}$ pH = -log(1.9287×10^{-5})= **4.7** [1] min 2sf	**1**
23(c)(i)	K_{pc} = (0.935 / 50) / (0.065 / 50) K_{pc} = **14.4** (14.38) [1] min 3sf	**1**
23(c)(ii)	**M1:** 14.4 = ((0.935 – x) / 50) / (x / 100) [1] ecf from **4(c)(i)** **M2:** x = **0.114** g [1] min 2sf ecf from M1	**2**

Question	Answer	Marks
24(a)	$[H^+][A^-] / [HA]$ [1]	**1**
24(b)(i)	$[H^+] = 3.9 \times 10^{-5}$ [1] $K_a = 1.5 \times 10^{-6}$ [1]	**2**
24(b)(ii)	5.82 [1]	**1**
24(c)	$4 \times {}^{3} = 1.1 \times 10^{-11}$ [1] $x = 1.4 \times 10^{-4}$ [1]	**2**

25(a)(i)	**M1:** CH_3CO_2H and $CH_3CO_2^-$ **M2:** due to buffering action / acting as a buffer solution **M3:** CH_3CO_2H reacts with NaOH / OH^- (forming $CH_3CO_2^-$ and water) **OR** OH^- reacts with H^+ and equilibrium $CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$ shifts to the right	**3**
25(a)(ii)	identifying $CH_3CO_2^-$ is present (with water) at the equivalence point **OR** $CH_3CO_2^-$ react with water forming OH^- **OR** titrating a weak acid with a strong base	**1**
25(b)	**M1:** moles $MnO_4^- = 0.025 \times 0.0201 = 5.025 \times 10^{-4}$ moles $V^{2+} = 5.025 \times 10^{-4} \times 5 / 3 = 8.375 \times 10^{-4}$ **M2:** moles $VO_3^- = 8.375 \times 10^{-4}$ mass of $NH_4VO_3 = 116.9 \times 8.375 \times 10^{-4} = 0.0979$ g **M3:** % Purity of $NH_4VO_3 = 100 \times 0.0979 / 0.15 = 65.3$ must be 3 sf	**3**

26(c)(i)	$_2C_4$ → BaC + CO_2 + CO **OR** BaC_2O_4 → BaC + 2CO + $½O_2$	**1**
26(c)(ii)	**M1:** [a] initial moles MnO_4^- = 0.0200 × 0.050 = 1.00×10^{-3} [b] moles Fe^{2+} = 0.050 × 0.0304 = 1.52×10^{-3} **M2:** [a] moles MnO_4^- unreacted = 1.52×10^{-3} / 5 = 3.04×10^{-4} [b] moles MnO_4^- reacted = $1.00 \times 10^{-3} - 3.04 \times 10^{-4} = 6.96 \times 10^{-4}$ **M3:** moles $C_2O_4^{2-}$ reacted = $6.96 \times 10^{-4} \times 5/2 = 1.74 \times 10^{-3}$ **M4:** mass of BaC_2O_4 = $225.3 \times 1.74 \times 10^{-3} = 0.392$ g % Purity of BaC_2O_4 = 100 × 0.392/0.50 = 78.4	**4**
26(d)	**M1:** $[OH^-] = 2 \times 0.12 = 0.24$ (mol dm^{-3}) $[H^+] = 1 \times 10^{-14}/0.24 = 4.17 \times 10^{-14}$ / pOH = –log(0.24) **OR** 0.62 **M2:** pH = $-\log[H^+]$ = 13.4 **OR** pH = 14 – 0.6 = 13.4	**2**

27(a)(i	$K_a = \frac{[H^+][Cl(CH_2)_3CO_2^-]}{[Cl(CH_2)_3CO_2H]}$ [1]	**1**
27(a)(ii)	$pK_a = -\log K_a$ **OR** $K_a = 10^{-pKa}$ [1]	**1**
27(a)(iii)	$[H^+] = 10^{-4.0}$ = **1×10^{-4}** [1]	**1**
27(a)(iv)	• $[HCl] = 1 \times 10^{-4}$ ecf 2(a)(iii) • $K_a = 10^{-4.52} = 3.02 \times 10^{-5}$ • $[Cl(CH_2)_3CO_2H] = (1 \times 10^{-4})^2 / 3.02 \times 10^{-5}$ $= 3.3 \times 10^{-4}$ ecf • $\frac{[HCl]}{[Cl(CH_2)_3CO_2H]} = \frac{1\times10^{-4}}{3.3\times10^{-4}} =$ **0.302** min 2sf ecf	**2**
27(b)	M1 $[H^+] = 10^{-5}$ **OR** 1×10^{-5} $K_a = [H^+][A^-] / [HA]$ **OR** pH = p*K*a + log $[A^-] / [HA]$ • ✓ [1] M2 moles of $A^- = (1.35 \times 10^{-5})(5 / 74) / (1 \times 10^{-5})$ moles of $A^- = 0.0912$ [1] ecf M3 mass of sodium propanoate = $0.0912 \times 96 =$ **8.76** [1] min 2sf ecf	**3**
27(c)	all of the (sodium) **propanoate** (ion) has been protonated / converted to (propanoic) acid / neutralised [1] **H^+** is in excess / **H^+** is 0.1 mol dm^{-3} (from the H_2SO_4) [1]	**2**

28(a)	M1 reference to **equilibrium** not being established / not at **equilibrium** [1] M2 concentration in water too high **or** conc in octan-1-ol too low owtte [1]	**2**
28(b)(i)	1.1 / 1.13 / 1.127 / 1.1272 [1]	**1**
28(b)(ii)	M1 $6.760 = (0.762 - x) / x$ [1] M2 $7.76x = 0.762$ $x = 0.0982$ g (correct value scores 2) [1] M3 0.0982 / 74 = 0.0013 / 0.00133 mol [1]	**3**
28(c)(i)	1.0×10^{-9} [1] $mol^3\ dm^{-9}$ [1]	**2**
28(c)(ii)	yellow precipitate / yellow solid / yellow crystals [1] common ion effect / K_{sp} has been exceeded [1]	**2**

Paper 4
Topic 4
Reaction Kinetics

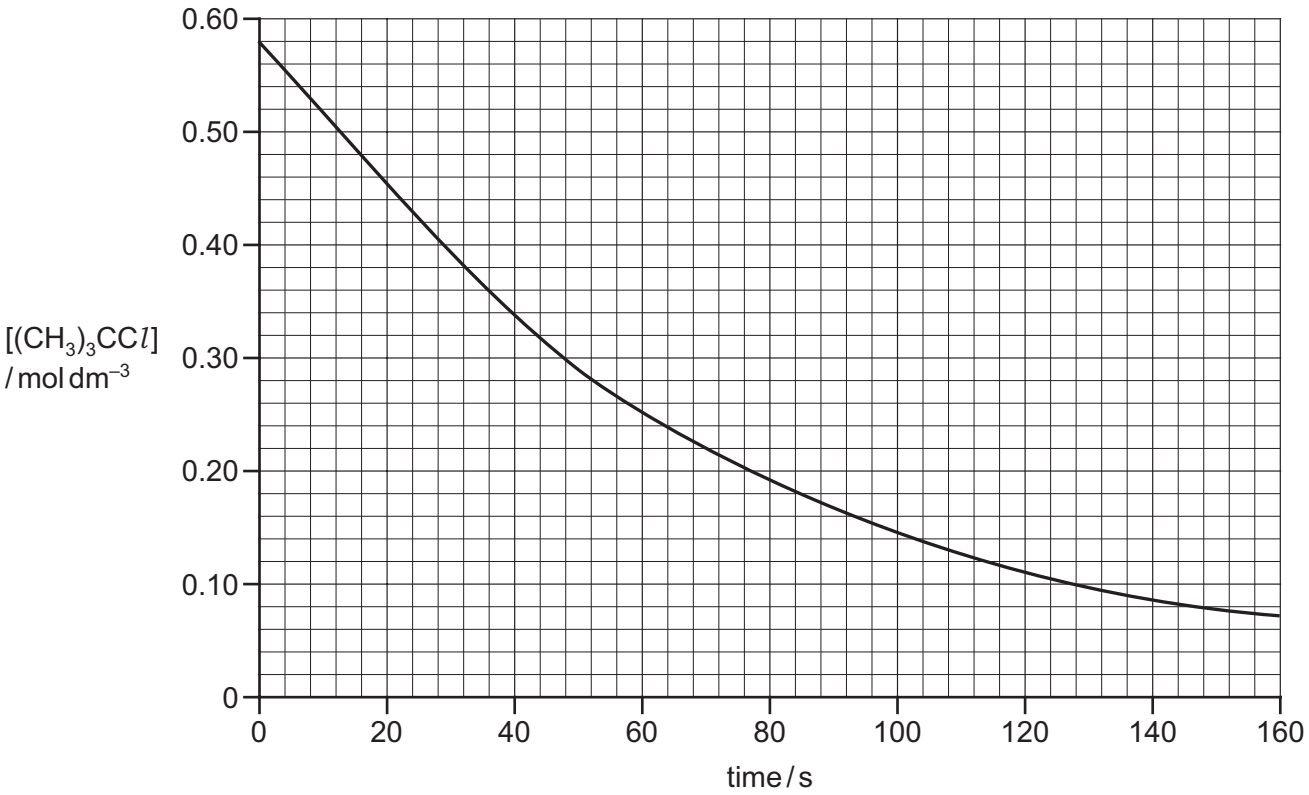
$$(CH_3)_3CCl(aq) + NaOH(aq) \rightarrow (CH_3)_3COH(aq) + NaCl(aq)$$

(a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

(b) The graph below shows the results of the experiment.



(i) What is meant by the *half-life* of a reaction?

.....

..... [1]

(ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

(iii) What would be the effect on the half-life of this reaction if the initial concentration of $[(CH_3)_3CCl]$ was **doubled**?

..... [1]

(c) (i) Use the graph in **(b)** to determine the rate of reaction at 80 s.
Show all your working.

rate = ... units ..... [2]

The rate equation for this reaction is shown.

$$\text{rate} = k[(CH_3)_3CCl]$$

(ii) Calculate the value of the rate constant, k, for this reaction and give its units.

k = ... units ..... [1]

[Total: 9]

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHCl CH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, given the following.

- a solution of 0.10 mol dm^{-3} 1-chloro-1-phenylethane, labelled **A**
- a solution of 0.10 mol dm^{-3} sodium hydroxide, labelled **B**
- 0.10 mol dm^{-3} HC*l*
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

.....

.....

.....

.....

.....

.....

.....

..... [4]

(b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[C_6H_5CHCl CH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

(i) Deduce the order of reaction with respect to each of $[C_6H_5CHCl CH_3]$ and $[OH^-]$. Explain your reasoning.

order with respect to $[C_6H_5CHCl CH_3]$ .....

.....

order with respect to $[OH^-]$ .....

rate = ... mol dm^{-3} s^{-1}

units of k = ...
[1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

(c) (i) Use your answers in **(b)(i)** to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

.....

..... [1]

D_2O and the proton NMR spectrum recorded, **fewer** peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, $C_6H_5CH(OH)CH_3$.
Use of the *Data Booklet* might be helpful.

δ / ppm	number of ^1H atoms responsible for the peak	group responsible for the peak	splitting pattern	result on shaking with D_2O
1.4				
2.7				
4.0				
7.2-7.4	5	C_6H_5	multiplet	peak remains

[4]

[Total: 16]

test performed	observation with NaC*l*	observation with NaI

[2]

Important information for this question

- In this question (pr) means 'a solution in propanone'.
- Sodium iodide is soluble in propanone giving Na^+(pr) and I^-(pr).
- Sodium chloride is insoluble in propanone.

The reaction between 2-chlorobutane and sodium iodide in propanone is shown.

$$CH_3CH_2CHClCH_3(pr) + Na^+(pr) + I^-(pr) \rightarrow CH_3CH_2CHICH_3(pr) + NaCl(s)$$

The rate of this reaction can be investigated by measuring the electrical conductivity of the reaction mixture. The electrical conductivity changes as the reaction progresses due to the precipitation of the NaC*l* produced.

(b) (i) Suggest how the electrical conductivity will change as the reaction proceeds. Explain your answer.

.....

..... [1]

(ii) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, using the following.

- an electrical conductance meter which measures the electrical conductivity of solutions
- solutions of known concentrations of 2-chlorobutane in propanone and sodium iodide in propanone
- stopclock
- access to standard laboratory equipment

.....

.....

.....

.....

.....

.....

.....

experiment	$[CH_3CH_2CHCl CH_3]$ / mol dm^{-3}	$[I^-]$ / mol dm^{-3}	relative rate
1	0.06	0.03	3
2	0.10	0.03	5
3	0.06	0.05	5
4	0.08	0.04	to be calculated

(i) Deduce the order of reaction with respect to each of $[CH_3CH_2CHCl CH_3]$ and $[I^-]$. Explain your reasoning.

order with respect to $[CH_3CH_2CHCl CH_3]$ .....

.....

order with respect to $[I^-]$ .....

.....
[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm^{-3} s^{-1}

units of *k* = ...
[1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structure of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 2-chlorobutane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

.....

..... [1]

(e) (i) State the number of peaks that would be seen in the carbon-13 NMR spectrum of $CH_3CH_2CHClCH_3$.

..... [1]

(ii) There are two isomers of $CH_3CH_2CHClCH_3$ that have **fewer** peaks in their carbon-13 NMR spectra than $CH_3CH_2CHClCH_3$.

Draw the structures of the isomers and state the number of peaks for each isomer.

isomer 1

number of peaks = ...

isomer 2

number of peaks = ...

[3]

4 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

.....

.....

..... [2]

(b) Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

(c) The rate of the reaction was measured at various concentrations of the two reactants, NO and Br_2, and the following results were obtained.

experiment	[NO] / mol dm^{-3}	[Br_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.03	0.02	3.4×10^{-3}
2	0.03	0.04	6.8×10^{-3}
3	0.09	0.04	6.1×10^{-2}
4	0.12	0.06	to be calculated

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[NO]^a[Br_2]^b$$

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

.....

..... [1]

.....

.....

.....

..... [2]

(iii) Use the data in the table to calculate the initial rate for experiment 4.

initial rate = ... mol dm^{-3} s^{-1} [1]

(iv) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

rate constant, *k* = ... units ..... [2]

(v) By considering the rate equation, explain why the rate decreases with decreasing temperature.

.....

..... [1]

(d) The reaction between X and Y was studied.

$$2X + Y \rightarrow Z$$

The following sequence of steps is a proposed mechanism for the reaction.

step 1 $2X \rightarrow V$
step 2 $V + Y \rightarrow Z$

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[X]^m[Y]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of *m* and *n* in the rate equation.

m = ... *n* = ...
[1]

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

(a) Define the term *rate of reaction*.

.....

..... [1]

(b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

..... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

The result of an experiment in which NO reacted with H_2 is shown in the table.

initial [NO] / mol dm^{-3}	initial [H_2] / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}

(c) Use the data and the rate equation to calculate a value for the rate constant *k*.
Give the units of *k*.

k = ...

units = ...
[2]

(d) A second experiment is performed at the same temperature. The initial concentration of $H_2(g)$ is 4.60×10^{-3} mol dm^{-3}. The initial rate of the reaction is 2.31×10^{-3} mol dm^{-3} s^{-1}.

Calculate the initial concentration of NO(g).

initial concentration of NO(g) = mol dm^{-3} [1]

[NO]	
[H_2]	
overall order	

[1]

(f) The reaction is believed to proceed in three steps.

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

(i) Deduce which of the three steps is the rate-determining step.

..... [1]

(ii) Explain your answer to **(i)**.

.....

.....

..... [1]

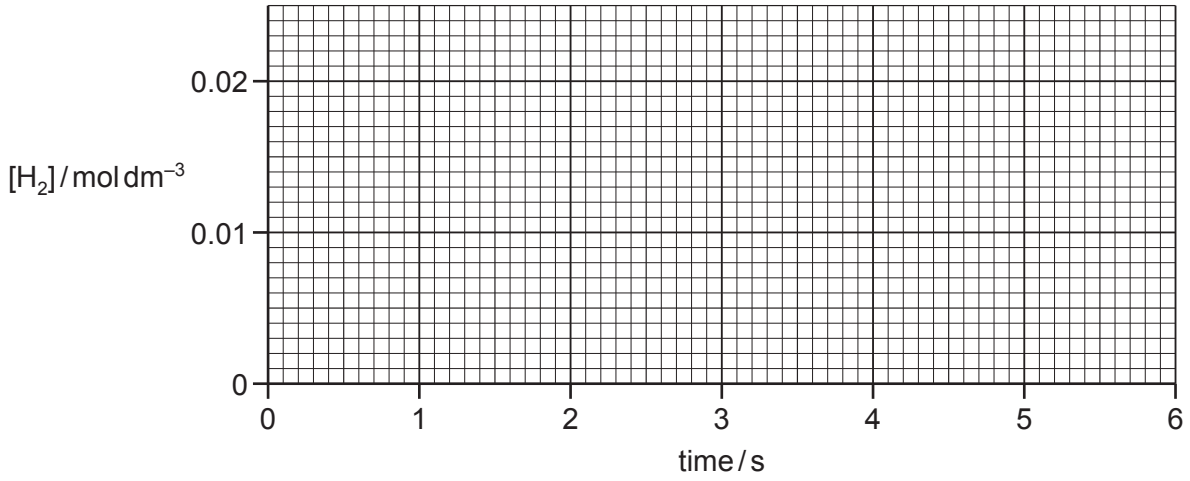
$H_2(g)$ is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

.....

..... [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of $H_2(g)$ during the first seconds under the conditions used.



[2]

(h) NO(g) acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how NO(g) acts as a catalyst in this process.

equation 1 .....

equation 2 .....

[1]

(ii) Explain why NO(g) can be described as a catalyst in this reaction.

.....

..... [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

.....

..... [1]

[Total: 14]

$$2IC\mathit{l}(g) + H_2(g) \rightarrow 2HC\mathit{l}(g) + I_2(g)$$

Experiments are performed using different starting concentrations of $IC\mathit{l}$ and H_2. The initial rate of each reaction is measured. The following results are obtained.

experiment	$[IC\mathit{l}]$ / mol dm^{-3}	$[H_2]$ / mol dm^{-3}	relative rate of reaction
1	4.00×10^{-3}	4.00×10^{-3}	1.00
2	4.00×10^{-3}	7.00×10^{-3}	1.75
3	4.00×10^{-3}	1.00×10^{-2}	2.50
4	5.00×10^{-3}	8.00×10^{-3}	2.50
5	7.00×10^{-3}	8.00×10^{-3}	3.50

(a) Identify a change, taking place in the reaction mixture, that would enable measurements of the rate of this reaction to be made.

..... [1]

(b) Use the data in the table to show that the reaction is first order with respect to $H_2(g)$.

.....

.....

.....

..... [1]

(c) Use the data in the table to show that the reaction is first order with respect to $IC\mathit{l}(g)$.

.....

.....

.....

..... [1]

(d) Complete the rate equation for the reaction between $IC\mathit{l}(g)$ and $H_2(g)$.

rate = ... [1]

k = ... [1]

(f) The reaction $2IC\mathit{l}(g) + H_2(g) \rightarrow 2HC\mathit{l}(g) + I_2(g)$ is first order with respect to $IC\mathit{l}(g)$ and first order with respect to $H_2(g)$.

Suggest a mechanism for this reaction. You should assume

- the mechanism has two steps,
- the first step is much slower than the second step.

first step ..... → .....

second step ..... → .....
[2]

(g) An alternative method is used to show that the reaction is first order with respect to $H_2(g)$. This method uses a large excess of $IC\mathit{l}(g)$ and measures how the concentration of $H_2(g)$ varies with time.

(i) Describe two ways of using these results to show the reaction is first order with respect to $H_2(g)$ concentration.

.....

.....

.....

.....

.....

..... [3]

(ii) Explain the reason for using a large excess of $IC\mathit{l}(g)$.

.....

..... [1]

(h) A chemical reaction may be speeded up by the presence of a catalyst.

Explain why a catalyst increases the rate of a chemical reaction.

.....

..... [1]

$$2NH_3 + Cl^- \rightarrow N_2H_4 + Cl^- + H_2O$$

A series of experiments was carried out at different concentrations of Cl^- and NH_3.

The table shows the results obtained.

experiment	$[Cl^-]$ / mol dm^{-3}	$[NH_3]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

(i) Use the data in the table to determine the order with respect to each reactant, Cl^- and NH_3.

Show your reasoning.

.....

.....

.....

.....

.....

..... [2]

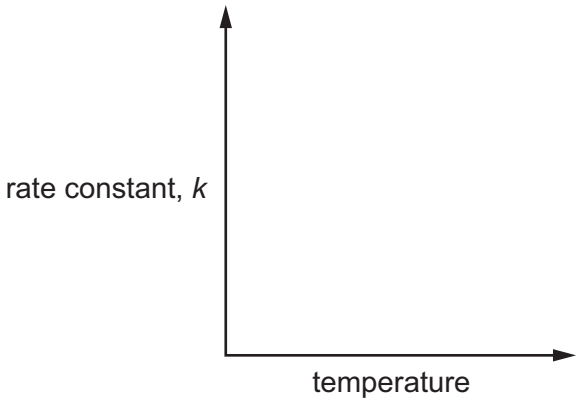
(ii) Write the rate equation for this reaction.

rate = ... [1]

(iii) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

k = ...

units = ...
[2]



[1]

(b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

(i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

.....

.....

..... [2]

A three-step mechanism for this reaction is shown.

step 1 $ClO^- + H_2O \rightarrow HClO + OH^-$

step 2 $I^- + HClO \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(ii) Use this mechanism to deduce the overall equation for this reaction.

..... [1]

(iii) Identify a step that involves a redox reaction. Explain your answer.

.....

..... [1]

[Total: 10]

$$CH_3COCH_3 + I_2 \xrightarrow{H^+ \text{ catalyst}} CH_3COCH_2I + HI$$

The rate equation was determined experimentally to be as shown.

$$\text{rate} = k[CH_3COCH_3][H^+]$$

(a) State the order of reaction with respect to

- CH_3COCH_3 .....
- I_2 .....
- H^+ .....

and state the overall order of this reaction. .....

[2]

(b) The rate of this reaction is 5.40×10^{-3} mol dm^{-3} s^{-1} when

- the concentration of CH_3COCH_3 is 1.50×10^{-2} mol dm^{-3}
- the concentration of I_2 is 1.25×10^{-2} mol dm^{-3}
- the concentration of H^+ is 7.75×10^{-1} mol dm^{-3}.

(i) Calculate the rate constant, *k*, for this reaction. State the units of *k*.

k = ...

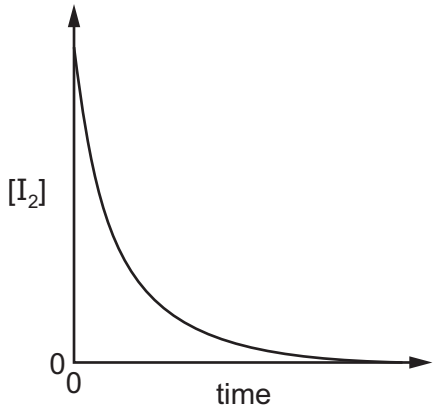
units = ...

[2]

(ii) Complete the table by placing **one** tick (✓) in each row to describe the effect of **decreasing** the temperature on the rate constant and on the rate of reaction.

	decreases	no change	increases
rate constant			
rate of reaction			

[1]



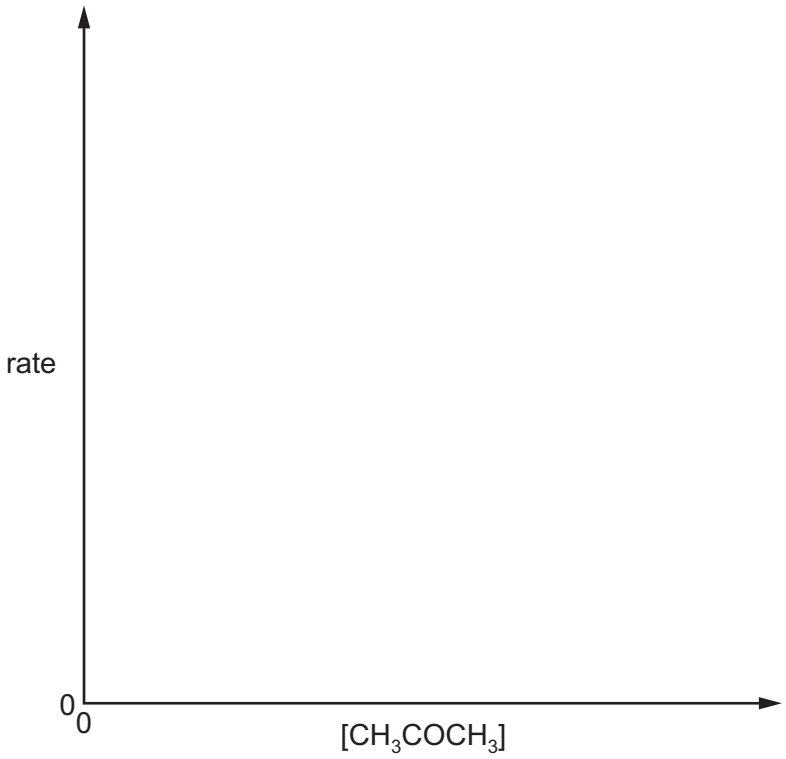
Describe how this graph could be used to determine the initial rate of the reaction.

.....

.....

..... [2]

(d) On the axes below, sketch a graph to show how the initial rate changes with different initial concentrations of CH_3COCH_3 in this reaction.



[1]

step 1 $Ce^{4+} + Mn^{2+} \rightarrow Ce^{3+} + Mn^{3+}$

step 2 $Ce^{4+} + Mn^{3+} \rightarrow Ce^{3+} + Mn^{4+}$

step 3 $Mn^{4+} + Tl^{+} \rightarrow Tl^{3+} + Mn^{2+}$

(i) Explain the meaning of the term *rate-determining step*.

.....

..... [1]

(ii) Use this mechanism to

- determine the overall equation for this reaction

.....

- suggest the role of Mn^{2+} ions in this mechanism. Explain your answer.

.....

.....

.....

[2]

[Total: 11]

$$C\ell NO_2(g) + NO(g) \rightleftharpoons NO_2(g) + C\ell NO(g)$$

In each $C\ell NO_2$ molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

(a) Draw a 'dot-and-cross' diagram for the $C\ell NO_2$ molecule.

[2]

(b) The reaction between $C\ell NO_2$ and NO is first order with respect to each reactant.

(i) Write the rate equation for this reaction.

rate = ... [1]

(ii) Deduce the units of the rate constant, *k*, when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in mol dm^{-3} s^{-1}.

..... [1]

(iii) State and explain whether or not the reaction **could** take place in a single step.

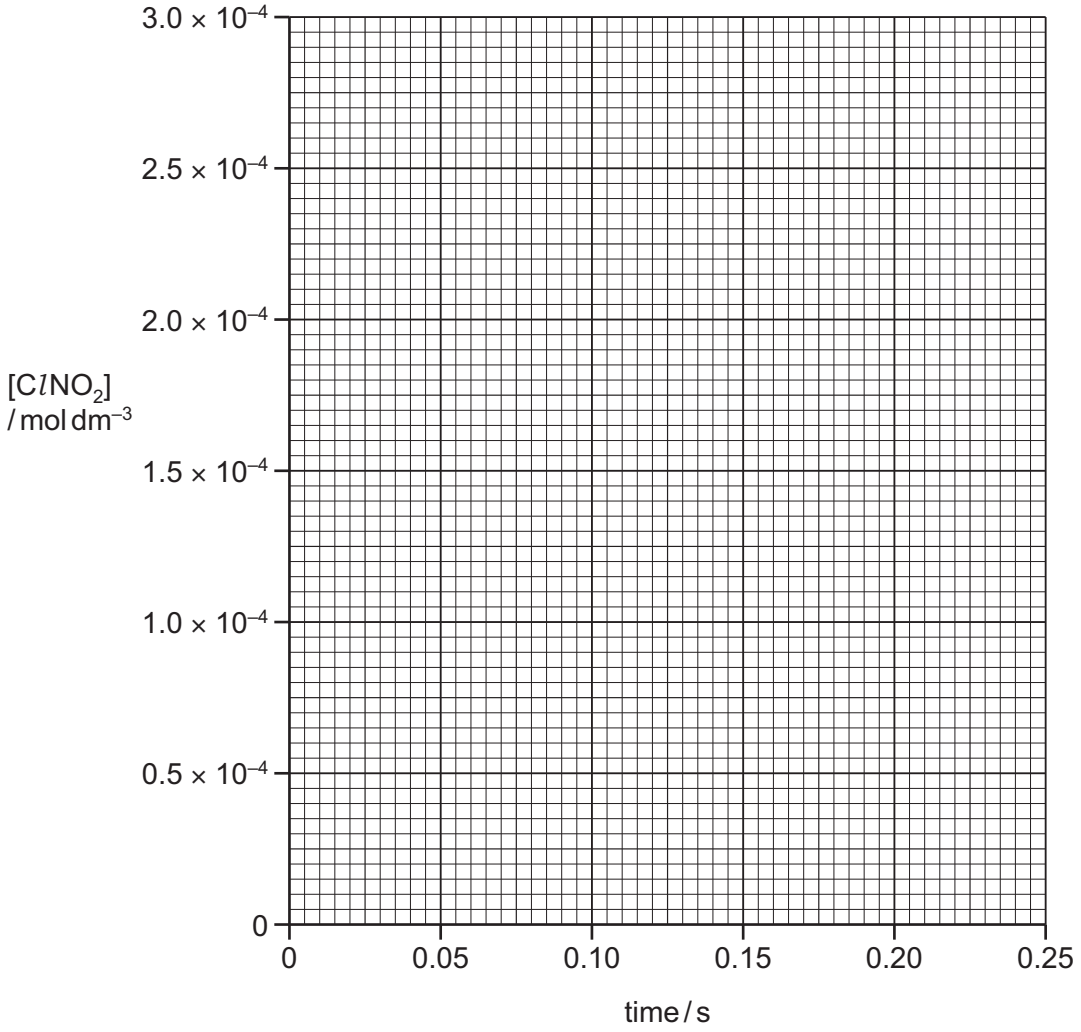
.....

.....

..... [1]

assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of $ClNO_2$ varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the NO_2 product at 0.20 seconds.

..... [1]

(iii) After 20 seconds the concentration of $ClNO_2$ remains constant.

Explain this observation.

..... [1]

[Total: 9]

half-life of a reaction .....

.....

rate-determining step .....

.....

[2]

(b) The reaction between hydroxide ions and bromomethane is first order with respect to $[OH^-]$ and first order with respect to $[CH_3Br]$.

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^-$$

Suggest a practical method that would confirm that the reaction is first order with respect to $[OH^-]$.

- Your method should include details of measurements that would be taken in order to calculate the rate of the reaction.
- You should include a method of presenting the results to show that the reaction is first order with respect to $[OH^-]$.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

..... [4]

In a particular experiment,

- $[CH_3CO_2CH_3] = 0.100\,mol\,dm^{-3}$
- $[OH^-] = 0.100\,mol\,dm^{-3}$
- rate of reaction = $2.06 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$.

Write a rate equation for this reaction and calculate the value of the rate constant, *k*, under these conditions. State the units of *k*.

rate = ...

k = ... units = ...
[3]

[Total: 9]

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

The mechanism involves the formation of the intermediate species, Mn^{2+}, in the first step which is subsequently used up in the second step.

State and use relevant electrode potentials, $E^{\ominus}$, to construct **two** equations to show how MnO_2 can catalyse this reaction.

.....

.....

.....

.....

.....

equation 1 .....

equation 2 .....

[3]

(b) The equation for the decomposition of hydrogen peroxide without a catalyst is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, k, of $2.0 \times 10^{-6}\,s^{-1}$ at 298 K.

Calculate the initial rate of decomposition of a $0.75\,mol\,dm^{-3}$ hydrogen peroxide solution at 298 K.

initial rate = ... $mol\,dm^{-3}\,s^{-1}$ [1]

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

step 2 $H^+ + IO^- \rightarrow HIO$

step 3 $HIO + I^- \rightarrow I_2 + OH^-$

step 4 $OH^- + H^+ \rightarrow H_2O$

Step 1 is the rate-determining step.

(i) State what is meant by the term *rate-determining step*.

.....

..... [1]

(ii) Use this mechanism to construct a balanced equation for this reaction.

..... [1]

(iii) Deduce the order of reaction with respect to each of the following.

H_2O_2 = ... I^- = ... H^+ = ... [1]

[Total: 7]

$$IO_3^- + 3SO_3^{2-} \rightarrow I^- + 3SO_4^{2-}$$

The initial rate of reaction was found to be first order with respect to IO_3^-, first order with respect to SO_3^{2-} and first order with respect to H^+.

(i) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... $mol\,dm^{-3}\,s^{-1}$

units of *k* = ...
[2]

(ii) The rate of reaction depends on the pH of the solution. Assume all other concentrations remain the same.

Use the expression $x = \frac{\text{rate at pH 5.00}}{\text{rate at pH 4.00}}$ to calculate the value of x.

x = ... [1]

[Total: 19]

13 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The rate equation for the forward reaction is shown.

$$\text{rate} = k[NO]^2[O_2]$$

(a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to $[O_2]$	
the overall order of reaction	

[1]

(b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	$[NO]$ / mol dm^{-3}	$[O_2]$ / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

(i) Use the data for experiment 1 to calculate the value of the rate constant, *k*. State the units of *k*.

k = ... units = ...
[2]

(ii) Calculate the value of [NO] in experiment 2.

[NO] = ... mol dm^{-3} [1]

(c) Define the term *rate-determining step*.

..... [1]

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

The rate equation for the reaction in the absence of any catalyst is shown.

$$\text{rate} = k[S_2O_8^{2-}][I^-]$$

(i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1 .....

step 2 .....

rate-determining step = ...

[2]

(ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, $[I^-] = 0.00780\,\text{mol}\,\text{dm}^{-3}$. Under the conditions used, the half-life of $[I^-]$ is 48 seconds.

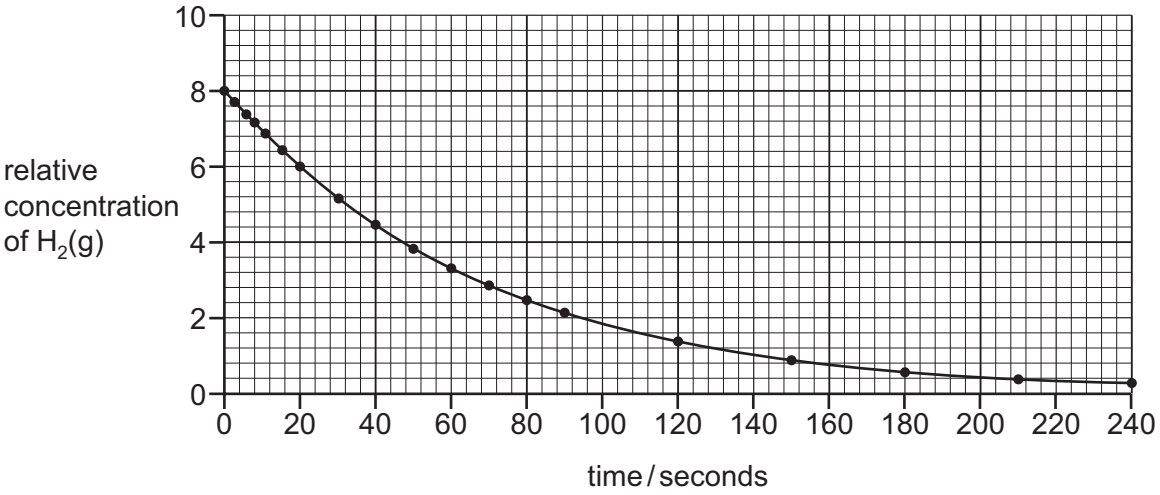
Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... $\text{mol}\,\text{dm}^{-3}$ [1]

[Total: 8]

14 The rate of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is studied.

(a) A small amount of $H_2(g)$ is mixed with a large excess of $I_2(g)$ at a temperature of 400 K and the reaction is monitored. The graph obtained is shown.



(i) Suggest why a large excess of $I_2(g)$ is used in this experiment.

..... [1]

(ii) The reaction is first order with respect to $H_2(g)$.

Use data from the graph to confirm this statement.

.....

.....

.....

..... [2]

experiment	$[H_2(g)]$ / mol dm^{-3}	$[I_2(g)]$ / mol dm^{-3}	rate of reaction / mol dm^{-3} s^{-1}
1	1.0×10^{-2}	1.0×10^{-2}	2.0×10^{-17}
2	1.0×10^{-1}	1.0×10^{-1}	2.0×10^{-15}
3	5.0×10^{-1}	5.0×10^{-1}	5.0×10^{-14}

(i) Use the data, and the order of reaction with respect to $H_2(g)$ given in **(a)(ii)**, to deduce the order of reaction with respect to $I_2(g)$.

Explain your answer, giving data in support of your explanation.

.....

.....

.....

..... [3]

(ii) Use information from **(a)(ii)** and your answer to **(b)(i)** to write the rate equation for the forward reaction.

rate = ... [1]

(iii) Use your rate equation and data from experiment 1 to calculate the value of the rate constant, *k*, for the forward reaction at 400 K. Include units for *k*.

k = ... units = ...
[2]

reactions are the same.

forward reaction	$H_2(g) + I_2(g) \rightarrow 2HI(g)$
backward reaction	$2HI(g) \rightarrow H_2(g) + I_2(g)$

(i) Use this information to explain what will happen if equal concentrations of HI(g), $H_2(g)$ and $I_2(g)$ are mixed at 400 K.

You should comment on:
- the relative initial rates of the forward and backward reactions
- the position of the equilibrium reached.

.....

.....

..... [1]

(ii) At 700 K the rate constant for the forward reaction is approximately 50 times greater than the rate constant for the backward reaction.

Use this information and the information in **(c)(i)** to deduce the signs of the ΔH values of the forward and backward reactions. Explain your answer.

.....

.....

.....

..... [2]

[Total: 12]

oxygen gas.

$$N_2O_5(solv) \rightarrow 2NO_2(solv) + \tfrac{1}{2}O_2(g)$$

(a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

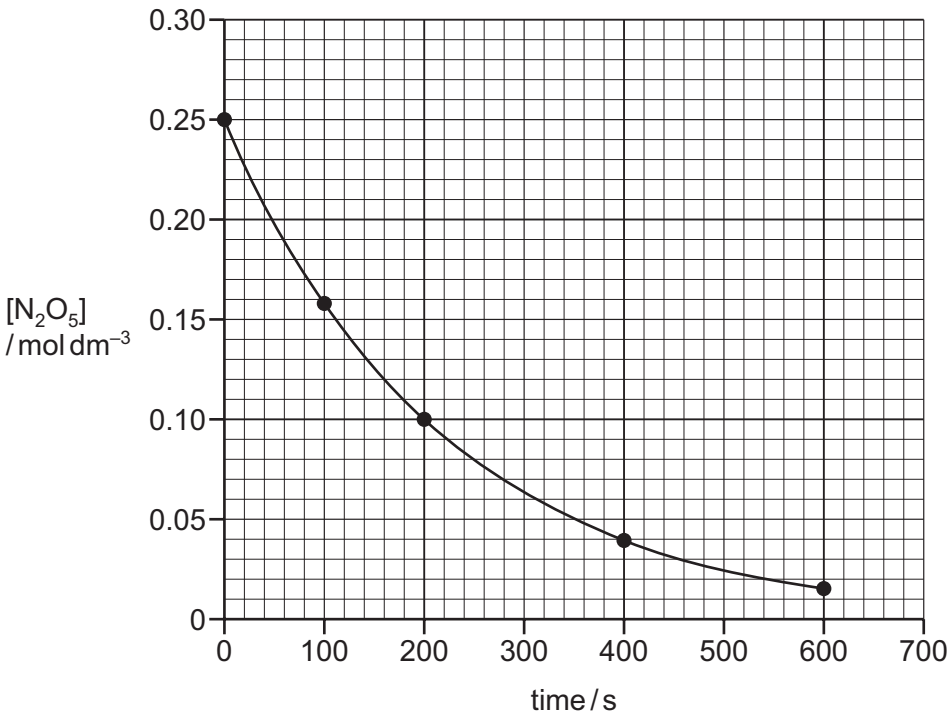
.....

..... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The graph shows the results obtained.



The reaction is first order with respect to N_2O_5. This can be confirmed from the graph using half-lives.

(i) Explain the term *half-life of a reaction*.

.....

..... [1]

half-life = ... s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

..... [1]

(c) (i) Use the graph in **5(b)** to determine the rate of reaction at 200 s. Show your working.

rate = ...

units = ...
[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to **(c)(i)** to calculate the value of the rate constant, k, for this reaction and state its units.

k = ... units ..... [1]

(d) Nitrogen dioxide reacts with ozone, O_3, as shown.

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

The rate equation for this reaction is rate = $k[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

.....

..... [2]

[Total: 9]

$$2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$$

A series of experiments is carried out using differen concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} min^{-1}
1	0.020	0.030	7.20×10^{-4}
2	0.020	0.120	2.88×10^{-3}
3	0.050	0.030	4.50×10^{-3}

(i) Explain the term *order of reaction*.

.....

..... [1]

(ii) Use the data in the table to determine the order of reaction with respect to each reactant, ClO_2 and OH^-.

Explain your reasoning.

.....

.....

.....

.....

.....

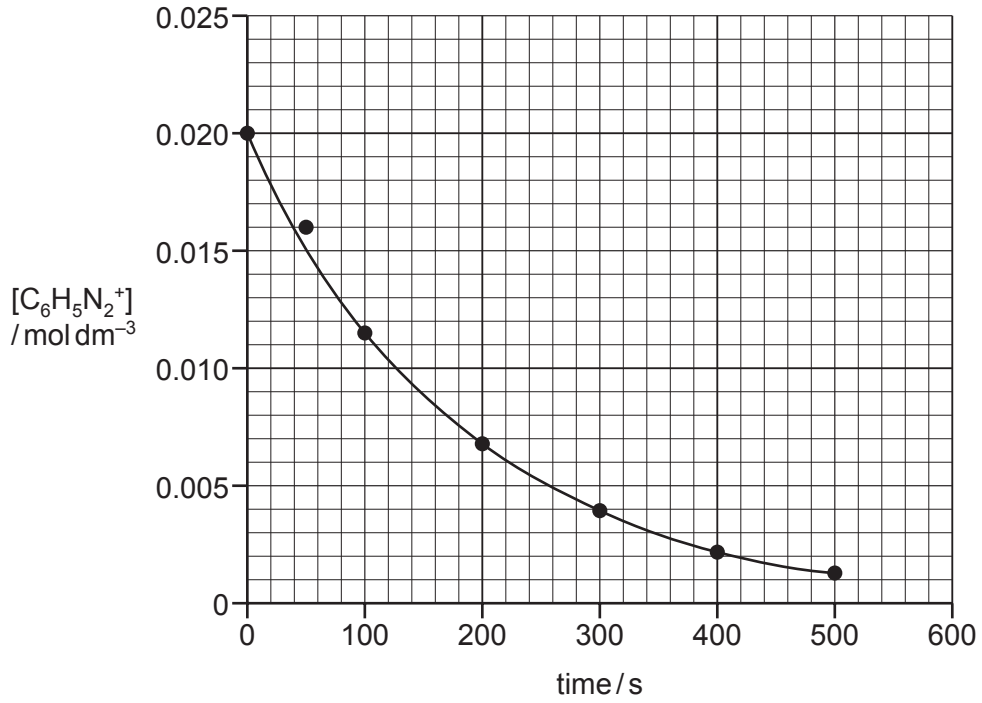
..... [2]

(iii) Use your answer to **(a)(ii)** to construct the rate equation for this reaction.

rate = ... [1]

(iv) Use your rate equation and the data from experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

The graph shows the results obtained.



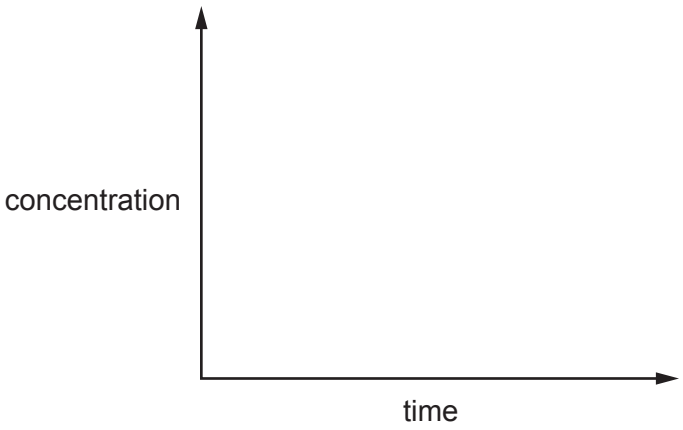
(i) Draw the structure of the organic product formed in this reaction.

[1]

(ii) Use the graph to determine the rate of reaction at 100 s. Show your working.

rate = ... mol dm^{-3} s^{-1} [1]

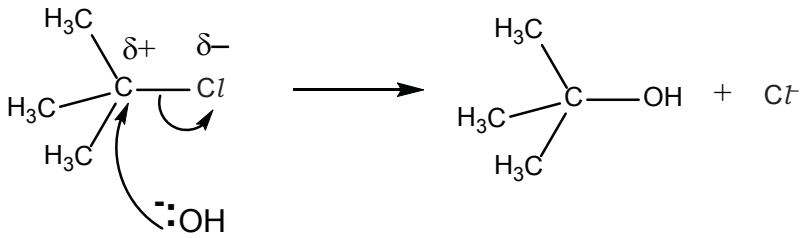
Use your graph to suggest how successive half-lives for a zero-order reaction vary as the concentration of a reactant decreases. Indicate this by placing a tick (✓) in the appropriate box in the table.



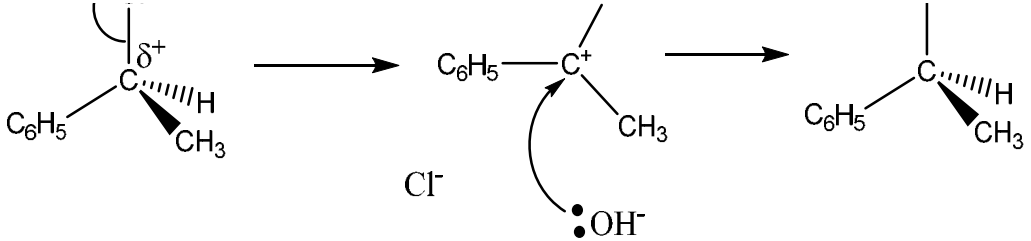
successive half-lives decrease	no change in successive half-lives	successive half-lives increase

[1]

[Total: 9]

Question	point	Marks
1 (a)	M1: dipole on C–C*l* bond M2: curly arrow breaking C–C*l* bond M3: curly arrow from the oxygen on $^{-}$OH (lone pair needs to be shown) to carbon in C–C*l* bond **and** C*l*$^{-}$ (ion) formed in the mechanism 	3
(b) (i)	time taken for the concentration of a reactant(s) to fall to half its original value	1
(ii)	evidence of a pair of construction lines on graph **and** $t_{½}$ = 49–53 s	1
(iii)	no effect / change	1
(c) (i)	evidence of tangent at 80 s **and** data used, e.g. 0.42 / 152 = 0.00263 units mol dm^{-3} s^{-1}	2
(ii)	correct use of answer to **(i)**/0.19 **and** s^{-1}	1
		9

2(a)	Any of the three methods possible. Any 4 of the 5 points for each method available for maximum 4 marks. Method 1 1 Ensure both solutions (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **B** and start the clock 3 at known time take out a sample / **X** and add it to ice-cold solvent 4 titrate against HCl 5 repeat at time at known time intervals Method 2 1 Ensure both solutions (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **B** and start the clock 3 at known time pour into ice-cold solvent or pour ice-cold solvent in 4 titrate against HCl 5 repeat with different concentrations of either A or B, or repeat using different times Method 3 1 Ensure both solutions (**A** and **B)** at 40 °C before mixing 2 mix known volumes of **A** and **B** and start the clock and add pH meter 3 at a known time . . . . 4 . . . . record the pH 5 repeat pH readings at known time intervals	**4**
2(b)(i)	from 1 and 3: when [RCl] is trebled, so is rate, so order w.r.t. [RCl] = 1	**1**
	from 1 and 2: when both concentrations are doubled, rate doubles so [OH^-] has no effect on rate, so order w.r.t.[OH^-] = 0	**1**
2(b)(ii)	rate = k[RCl] AND units: sec^{-1} 1 / s	**1**
2(b)(iii)	relative rate = 2.0	**1**

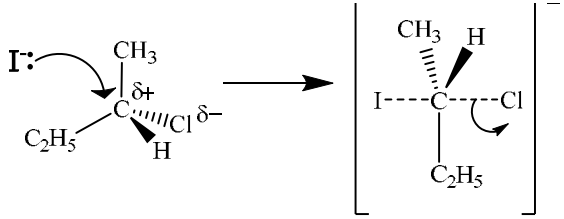
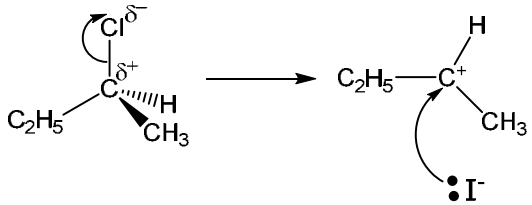
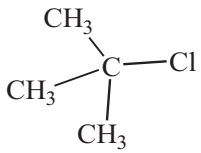
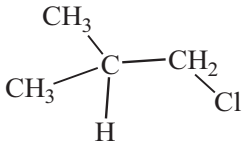


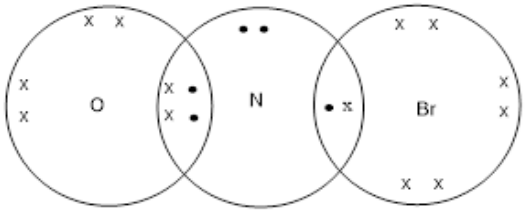
	C-C*l* dipole and first curly arrow	**1**
	intermediate cation	**1**
	OH^- with lone pair and curly arrow	**1**
2(c)(ii)	Beginning with candidate's mechanism in (c)(i): **If S_N1:** racemate / mixture of / two optical isomers will be formed, because: the intermediate is planar / has a plane of symmetry / OH^- can approach from top or bottom or from any direction **If S_N2:** one optical isomer because attack always from fixed direction / from same side / the "configuration" always inverts / there is an asymmetric transition state	**1**
2(d)(i)		

δ value	number of H atoms	group	splitting	result with D_2O
1.4	**3**	**C 3 / methyl**	**doublet**	**peak remains**
2.7	**1**	**O / hydroxyl / alcohol**	**s**	**peak disappears**
4.0	**1**	**CH**	**quartet**	**peak remains**

the three groups are in their correct places wrt the δ values	**1**
no. of H atoms for each peak agrees with group column	**1**
splitting patterns doublet, singlet and quartet are assigned to correct groups	**1**
peak identified as OH disappears with D_2O, no other peak disappears	**1**

3(a)	Add $AgNO_3$ Cl^- gives a white ppt **and** I^- gives a yellow ppt.	**1**
	Add $NH_3(aq)$; ppt dissolves **and** ppt is insoluble	**1**
3(b)(i)	conduc **decreases** during the reaction, AND number of Na^+ / I^- / **ions** are **decreased** / used up (from solution)	**1**
3(b)(ii)	(Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing) mix **known volumes and** start the clock / timing clearly mentioned/implied measure conductance / conductivity at regular intervals / every measured time [method A] OR measure the time for conductance to go to zero / a specific value / to be constant [method B] prepare a curve of conductance vs. time [related to method A] OR prepare a curve of conductance vs. concentration [related to method A] OR repeating the experiment at different concentrations [related to method A and B] any 3 points	**3**
3(c)(i)	[R-Cl]: rate increases by 5 / 3 when concentration increases by 10 / 6 (5 / 3), so order = 1	**1**
	[I^-]: rate increases by 5 / 3 when concentration increases by 5 / 3, so order = 1	**1**
3(c)(ii)	rate = $k[I^-][CH_3CH_2CHClCH_3]$ AND units of k = $dm^3\ mol^{-1}\ s^{-1}$	**1**
3(c)(iii)	relative rate = 5 / 5.3	**1**

	S_N2  S_N1 	
	C-C*l* dipole AND C-C*l* curly arrow	**1**
	intermediate cation OR 5-valent transition state (charge essential)	**1**
	I^- with lone pair AND other curly arrow	**1**
3(d)(ii)	If S_N1 in 2(d)(i) **mixture of / two** optical isomers will be formed, AND the intermediate can be formed by the I^- approaching from top or bottom plane If S_N2 in 2(d)(i) **one optical isomer** AND attack always from fixed direction / opposite side	**1**
3(e)(i)	**4** peaks	**1**
3(e)(ii)	 	**1 + 1**
	number of peaks = 2 number of peaks = 3	**1**

	Br_2: Br 0 to −1 (and reduced)	1
4(b)		
	3 bonding pairs around N (in a structure involving NOBr)	**1**
	rest of molecule correct	**1**
4(c)(i)	**power** to which a concentration of a reactant is raised in the **rate equation**	**1**
4(c)(ii)	using expt. 2 and 3 a = 2 **or** [NO] 2nd order **and** conc × 3 rate × 9 **or** $6.1 \times 10^{-2} / 6.8 \times 10^{-3} = (0.09/0.03)^a$	**1**
	using expt. 1 and 2 b = 1 **or** $[Br_2]$ 1st order **and** conc × 2 rate × 2 **or** $6.8 \times 10^{-3} / 3.4 \times 10^{-3} = (0.04/0.02)^b$	**1**
4(c)(iii)	initial rate = 0.16(32)	**1**
4(c)(iv)	$(0.0034 = k(0.03)^2(0.02))$ k = **188.9**	**1**
	$mol^{-2}\,dm^6\,s^{-1}$	**1**
4(c)(v)	*k* decreases (as rate decreases)	**1**
4(d)	m = 2 **and** n = 0	**1**

5(a)	change in amount / mass / concentration of reactant / product per time	**1**
5(b)	decrease in volume or pressure	**1**
5(c)	8.13×10^4 / 81280 / 81300	**1**
	$mol^{-2}\ dm^6\ s^{-1}$	**1**
5(d)	$\sqrt{}(0.00231 / (0.0046 \times 81280)) = 2.49 \times 10^{-3}$	**1**
5(e)	2, 1, 3	**1**
5(f)(i)		**1**
5(f)(ii)	the total of steps 1 and 2 / the components of 2 are two NO and one H_2	**1**
5(g)(i)	time for amount or mass or concentration to halve	**1**
5(g)(ii)	0.02 at start and 0.01 after 2 seconds	**1**
	0.005 after 4 seconds and 0.0025 after 6 seconds	**1**
5(h)(i)	$NO + ½\ O_2 \rightarrow NO_2$ **or** $NO + O_2 \rightarrow NO_2 + ½\ O_2$ **AND** $NO_2 + SO_2 \rightarrow NO + SO_3$	**1**
5(h)(ii)	(NO is) regenerated / reformed	**1**
5(h)(iii)	$SO_3 + H_2O \rightarrow H_2SO_4$ **AND** acid rain or consequence of this described	**1**

6(a)	colorimetry / (change) in colour / less light transmission / measure absorbance	**1**
6(b)	Exp 1 and 2: rate × 1.75 and [H_2] × 1.75 (when [IC*l*] no change) **or** calculation e.g.: order = (0.007 / 0.004) / (1.75 / 1.00) = 1 **or** Exp 1 and 3: rate × 2.5 and [H_2] × 2.5 (when [IC*l*] no change) **or** Exp 2 and 3: rate × 10 / 7(1.43) and [H_2] × 10 / 7(1.43) (when [IC*l*] no change)	**1**
6(c)	Exp 4 and 5: rate × 1.4 and [IC*l*] × 1.4 (when [H_2] no change) **or** calculation	**1**
6(d)	(rate=) k[IC*l*][H_2]	**1**
6(e)	62 500 **or** 6.25×10^4	**1**
6(f)	IC*l* + H_2 → HC*l* + HI **or** IC*l* + H_2 → IC*l*H_2 **or** IC*l* + H_2 → ½I_2 + C*l*H_2	**1**
	HI + IC*l* → HC*l* + I_2 **or** IC*l*H_2 + IC*l* → 2HC*l* + I_2 **or** C*l*H_2 + IC*l* → 2HC*l* + ½I_2	**1**

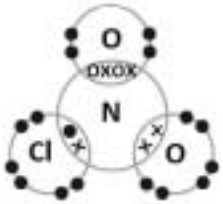
6(g)(i)	part mark 1: plot a graph of concentration of $[H_2]$ against time part mark 2: constant half-life (showing it is 1st order) part mark 3: draw tangent **AND** determine gradient (on conc vs time graph) **or** draw two tangents to determine two gradients (rate) (on conc vs time graph) part mark 4: if conc 1 (at time 1) / conc 2 (at time 2) = gradient 1 / gradient 2 part mark 5: plot a graph of rate against concentration of $[H_2]$ part mark 6: gives a straight-line through the origin of graph for part mark 5 2 parts = 1 mark 3 parts = 2 marks 4 parts = 3 marks	**3**
6(g)(ii)	[IC*l*] doesn't change ***or*** [IC*l*] only changes slightly	**1**
6(h)	provides an alternative route of lower activation energy / E_a **or** to lower E_a and more molecules with $E \geqslant E_a$	**1**

7(a)(i)	**M1**: using expt 2 and 3, $[NH_3] \times 2$, rate $\times$ 4 so order with respect to $[NH_3] = 2$ **M2**: using expt 1 and 2, $[C\mathit{l}O^-] \times 2$ and $[NH_3] \times 2$, as rate $\times$ 8 ($=2^2$ * x) so order with respect to $[C\mathit{l}O^-] = 1$	**2**
7(a)(ii)	rate = $k[NH_3]^2[C\mathit{l}O^-]$	**1**
7(a)(iii)	**M1:** $k = 0.256 / (0.200 \times 0.100^2)$ $k = 128$ **M2:** Units $dm^6\ mol^{-2}\ s^{-1}$	**2**
7(a)(iv)	curve / line showing k increasing as temperature increases	**1**
7(b)(i)	**M1:** plot a graph of $[I^-]$ against time **M2:** constant half-lives	**2**
7(b)(ii)	$C\mathit{l}O^- + I^- \rightarrow IO^- + C\mathit{l}^-$	**1**
7(b)(iii)	step 2 **and** Cl is reduced / oxid no. decreases / oxid no. +1 → –1 ***or*** step 2 **and** I is oxidised / oxid no. increases / oxid no. –1 → +1	**1**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>8(a)</td><td>$_3COCH_3$ = 1
I_2 = 0
H^+ = 1
overall order = 2 M1 3 orders [1] M2 overall order based on their M1 [1]</td><td>2</td></tr>
<tr><td>8(b)(i)</td><td>k = $5.40 \times 10^{-3} / (1.50 \times 10^{-2} \times 7.75 \times 10^{-1})$
k = 0.46(452) [1] $dm^3\ mol^{-1}\ s^{-1}$ [1] 2sf min</td><td>2</td></tr>
<tr><td>8(b)(ii)</td><td><table><tr><td></td><td>decreases</td><td>no change</td><td>increases</td></tr><tr><td>rate constant</td><td>✓</td><td></td><td></td></tr><tr><td>rate of reaction</td><td>✓</td><td></td><td></td></tr></table>both [1]</td><td>1</td></tr>
<tr><td>8(c)</td><td>draw a tangent at time, t=0 [1]

measure the gradient / slope of the tangent [1]</td><td>2</td></tr>
<tr><td>8(d)</td><td>straight line graph starting at 0,0 and showing rate α $[CH_3COCH_3]$ [1]</td><td>1</td></tr>
<tr><td>8(e)(i)</td><td>s step / reaction (in the mechanism) [1]</td><td>1</td></tr>
<tr><td>8(e)(ii)</td><td>$2Ce^{4+} + Tl^+ \rightarrow Tl^{3+} + 2Ce^{3+}$ [1]

catalyst and (used in step 1 and) regenerated / reformed in step 3 / end of the reaction [1]</td><td>2</td></tr>
</table>

Question	Answer	Marks
9(a)	 **M1:** eight electrons around N atom [N=O, N-O, N-C*l* with N-O as dative] **M2:** all other electrons correct	**2**
9(b)(i)	(rate =) k[C*l*NO_2][NO]	**1**
9(b)(ii)	mol^{-1} dm^3 s^{-1}	**1**
9(b)(iii)	Yes **AND** number of moles of reactants in overall equation is the same as order in rate equation	**1**
9(c)(i)	• straight line with a negative gradient • starting at 2.0×10^{-4} • reaches at 1.8×10^{-4} at 0.2 seconds Award 1 mark for two points, award 2 marks for all three points	**2**
9(c)(ii)	2×10^{-5} ($mol\ dm^{-3}$)	**1**
9(c)(iii)	The reaction has reached equilibrium	**1**

Question	Answer	Marks
10(a)	**M1:** the time taken for the amount/concentration or a reactant to halve **M2:** the slowest step	**2**
10(b)	• Use an excess of CH_3Br • (Several experiments with) different initial [OH] • control / equilibrate temperatures • measure time • find $[OH^-]$ by sample and titrate or use of pH probe **or** find $[Br^-]$ by sample and reference to use of Ag^+. • processing of results – plot graph of $[OH^-]$ vs rate or evaluate rate is proportional to $[OH^-]$ numerically Alternative approach: • Use an excess of CH_3Br • One experiment with known initial $[OH^-]$ • control / equilibrate temperatures • measure time • find $[OH^-]$ by sample and titrate or use of pH probe **or** find $[Br^-]$ by sample and reference to use of Ag^+ and describes how to calculate $[OH^-]$. • processing of results – plot graph of $[OH^-]$ vs time and look for constant half-life Award 1 mark for each correctly identified point.	**4**
10(c)	**M1:** rate = k[ester]$[OH^-]$ **M2:** value of k = 0.206 **M3:** units $mol^{-1}dm^3s^{-1}$	**3**

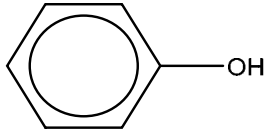
Question	Answer	Marks
11(a)	**M1** data seen H_2O_2/H_2O +1.77V and MnO_2/Mn^{2+} +1.23 V and O_2/H_2O_2 +0.68 V **OR** E_{cell}= 0.55 V (first step) **and** 0.54 V (second step) **M2** $MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + O_2 + 2H_2O$ **M3** $Mn^{2+} + H_2O_2 \rightarrow MnO_2 + 2H^+$	**3**
11(b)	rate = $2.0 \times 10^{-6} \times 0.75$ = **1.5×10^{-6}**	**1**
11(c)(i)	slowest step in overall reaction	**1**
11(c)(ii)	$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ **OR** $H_2O_2 + 2HI \rightarrow I_2 + 2H_2O$	**1**
11(c)(iii)	H_2O_2 = 1 **AND** I^- = 1 **AND** H^+ = 0	**1**

12(g)(i)	**M1** Rate = $k[IO_3^-][SO_3^{2-}][H^+]$ **M2** units = $mol^{-2}dm^6s^{-1}$	**2**
12(g)(ii)	0.10	**1**

Question	Answer	Marks
13(a)	<table><tr><td>the order of reaction with respect to [NO]</td><td>2</td></tr><tr><td>the order of reaction with respect to [O2]</td><td>1</td></tr><tr><td>the overall order of reaction</td><td>3</td></tr></table> **ALL CORRECT** [1]	**1**
13(b)(i)	$k = (1.51 \times 10^{-4}) / (0.003^2 \times 0.00200)$ k = **8389** [1] min 2sf $mol^{-2}\ dm^6\ s^{-1}$ [1]	**2**
13(b)(ii)	$8400 = (6.05 \times 10^{-5}) / (x^2 \times 0.005)$ $x = \sqrt{(6.05 \times 10^{-5}) / (8400 \times 0.005)}$ x = **0.00120 / 1.20** $\times$ **10^{-3}** [1] min 2sf ecf from Q1bi	**1**
13(c)	slow(est) [1]	**1**
13(d)(i)	**correct RDS identified** as step 1 with **only one $S_2O_8^{2-}$** and **one I^-** [1] overall mechanism adds up to chemical equation and no cancellable species on LHS / RHS in each of the equations [1] **M2 DEP** on one $S_2O_8^{2-}$ and one I^- in step 1 e.g. step 1 $S_2O_8^{2-} + I^- \rightarrow SO_4^{2-} + SO_4I^-$ RDS = step 1 step 2 $SO_4I^- + I^- \rightarrow SO_4^{2-} + I_2$	**2**
13(d)(ii)	no. $t$of $_{1/2}$ = 192 / 48 = 4 $[I^-]$ = 0.0078 / 16 = **4.9** $\times$ **10^{-4}** [1] min 2sf	**1**

Question	Answer	Marks
14(a)(i)	so it won't change / so it stays constant [1]	**1**
14(a)(ii)	constant half-life / both half-lives = 45–55 [1] two half-lives taken (evidence needed) [1]	**2**
14(b)(i)	first order [1] any two rows of data quoted, effect of $[H_2]$ specified [1] effect of $[I_2]$ specified and linked to first order [1]	**3**
14(b)(ii)	rate = $k[H_2][I_2]$ [1]	**1**
14(b)(iii)	2×10^{-13} [1] $mol^{-1}\ dm^3\ s^{-1}$ [1]	**2**
14(c)(i)	forward reaction is faster than backward reaction **and** reaches equilibrium on product side / to the right [1]	**1**
14(c)(ii)	forward reaction is negative **AND** backward reaction is positive [1] equilibrium position further left at higher T [1]	**2**

Question	Answer	Marks
15(a)	meas volume / amount of oxygen formed / mass lost / and time / against time / per unit time **OR** measure absorbance / transmission against time / per unit time	**1**
15(b)(i)	time taken for the concentration / mass / amount of a reactant to fall to half (its original value) / to halve	**1**
15(b)(ii)	$t_{1/2}$ = 150 s **AND** evidence on graph / paper of one half-life	**1**
15(b)(iii)	no change	**1**
15(c)(i)	**M1:** evidence on graph of tangent **AND** 4 to 5 $\times$ 10^{-4} **M2:** mol dm^{-3} s^{-1}	**2**
15(c)(ii)	**(c)(i)** / 0.10 **AND** s^{-1}	**1**
15(d)	**M1:** $NO_2 + O_3 \rightarrow NO_3 + O_2$ **M2:** $NO_2 + NO_3 \rightarrow N_2O_5$	**2**

16(a)(i)	the power to which a concentration of a reactant is raised in the rate equation / law	**1**
16(a)(ii)	**M1:** (using expt 1 and 3) as $[ClO_2] \times 2.5$ rate $\times 6.25$ so 2nd order **M2:** (using expt 1 and 2) as $[OH^-] \times 4$ rate $\times 4$ so 1st order	**2**
16(a)(iii)	rate = $k[ClO_2]^2[OH^-]$	**1**
16(a)(iv)	**M1:** k = rate / $[ClO_2]^2[OH^-]$ $k = 7.20 \times 10^{-4} / (0.02)^2(0.03)$ $k = 60$ **M2:** $mol^{-2}\ dm^6\ min^{-1}$	**2**
16(b)(i)	structure of phenol: C_6H_5OH **OR** 	**1**
16(b)(ii)	tangent drawn correctly **AND** rate = $0.015 / 260 = 5.8 \times 10^{-5}$ **ALLOW** values consistent with tangent drawn at 100 sec	**1**
16(c)	 **AND** half-life decreases (1st box)	**1**

Paper 4
Topic 5
Entropy And Gibbs Free Energy

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^{\ominus} = +241\,kJ\,mol^{-1}$$

.....

..... [1]

The free energy change, $\Delta G^{\ominus}$, for this reaction at 1000 K is +51 kJ mol^{-1}.

(ii) Calculate the value of $\Delta S^{\ominus}$ for this reaction, stating its units.

$\Delta S^{\ominus}$ = ... units ..... [2]

(d) How would the value of $\Delta G^{\ominus}$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

.....

.....

..... [2]

[Total: 10]

$Cd^{2+}(aq) + 4CH_3NH_2(aq) \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}(aq)$ $K_{stab} = 3.6 \times 10^6$ equilibrium **I**

$Cd^{2+}(aq) + 2H_2NCH_2CH_2NH_2(aq) \rightleftharpoons [Cd(H_2NCH_2CH_2NH_2)_2]^{2+}(aq)$ $K_{stab} = 4.2 \times 10^{10}$ equilibrium **II**

(a) (i) Write an expression for the stability constant, K_{stab}, for equilibrium **I**, and state its units.

K_{stab} =

units .....
[2]

Cadmium ions are poisonous and need to be removed from some water supplies. This is often done by adding a complexing agent.

(ii) In a sample of ground water the concentration of $Cd^{2+}(aq)$ is 1.00×10^{-4} mol dm^{-3}.

Calculate the concentration of $CH_3NH_2(aq)$ needed to reduce the concentration of $Cd^{2+}(aq)$ in this dilute solution by a factor of one thousand.

concentration of $CH_3NH_2(aq)$ = ... mol dm^{-3} [2]

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}
I	–57.3	–37.4	–66.8
II	–56.5	–60.7	to be calculated

(i) Suggest a reason why the $\Delta H^{\ominus}$ values for the two equilibria are very similar.

.....

..... [1]

(ii) Calculate $\Delta S^{\ominus}$ for equilibrium **II**.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} [1]

(iii) Suggest a reason for the difference between the $\Delta S^{\ominus}$ you have calculated for equilibrium **II** and that for equilibrium **I** given in the table.

.....

.....

..... [1]

(iv) Which of the two complexes is the more stable? Give a reason for your answer.

.....

..... [1]

[Total: 8]

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

(a) State and explain whether the following processes will lead to an increase or decrease in entropy.

(i) the reaction of magnesium with hydrochloric acid

entropy change .....

explanation .....

[1]

(ii) solid potassium chloride dissolving in water

entropy change .....

explanation .....

[1]

(iii) steam condensing to water

entropy change .....

explanation .....

[1]

(b) Magnesium carbonate can be decomposed.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +117\,kJ\,mol^{-1}$$

Standard entropies are shown in the table.

substance	$MgCO_3(s)$	$MgO(s)$	$CO_2(g)$
$S^{\ominus}$ / J mol^{-1} K^{-1}	+65.7	+26.9	+214

(i) Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [3]

(ii) Explain, with reference to $\Delta G^{\ominus}$, why this reaction becomes more feasible at higher temperatures.

.....

..... [1]

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \quad \Delta H^{\ominus} = +130\,kJ\,mol^{-1}$$
$$\Delta S^{\ominus} = +316\,J\,mol^{-1}\,K^{-1}$$

Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible). Show your working.

temperature = ... K [2]

(d) The solubility of Group 2 sulfates decreases down the Group.

Explain this trend.

.....

.....

.....

..... [2]

[Total: 11]

4 Silicon tetrachloride, $SiCl_4$, is formed when silicon reacts with chlorine under suitable conditions. It is a colourless liquid with a low boiling point.

(a) Explain why $SiCl_4$ has a low boiling point.

.....

.....

..... [2]

(b) $SiCl_4$ reacts with water to produce an acidic solution.

(i) Write an equation for this reaction.

..... [1]

(ii) Describe **two** visual observations when silicon tetrachloride is added drop by drop to a small amount of water.

1 .....

2 .....
[2]

(iii) A sample of 0.8505 g of $SiCl_4$ is added to 800 cm^3 of water. All of the soluble acidic product is dissolved in the water.

Calculate the pH of the solution obtained.

pH = ... [3]

reaction 1 $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$ $\Delta S^{\ominus} = -225.7\,J\,K^{-1}\,mol^{-1}$

standard entropy of silicon, $S^{\ominus}$ Si(s)	$18.7\,J\,K^{-1}\,mol^{-1}$
standard entropy of silicon tetrachloride, $S^{\ominus}$ $SiCl_4$ (l)	$239.0\,J\,K^{-1}\,mol^{-1}$

Calculate the standard entropy of chlorine, $S^{\ominus}$ Cl_2(g). Show all your working.

$S^{\ominus}$ Cl_2(g) = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) Explain why the entropy change for reaction 1 is negative.

.....

..... [1]

(d) The standard enthalpy change of formation of silicon tetrachloride, $\Delta H_f^{\ominus}$ $SiCl_4$(l), is $-640\,kJ\,mol^{-1}$.

Reaction 1 is spontaneous at lower temperatures, but it is not spontaneous at very high temperatures.

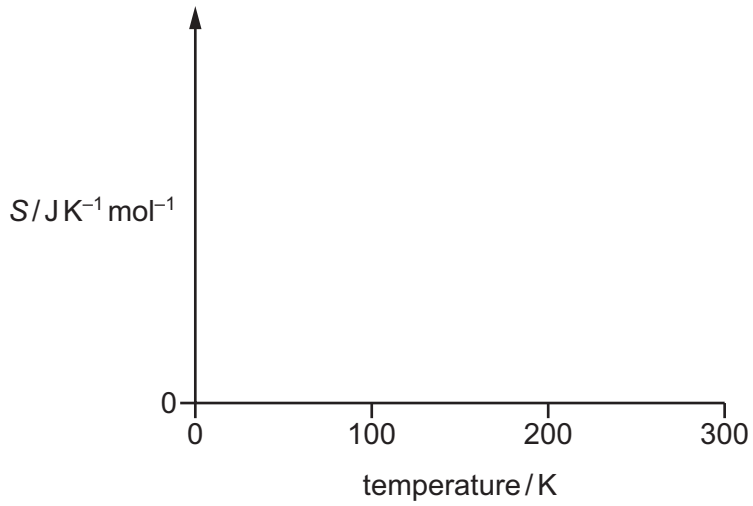
Calculate the temperature above which reaction 1 is **not** spontaneous.

temperature = ... K [2]

[Total: 13]

(a) Assume the entropy, *S*, for H_2O is zero at 0 K.

Sketch a graph on the axes to show how the entropy changes for H_2O between 0 K and 300 K.



[2]

(b) Place **one tick** (✓) in **each row** of the table to show the sign of the entropy changes, ΔS.

	ΔS is negative	ΔS is positive
solid dissolving in water		
water boiling to steam		

[1]

(c) The equation for a reaction that produces methanol is shown.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$$

Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH, for this gas phase reaction.

ΔH = ... kJ mol^{-1} [2]

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \qquad \Delta H^{\ominus} = -131\,kJ\,mol^{-1}$$

Standard entropies are shown in the table.

substance	$CO_2(g)$	$H_2(g)$	$CH_3OH(l)$	$H_2O(l)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+214	+131	+127	+70

(i) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

$\Delta S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

.....

..... [1]

	$\Delta H_f^\ominus$ / kJ mol^{-1}	$S^\ominus$ / J K^{-1} mol^{-1}
$NH_2Cl(g)$	+80.1	+241
$NH_3(g)$	–45.9	+198
$N_2H_4(g)$	+95.4	+237
$HCl(g)$	–92.3	+187

(i) Define the meaning of the term *entropy*.

.....

..... [1]

Hydrazine, N_2H_4, can be produced from chloramine and ammonia as shown.

$$NH_2Cl(g) + NH_3(g) \rightarrow N_2H_4(g) + HCl(g)$$

(ii) Calculate the standard entropy change, $\Delta S^\ominus$, for this reaction.

$\Delta S^\ominus$ = ... J K^{-1} mol^{-1} [1]

(iii) Calculate the standard enthalpy change, $\Delta H^\ominus$, for this reaction.

$\Delta H^\ominus$ = ... kJ mol^{-1} [1]

(iv) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for this reaction at 298 K.

$\Delta G^\ominus$ = ... kJ mol^{-1} [2]

(v) Explain, with reference to $\Delta G^\ominus$, why this reaction becomes **less** feasible at higher temperatures.

.....

.....

.....

..... [1]

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is ..... because .....

.....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is ..... because .....

.....

- the change corresponding to the lattice energy of calcium chloride, ΔH_{latt} $CaCl_2(s)$, takes place

The entropy change is ..... because .....

.....
[3]

(c) The reaction $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$ is not spontaneous at room temperature.

(i) Give the full name for the term $\Delta G^{\ominus}$.

..... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation .....

.....

.....

.....
[2]

[Total: 7]

substance	standard entropy, $S^\ominus$ / J K^{-1} mol^{-1}
PbO_2(s)	77
PbO(s)	69
O_2(g)	205

Lead(IV) oxide, PbO_2, decomposes to lead(II) oxide, PbO, and oxygen when heated.

$$2PbO_2(s) \rightarrow 2PbO(s) + O_2(g) \qquad \Delta H^\ominus = +118\,kJ\,mol^{-1}$$

(a) Use the data to calculate the value of $\Delta S^\ominus$ for this reaction.

$\Delta S^\ominus$ = ... J K^{-1} mol^{-1} [2]

(b) Use the value of $\Delta H^\ominus$ and your answer to **(a)** to calculate the temperature at which this reaction becomes feasible.

T = ... K [3]

(c) Solid lead(II) oxide can be made by heating lead metal in air.

Predict the **sign** of the standard entropy change of this reaction. Explain your answer.

.....

..... [1]

[Total: 6]

$$AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq) \qquad \Delta H^{\ominus}_{sol} = +65.5\,kJ\,mol^{-1}$$

Standard entropies are shown in the table.

species	$AgCl(s)$	$Ag^+(aq)$	$Cl^-(aq)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+96.2	+72.7	+56.5

(i) Calculate the standard entropy change of solution, $\Delta S^{\ominus}$.

$\Delta S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ [1]

(ii) Explain, with the aid of a calculation, why $AgCl$ is insoluble in water at 25 °C.

You should use data from this question and your answer to **(b)(i)**.

.....

..... [3]

[Total: 10]

10 $EDTA^{4-}$, is a polydentate ligand.

(a) (i) Explain what is meant by the term *polydentate ligand*.

.....

.....

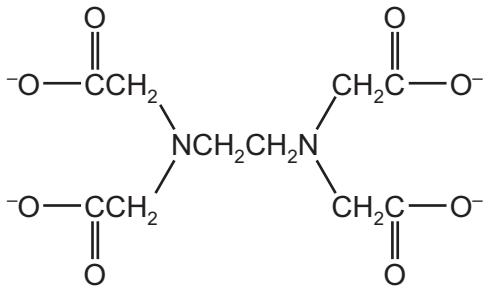
..... [2]

(ii) When a solution containing $EDTA^{4-}$ is added to a solution containing $[Cd(H_2O)_6]^{2+}$ a new complex is formed, $[CdEDTA]^{2-}$.

equilibrium **1** $[Cd(H_2O)_6]^{2+} + EDTA^{4-} \rightleftharpoons [CdEDTA]^{2-} + 6H_2O$

Circle, on the structure of $EDTA^{4-}$, the **six** atoms that form bonds with the metal ion.

$EDTA^{4-}$



[1]

(iii) Write an expression for the stability constant, K_{stab1}, for equilibrium **1**, and state its units.

K_{stab1} =

units = ...
[2]

equilibrium **2** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ $K_{stab2} = 3.60 \times 10^6$

equilibrium **3** $[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4H_2O$ $K_{stab3} = 4.20 \times 10^{10}$

An equilibrium is set up between these two complexes as shown in equilibrium **4**.

equilibrium **4** $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 2en \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+} + 4CH_3NH_2$ $\Delta H^\ominus = +0.840\,kJ\,mol^{-1}$ $\Delta S^\ominus = +80.9\,J\,K^{-1}\,mol^{-1}$

(i) K_{eq4} is the equilibrium constant for equilibrium **4**.

Write an expression for K_{eq4} in terms of K_{stab2} and K_{stab3}.

K_{eq4} =

[1]

(ii) Calculate the value of the standard Gibbs free energy change, $\Delta G^\ominus$, for equilibrium **4** at 298 K.

$\Delta G^\ominus$ = ... $kJ\,mol^{-1}$ [2]

(iii) State how the value of $\Delta G^\ominus$ changes as the temperature increases. Explain your answer.

.....

.....

..... [1]

[Total: 9]

.....

..... [1]

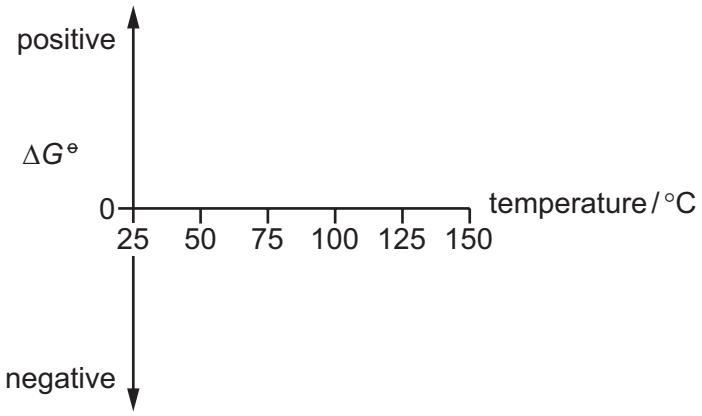
(ii) Place one tick (✓) in each row of the table to show the sign of each entropy change, ΔS.

process	ΔS is negative	ΔS is zero	ΔS is positive
NaCl dissolving in water			
water solidifying to ice			

[1]

(iii) The evaporation of one mole of water has a standard Gibbs free energy change, $\Delta G^{\ominus}$, of +8.6 kJ at 25 °C.

Sketch a graph on the axes to show how $\Delta G^{\ominus}$ changes for this process between 25 °C and 150 °C at 101 kPa.



[2]

(d) The reaction between A and B is feasible at low temperatures but is **not** feasible at high temperatures.

$$A + B \rightleftharpoons C + D$$

Deduce the signs of ΔH and ΔS for this reaction and explain why the feasibility changes with temperature.

sign of ΔH = ... sign of ΔS = ...

.....

.....

.....

..... [2]

[Total: 15]

species	$S^{\ominus}$ / J K^{-1} mol^{-1}
$H_2O(l)$	+70
$H_2(g)$	+131
$O_2(g)$	+205

(i) Calculate $\Delta S^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} [1]

(ii) $\Delta H^{\ominus}$ for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ is +572 kJ mol^{-1}.

Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [2]

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction.
Explain your answer.

.....

..... [1]

[Total: 9]

species	$S^{\ominus}$ / J K^{-1} mol^{-1}
HCl(g)	+187
H_2(g)	+131
Cl_2(g)	+223

(i) Calculate $\Delta S^{\ominus}$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$.

$\Delta S^{\ominus}$ = ... J K^{-1} mol^{-1} [1]

(ii) $\Delta H^{\ominus}$ for the reaction $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$ is +185 kJ mol^{-1}.

Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [2]

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction. Explain your answer.

.....

..... [1]

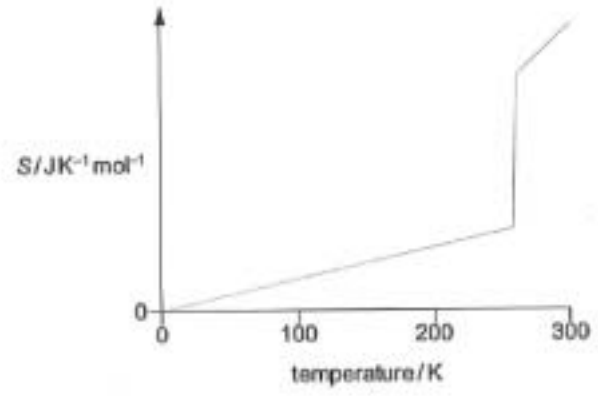
[Total: 9]

1 (c) (i)	$\Delta S^{\ominus}$ will be positive, because more gas moles on the RHS / products	[1]
(ii)	$\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus}) / T = (241 - 51)/1000 = 0.19$ OR 190 $kJ\,mol^{-1}K^{-1}$ OR $J\,mol^{-1}K^{-1}$	[1] [1]
(d)	$\Delta G^{\ominus}$ will become less positive/more negative as T increases, …because $\Delta S^{\ominus}$ is positive (*or* $-T\Delta S^{\ominus}$ is more negative) …therefore the reaction becomes more feasible / spontaneous as T increases	[2]

Question	Answer	Marks
2 (a) (i)	$K_{stab} = \frac{[Cd(CH_3NH_2)_4^{2+}]}{[Cd^{2+}]\,[CH_3NH_2]^4}$ units: $mol^{-4}\,dm^{12}$	2
(ii)	$Cd^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4]^{2+}$ at start: 1×1^{-4} **0** at eqm: 1×10^{-7} **y** **$1 \times 10^{-4} - 1 \times 10^{-7}$** **or 9.99×10^{-5} or 1.0×10^{-4}** $9.99 \times 10^{-5} / (y^4 \times 10^{-7}) = 3.6 \times 10^6$ and y = $\sqrt[4]{(9.99 \times 10^{-5}) / (1 \times 10^{-7} \times 3.6 \times 10^6)}$ = **0.129 / 0.13**	2
(b) (i)	(each complex is formed by) making (4 ×)N-Cd bonds and breaking (6 ×) O-Cd bonds ***or*** same types of / similar bonds forming / breaking ***or*** same number of bonds forming / breaking	1
(ii)	$\Delta S = (\Delta H - \Delta G) / T = (60.7 - 56.5) \times 1000 / 298$ = (+)**14** / (+)**14.1**	1
(iii)	fewer moles (of solutes) are forming (one mole of) the complex (so less loss of disorder) ***or*** one *en* displaces two H_2O whereas one CH_3NH_2 only displaces one H_2O	1
(iv)	The $[Cd(H_2NCH_2CH_2NH_2)_2]^{2+}$ / equilibrium 2 complex (is more stable) because: *either* K_{stab} is greater or $\Delta G^{\ominus}$ is more negative.	1
		[Total: 8]

3(a)(i)	(entropy) increases / is positive **and** H_2 / gas is formed	1 **1**
3(a)(ii)	(entropy) increases / is positive **and** (KCl (aq)) solution has (free) moving / mobile ions / aqueous ions	1 **1**
3(a)(iii)	(entropy) decreases / is negative **and** decrease in **gas**	1 **1**
3(b)(i)	$\Delta S^{\ominus} = 26.9 + 214 - 65.7 = (+)\,175.2$ (J K^{-1} mol^{-1}) $\Delta G^{\ominus} = 117 - (298 \times 175.2 / 1000)$ **OR** $\Delta G^{\ominus} = 117\,000 - (298 \times 175.2)$ $\Delta G^{\ominus} = +64.8$ (kJ mol^{-1})	1 1 1 **3**
3(b)(ii)	TΔS is more positive than ΔH / TΔS increases / –TΔS more negative **and** ΔG is negative / decrease / less positive	1 **1**
3(c)	use of $\Delta G = 0$ or $\frac{T\Delta S}{\Delta H} = 1$ T = 130 / (316 / 1000) = **410 / 411 / 412 / 411.4** (K)	1 1 **2**
3(d)	hydration enthalpy and lattice energy **both** more endothermic / more positive / less exothermic / less negative (down the group) ΔH_{hyd} decreases more / faster **and** ΔH_{sol} becomes (more) endothermic / (more) positive / less exothermic / less negative	1 1 **2**
		Total: 11

4(a)	sim molecular / simple covalent	**1**
	weak London forces / id-id forces / VDW forces ***or*** London forces / id-id forces / VDW forces **AND** small amount of energy to break	**1**
4(b)(i)	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ or $SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$	**1**
4(b)(ii)	white solid	**1**
	steamy fumes / white fumes / misty fumes	**1**
4(b)(iii)	moles of $SiCl_4$ = 0.8505 / 170.1 = 0.005	**1**
	conc of H^+ (0.005) $\times$ 4 / 0.8 = 0.025	**1**
	pH = –log(0.025) = 1.6	**1**
4(c)(i)	–225.7 = 239.0 – (18.7 + 2x)	**1**
	x = +223	**1**
4(c)(ii)	decrease in number of **moles** of **gas** /more **moles** of **gas** on left / reactants (ora)	**1**
4(d)	use of $\Delta G = \Delta H - T\Delta S$ with $\Delta G = 0$ / $\Delta G > 0$ **or** T = $\Delta H / \Delta S$ or T = (640 000 / 225.7)	**1**
	2836 / 2840 (2835.6)	**1**



M1 continuous increase in *S* from 0–300 K (excluding m.p.) [1]
M2 steep vertical increase in *S* **ONLY** at the m.p. **AND** continuous increase in *S* after m.p. [1]

5(b) [1] for each correct tick

	negative $\Delta S^{\ominus}$	positive $\Delta S^{\ominus}$
solid dissolving in water		✓
water boiling to steam		✓

1

5(c) $\Delta H^{\ominus}$ = (2 × C=O) + (3 × H-H) – (3 × C-H) – (C-O) – (3xO-H)
$\Delta H^{\ominus}$ = (2 × 805) + (3 × 436) – (3 × 410)– (1 × 360) – (3 × 460) [1]
$\Delta H^{\ominus}$ = 1610 + 1308 – 1230 – 360 – 1380 = **– 52** (kJ mol^{-1}) [1] ecf correct answer scores [2]

2

5(d)(i) $\Delta S^{\ominus}$ = 127 + 70 – (214 + 3 × 131) [1]
= – 410 (J K^{-1} mol^{-1}) [1] ecf correct answer scores [2]

2

5(d)(ii) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ [1]
$\Delta G^{\ominus}$ = –131 – (298 × –0.41) = **– 8.8(2)** (kJ mol^{-1}) [1] correct answer scores [2]

2

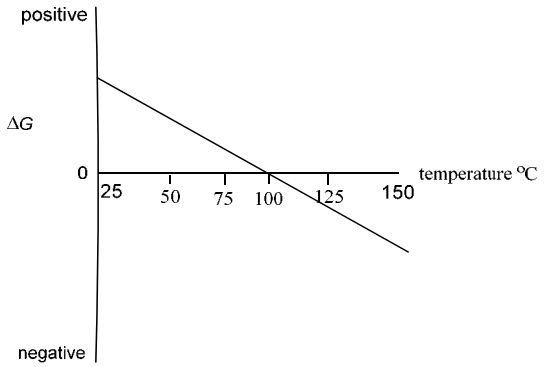
6(c)(i)	(entropy) is a measure of the disorder/randomness of a system	**1**
6(c)(ii)	ΔS^{o-} = 237 + 187 – (241 + 198) = –15.0 (J K^{-1} mol^{-1})	**1**
6(c)(iii)	ΔH^{o-} = 95.4–92.3 – (80.1–45.9) = –31.1 (kJ mol^{-1})	**1**
6(c)(iv)	$\Delta G^{o-} = \Delta H^{o-} - T\Delta S^{o-}$ [1] ΔG^{o} = -31.1 – (298 × -0.015) = –26.6 (kJ mol^{-1}) [1]	**2**
6(c)(v)	(at higher temperatures) $T\Delta S^{o-}$ becomes more negative so ΔG^{o-} becomes more positive **OR** (at high temperatures) $-T\Delta S^{o}$ is becomes more positive so ΔG^{o} becomes more positive	**1**

Question	Answer	Marks
7(a)	**measure / degree** of **disorder / randomness** of a system	**1**
7(b)	**M1:** negative – molecules have less energy in the system **M2:** positive – solid being converted into an aqueous solution **M3:** negative – gaseous ions being converted into a solid	**3**
7(c)(i)	(standard) Gibbs free energy change	**1**
7(c)(ii)	**M1:** $(\Delta)G = \Delta H - T\Delta S$ **M2:** description of calculating the minimum value of T for which ΔG is zero / becomes negative **OR** $T = \Delta H / \Delta S$ [1]	**2**

Question	Answer	Marks
8(a)	**M1:** correct use of stoichiometry **M2:** answer + 189	**2**
8(b)	**M1:** States or uses correct form of Gibbs equation $\Delta G = \Delta H - T\Delta S$ **M2:** appreciates / includes $\Delta G = 0$ at temperature required **M3:** uses 1000 correctly and answer +624(.339) Award 3 marks for correct answer	**3**
8(c)	negat **and** decrease in number / amount of gas molecules	**1**

9(b)(i)	$\Delta S^{\ominus}$ = 72.7 + 56.5 -96.2 = +**33.0** J K^{-1} mol^{-1}	**1**
9(b)(ii)	**M1** $\Delta G = \Delta H^{\ominus} - T\Delta S^{\ominus}$ **M2** ΔG = (65.5)- (298x0.033) = +**55.7** kJ mol^{-1} min 3sf **M3** ΔG = positive so not feasible/spontaneous	**3**

Question	Answer	Marks
10(a)(i)	**M1** (a species) that donates/uses a many lone pairs/more than one lone pair **M2** to form a dative/coordinate to a metal atom/metal ion/TM/TE/metal **OR** **M1** (a species) that donates/uses lone pairs to form many/more than one **M2** dative/coordinate bond to a metal atom/metal ion/TM/TE/metal	**2**
10(a)(ii)	structure of EDTA any **six** atoms circled of 2 N & 4 O	**1**
10(a)(iii)	**M1** $K_{stab1} = \dfrac{[[CdEDTA]^{2-}]}{[[Cd(H_2O)_6]^{2+}][EDTA^{4-}]}$ **M2** units = $mol^{-1}\ dm^3$	**2**
10(b)(i)	$K_{eq4} = K_{stab3}/K_{stab2}$	**1**
10(b)(ii)	**M1** $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ $\Delta G^{\ominus} = 0.84 - (298*0.0809)$ **M2** $\Delta G^{\ominus}$ = **-23.3** ($kJ\ mol^{-1}$) **3sf min**	**2**
10(b)(iii)	more negative as $T\Delta S$ increases **OR** more negative as ΔS is positive	**1**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>11(c)(i)</td><td>measure / degree of (dis)order / randomness (of a system)
OR the number of possible arrangements of the particles and their energy (in a given system)</td><td>1</td></tr>
<tr><td>11(c)(ii)</td><td><table>
<tr><td></td><td>ΔS is negative</td><td>ΔS is zero</td><td>ΔS is positive</td></tr>
<tr><td>solid dissolving in water</td><td></td><td></td><td>✓</td></tr>
<tr><td>water solidifying to ice</td><td>✓</td><td></td><td></td></tr>
</table></td><td>1</td></tr>
<tr><td>11(c)(iii)</td><td> 

two correct for 1 mark, three correct for two marks:
• starting at +8.6 kJ / in positive region close to the y-axis
• line passes through x-axis around 100°C
• negative gradient straight / curve line through the x-axis (no clear positive inflexions)</td><td>2</td></tr>
<tr><td>11(d)</td><td>M1: ΔH negative / – , ΔS negative / –

M2: as temperature increase, ΔG becomes (more) positive / less negative ora
OR at low(er) T, (ΔH more negative than TΔS) so ΔG is negative
OR at high(er) T, (ΔH less negative than TΔS) so ΔG is positive</td><td>2</td></tr>
</table>

12(e)(i)	ΔS = 262 + 205 – 140 = (+) **327** (J K^{-1} mol^{-1}) [1]	**1**
12(e)(ii)	ΔG = ΔH – TΔS **OR** use of Gibbs equation [1] ΔG = 572 – (298 × 0.327) = (+)**474.6** (kJ mol^{-1}) [1] min 3sf ecf 1e(i)	**2**
12(e)(iii)	becomes more feasible / spontaneous as TΔS is more positive / –TΔS becomes more negative • ✓	**1**

13(e)(i)	–20 [1]	**1**
13(e)(ii)	states / uses correct Gibbs equation [1] answer = 190 / 191 / 190.0 [1]	**2**
13(e)(iii)	Becomes less feasible / less spontaneous / **AND** because ΔS is negative / TΔS becomes more negative / –TΔS becomes more positive [1]	**1**

Paper 4
Topic 6
Transition Elements

(a) What is meant by the term *transition element*?

.....

..... [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(ii) Which of the following species can act as a ligand?
Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$H_2NCH_2CH_2NH_2$		
NH_4^+		

[2]

(c) Manganese ions, $Mn^{2+}(aq)$, show some similar chemical properties to those of copper(II) ions, $Cu^{2+}(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the manganese species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of manganese species formed	type of reaction
$Mn^{2+}(aq)$ + NaOH(aq)		
$Mn^{2+}(aq)$ + concentrated HCl		
$Mn^{2+}(aq)$ + $H_2O_2(aq)$		

[5]

Complete the electronic structures for

a cobalt atom, $1s^2 2s^2 2p^6$.....

cobalt in the +3 oxidation state. $1s^2 2s^2 2p^6$.....

[2]

(b) (i) In an aqueous solution of cobalt(II) sulfate the cobalt forms complex ions.

What is meant by the term *complex ion*?

.....

..... [1]

(ii) State **two** chemical properties of cobalt, other than the formation of complexes, that are **not** shown by a typical s-block element.

.....

..... [2]

(c) Cobalt(II) ions, $Co^{2+}(aq)$, show some chemical properties similar to those of copper(II) ions, $Cu^{2+}(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the cobalt species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of cobalt species formed	type of reaction
$Co^{2+}(aq)$ + an excess of $NH_3(aq)$		
$Co^{2+}(aq) + OH^-(aq)$		
$Co^{2+}(aq) + S_2O_8^{2-}(aq)$		

[5]

Compound **Q** is a superconductor and contains 13.4% yttrium, 41.2% barium, 28.6% copper and 16.8% oxygen by mass.

(i) Show that the empirical formula of **Q** is $YBa_2Cu_3O_7$. Show all your working.

[1]

(ii) The table shows the oxidation numbers of yttrium, barium and oxygen in **Q**.

element	oxidation number
yttrium	+3
barium	+2
oxygen	–2

Calculate the **average** oxidation number of copper in **Q**.

[1]

(iii) Hence deduce the oxidation number of **each** of the **three** copper atoms in **Q**.

[1]

[Total: 13]

- the cobalt atom, Co $1s^2 2s^2 2p^6$ .....
- the cobalt(II) ion, Co^{2+} $1s^2 2s^2 2p^6$ .....

[1]

(ii) State the colours you would observe when concentrated HCl(aq) is added to an aqueous solution of cobalt(II) nitrate, $Co(NO_3)_2$.
Give the formulae and geometry of the complexes formed.

.....

.....

.....

.....

..... [5]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.

$Ni(R_3P)_2I_2$

$Ni(R_3P)_2I_2$

$Co(R_3P)_2I_2$

[3]

[Total: 9]

(i) Suggest the *type of isomerism* shown by these complex ions.

..... [1]

(ii) Explain why these two complex ions

- are coloured, ...

.....

.....

.....

- have **different** colours. .....

.....

.....

.....
[4]

(i) Draw diagrams to show the three-dimensional structures of the two isomers.

isomer 1

isomer 2

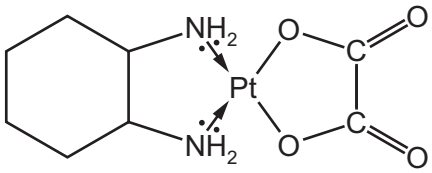
[2]

(ii) Comment on the polarity of the two isomers of $Pt(NH_3)_2Cl_2$. Explain your answer.

.....

..... [1]

Oxaloplatin is another successful anti-cancer drug in which the stereochemistry around the platinum atom is the same as that in $Pt(NH_3)_2Cl_2$.



oxaloplatin

(iii) Explain why there are no isomers of oxaloplatin.

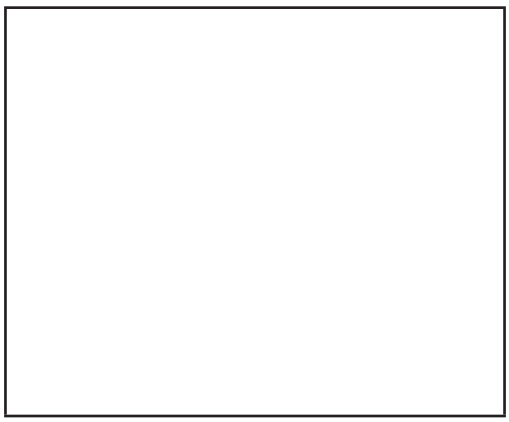
.....

..... [1]

(i) What does this indicate about the stereochemistry around the nickel atom?

..... [1]

(ii) Draw a three-dimensional diagram showing the structure of this complex.



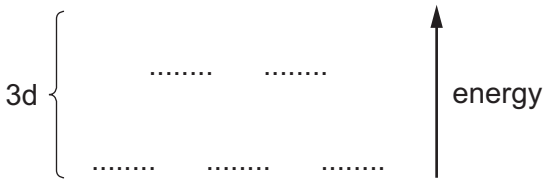
[1]

[Total: 6]

Fe $1s^2 2s^2 2p^6$..... [1]

(ii) In some of its complexes, the Fe^{3+} ion has **only one** unpaired electron in its d orbitals.

Using the symbols ↑ and ↓ to represent electrons of opposite spins, complete the following diagram to show the d orbital electronic configuration of **this** Fe^{3+} ion.



[1]

(b) A solution containing a mixture of $Sn^{2+}(aq)$ and $Sn^{4+}(aq)$ is added to a solution containing a mixture of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$.

Use $E^{\ominus}$ data from the *Data Booklet* to predict the reaction that might take place when the two solutions are mixed, and write an equation for the reaction.

.....

.....

..... [2]

$[Fe(H_2O)_6]^{3+}$ + F^- ⇌ $[Fe(H_2O)_5F]^{2+}$ + H_2O equilibrium **1** $K_{stab} = 2.0 \times 10^5\,mol^{-1}\,dm^3$
violet colourless

$[Fe(H_2O)_6]^{3+}$ + SCN^- ⇌ $[Fe(H_2O)_5SCN]^{2+}$ + H_2O equilibrium **2** $K_{stab} = 1.0 \times 10^3\,mol^{-1}\,dm^3$
violet deep-red

(i) Predict and explain the **sequence** of colour changes you would observe in each of the following experiments.

- A few drops of KSCN(aq) are added to 5 cm^3 of Fe^{3+}(aq), followed by a few drops of KF(aq).

.....

.....

.....

- A few drops of KF(aq) are added to 5 cm^3 of Fe^{3+}(aq), followed by a few drops of KSCN(aq).

.....

.....

.....

[4]

(ii) What *type of reaction* is occurring during the experiments in **(i)**?

..... [1]

[Total: 9]

P41/O/N/16/Q1

7 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar] .....
- copper ion in the +2 oxidation state [Ar] .....

[2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

(i) Name the *type of reaction* occurring here.

..... [1]

(ii) State the colours of these two complex ions.

$[Cu(H_2O)_6]^{2+}$ ..... $[CuCl_4]^{2-}$ ..... [1]

(iii) State the shape of the $[CuCl_4]^{2-}$ ion.

..... [1]

(iv) Write the expression for the stability constant, K_{stab}, for this equilibrium.

K_{stab} =

[1]

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \quad \text{equilibrium 1}$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O \quad \text{equilibrium 2}$$

(i) What is meant by the term *bidentate ligand*?

.....

..... [2]

	stability constant, K_{stab}
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.94×10^7
$[Cu(en)(H_2O)_4]^{2+}$	3.98×10^{10}

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

.....

..... [1]

(d) Nickel forms the complex ion $[Ni(en)_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

(i) Name the type of stereoisomerism displayed by $[Ni(en)_3]^{2+}$.

..... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[Ni(en)_3]^{2+}$.

[3]

(e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

(i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

.....

..... [2]

(ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

(ii) Name the *type of reaction* occurring during this polymerisation.

..... [1]

(iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

..... [1]

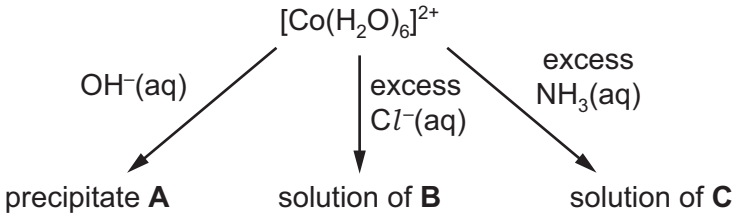
[Total: 20]

Explain what is meant by the term *transition element*.

.....

..... [1]

(b) The following scheme shows some reactions of $[Co(H_2O)_6]^{2+}$.



(i) State the formula of each of the following.

A .....

B .....

C .....

[2]

(ii) State the colour of the following solutions.

$[Co(H_2O)_6]^{2+}$ .....

solution of **B** .....

solution of **C** .....

[2]

(c) Define the term *standard electrode potential*.

.....

.....

..... [2]

(i) Complete the table with the substance used to make the electrode in each of these half-cells.

half-cell	electrode
Co^{2+}/Co	
Fe^{3+}/Fe^{2+}	

[1]

(ii) Write the equation for the overall cell reaction.

..... [1]

(iii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(e) The electrochemical cell in **(d)** was set up again but this time the concentration of $Co^{2+}(aq)$ was $0.050\,mol\,dm^{-3}$.

The Nernst equation can be used to calculate the value of an electrode potential at different concentrations.

$$E = E^{\ominus} + (0.059/z)\log[Co^{2+}(aq)] \qquad \text{Nernst equation}$$

(i) Use the *Data Booklet* and the Nernst equation to calculate the value of E for the Co^{2+}/Co half-cell in this experiment.

E for Co^{2+}/Co = ... V [1]

(ii) Suggest how this change will affect the overall cell potential, E_{cell}, compared to $E^{\ominus}_{cell}$ in **(d)(iii)**.
Circle your answer.

less positive no change more positive

[1]

(f) Iron(III) ions can oxidise vanadium metal.

Construct an equation for the reaction of an excess of iron(III) ions with vanadium metal.
Use of the *Data Booklet* will be helpful.

..... [2]

[Total: 14]

(i) State what is meant by the terms

monodentate, ...

.....

ligand. .....

.....
[2]

Silver ions, Ag^+, react with cyanate ions to form a linear complex.

(ii) Suggest the formula of this complex, including its charge.

..... [2]

(e) When heated with HC*l*(aq), organic isocyanates, RNCO, are hydrolysed to the amine salt, RNH_3Cl, and CO_2.

$$RNCO + H_2O + HCl \rightarrow RNH_3Cl + CO_2$$

A 1.00 g sample of an organic isocyanate, RNCO, was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous $Ba(OH)_2$ according to the equation shown. The solid $BaCO_3$ precipitated weighed 1.66 g.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$$

(i) Calculate the number of moles of $BaCO_3$ produced.

moles of $BaCO_3$ = ... [1]

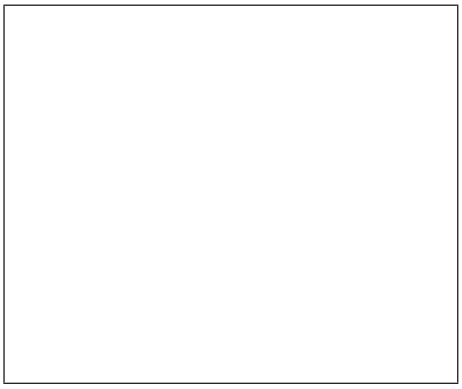
(ii) Hence calculate the M_r of the organic isocyanate RNCO.

M_r of RNCO = ... [1]

(iii) Use your M_r value calculated in **(ii)** to suggest the molecular formula of the organic isocyanate RNCO.

molecular formula of RNCO ..... [1]

(iv) Suggest a possible structure of the amine RNH_2, which forms the amine salt, RNH_3Cl.



[1]

(a) (i) Determine the oxidation state of the cobalt in these complex ions.

..... [1]

(ii) Name the **two** types of reaction undergone by the cobalt ions during the formation of these complex ions.

.....

..... [2]

(iii) The complex $[Co(NH_3)_4Cl_2]^+$ shows isomerism.

Draw three-dimensional structures of the two isomers, and suggest the type of isomerism shown here.

isomer 1

isomer 2

type of isomerism .....
[3]

(b) (i) What is meant by the term *co-ordination number*?

.....

..... [1]

complex	metal ion	ligand	co-ordination number	formula of complex	charge on complex
C	Cr^{3+}	CN^-			3–
D	Ni^{2+}	$H_2NCH_2CH_2NH_2$	6		
E	Pt^{2+}	Cl^-			2–
F	Fe^{3+}	$^-O_2C–CO_2^-$		$[Fe(O_2CCO_2)_3]$	

[6]

(c) Iron(III) forms complexes in separate reactions with both SCN^- ions and Cl^- ions.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq) \qquad \text{equilibrium 1}$$

$$Fe^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [FeCl_4]^-(aq) \qquad \text{equilibrium 2}$$

(i) Write the expressions for the stability constants, K_{stab}, for these two equilibria. Include units in your answers.

K_{stab1} =

units = ...

K_{stab2} =

units = ...

[3]

(ii) An equilibrium can be set up between these two complexes as shown in equilibrium 3.

$$[FeCl_4]^-(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq) + 4Cl^-(aq) \qquad \text{equilibrium 3}$$

Write an expression for K_{eq3} in terms of K_{stab1} and K_{stab2}.

K_{eq3} = ... [1]

(iii) The numerical values for these stability constants are shown.

$$K_{stab1} = 1.4 \times 10^2 \qquad K_{stab2} = 8.0 \times 10^{-2}$$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = ... units = ...

[2]

Each isomer contains a six co-ordinated Cr(III) ion in an octahedral complex.
Water molecules not directly bonded with the Cr atom are held in the crystal lattice as water of crystallisation.
The Cr–C*l* bond is not easily broken and so chloride bonded with the Cr(III) ion in the complex does not react.

1.00 g samples of three of the isomers, **A**, **B** and **C**, were dissolved in separate samples of water. An excess of $AgNO_3(aq)$ was added to each and the mass of Ag*Cl*(s) formed was measured.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

The number of moles of Ag*Cl*(s) formed was calculated. The table shows the results.

isomer	moles of Ag*Cl* formed from 1.00 g of isomer
A	3.75×10^{-3}
B	7.50×10^{-3}
C	1.13×10^{-2}

(i) Calculate the M_r of $Cr(H_2O)_6Cl_3$.

M_r $Cr(H_2O)_6Cl_3$ = ... [1]

(ii) Use the data in the table above to calculate the value of n for each of the isomers, **A**, **B** and **C**. Complete the table below with the values of n and the molecular formula of each isomer, in the style of the general formula given above.

Show your working for at least one calculation of n.

isomer	n	molecular formula
A		
B		
C		

[2]

(i) Name the *type of isomerism* shown by $Ni(R_3P)_2(CN)_2$.

..... [1]

(ii) Draw structures of these two isomers.

isomer 1

isomer 2

[1]

(iii) State which isomer has a dipole moment. Explain your answer.

.....

..... [1]

[Total: 6]

(i) What is meant by the terms *bidentate* and *ligand*?

bidentate .....

ligand .....

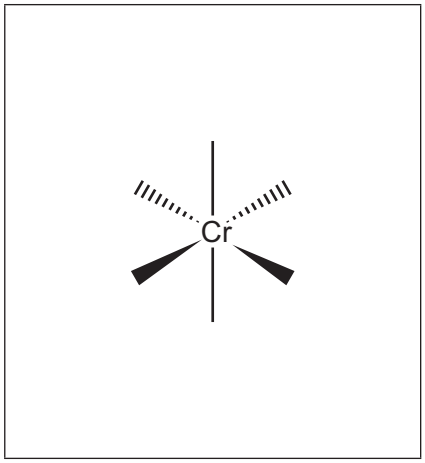
.....

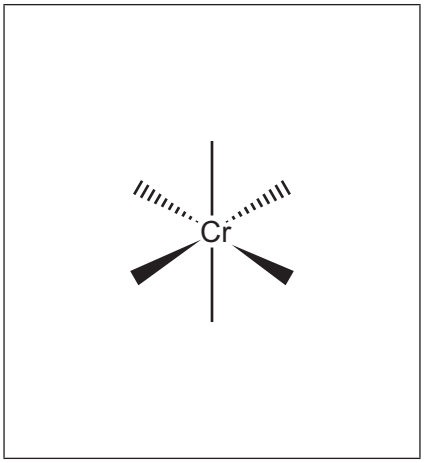
[2]

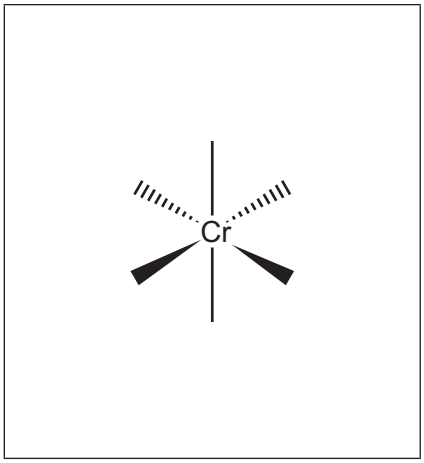
(ii) There are three isomeric complex ions with the formula $[Cr(en)_2Cl_2]^+$.

Complete the three-dimensional diagrams of the isomers in the boxes.

You may use  to represent *en*.







[3]

(b) Copper forms complexes with NH_3 and *en* according to equlibria 1 and 2.

equilibrium 1 $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

equilibrium 2 $Cu^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq)$

(i) Write the expressions for the stability constants, K_{stab1} and K_{stab2}, for equilibria 1 and 2. Include units in your answers.

K_{stab1} =

units = ...

K_{stab2} =

units = ...

[3]

equilibrium 3 $[Cu(NH_3)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cu(en)_2]^{2+}(aq) + 4NH_3(aq)$

Write an expression for the equilibrium constant, K_{eq3}, in terms of K_{stab1} and K_{stab2}.

K_{eq3} = ... [1]

(iii) The numerical values for these stability constants are shown.

$$K_{stab1} = 1.2 \times 10^{13} \qquad K_{stab2} = 5.3 \times 10^{19}$$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = ... unit = ...
[2]

(c) $\Delta S^{\ominus}$ values for equilibria 1 and 2 differ greatly, as can be seen in the table. All values are at a temperature of 298 K.

equilibrium	$\Delta H^{\ominus}$ / kJ mol^{-1}	$\Delta S^{\ominus}$ / J K^{-1} mol^{-1}	$\Delta G^{\ominus}$ / kJ mol^{-1}
1	–92	–60	–74
2	–100	+40	

(i) Explain why $\Delta S^{\ominus}_{eq2}$ is so different from $\Delta S^{\ominus}_{eq1}$.

.....

..... [1]

(ii) Calculate $\Delta G^{\ominus}_{eq2}$ at 298 K.

$\Delta G^{\ominus}_{eq2}$ = ... kJ mol^{-1}
[2]

(iii) What conclusion can be made about the relative feasibility of equilibria 1 and 2?

Explain your answer.

..... [1]

(iv) Using data from the table, suggest a value of $\Delta H^{\ominus}$ for equilibrium 3.

..... [1]

(v) State the *type of reaction* that is occurring in equilibrium 2.

..... [1]

density of cobalt .....

explanation .....

.....

melting point of cobalt .....

explanation .....

.....

[3]

(b) Transition metals can form complexes.

What is meant by the term *transition metal complex*?

.....

..... [1]

(c) **(i)** Cobalt can form the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
These two compounds are structural isomers.

Define the term *structural isomer*.

.....

..... [1]

(ii) Draw a three-dimensional diagram to show the structure of the ion $[Co(NH_3)_5Br]^{2+}$.
Name its shape.

$[Co(NH_3)_5Br]^{2+}$

shape ..... [1]

(iii) State the type of bonding between the cobalt ion and NH_3 groups in the $[Co(NH_3)_5Br]^{2+}$ ion.

..... [1]

- $[Co(NH_3)_5Br]^{2+}$ oxidation number of Co = ...
- $[Co(NH_3)_5SO_4]^{+}$ oxidation number of Co = ...

[1]

(d) Solutions of the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be distinguished from each other by simple chemical tests.
Assume that any species bonded to the cobalt ion does not react in these tests.

Complete the table with two **different** tests that could be used to positively identify each compound. Give the expected observation with each compound.

test	observation with $[Co(NH_3)_5Br]SO_4(aq)$	observation with $[Co(NH_3)_5SO_4]Br(aq)$

[2]

(e) The two compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are different colours.

Explain why the colours of the two compounds are different.

.....

.....

..... [2]

(f) Some transition metals and their compounds act as catalysts. The catalysis can be classified as heterogeneous or homogeneous.

Complete the table by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

	heterogeneous	homogeneous
Fe in the Haber process		
Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction		
NO_2 in the oxidation of SO_2		
V_2O_5 in the Contact process		

[2]

.....

..... [1]

(b) Platinum can form the compound $[Pt(NH_3)_4Cl_2][PtCl_4]$.

State the co-ordination numbers and the oxidation numbers of the platinum in the two ions of this compound.

	co-ordination number	oxidation number
$[Pt(NH_3)_4Cl_2]^{2+}$		
$[PtCl_4]^{2-}$		

[2]

(c) Draw three-dimensional diagrams to show the structures of the two isomers of $[Pt(NH_3)_4Cl_2]^{2+}$.

[2]

(d) Solutions of the compounds $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ can be distinguished from each other by a simple chemical test. Assume that any species bonded to the platinum ion does not react in this test.

Complete the table with a test that could be used to positively identify each compound. Give details of expected observations with each compound.

test	observation with $[Pt(NH_3)_4Cl_2]Br_2$	observation with $[Pt(NH_3)_4Br_2]Cl_2$

What type of isomerism is shown by the following complexes?
You should answer **geometrical**, **optical**, **both** or **neither**.

octahedral $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$ .....

square planar $[Ni(CN)_2Cl_2]^{2-}$ .....

tetrahedral $[CuBr_2Cl_2]^{2-}$ .....
[3]

(f) Many enzymes contain transition metal complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

.....

.....

.....

..... [3]

[Total: 13]

(a) Complete the electronic configurations of a Cu atom and a Cu^+ ion.

Cu atom $1s^2 2s^2 2p^6$ .....

Cu^+ ion $1s^2 2s^2 2p^6$ .....

[2]

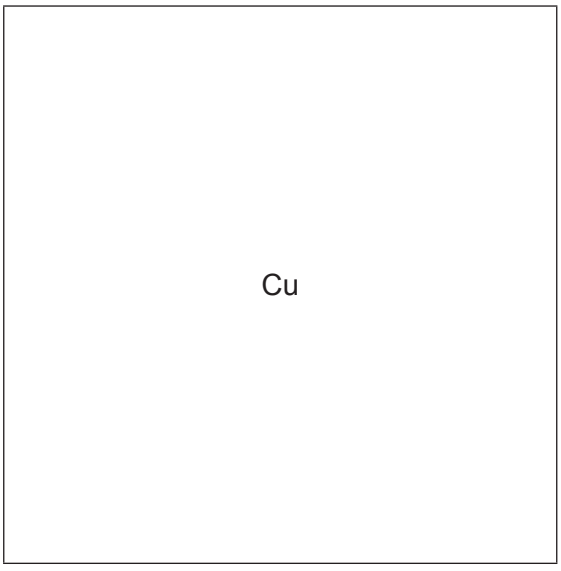
(b) Cu^+ ions form a linear complex with Cl^- ions, which are monodentate ligands.

Draw the structure of this complex and include its overall charge.

[2]

(c) Cu^{2+} ions exist as $[Cu(H_2O)_6]^{2+}$ complex ions in aqueous solution.

Complete a three-dimensional diagram to show the shape of this complex.
Name its shape.
Label and state the value of one bond angle.



name of shape .....

[2]

$$[Cu(H_2O)_6]^{2+} \xrightarrow[\text{reaction 1}]{\text{dropwise } NH_3(aq)} \mathbf{A} \xrightarrow[\text{reaction 2}]{\text{excess } NH_3(aq)} \mathbf{B}$$

For each reaction, describe what you would see and write an equation.

reaction 1

observation .....

.....

equation .....

reaction 2

observation .....

.....

equation .....

[4]

(e) $EDTA^{4-}$ is a polydentate ligand. When a solution of $EDTA^{4-}$ is added to a solution containing $[Cu(H_2O)_6]^{2+}$ a new complex is formed. The formula of this complex is $[CuEDTA]^{2-}$.

(i) Name the type of reaction occurring here.

..... [1]

(ii) Write an expression for the stability constant, K_{stab}, of $[CuEDTA]^{2-}$ in this reaction.

[1]

(iii) The numerical value of the K_{stab} of $[CuEDTA]^{2-}$ is 6.3×10^{19} at 298 K.

State what this tells us about the $[CuEDTA]^{2-}$ complex ion.

..... [1]

(i) Explain what is meant by the term *bidentate ligand*.

.....

.....

.....

..... [2]

(ii) When ethanedioate ions are added to a solution of zirconium ions, Zr^{4+}, a complex ion containing four $C_2O_4^{2-}$ ions and one Zr^{4+} ion is formed. All four ethanedioate ions act as bidentate ligands in this complex.

Give the formula of this complex ion and explain why this complex is not octahedral.

.....

.....

.....

..... [2]

[Total: 17]

Both these ions form complexes.

(a) Complete the electronic configurations of a Co atom and a Co^{2+} ion.

Co atom $1s^2 2s^2 2p^6$ .....

Co^{2+} ion $1s^2 2s^2 2p^6$ .....

[2]

(b) One Co^{2+} ion can form a tetrahedral complex ion with four Cl^- ions. This complex is blue.

(i) What is meant by the term *complex ion*?

.....

..... [1]

(ii) Draw the tetrahedral complex ion formed by one Co^{2+} ion with four Cl^- ions. Your drawing should clearly show three-dimensional shape, and should include the overall charge on the ion.

Co

[2]

(iii) Explain why many transition metal complexes are coloured.

.....

.....

.....

.....

..... [3]

(iv) Using ideas from your answer to **(iii)** suggest why the colour of the complex formed by one Co^{2+} ion with four Cl^- ions is **blue**.

.....

colour change .....

type of reaction .....
[2]

(d) $Co^{2+}(aq)$ can be oxidised to $Co^{3+}(aq)$.

(i) Use the *Data Booklet* to suggest a suitable oxidising agent for this reaction.

..... [1]

(ii) Calculate the $E^{\ominus}_{cell}$ of this reaction.

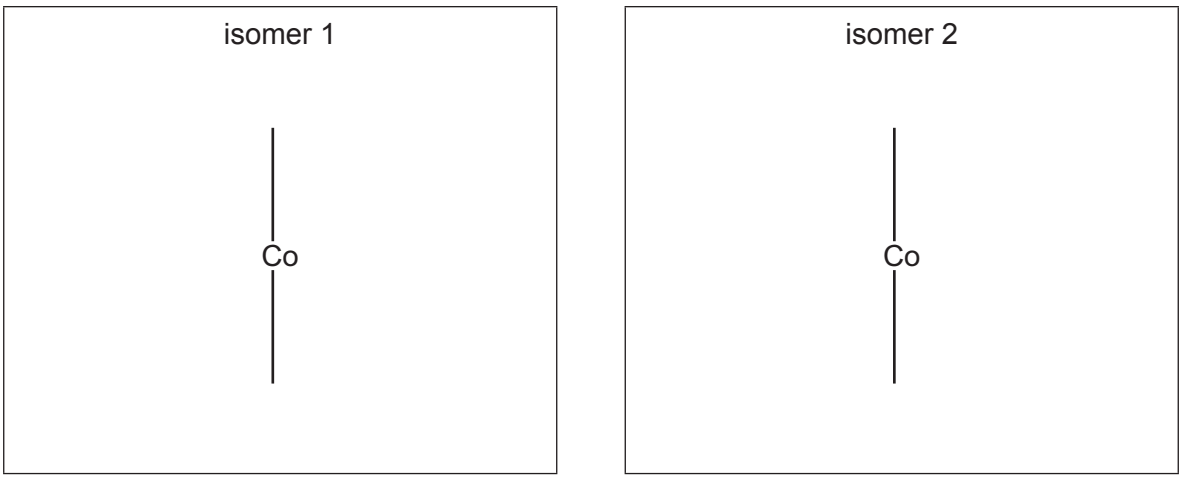
$E^{\ominus}_{cell}$ = ... V [1]

(iii) Write an equation for the reaction between Co^{2+} and the oxidising agent you chose in **(d)(i)**.

..... [1]

(e) Cobalt(III) forms two isomeric octahedral complexes with the formula $[Co(NH_3)_3(NO_2)_3]$. The NO_2^- ion is monodentate.

Complete the diagrams to show the three-dimensional structures of the two isomers and suggest the type of isomerism shown here.



type of isomerism .....
[3]

P41/O/N/18/Q2

17 **(a)** Ethanedioate ions, $C_2O_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

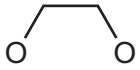
.....

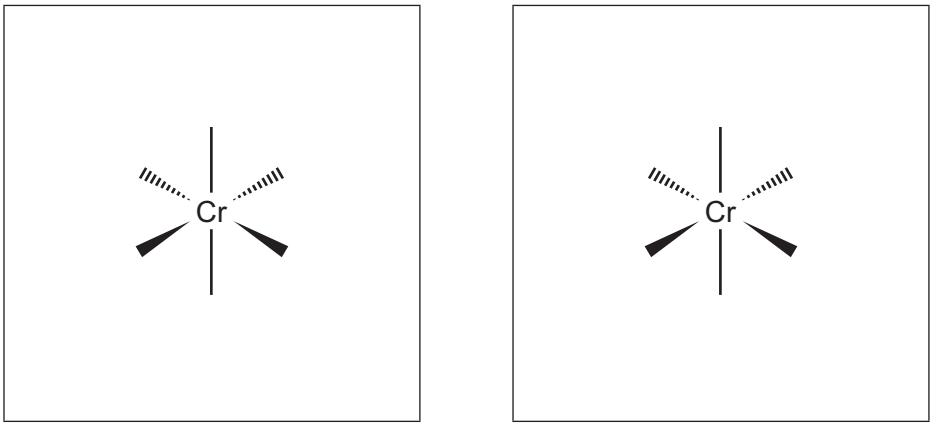
.....

..... [1]

(b) $Cr^{3+}(aq)$ and $C_2O_4^{2-}(aq)$ ions form the complex ion $[Cr(C_2O_4)_2(H_2O)_2]^-$.

Draw **two** stereoisomers of this complex ion.

You may use  to represent $C_2O_4^{2-}$.



[2]

(c) The solubility of calcium ethanedioate, CaC_2O_4, is 6.65×10^{-3} g dm^{-3} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of CaC_2O_4. Include its units.

K_{sp} =

units = ...
[2]

(ii) Calculate the numerical value of K_{sp} CaC_2O_4 at 298 K. Give your answer in **standard form** to **two** significant figures.

K_{sp} CaC_2O_4 = ... [2]

	number of **unpaired** electrons	
	3d	4s
Cr		
Mn		
Fe		

[2]

(b) Solid potassium manganate(VII), $KMnO_4$, decomposes on heating to form manganese(IV) oxide, potassium manganate(VI) and a colourless gas.

Construct an equation for this reaction.

..... [2]

(c) Explain the origin of colour in transition element complexes.

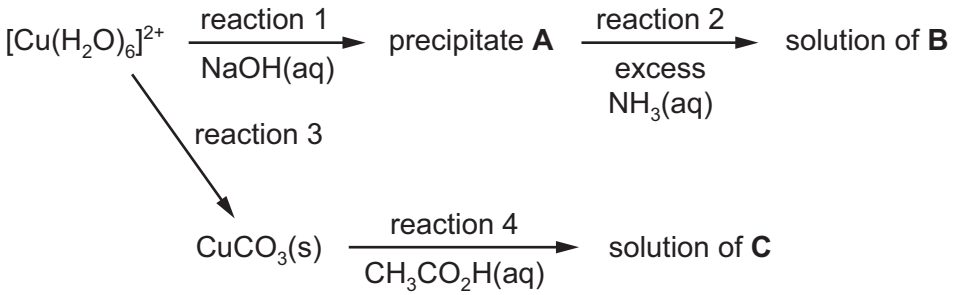
.....

.....

.....

.....

..... [3]



(i) Write the formulae of

precipitate **A**, ...

complex ion **B**, ...

compound **C**. .....

[3]

(ii) Identify a suitable reagent for reaction 3.

..... [1]

(iii) Write an equation for reaction 4.

..... [1]

(iv) Describe **two** visual observations that would be made during reaction 4.

.....

..... [1]

(e) Platin, $Pt(NH_3)_2Cl_2$, is a neutral complex of platinum(II).

Explain why $Pt(NH_3)_2Cl_2$ has no charge.

.....

..... [1]

Draw the structure of *trans*-platin. State its shape and the C*l*–Pt–C*l* bond angle.

shape ..... C*l*–Pt–C*l* bond angle .....

[2]

(ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

.....

.....

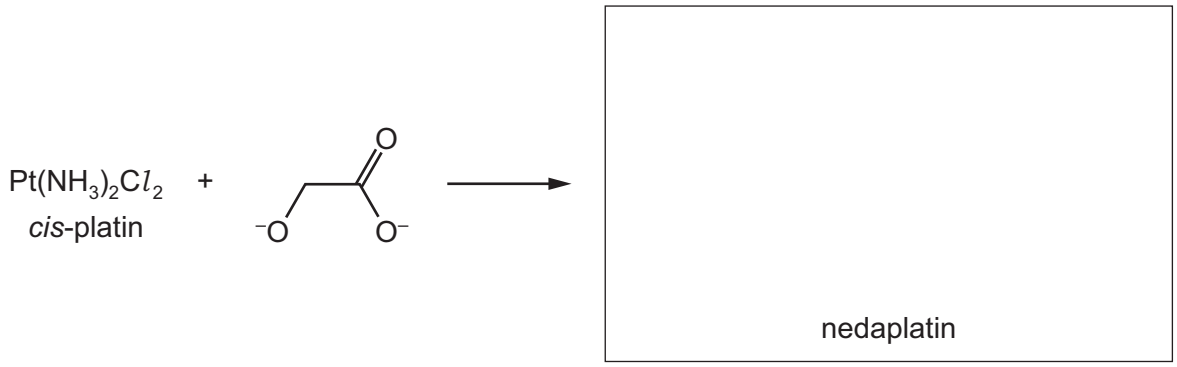
.....

..... [2]

(g) The use of *cis*-platin can cause side effects so nedaplatin has been developed.

Nedaplatin can be synthesised from *cis*-platin, $Pt(NH_3)_2Cl_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[1]

[Total: 19]

19 **(a)** Complete the electronic configuration for Cu and Cu^{2+}.

[2]

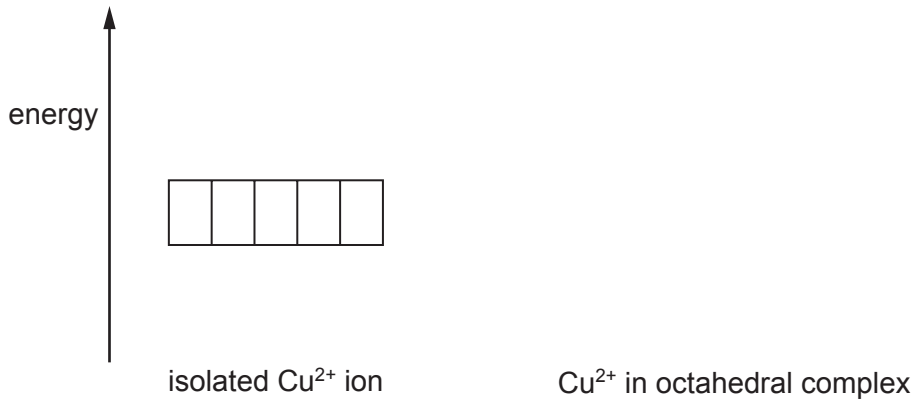
(b) **(i)** The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Explain what is meant by the term *degenerate* in this context.

.....

..... [1]

(ii) Complete the diagram to describe the splitting of the 3d orbital energy levels in an octahedral complex.



[1]

Explain what is meant by the term *bidentate*.

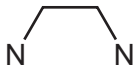
.....

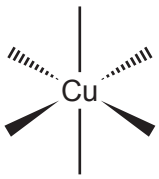
.....

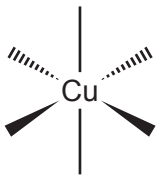
..... [1]

(ii) Cu^{2+} ions and *en* form the complex ion $[Cu(en)_3]^{2+}$.

Draw the two optical isomers of this complex ion.

You may use  to represent *en*.

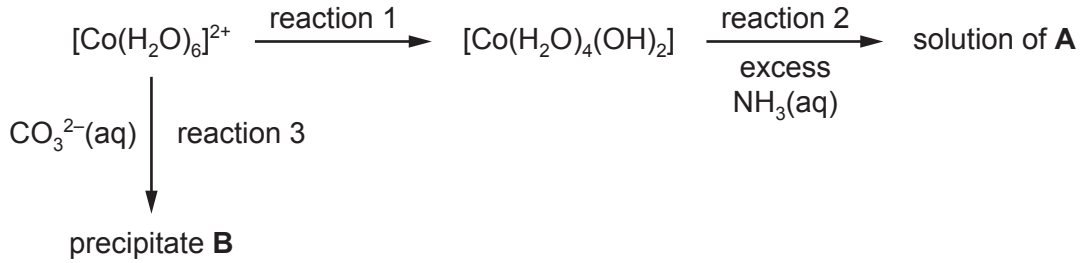




[2]

[Total: 7]

20 **(a)** The reaction scheme shows some reactions of $[Co(H_2O)_6]^{2+}$.



(i) Write the formulae of the following species.

A .....

B .....

[2]

(ii) State a suitable reagent for reaction 1.

..... [1]

(iii) Write an equation for reaction 2.

..... [1]

(iv) Write an ionic equation for reaction 3.

..... [1]

(b) Co^{2+} ions catalyse the oxidation of 2,3-dihydroxybutanedioate ions, $C_4H_4O_6^{2-}$, to methanoate ions, HCO_2^-, carbon dioxide and water.

(i) What property of transition elements allows Co^{2+} ions to act as a catalyst?

..... [1]

(ii) Draw the structure of the 2,3-dihydroxybutanedioate ion.

[1]

(iii) Complete the equation for the oxidation of 2,3-dihydroxybutanedioate. Use [O] for the oxidising agent in this reaction.

$C_4H_4O_6^{2-}$ + ... → ..... [1]

(i) Draw the structures of these isomers.

cis isomer	*trans* isomer

[2]

(ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

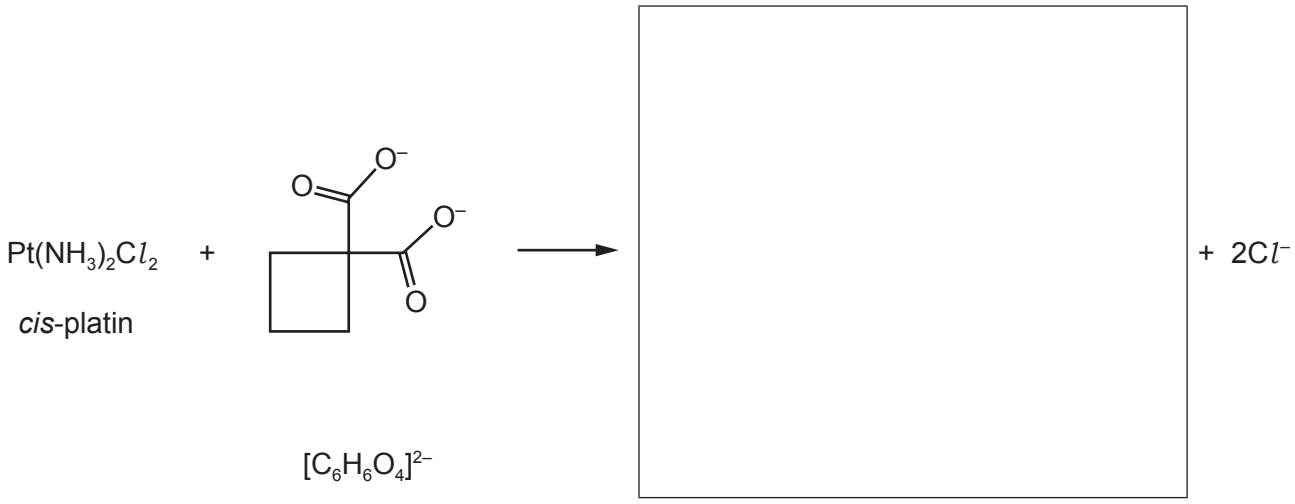
.....

.....

.....

..... [2]

Carboplatin can be synthesised from *cis*-platin, $Pt(NH_3)_2Cl_2$, by replacing the two chloride ion ligands with a **single** cyclobutane-1,1-dicarboxylate ion ligand as shown.



cis-platin

$[C_6H_6O_4]^{2-}$

cyclobutane-1,1-dicarboxylate ion

carboplatin

Suggest the structure for carboplatin and draw it in the box. [1]

[Total: 13]

P41/M/J/19/Q1

21 **(a)** Aqueous solutions of copper(II) salts contain the blue-coloured $[Cu(H_2O)_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

  ionic equation .....

  type of reaction .....

  colour and state of the copper-containing product .....

- reaction with concentrated hydrochloric acid

  ionic equation .....

  type of reaction .....

  colour and state of the copper-containing product .....

[6]

(b) Chloride ions can be identified using aqueous silver nitrate, $AgNO_3(aq)$.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

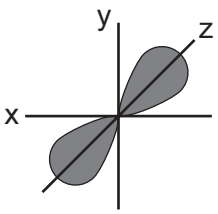
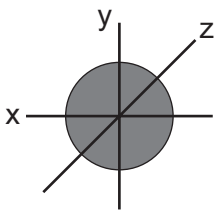
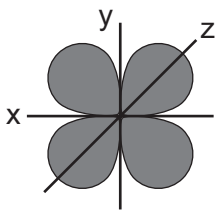
0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3. A 25.00 cm^3 sample of this solution is titrated with 0.0500 mol dm^{-3} $AgNO_3(aq)$. The titration requires 22.40 cm^3 of 0.0500 mol dm^{-3} $AgNO_3(aq)$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

22 **(a)** Sketches of the shapes of some atomic orbitals are shown.

Identify the type of orbital, s, p, or d.

shape of orbital			
type of orbital			

[1]

(b) Cadmium forms the two ions, Cd_2^{2+} and Cd^{2+}. The electronic configuration of cadmium in these ions is shown.

- [Kr] $4d^{10}5s^1$
- [Kr] $4d^{10}$

Use this information to explain why cadmium is **not** a transition element.

.....

..... [1]

(c) Methylamine, CH_3NH_2, is a monodentate ligand.

(i) State what is meant by the term *monodentate* in this context.

.....

..... [1]

equilibrium **1** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O \quad \Delta H_r^{\ominus} = -57\,kJ\,mol^{-1}$

(ii) Complete the three-dimensional diagrams to show the isomers of $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$.

Use L to represent CH_3NH_2 in your diagrams.

[2]

(d) (i) State what is meant by the term *stability constant*.

.....

..... [1]

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$, for equilibrium **1**. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$			

explanation .....

.....

[2]

The values for the stability constants for two Cd^{2+} complexes are shown.

	K_{stab}
$[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$	4.0×10^6
$[CdEDTA]^{2-}$	4.0×10^{16}

(iii) A solution containing equal numbers of moles of CH_3NH_2 and EDTA is added to $[Cd(H_2O)_6]^{2+}$.

Predict which complex is formed in the larger amount. Explain your answer.

.....

..... [1]

(e) Methylamine is a Brønsted-Lowry base.

Write an equation showing how methylamine dissolves in water to give an alkaline solution.

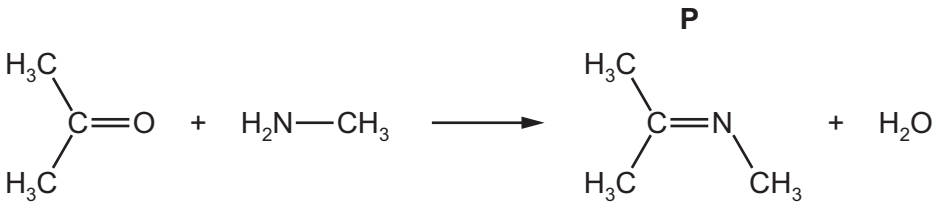
..... [1]

(f) Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

..... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

..... [1]

[Total: 13]

20 copper(I) and silver(I) salts are colourless.

Suggest why.

.....

.....

.....

..... [2]

(c) Consider the following two equilibria and associated data values at 298 K.

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ equilibrium **1** $K_{sp} = 5.0 \times 10^{-13}\,mol^2\,dm^{-6}$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ equilibrium **2** $K_{stab} = 1.7 \times 10^{7}\,mol^{-2}\,dm^{6}$

The equilibrium constant for equilibrium **1** is the solubility product, K_{sp}, of AgBr(s). The equilibrium constant for equilibrium **2** is the stability constant, K_{stab}, for the formation of $[Ag(NH_3)_2]^+(aq)$.

(i) Calculate the solubility of AgBr at 298 K in mol dm^{-3}.

solubility of AgBr = ... mol dm^{-3} [1]

(ii) Use Le Chatelier's principle as applied to equilibria **1** and **2** to suggest why AgBr(s) dissolves in concentrated $NH_3(aq)$.

.....

.....

.....

..... [2]

(iii) Use equilibria **1** and **2** to construct an equation for the reaction of AgBr(s) with concentrated $NH_3(aq)$. This is equilibrium **3**.

..... equilibrium **3** [1]

(iv) Write an expression for the equilibrium constant of equilibrium **3**, K_{eq3}, in terms of K_{sp} for equilibrium **1** and K_{stab} for equilibrium **2**.

K_{eq3} =

24 **(a)** Sketch the shape of a d orbital.

[1]

(b) **(i)** Explain what is meant by the term *transition element*.

.....

..... [1]

Transition elements can form complex ions which contain ligands.

(ii) Name the *type of bonding* that occurs between a ligand and a transition element.

..... [1]

(c) Give the formulae of two oxides of iron. State the oxidation number of iron in each compound.

.....

..... [1]

(d) CO and CN^- are monodentate ligands.

Complete the table for the following two complexes.

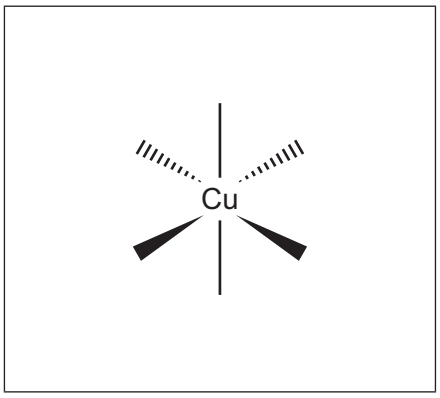
metal ion	ligand	co-ordination number	formula of complex ion	charge of complex ion
Ni^{2+}	CO	4		
Fe^{3+}	CN^-			3-

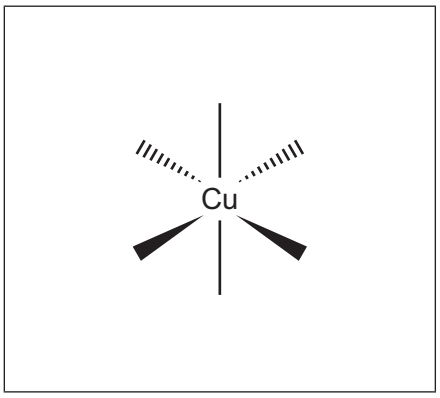
[2]

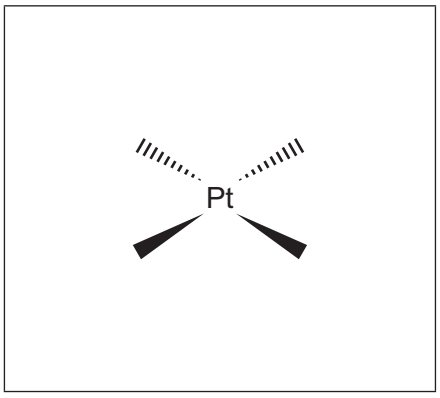
(i) Name this type of isomerism.

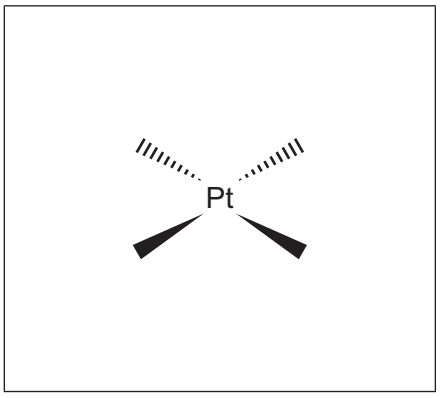
..... [1]

(ii) Complete the three-dimensional diagrams of the two isomers for $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$.









[2]

$[Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$ equilibrium **4**

$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \rightleftharpoons [Cu(H_2O)_4(NH_3)_2]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 5.01 \times 10^{7}$ equilibrium **5**

(i) Write an expression for the stability constant, K_{stab}, for equilibrium **5**. State its units.

K_{stab} =

units = ...
[2]

(ii) The standard entropy change, $\Delta S^{\ominus}$, for equilibrium **4** is $+23\,J\,K^{-1}\,mol^{-1}$ and for equilibrium **5** is $-8.4\,J\,K^{-1}\,mol^{-1}$.

Suggest an explanation for this difference by reference to both equilibria.

.....

.....

..... [1]

(iii) Of the three copper complexes in equilibria **4** and **5**, state the formula of the copper complex that is the most stable and explain your choice.

copper complex .....

explanation .....

.....
[1]

[Total: 13]

25 Manganese, chromium and ruthenium are all transition elements.

(a) Explain what is meant by a *transition element*.

.....

.....

..... [1]

(b) $MnO_4^-(aq)$ and $Cr_2O_7^{2-}(aq)$ act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of Sn^{2+} to give a solution of Sn^{4+}. Solutions containing Sn^{2+} and solutions containing Sn^{4+} are colourless.

(i) Describe the colour change seen when an excess of $Sn^{2+}(aq)$ is added separately to

- dilute acidified $MnO_4^-(aq)$

from ..... to .....

- dilute acidified $Cr_2O_7^{2-}(aq)$.

from ..... to .....
[1]

(ii) Write an equation for the reaction between $Sn^{2+}(aq)$ and acidified $Cr_2O_7^{2-}(aq)$.

..... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one Ru^{2+} ion, one Cl^- ion, one SO_2 molecule and the remaining ligands are NH_3 molecules.

The SO_2 molecule acts as a monodentate ligand and is attached to the Ru^{2+} ion via the sulfur atom. **X** exists in two isomeric forms.

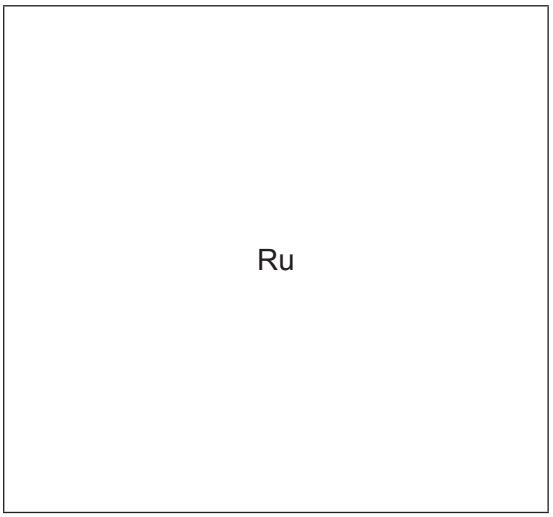
(i) State what is meant by a *co-ordination number of six*.

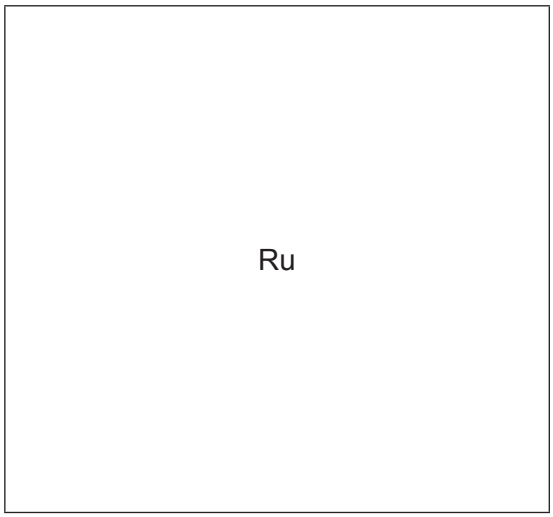
..... [1]

(ii) State the formula of **X**. Include its charge.

..... [1]

- the three-dimensional shapes of the two isomers
- how each ligand is attached to the central ruthenium ion.





[3]

(iv) Suggest the type of isomerism shown by **X**.

..... [1]

(v) Explain the origin of colour in a transition element complex such as **X**.

.....

.....

.....

.....

.....

.....

..... [3]

[Total: 12]

26 Many copper compounds, such as $CuSO_4$ and $Cu(NO_3)_2$ contain Cu^{2+} ions. Aqueous solutions of this ion contain the $[Cu(H_2O)_6]^{2+}$ complex ion, in which water behaves as a monodentate ligand.

(a) Explain what is meant by the term *monodentate ligand*.

.....

..... [1]

(b) Copper(II) sulfate solution, $CuSO_4(aq)$, undergoes visible changes with certain reagents.

Complete the table below.

reagent added to a solution of $CuSO_4(aq)$	observations	formula of the copper(II) compound or complex ion that is formed
a few drops of $NH_3(aq)$		
an excess of $NH_3(aq)$		
an excess of NaOH(aq)		
an excess of concentrated HC*l*(aq)		

[4]

(c) When water is added to concentrated aqueous cobalt(II) chloride the colour of the solution changes from blue to pink. Explain this observation.

No equation is needed, but you should include reference to electron movement between orbitals in your answer.

.....

.....

.....

.....

.....

.....

.....

.....

[3]

Use data from the *Data Booklet* to explain this observation. Include an equation in your answer.

Reference to electron movement between orbitals is not needed.

.....

.....

..... [2]

(e) If a solution of chloride ions is added to a solution containing $[Fe(H_2O)_6]^{3+}$ an equilibrium is established.

$$[Fe(H_2O)_6]^{3+} + 4Cl^- \rightleftharpoons [FeCl_4]^- + 6H_2O$$

(i) Write an expression for the stability constant of $[FeCl_4]^-$, K_{stab}.

K_{stab} =

[1]

(ii) For the above equilibrium the numerical value of K_{stab} = 0.080.

Calculate the concentration of $[Fe(H_2O)_6]^{3+}$ in a solution in which the concentration of Cl^- is 2.0 mol dm^{-3} and the concentration of $[FeCl_4]^-$ is 0.10 mol dm^{-3}.

concentration of $[Fe(H_2O)_6]^{3+}$ = ... mol dm^{-3} [1]

[Total: 12]

27 **(a)** An aqueous solution of cobalt(II) contains the $[Co(H_2O)_6]^{2+}$ complex ion.

(i) Define the term *complex ion*.

.....

..... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of $[Co(H_2O)_6]^{2+}$ with aqueous sodium hydroxide

  colour and state of the cobalt-containing species .....

  ionic equation .....

  type of reaction .....

- the reaction of $[Co(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

  colour and state of the cobalt-containing species .....

  ionic equation .....

  type of reaction .....

[6]

(b) When concentrated hydrochloric acid is added to a solution containing $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed and the following equilibrium is established.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$. Explain your answer.

.....

.....

..... [2]

Complete the three-dimensional diagrams to show the two isomers of $[Co(NH_3)_3Cl_3]$.

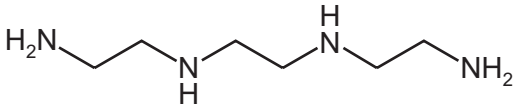
Suggest the type of stereoisomerism.

type of stereoisomerism .....

[2]

(d) Compound **X**, $C_6H_{18}N_4$, is a tetradentate ligand.

X



(i) Suggest why one molecule of **X** can form four dative bonds.

.....

.....

..... [1]

(ii) $C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion.

Construct an equation for this reaction.

..... [1]

[Total: 13]

P41/M/J/20/Q10

28 **(a)** The electronic configuration of transition element **Q** is [Ar] $3d^2$ $4s^2$.

Predict the likely oxidation states of element **Q** in compounds.

..... [1]

(b) Suggest why transition elements often show variable oxidation states in their compounds, but typical s-block elements such as calcium do not.

.....

..... [1]

(c) Many enzymes contain transition element complexes.

Describe, with the aid of a suitably labelled diagram, how an enzyme catalyses the breakdown of a substrate molecule.

.....

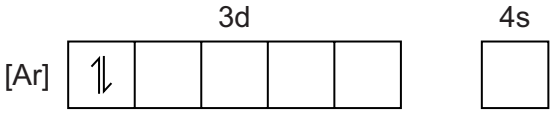
.....

.....

..... [3]

[Total: 5]

29 **(a)** Complete the electronic configuration of an isolated gaseous nickel(II) ion, Ni^{2+}.



[1]

(b) Explain the origin of colour in transition element complexes.

.....

.....

.....

.....

.....

..... [4]

(c) Hexaaquanickel(II) ions are green. They form a green precipitate with hydroxide ions, OH^-, in equilibrium **1** and a blue complex with ammonia, NH_3, in equilibrium **2**.

equilibrium **1** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightleftharpoons Ni(OH)_2 + 6H_2O$
green ppt.

equilibrium **2** $[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$
blue

Use Le Chatelier's principle to suggest explanations for the following observations.

(i) Explain why when aqueous NH_3 is added dropwise to $[Ni(H_2O)_6]^{2+}$ a green precipitate is formed.

.....

.....

..... [1]

(ii) Explain why when a large excess of aqueous NH_3 is added to $[Ni(H_2O)_6]^{2+}$, the green precipitate dissolves and a blue solution is formed.

.....

.....

Draw diagrams to show the two isomers of $[NiBr_2(CN)_2]^{2-}$. Name the type of stereoisomerism.

isomer 1	isomer 2

type of stereoisomerism .....

[2]

[Total: 9]

30 A solution is made by dissolving $CuSO_4 \cdot 5H_2O$ in an excess of aqueous ammonia. This solution contains the copper complex $[Cu(NH_3)_4]^{2+}$.

(a) (i) Write an expression for the K_{stab} of $[Cu(NH_3)_4]^{2+}$.

K_{stab} =

[1]

(ii) State the colour of the solution of $[Cu(NH_3)_4]^{2+}$.

..... [1]

The solution of $[Cu(NH_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $Cu(OH)_2$ forms and is collected.

A sample of $Cu(OH)_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $Cu(OH)_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[Cu(NH_3)_4]^{2+}$, **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of $[Cu(NH_3)_4]^{2+}$ to form $Cu(OH)_2$ as the aqueous solution of $[Cu(NH_3)_4]^{2+}$ is heated.

..... [1]

(c) Suggest an equation for the reaction of $Cu(OH)_2$ with concentrated hydrochloric acid, forming **Y**.

..... [2]

(d) Complete the table with the colour and geometry of complex **Y** and the colour, geometry and formula of complex **Z**.

	Y	**Z**
colour of complex		
geometry of complex		
formula of complex		

[2]

.....

.....

.....

.....

.....

.....

.....

..... [5]

[Total: 12]

P41/O/N/20/Q6

31 **(a)** When 1.0 mol dm^{-3} $Na_2S_2O_3$(aq) is added to a solution containing Ag^+(aq) ions, a linear complex, **P**, is formed. $S_2O_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

.....

..... [2]

(ii) Give the formula of **P**, including its charge.

..... [1]

(b) When 1.0 mol dm^{-3} NaCN(aq) is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when NaCN(aq) is added to a solution of **P**.

..... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

.....

.....

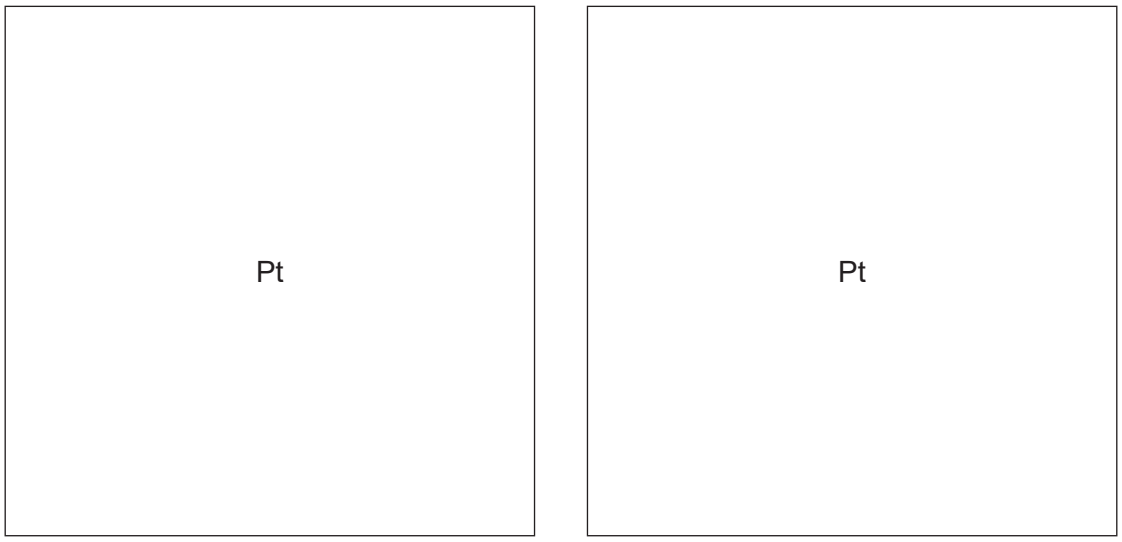
..... [1]

(iii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.



[1]

(ii) Describe the geometry of $[Pt(CN)_2Cl_2]^{2-}$.

..... [1]

(iii) Name the type of stereoisomerism shown by $[Pt(CN)_2Cl_2]^{2-}$.

..... [1]

[Total: 9]

32 **(a)** Define the term *transition element*.

.....

..... [1]

(b) (i) Complete the electronic configuration of an isolated gaseous Fe^{3+} ion.

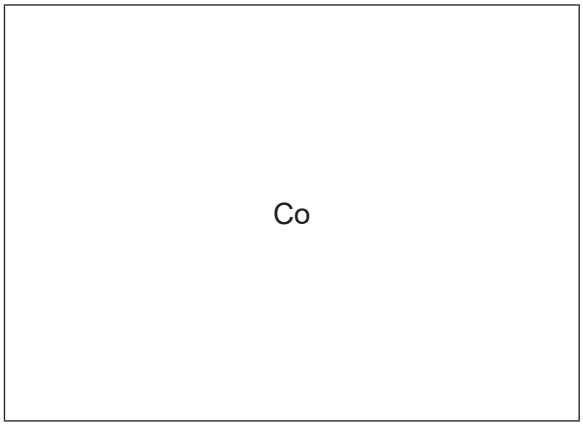
$1s^2$ ..... [1]

(ii) Name **two** transition elements whose isolated gaseous **atoms** have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion.

..... [1]

(c) Cobalt(II) sulfate is added to water to form a pink solution containing complex ion **P**. An excess of concentrated hydrochloric acid is added to this solution to form a blue solution containing complex ion **Q**.

(i) Complete the diagram to show the three-dimensional structure of **Q**.
State the charge on this complex ion.



charge .....

[2]

(ii) Name the type of reaction in which **P** forms **Q**.

..... [1]

(iii) Explain why solutions that contain transition element ions are often coloured.

.....

.....

.....

.....

.....

.....

.....

..... [2]

(d) A solution of the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, is added to an aqueous solution of cobalt(II) sulfate. Oxygen is then bubbled into the mixture forming a complex ion with the formula $[Co(H_2NCH_2CH_2NH_2)_3]^{3+}$.

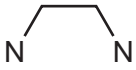
This complex ion exists as a mixture of two isomers. The geometry of both of these isomeric complexes is octahedral.

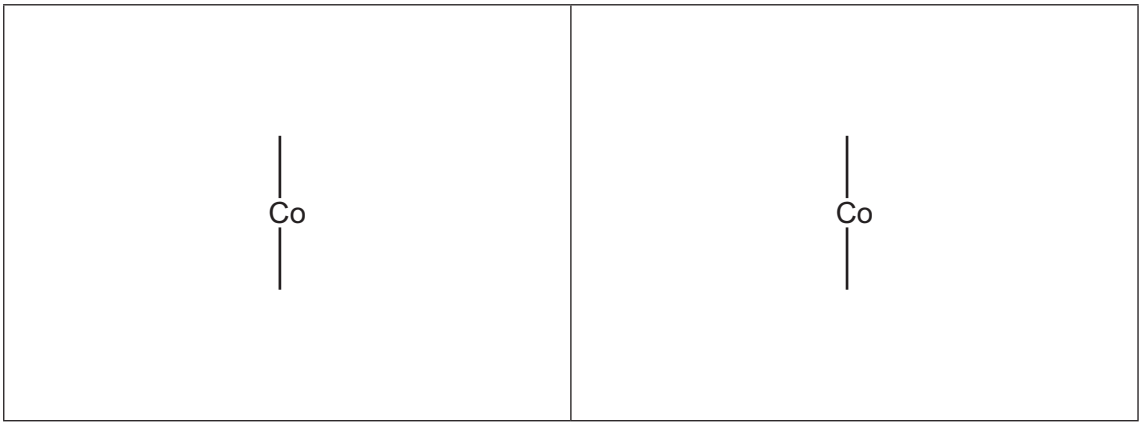
(i) In this reaction, cobalt undergoes **two** types of reaction. One type of reaction is the same as that described in **(c)(ii)**.

Name the **other** type of reaction that cobalt undergoes.

..... [1]

(ii) Draw the three-dimensional structures of the two isomeric complexes in the boxes.

You may use  to represent a molecule of $H_2NCH_2CH_2NH_2$.



[2]

(iii) Name the type of stereoisomerism shown by these two isomeric complexes.

..... [1]

(iv) State the co-ordination number of cobalt in these two isomeric complexes.

..... [1]

complex	K_{stab}
$[Hg(CN)_4]^{2-}$	2.5×10^{41}
$[HgCl_4]^{2-}$	1.7×10^{16}
$[HgI_4]^{2-}$	2.0×10^{30}

(i) Write an expression for the K_{stab} of $[Hg(CN)_4]^{2-}$.

K_{stab} =

[1]

(ii) An aqueous solution containing Hg^{2+} is added to a solution containing equal concentrations of CN^-(aq), Cl^-(aq) and I^-(aq). The mixture is left to reach equilibrium.

Predict which of the complexes $[Hg(CN)_4]^{2-}$, $[HgCl_4]^{2-}$ and $[HgI_4]^{2-}$ is present in the resulting mixture in the highest concentration and which is present in the lowest concentration. Explain your answer.

.....

.....

.....

..... [2]

[Total: 20]

33 **(a)** Explain why chromium complexes are coloured.

.....

.....

.....

.....

..... [4]

(b) Four different compounds can be obtained when anhydrous chromium(III) chloride reacts with water under various conditions. When samples of each compound are reacted separately with aqueous silver nitrate, different amounts of silver chloride are precipitated. The precipitation leaves the complex ions **P**, **Q**, **R** and **S** in solution.

formula of compound	moles of $AgCl$ precipitated per mole of complex ion	complex ion	property of complex ion
$CrCl_3(H_2O)_6$	3	**P**	non-polar
$CrCl_3(H_2O)_5$	2	**Q**	polar
$CrCl_3(H_2O)_4$	1	**R**	polar
$CrCl_3(H_2O)_4$	1	**S**	non-polar

(i) Draw three-dimensional diagrams for the structures of complex ions **P**, **Q**, **R** and **S**. Include the charges for each complex ion.

P

Cr

Q

Cr

R

Cr

S

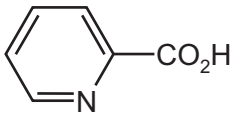
Cr

.....

..... [1]

(c) The structure of picolinic acid is shown.

picolinic acid



The conjugate base of picolinic acid is a bidentate ligand, **Z**.

(i) Define the term *bidentate ligand*.

.....

..... [2]

(ii) Draw the structure of **Z**.

[1]

(iii) **Z** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number ..... geometry ..... [1]

(d) $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.

(i) Deduce the oxidation numbers of chromium in $(NH_4)_2Cr_2O_7$ and in Cr_2O_3.

$(NH_4)_2Cr_2O_7$ ..... Cr_2O_3 ..... [1]

(ii) Construct an equation for the thermal decomposition of $(NH_4)_2Cr_2O_7$.

..... [1]

[Total: 15]

34 **(a)** **(i)** Define the term *transition element*.

.....

..... [1]

(ii) State how the melting point and density of iron compare to those of calcium.

.....

..... [1]

(b) **(i)** Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

.....

.....

..... [2]

(ii) Draw a fully labelled diagram of the apparatus that can be used to measure the cell potential of a cell composed of a Cu(II)/Cu electrode and an Fe(III)/Fe(II) electrode. Include all necessary reactants.

[3]

(i) Use equations to show the catalytic role of Fe^{3+} in this reaction.

[2]

(ii) $Fe^{3+}(aq)$ can oxidise $I^-(aq)$, whereas $[Fe(CN)_6]^{3-}(aq)$ cannot oxidise $I^-(aq)$.

Use $E^\ominus$ values to explain these observations.

.....

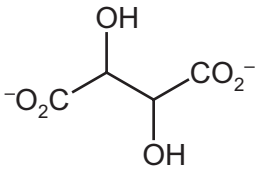
.....

.....

..... [2]

(d) When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions are mixed the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an $Fe^{3+}(aq)$ catalyst.
The overall equation for this reaction is shown.

tartrate ions



$$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

(i) Suggest why this reaction is slow without the Fe^{3+} catalyst.

.....

..... [1]

(ii) Use the overall equation to deduce the half-equation for the oxidation of tartrate ions, $C_4H_4O_6^{2-}$, to carbon dioxide, CO_2, and methanoate ions, HCO_2^-.

$C_4H_4O_6^{2-}$ + ... $\rightleftharpoons$ ..... [1]

or with an excess of aqueous ammonia.

Give the following information about these reactions.

(i) reaction 1: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous of sodium hydroxide

colour and state of the copper-containing species .....

ionic equation .....

type of reaction .....

[3]

(ii) reaction 2: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

colour and state of the copper-containing species .....

ionic equation .....

type of reaction .....

[3]

(b) Copper(I) oxide is added to hot dilute sulfuric acid. A blue solution, **X**, and a red-brown solid, **Y**, form.

Suggest the identities of **X** and **Y**. Name the type of reaction.

X .....

Y .....

type of reaction .....

[2]

[Total: 8]

36 **(a)** An aqueous solution of chromium(III) contains the green $[Cr(H_2O)_6]^{3+}$ complex ion.

(i) Complete the electronic configuration of an isolated, gaseous Cr^{3+} ion.

$1s^2$ ..... [1]

(ii) Define the term *complex ion*.

.....

..... [1]

(b) $[Cr(H_2O)_6]^{3+}(aq)$ shows some similar chemical properties to $[Co(H_2O)_6]^{2+}(aq)$.

Samples of $[Cr(H_2O)_6]^{3+}$ are reacted separately with either NaOH(aq), $H_2O_2(aq)$, or excess $NH_3(aq)$.

Use this information and the *Data Booklet* to suggest the formula of the chromium species formed. State the type of reaction taking place in each case.

reagent added to $[Cr(H_2O)_6]^{3+}(aq)$	formula of chromium species formed	type of reaction
NaOH(aq)		
$H_2O_2(aq)$		
an excess of $NH_3(aq)$		

[5]

(c) $[Cr(H_2O)_6]^{2+}$ and $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ are both complexes of chromium(II) and have different colours.

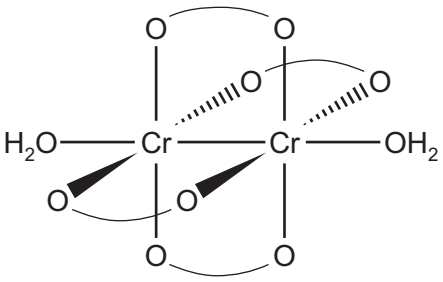
Explain why the colours of these complexes are different.

.....

.....

.....

..... [2]



(i) Water and ethanoate ions behave as different types of ligand in this complex.

Suggest an explanation for this statement.

.....

..... [1]

(ii) Deduce the coordination number of Cr and the geometry around each Cr atom in this structure.

coordination number .....

geometry around Cr atom .....
[1]

(iii) State the type of bond between the two atoms in the Cr–Cr bond.

..... [1]

(e) The $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ complex reacts with aqueous acid to form $Cr^{2+}(aq)$ ions.

$Cr^{2+}(aq)$ ions react with $O_2(aq)$ under acidic conditions. $Cr^{3+}(aq)$ ions are formed.

Use the *Data Booklet* to answer the following questions.

(i) Construct an ionic equation for the reaction of $Cr^{2+}(aq)$ with $O_2(aq)$ under acidic conditions.

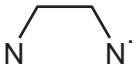
..... [2]

(ii) Calculate $E^{\ominus}_{cell}$ for the reaction in **(e)(i)**.

$E^{\ominus}_{cell}$ = ... V [1]

[Total: 15]

37 The complex $[Ru(en)_3]^{3+}$ shows stereoisomerism. The ligand en is bidentate.

Draw three-dimensional diagrams to show the two isomers of $[Ru(en)_3]^{3+}$. Represent the ligand en by using  .

Name the type of stereoisomerism.

isomer 1

Ru

isomer 2

Ru

type of stereoisomerism .....
[3]

(b) (i) An electrochemical cell consists of a Br_2/Br^- half-cell and a Ag^+/Ag half-cell, under standard conditions.

Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$. Deduce the direction of electron flow in the wire through the voltmeter between these two half-cells.

$E^{\ominus}_{cell}$ = ... V

direction of electron flow from ..... to ..... [1]

(ii) Water is added to the Ag^+/Ag half-cell in **(b)(i)**.

Suggest the effect of this addition on the E_{cell}. Place a tick (✓) in the appropriate box.

less positive	no change	more positive

Explain your answer.

.....

.....

equilibrium 1 $AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

(i) Define the term *ligand*.

.....

..... [1]

(ii) Write an expression for the equilibrium constant, K_c, for equilibrium 1.

K_c =

[1]

(iii) Some additional data are given about the dissolution of AgBr in $S_2O_3^{2-}(aq)$.

equilibrium constant	numerical value
solubility product, K_{sp}, of AgBr	5.4×10^{-13}
stability constant, K_{stab}, of $[Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}

Use your answer to **(c)(ii)** and these data to calculate K_c for equilibrium 1. Include the units for K_c.

K_c = ... units ..... [2]

(d) The numerical values for the stability constants, K_{stab}, of two other silver(I) complexes are given.

silver(I) complex	numerical value of K_{stab}
$[Ag(CN)_2]^-$	5.3×10^{18}
$[Ag(NH_3)_2]^+$	1.6×10^7

An aqueous solution containing Ag^+ is added to a solution containing equal concentrations of $CN^-(aq)$, $NH_3(aq)$ and $S_2O_3^{2-}(aq)$. The mixture is left to reach equilibrium.

Deduce the relative concentrations of $[Ag(CN)_2]^-$, $[Ag(NH_3)_2]^+$ and $[Ag(S_2O_3)_2]^{3-}$ present in the resulting mixture. Explain your answer.

..... > ..... > .....

highest concentration lowest concentration

.....

..... [2]

P41/O/N/21/Q5

38 **(a)** $[MnCl_4]^{2-}$ is a complex ion.

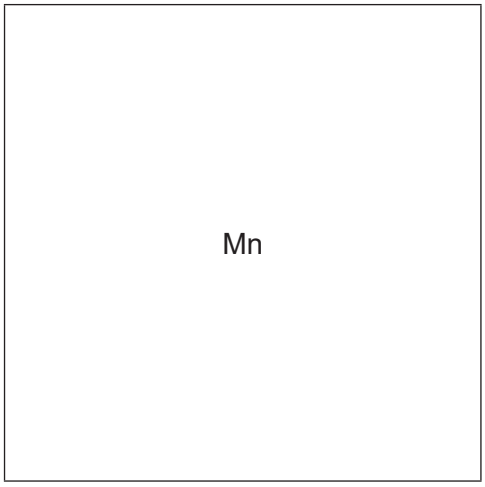
(i) Deduce the oxidation state of manganese in $[MnCl_4]^{2-}$.

oxidation state = ... [1]

(ii) The $[MnCl_4]^{2-}$ complex does **not** contain any 180° bond angles.

Draw a three-dimensional diagram to show the shape of the $[MnCl_4]^{2-}$ complex.

State one bond angle on your diagram.



[2]

(b) A solution of cobalt(II) sulfate contains the complex ion $[Co(H_2O)_6]^{2+}$.

A solution containing $[Co(H_2O)_6]^{2+}$ is reacted separately with an excess of each of NaOH(aq), NH_3(aq) and NaCl(aq).

Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.

(i) $[Co(H_2O)_6]^{2+}$ and an excess of NaOH(aq)

equation .....

observation .....

[2]

(ii) $[Co(H_2O)_6]^{2+}$ and an excess of NH_3(aq)

equation .....

observation .....

[2]

equation .....

observation .....

[2]

(iv) Name the type of reaction that occurs in **(b)(iii)**.

..... [1]

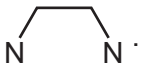
(c) Cobalt forms the complex ion $[Co(NH_3)_2(en)_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$. The complex ion shows both geometrical and optical isomerism.

(i) Define the term *bidentate ligand*.

.....

..... [2]

(ii) Draw three-dimensional diagrams for the two **optical** isomers of $[Co(NH_3)_2(en)_2]^{2+}$.

Each en ligand can be represented using 

.

Co

Co

[2]

[Total: 14]

39 An excess of sodium iodide is added to a solution of copper(II) sulfate. Iodine and a white precipitate of copper(I) iodide are formed.

(a) Write an equation for the reaction that occurs.

..... [1]

(b) (i) Explain why the copper(II) sulfate solution is coloured.

.....

.....

.....

.....

..... [4]

(ii) Suggest why the precipitate of copper(I) iodide is white.

.....

..... [1]

(c) Use suitable $E^{\ominus}$ values from the *Data Booklet* to predict whether iodide ions can reduce Cu^{2+} to Cu^{+} under standard conditions. Explain your answer.

.....

.....

..... [2]

(d) An excess of sodium iodide is added to copper(II) sulfate solution. Copper(I) iodide forms as a precipitate. After precipitation, $[Cu^{+}]$ is much lower than $1.0\,mol\,dm^{-3}$.

Use this information and your answer to **(c)** to explain how the relevant electrode potentials change and hence why I^{-} ions can reduce Cu^{2+} ions.

.....

.....

.....

.....

..... [2]

40 Transition elements form complexes.

(a) Molybdenum, Mo, forms an octahedral complex consisting of one Mo atom surrounded by carbon monoxide, CO, molecules. CO is a monodentate ligand. Iron forms an octahedral complex consisting of one Fe^{3+} and a number of cyanide, CN^-, ions. CN^- is a monodentate ligand.

(i) Define the term *monodentate ligand*.

.....

..... [1]

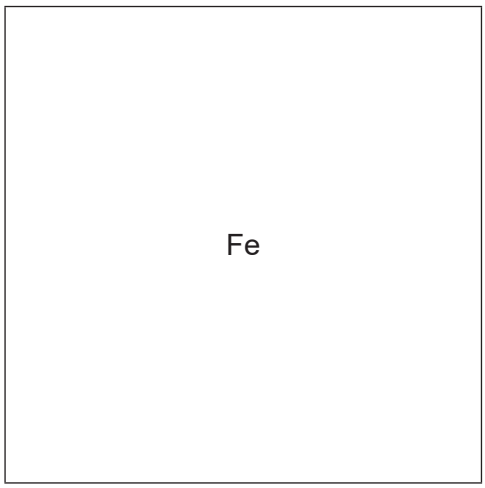
(ii) Complete the table by stating the formulae and charges of the complexes described.

	formula	charge
molybdenum complex		
iron(III) complex		

[2]

(iii) Draw a three-dimensional diagram to show the shape of this iron(III) complex.

Label one 180° bond angle on your diagram.



[1]

(b) An excess of aqueous ammonia is added to dilute copper(II) sulfate solution. A dark blue complex, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, is formed.

(i) Write an ionic equation for this reaction.

..... [1]

.....

.....

.....

.....

.....

..... [4]

(c) An excess of concentrated hydrochloric acid is added to the dark blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. A new complex, **Z**, is formed. The colour of the solution changes.

(i) Write an equation for the formation of **Z** from the solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. Include the formula and charge of **Z**.

..... [2]

(ii) Name the type of reaction when **Z** forms from $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

..... [1]

(iii) State the geometry of **Z**.

..... [1]

(iv) State the colour of a solution of **Z**.

..... [1]

(v) Explain why the colour of a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is different from the colour of a solution of **Z**. You should refer to the energies of the orbitals involved in your answer.

.....

..... [1]

[Total: 15]

41 An excess of aqueous ammonia is added to a solution containing the complex ion $[Co(H_2O)_6]^{2+}$.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

(a) Complete the sentence to describe the colour change that will be seen during this reaction.

The colour changes from ..... to ..... . [1]

(b) Write an expression for the stability constant, K_{stab}, of $[Co(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(c) The numerical value of K_{stab} of $[Co(NH_3)_6]^{2+}$ is 7.7×10^4.

What deduction about the properties of $[Co(NH_3)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ can be made from this K_{stab} value?

..... [1]

(d) Oxygen can oxidise $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ under standard conditions in alkaline solutions.

$$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+} \qquad E^\ominus = +0.10\,V$$

(i) Use this information and the *Data Booklet* to calculate the $E^\ominus_{cell}$ value for this oxidation of $[Co(NH_3)_6]^{2+}$.

.....

.....

$E^\ominus_{cell}$ = ... V
[1]

(ii) Write an ionic equation for this oxidation of $[Co(NH_3)_6]^{2+}$.

..... [1]

(iii) Predict, by selecting suitable data from the *Data Booklet*, whether oxygen can oxidise $Co^{2+}(aq)$ in **acidic** solution, in the absence of ammonia. Explain your answer.

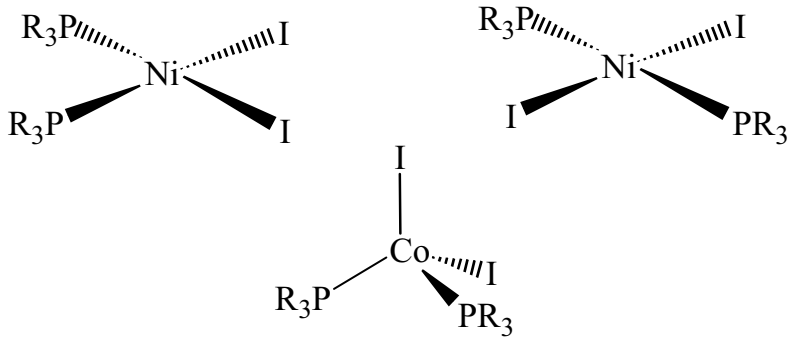
.....

..... [2]

<table>
<tr><th>Question</th><th>point</th><th>Marks</th></tr>
<tr><td>1 (a)</td><td>forms (one or more) ions
with incomplete d orbital(s)/sub-shells/shells</td><td>1</td></tr>
<tr><td>(b) (i)</td><td>dative (covalent) or co-ordinate</td><td>1</td></tr>
<tr><td>(ii)</td><td>
<table>
<tr><td>species</td><td>can act as a ligand</td><td>cannot act as a ligand</td></tr>
<tr><td>NO_3^-</td><td>✓</td><td></td></tr>
<tr><td>BF_3</td><td></td><td>✓</td></tr>
<tr><td>$H_2NCH_2CH_2NH_2$</td><td>✓</td><td></td></tr>
<tr><td>NH_4^+</td><td></td><td>✓</td></tr>
</table>
</td><td>2</td></tr>
<tr><td>(c) (i)</td><td>
<table>
<tr><th></th><th>formula of manganese species formed</th><th>type of reaction</th></tr>
<tr><td>$Mn^{2+}(aq)$ + NaOH (aq)</td><td>$Mn(OH)_2$
$Mn(H_2O)_4(OH)_2$

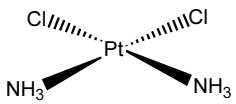
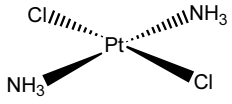
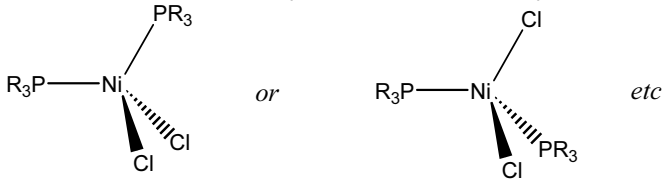
$Mn(OH)_3$</td><td>precipitation</td></tr>
<tr><td>$Mn^{2+}(aq)$ + concentrated HCl</td><td>$MnCl_4^{2-}$
$MnCl_6^{4-}$</td><td>ligand exchange / substitution</td></tr>
<tr><td>$Mn^{2+}(aq)$ + aqueous H_2O_2</td><td>Mn^{3+}</td><td>redox / oxidation</td></tr>
</table>
</td><td>5</td></tr>
<tr><td></td><td></td><td><u>9</u></td></tr>
</table>

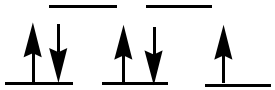
<table>
<tr><td>2 (a)</td><td>Co $3s^2 3p^6 3d^7 4s^2$ [1]
Co^{3+} $3s^2 3p^6 3d^6$ [1]</td><td>2</td><td></td></tr>
<tr><td>(b) (i)</td><td>atom or ion, bonded to (one or more), ligands</td><td>1</td><td></td></tr>
<tr><td>(ii)</td><td>any two from:
two (or more) oxidation states,
catalytic activity,
coloured ions or compounds</td><td>2</td><td></td></tr>
<tr><td>(c)</td><td>
<table>
<tr><th></th><th>transition element species formed</th><th>type of reaction</th></tr>
<tr><td>$Co^{2+}(aq)$ + an excess of $NH_3(aq)$</td><td>$[Co(NH_3)_6]^{2+}$ or
$[Co(NH_3)_4]^{2+}$ or
$[Co(NH_3)_4(H_2O)_2]^{2+}$</td><td>ligand exchange</td></tr>
<tr><td>$Co^{2+}(aq)$ + $OH^-(aq)$</td><td>$Co(OH)_2$ or
$Co(OH)_2(H_2O)_4$</td><td>precipitation or
acid-base</td></tr>
<tr><td>$Co^{2+}(aq)$ + $S_2O_8^{2-}(aq)$</td><td>$[Co(H_2O)_6]^{3+}$ or
Co^{3+} or
$Co_2(SO_4)_3$</td><td>redox or
oxidation or
reduction of $S_2O_8^{2-}$</td></tr>
</table>
</td><td>5</td><td></td></tr>
<tr><td>(d) (i)</td><td>Y 13.4 / 88.9 or 0.15 Ba 41.2 / 137 or 0.3 Cu 28.6 / 63.5 or 0.45 O 16.8 / 16 or 1</td><td>1</td><td></td></tr>
<tr><td>(ii)</td><td>= 7 / 3 or (+) 2.3</td><td>1</td><td></td></tr>
<tr><td>(iii)</td><td>two Cu are + 2 and one Cu is + 3</td><td>1</td><td></td></tr>
<tr><td></td><td></td><td></td><td>[Total: 13]</td></tr>
</table>

3 (a) (i)	Co: ...$3s^2 3p^6 3d^7 4s^2$ Co^{2+}: ...$3s^2 3p^6 3d^7$	[1]
(ii)	solution starts pink turns blue pink is $[Co(H_2O)_6]^{2+}$ blue is $[CoCl_4]^{2-}$ this complex is tetrahedral	[1] [1] [1] [1] [1]
(b)		[1] [1] [1]

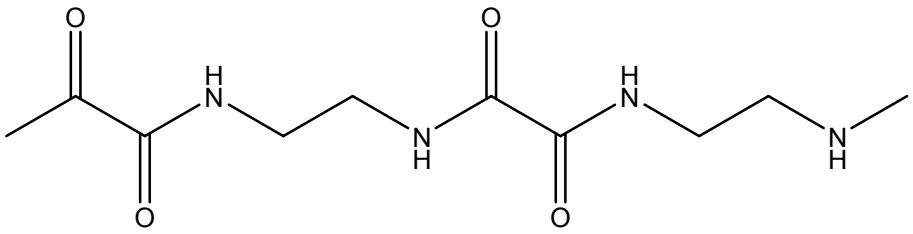
P41/M/J/16/Q8b

(4) (i)	*cis–trans* OR geometrical	[1]
(ii)	in a complex the d–orbitals are split into 2 energy levels colour is due to absorption of light (in visible region) electron promotion to higher orbital absorbs a photon the d–d energy gap is different for the two complexes, hence different colours	[1] [1] [1] [1]

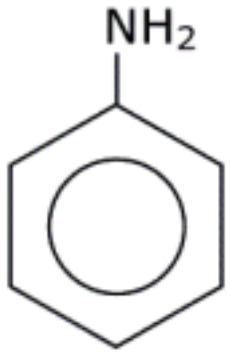
Question	P42/M/J/16/Q410	Marks
5 (a) (i)	 (cis)  (trans)	2
(ii)	***cis*** is (more) **polar** due to both $Cl^{(\delta-)}$ on same side **or** ***cis*** is (more) **polar** as dipoles do not cancel / unsymmetrical **or** **trans** is **non-polar** as it is bond dipoles cancel	1
(iii)	(This can only be *cis*) its mirror image is the same / superimposable **or** the distance between two coordinating nitrogens / oxygens is too small to bond *trans* **or** difficult for the NH_2 and O to change places (since 5-memebered rings can only bridge adjacent positions)	1
(b) (i)	It's not square planar **or** it's tetrahedral	1
(ii)	must be 3D structure (i.e. tetrahedral-like)  *or* *etc*	1
		[Total: 6]

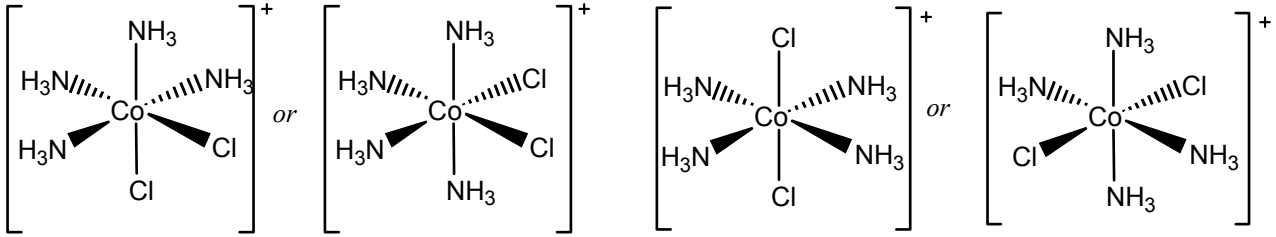
Question	P42/M/J/16/Q1010	Marks
6 (a) (i)	Fe is …$3s^2 3p^6 3d^6 4s^2$	1
(ii)		1
(b)	$E^\ominus$ values: Sn^{4+}/Sn^{2+} = +0.15(V); Fe^{3+}/Fe^{2+} = +0.77(V) **or** $E^\ominus_{cell}$ = +0.62 (V) (Sn^{2+} will reduce Fe^{3+}) $Sn^{2+} + 2Fe^{3+} \rightarrow 2Fe^{2+}$	2
(c) (i)	*essential mark* K_{stab} / stability: $[Fe(H_2O)_5F]^{2+} > [Fe(H_2O)_5SCN]^+$ $(> [Fe(H_2O)_6]^{2+})$ *observations* (violet) → deep-red (deep-red) → colourless (violet) → colourless which stays colourless / does not change	4
(ii)	**ligand** displacement / exchange / substitution	1
		[Total: 9]

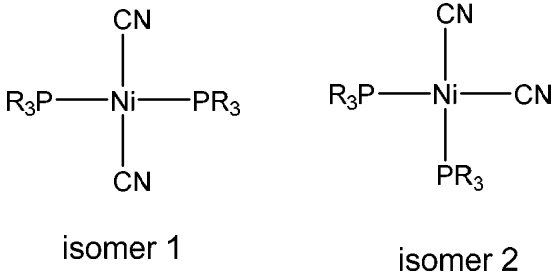
Question	P41/O/N/16/Q1	Mark
7(a)	Cu [Ar] $3d^{10}4s^1$ Cu^{2+} [Ar] $3d^9$ ($4s^o$)	1 1 **2**
7(b)(i)	**ligand** exchange / replacement / displacement / substitution	1 **1**
7(b)(ii)	$[Cu(H_2O)_6]^{2+}$ blue **and** $[CuCl_4]^{2-}$ yellow **OR** yellow / green **OR** green / yellow	1 **1**
7(b)(iii)	tetrahedral	1 **1**
7(b)(iv)	$K_{stab} = [CuCl_4^{2-}] / [Cu(H_2O)_6^{2+}][Cl^-]^4$	1 **1**
7(c)(i)	a species that contains **two lone pairs** that (each) form a co-ordinate / dative bond **OR** are donated (to a metal ion / atom)	1 1 **2**
7(c)(ii)	equilibrium 2 lies more to the RHS / favours forward reaction more	1 **1**
7(d)(i)	**optical**	1 **1**
7(d)(ii)	3D correct for octahedral one correct structure with 3D	1 1

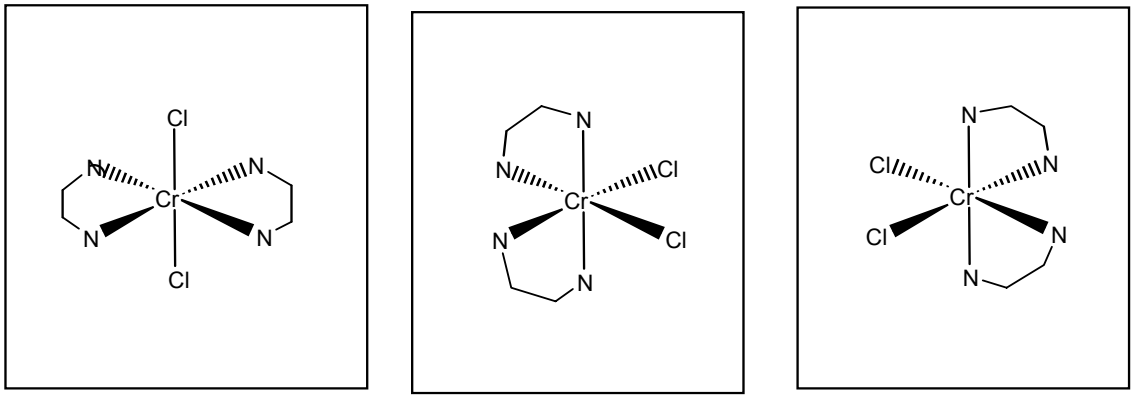
Question	Answer	Mark
		3
7(e)(i)	lone pair receive / accepts a proton / H^+	1 1 2
7(e)(ii)	$H_2NCH_2CH_2NH_2 + 2HCl \rightarrow ClH_3NCH_2CH_2NH_3Cl$ **OR** $H_2NCH_2CH_2NH_2 + 2H^+ \rightarrow H_3N^+CH_2CH_2N^+H_3$	 1 1
7(f)(i)	amide bond, displayed or –CONH– rest of the molecule with continuation bonds 	1 1 2
7(f)(ii)	condensation / addition – elimination	1 1
7(f)(iii)	any named polyalkene / eg polyethene, PVC **allow** Bakelite or Kevlar	1 1
		20

Question	P41/O/N/16/Q4	Mark
8(a)	(an element) forming one or more (stable) **ions** or **compounds** or **oxidation states** with **partially filled / incomplete d orbitals**	1 **1**
8b)(i)	**A** $Co(OH)_2$ **OR** $Co(H_2O)_4(OH)_2$ **B** $[CoCl_4]^{2-}$ **C** $[Co(NH_3)_6]^{2+}$ **OR** $[Co(NH_3)_6]^{3+}$ two correct = 1 mark three correct = 2 marks	 **2**
8(b)(ii)	$_2O)_6]^{2+}$ pink solution of **B** blue solution of **C** brown/yellow/orange	
	two correct = 1 mark three correct = 2 marks	 **2**

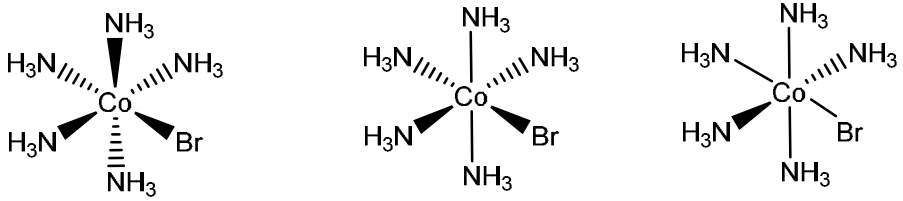
9(d)(i)	*monodentate*: (a species that) forms **one** dative / coordinate bond	**1**
	ligand: a species that uses a lone pair of electrons to form a dative / coordinate bond to **a metal atom / metal ion**	**1**
9(d)(ii)	$[Ag(NCO)_2]^-$ or $[Ag(OCN)_2]^-$ correct formula	**1**
	correct charge	**1**
9(e)(i)	$n(BaCO_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3}$ mol	**1**
9(e)(ii)	$n(RNCO) = 8.41 \times 10^{-3}$ mol, so $M_r = 1 / (8.41 \times 10^{-3})$ = **119**	**1**
9(e)(iii)	molecular formula = C_7H_5NO	**1**
9(e)(iv)		**1**

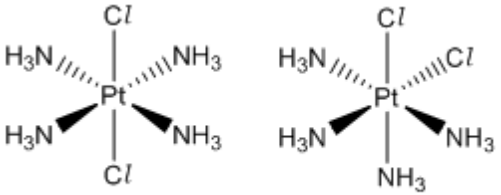
10(a)(ii)	oxidation	**1**
	ligand displacement / replacement / exchange / substitution	**1**
10(a)(iii)	 cis trans	**1 + 1**
	geometrical or cis-trans	**1**
10(b)(i)	The number of bonds / atoms bonded to **an atom / ion / species / metal**	**1**
10(b)(ii)	**C** 6 $[Cr(CN_6]$ – **D** – $[Ni(NH_2CH_2CH_2NH_2)_3]$ 2+/+2 **E** 4 $[Pt\ l_4]$ – **F** 3 – 3–/–3	**6**
10(c)(i)	$K_{stab(1)} = [FeSCN^{2+}]/([Fe^{3+}][SCN^-])$ $mol^{-1}\ dm^3$ $K_{stab(2)} = [FeCl_4^-]/([Fe^{3+}][Cl^-]^4)$ $mol^{-4}\ dm^{12}$	**3**
10(c)(ii)	$K_{eq(3)} = K_{stab(1)} / K_{stab(2)}$	**1**
10(c)(iii)	$K_{eq(3)} = 1750$	**1**

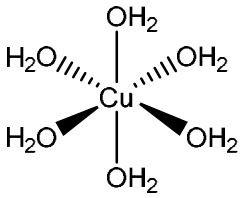
11(a)(i)	M_r = 52 + 6 × 18 + 3 × 35.5 = 266.5	**1**
11(a)(ii)	1.00g = 1 / 266.5 **OR** 3.75 × 10^{-3} moles (of complex in 1g) for **A**, n=2 **AND** $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ for **B**, n=1 **AND** $[Cr(H_2O)_5Cl]Cl_2.H_2O$ for **C**, n=0; **AND** $[Cr(H_2O)_6]Cl_3$	**2**
11(b)(i)	Geometric(al) / cis-trans	**1**
11(b)(ii)		**1**
11(b)(iii)	isomer 2 AND dipoles do not cancel OR CN^- are on the same side of the molecule	**1**
	Total:	**6**

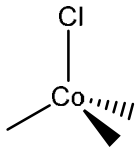
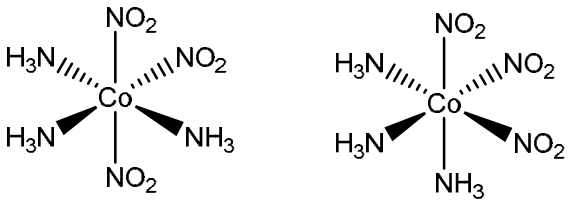
12(a)(i)	*bidentate*: (a species that) forms **two** dative bonds / donates **two** lone pairs	**1**
	ligand: a species that uses a **lone pair** to form a **dative** bond to **a metal atom / metal ion**	**1**
12(a)(ii)	 each structure [1] x 3	**3**
12(b)(i)	$K_{stab1} = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3]^4$	**1**
	$K_{stab2} = [Cu(en)_2^{2+}]/[Cu^{2+}][en]^2$	**1**
	$mol^{-4}\ dm^{12}$ AND $mol^{-2}\ dm^6$	**1**
12(b)(ii)	$K_{eq3} = K_{stab2} / K_{stab1}$	**1**
12(b)(iii)	$K_{eq3} = K_{stab2} / K_{stab1} = 4.4(2) \times 10^6$	**1**
	$mol^2\ dm^{-6}$	**1**
12(c)(i)	(ΔS_{eq1} is negative as) **more / 5** moles of reactants are forming (one mole of) the complex OR (ΔS_{eq2} is positive as) **fewer / 3** moles of reactants are forming (one mole of) the complex	**1**
12(c)(ii)	ΔG = −100 − 298 × 40 / 1000 OR $\Delta G = \Delta H - T\Delta S$	**2** **1**

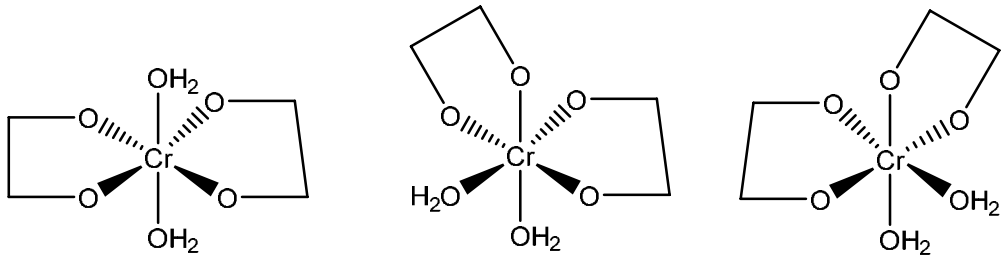
12(c)(iii)	Since (ΔG_{eq2}) is **more** negative (than ΔG_{eq1}) AND equilibrium 2 is more feasible	**1**
12(c)(iv)	$\Delta H_{(3)} = -8$ (kJ mol^{-1})	**1**
12(c)(v)	**ligand** exchange / replacement / substitution / displacement	**1**
	Total:	**17**

	(melting point) due to stronger attraction to cations as more delocalised electrons	**1**
13(b)	(a molecule or ion) formed by a **central** metal **atom / ion** surrounded by (one or more) **ligands**	**1**
13(c)(i)	same number and type of <u>atoms</u> **and** different structural formula	**1**
13(c)(ii)	octahedral **AND** 3D structure of $[Co(NH_3)_5Br]^{2+}$ e.g. 	**1**
13(c)(iii)	co-ordinate / dative covalent	**1**
13(c)(iv)	+3 for **both**	**1**
13(d)	(HNO_3) Ag^+ / $AgNO_3$ cream(–yellow) ppt. (of AgBr) **and** no reaction / white ppt. for other isomer	**1**
	$Ba(OH)_2$ / $Ba^{2+}(aq)$ / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) **and** no reaction for other isomer	**1**
13(e)	(d-d) energy gap / ΔE is different	**1**
	<u>absorb</u> different wavelength / frequency (of light)	**1**
13(f)	<table><tr><th></th><th>heterogeneous</th><th>homogeneous</th></tr><tr><td>Fe in the Haber process</td><td>✓</td><td></td></tr><tr><td>Fe^{2+} in the I^- / $S_2O_8^{2-}$ reaction</td><td></td><td>✓</td></tr><tr><td>NO_x in the oxidation of</td><td></td><td></td></tr></table>	**2**

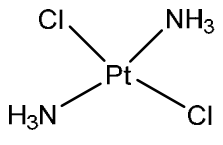
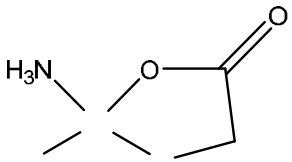
<table>
<tr><td>14(a)</td><td>central metal atom/ion surrounded by (one or more) ligands</td><td>1</td></tr>
<tr><td>14(b)</td><td>
<table>
<tr><td></td><td>co-ordination number</td><td>oxidation number</td></tr>
<tr><td>$[Pt(NH_3)_4Cl_2]^{2+}$</td><td>6</td><td>+4</td></tr>
<tr><td>$[PtCl_4]^{2-}$</td><td>4</td><td>+2</td></tr>
</table>
</td><td>2</td></tr>
<tr><td>14(c)</td><td> 
</td><td>2</td></tr>
<tr><td rowspan="2">14(d)</td><td>$_3$ +) $AgNO_3$ reagent</td><td>1</td></tr>
<tr><td>$[Pt(NH_3)_4Cl_2]Br_2$ with cream ppt. (of AgBr) and $[Pt(NH_3)_4Br_2]Cl_2$, with white ppt. (of AgCl) observation with both</td><td>1</td></tr>
<tr><td rowspan="3">14(e)</td><td>octahedral: both</td><td>1</td></tr>
<tr><td>square planar: geometric</td><td>1</td></tr>
<tr><td>tetrahedral: neither</td><td>1</td></tr>
</table>

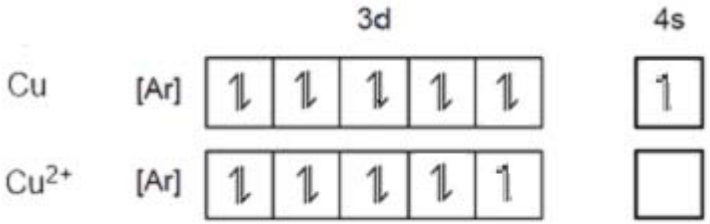
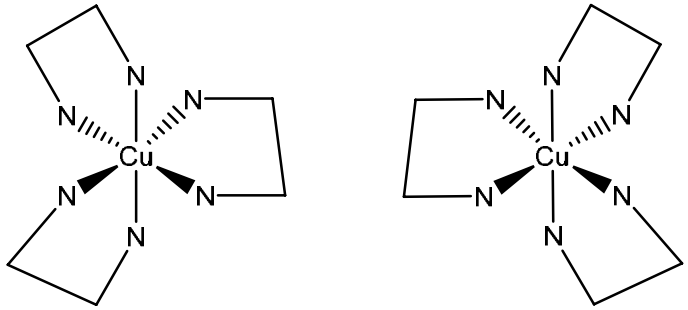
15b)	Cl-Cu-Cl	**1**
	one minus charge	**1**
15(c)		**1**
	octahedral **and** 90° or 180° labelled correctly on diagram as appropriate	**1**
15(d)	reaction 1: blue ppt / blue **solid**	**1**
	$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ or $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ or $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(OH)_2(H_2O)_4 + 2NH_4^+$	**1**
	reaction 2: deep / dark / royal blue solution	**1**
	$Cu(OH)_2 + 4NH_3 + 2H_2O \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$ or $Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$ or $Cu(OH)_2(H_2O)_4 + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$	**1**
15	exchange / displacement / replacement / substitution	**1**
15e)(ii)	$K_{stab} = [[CuEDTA]^{2-}] / [[Cu(H_2O)_6]^{2+}][[EDTA]^{4-}]$	**1**
15(e)(iii)	stable / more stable than $[Cu(H_2O)_6]^{2+}$	**1**
15(f)(i)	donates lone pairs / forms dative / co-ordinate bonds to (central) metal atom / metal ion	**1**
	donates two lone pairs / forms two (dative or coordinate) bonds	**1**

16(b)(ii)	charge is 2–	**1**
		**1**
16(b)(iii)	d-orbitals are split into two groups of orbitals	**1**
	absorption of light	**1**
	an electron is excited / (during) electron promotion (to a higher d-orbital)	**1**
16(b)(iv)	blue light is not absorbed **or** absorb (wavelength / frequency of) red and yellow / orange / green **or** absorbs least in the blue region	**1**
16(c)	(b goes) pink	**1**
	ligand exchange / ligand substitution	**1**
16(d)(i)	F_2 or $S_2O_8^{2-}$	**1**
16(d)(ii)	+1.05 or +0.19	**1**
16(d)(iii)	$2Co^{2+} + F_2 \rightarrow 2Co^{3+} + 2F^-$ **or** $2Co^{2+} + S_2O_8^{2-} \rightarrow 2Co^{3+} + 2SO_4^{2-}$	**1**
16e)		**1**

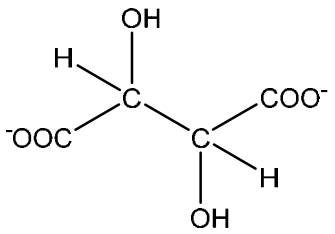
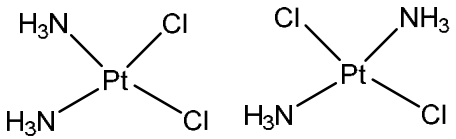
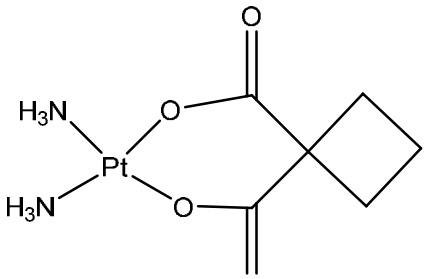
17(a)	species that forms **dative bond**(s) to a (central) **metal atom / ion**	**1**
17(b)	 any two structures [1] × 2	**2**
17(c)(i)	$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ [1] units $mol^2\ dm^{-6}$ [1]	**2**
17(c)(ii)	$[Ca^{2+}] = [C_2O_4^{2-}] = 6.65 \times 10^{-3}/128.1 = 5.19 \times 10^{-5}\ mol\ dm^{-3}$ [1] $K_{sp} = (5.19 \times 10^{-5})^2$ = **2.7×10^{-9}** $mol^2\ dm^{-6}$ [1]	**2**

18(a)	[1] for each column number of unpaired electrons in element / 3d / Cr / 5 / 1 Mn / 5 / 0 Fe / 4 / 0	**2**
18(b)	$2KMnO_4 \rightarrow K_2MnO_4 + O_2 + MnO_2$ formulae of K_2MnO_4 and O_2 [1] rest of the equation [1]	**2**
18(c)	**M1 d** orbitals split into two levels / lower and upper orbitals [1] **M2** visible light is **absorbed** and the complementary colour observed [1] **M3 electron**(s) promoted / excited [1]	**3**
18(d)(i)	precipitate **A** $[Cu(H_2O)_4(OH)_2]$ **OR** $Cu(OH)_2$ [1] solution **B** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [1] solution **C** $Cu(CH_3CO_2)_2$ [1]	**3**
18(d)(ii)	Na_2CO_3 **or** CO_3^{2-}	**1**
18(d)(iii)	$CuCO_3 + 2CH_3CO_2H \rightarrow Cu(CH_3CO_2)_2 + CO_2 + H_2O$	**1**
18(d)(iv)	any **two** for one mark • fizzing / bubbles / effervescence • solid **disappears** • green / blue solution (formed)	**1**

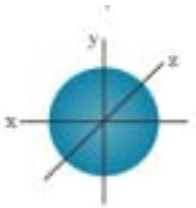
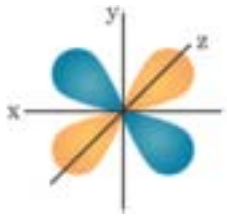
18(e)	sum of the charges of the (four) ligands equals the oxidation number / charge of Pt **OR** a calculation Pt +2, NH_3 neutral / no charge, both Cl^-'s –1 (so no overall charge)	**1**
18(f)(i)	 [1] square planar **and** 180° [1]	**2**
18(f)(ii)	**M1** this can **bond / bind** with **DNA** [1] **M2** which prevents replication of the DNA / strand **OR** prevents cell division [1]	**2**
18(g)		**1**

19(a)	 [1] × 2	**2**
19(b)(i)	orbitals have the same energy	**1**
19(b)(ii)	d-d splitting seen, leading to 2 upper and 3 lower orbitals	**1**
19(c)	an ion / molecule that donates two pairs of electrons	**1**
19(d)	 one correct [1] two correct and mirror images of each other [1]	**2**

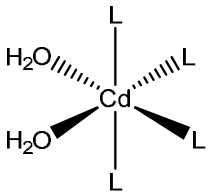
Question	P42/O/N/18/Q3	Marks
20(a)(i)	so of **A** $[Co(NH_3)_6]^{2+}$ [1] precipitate **B** $CoCO_3$ [1]	**2**
20(a)(ii)	NaOH(aq) / OH^-(aq)	**1**

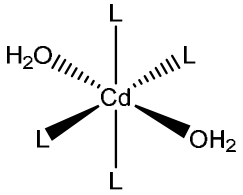
20 (a)(iv)	$[Co(H_2O)_6]^{2+} + CO_3^{2-} \rightarrow CoCO_3 + 6H_2O$	**1**
20(b)(i)	variable oxidation states	**1**
20(b)(ii)		**1**
20(b)(iii)	$C_4H_4O_6^{2-} + 3[O] \rightarrow 2HCO_2^- + 2CO_2 + H_2O$	**1**
20(c)(i)	 cis trans square planar shape of one isomer [1] both isomers drawn and assigned as cis and trans correctly [1]	**2**
20(c)(ii)	this can react / bond / bind with <u>DNA</u> [1] which prevents replication of the strand / prevents cell division / prevents mitosis [1]	**2**
20(d)		**1**

21(a)	**M1**	$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$	**6**
	M2	precipitation	
	M3	blue precipitate	
	M4	$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow CuCl_4^{2-} + 6H_2O$	
	M5	**ligand** exchange / displacement / substitution / replacement	
	M6	yellow solution	
21(b)	**M1**	amount of $Ag^+ = 0.050 \times 0.0224 = 1.12 \times 10^{-3}$ mol (in 25 cm^3) amount of $Ag^+ = 1.12 \times 10^{-3} \times 4$ = **4.48×10^{-3} mol (in 100 cm^3)**	**3**
	M2	amount of Cl^- = 4.48×10^{-3} mol (in 100 cm^3) mass of Cl^- = $4.48 \times 10^{-3} \times 35.5$ = 0.159 g (in 100 cm^3) mass of S = 0.303 – 0.159 = **0.144 g (in 100 cm^3)** ecf	
	M3	moles of S = 0.144 / 32.1 = 4.49×10^{-3} molar ratio S : Cl 1:1 → **SCl** ecf	

<table>
<tr><td>22(a)</td><td>
<table>
<tr><td> 
</td><td> 
</td><td> 
</td></tr>
<tr><td>p</td><td></td><td>d</td></tr>
</table>
All shapes required for mark
</td><td>1</td></tr>
<tr><td>22(b)</td><td>both cadmium ions have full d subshells</td><td>1</td></tr>
<tr><td>22(c)(i)</td><td>donates one lone pair to the central metal ion</td><td>1</td></tr>
<tr><td>22(c)(ii)</td><td>M1 one 3D diagram of $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$

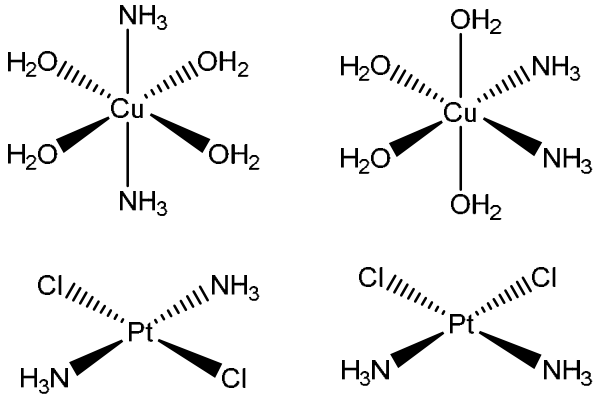
M2 cis and trans structures

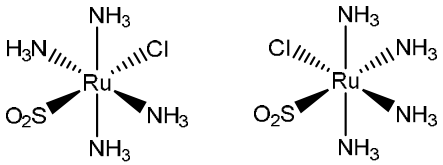
 


</td><td>2</td></tr>
<tr><td>22(d)(i)</td><td>equilibrium constant for the formation of a complex ion in solution / solvent [1]</td><td>1</td></tr>
</table>

<table>
<tr><td>22(d)(ii)</td><td>
<table>
<tr><td></td><td>decreases</td><td>no change</td><td>increases</td></tr>
<tr><td>K_{stab}</td><td>✓</td><td></td><td></td></tr>
<tr><td>$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$</td><td>✓</td><td></td><td></td></tr>
</table>
M1 both ticks correct [1]
M2 equilibrium moves to the left as the (forward) reaction is exothermic [1]</td><td>2</td></tr>
<tr><td>22(d)(iii)</td><td>$[CdEDTA]^{2-}$ and larger K_{stab} value</td><td>1</td></tr>
<tr><td>22(e)</td><td>$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$</td><td>1</td></tr>
<tr><td>22(f)(i)</td><td>$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$
M1 Correct formulae of CH_3COCl or $CH_3CONHCH_3$
M2 rest of the equation</td><td>2</td></tr>
<tr><td>22(f)(ii)</td><td>condensation or addition-elimination</td><td>1</td></tr>
</table>

23(a)(i)	$3s^2 3p^6 3d^9$ [1]	**1**
23(a)(ii)	$[Cu(H_2O)_6]^{2+}$ (pale) blue $CuCl_4^{2-}$ yellow **both** [1]	**1**
23(a)(iii)	M1 energy gap/ΔE is **different** (for the ligands) [1] M2 different frequency / wavelength of light **absorbed / transmitted / reflected** [1]	**2**
23(b)	(Cu^+/Ag^+) d-shell is full / complete **OR** d-orbital**s** are full [1] M2 no electrons can be promoted [1]	**2**
23(c)(i)	solubility = $\sqrt{5.0 \times 10^{-13}}$ = **7.1 × 10^{-7}** (mol dm^{-3}) [1] min 2sf	**1**
23(c)(ii)	M1 (in conc. NH_3) [NH_3] increases **and** equilibrium 2 shifts to the right [1] M2 [Ag^+] decreases **and** equilibrium **1** shifts to the right [1]	**2**
23(c)(iii)	$AgBr + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Br^-$ [1]	**1**
23(c)(iv)	$K_{eq3} = K_{sp} \times K_{stab}$ [1] **ALLOW** $K_{eq3} = [Ag(NH_3)_2^+][Br^-]/[NH_3]^2$	**1**

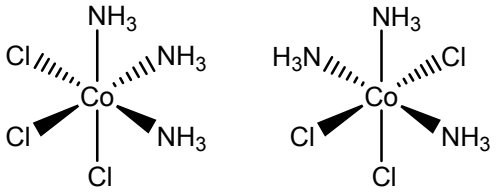
24(b)(i)	(elements) forming one or more (stable) **ions** with incomplete / partially filled **d** orbital(s) / sub-shell [1]	**1**
24(b)(ii)	dative covalent / coordinate [1]	**1**
24c)	FeO and +2 Fe_2O_3 and +3 all [1] **ALLOW** Fe_3O_4 and +3 and +2	**1**
24(d)	<table><tr><th>metal ion</th><th>ligand</th><th>co-ordination number</th><th>formula of complex ion</th><th>charge of complex ion</th></tr><tr><td>Ni^{2+}</td><td>CO</td><td>4</td><td>**$Ni(CO)_4$**</td><td>**2+**</td></tr><tr><td>Fe^{3+}</td><td>CN^-</td><td>**6**</td><td>**$Fe(CN_6$**</td><td>3-</td></tr></table> mark as • ✓ • ✓ [2]	**2**
3(e)(i)	cis isomerism [1] **ALLOW** geometric(al)	**1**
24(e)(ii)	 one correct pair [1] two correct pairs [2]	**2**
24(f)(i)	$[Cu(H_2O)_4(NH_3)_2]^{2+}$	**2**

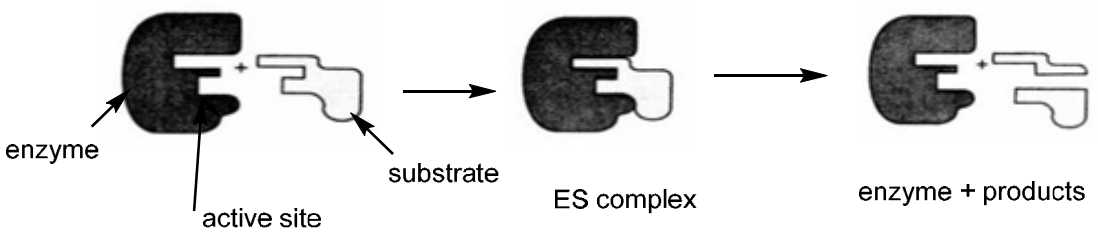
25(b)(i)	purple to pale pink / colourless **AND** orange to green	**1**
25(b)(ii)	$3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$	**1**
25(c)(i)	• six • coordinate bonds / dative bonds / lone pairs donated • to the (central) metal ion award 1 mark for all three points	**1**
25(c)(ii)	$[Ru(NH_3)_4Cl(SO_2)]^+$	**1**
25(c)(iii)	 **M1:** six correct ligands around Ru, bonds are shown from S of SO_2 **M2:** 3-D bonds used correctly for octahedral **M3:** cis and trans isomers shown	**3**
25(c)(iv)	cis-trans or geometric(al) [1]	**1**
25(c)(v)	**M1:** complexes have two sets of **d orbital(s)** of different energy **OR d-orbitals** splits into two sets (of orbitals) **M2:** visible light **absorbed** (and complementary colour observed) **M3**: **electron**(s) promoted / excited **OR electron**(s) moves to higher (d–) orbital	**3**

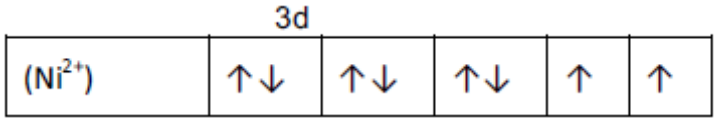
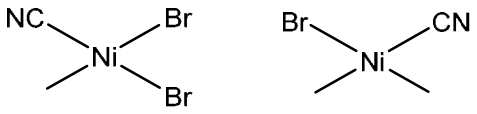
<table>
<tr><td>26(a)</td><td>donates one pair of electrons / forms one coordinate bond</td><td>1</td></tr>
<tr><td>26(b)</td><td>
<table>
<tr><th>Reagent added to a solution of $CuSO_4(aq)$</th><th>Observations</th><th>Formula of the copper(II) compound or complex ion that is formed</th></tr>
<tr><td>a few drops of dilute ammonia</td><td>blue ppt</td><td>$Cu(OH)_2$ or $Cu(OH)_2(H_2O)_4$</td></tr>
<tr><td>an excess of dilute ammonia</td><td>deep blue solution</td><td>$[Cu(NH_3)_4]^{2+}$ or
$[Cu(NH_3)_4(H_2O)_2]^{2+}$</td></tr>
<tr><td>an excess of aqueous sodium hydroxide</td><td>blue ppt</td><td>$Cu(OH)_2$ or $Cu(OH)_2(H_2O)_4$</td></tr>
<tr><td>an excess of conc HCl.</td><td>green-yellow /
yellow-green / yellow</td><td>$[CuCl_4]^{2-}$</td></tr>
</table>
Award 1 mark for each correct observation and formula in a row of the table.</td><td>4</td></tr>
<tr><td>26(c)</td><td>• ligand exchange
• magnitude of d-orbital splitting changes / ΔE for d-orbitals changes / energy gap between d-orbitals changes
• change in colour / frequency / wavelength of light absorbed
• electrons are promoted/excited to higher d

Award 1 mark for two points, award 2 marks for three points, award 3 marks for all four points</td><td>3</td></tr>
<tr><td>26(d)</td><td>M1: E^o values 1.36 and 0.77 quoted

M2: $2FeSO_4 + Cl_2 \rightarrow Fe_2(SO_4)_2Cl_2$ or $2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$</td><td>2</td></tr>
<tr><td>26(e)(i)</td><td>$[[FeCl_4]^-] / [[Fe(H_2O)_6]^{3+}][Cl^-]^4$</td><td>1</td></tr>
<tr><td>26(e)(ii)</td><td>0.078(125)</td><td>1</td></tr>
</table>

27(a)(ii)	M1: blue ppt/solid M2: $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ **OR** $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$ M3: precipitation/ acid-base M4: blue solution M5: $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ M6: **ligand** exchange/displacement/substitution/replacement	**6**
27(b)	• solution turns blue → pink • a white ppt. of AgC*l* forms • equilibrium shifts to the left / $[Cl^-]$ decreases Two correct responses = 1 mark Three correct responses = 2 marks	**2**
27(c)	 geometric **ALLOW** cis-trans Two correct responses = 1 mark Three correct responses = 2 marks	**2**
27(d)(i)	**each nitrogen** / the four nitrogen's has a **lone pair of electrons** (to the metal ion) Two correct responses = 1 mark	**1**
27(d)(ii)	$[Co(H_2O)_6]^{2+} + C_6H_{18}N_4 \rightarrow [Co(C_6H_{18}N_4)]^{2+} + 6H_2O$ **OR** $[Co(H_2O)_6]^{2+} + C_6H_{18}N_4 \rightarrow [Co(C_6H_{18}N_4)(H_2O)_2]^{2+} + 4H_2O$	**1**

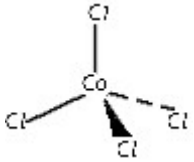
Question	P41/M/J/20/Q10	Marks
28(a)	+4 **and** any of +1, +2, +3	**1**
28(b)	close similarity of energy of the 4s and 3d sub-shells	**1**
28(c)	diagrams  M1 (can be in words or diagram) substrate shape is complementary to active site M2 (can be in words or diagram) the substrate bind / bonds / fits into the active site M3 (can be in words or diagram) products are released M4 (words) lower E_A / bonds weakened (in substrate) Any three points	**3**

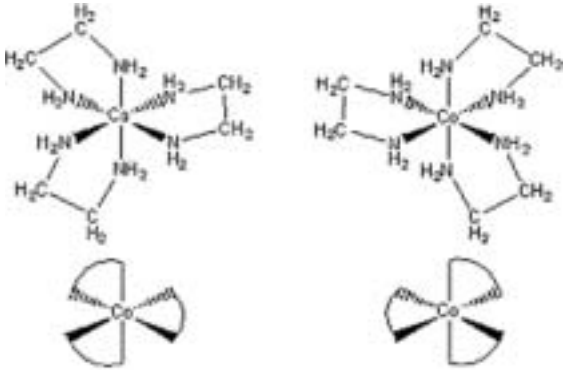
29(a)		**1**
29(b)	**M1** **d** orbitals **split** into **two levels/** lower and upper orbitals **M2** **electron**(s) promoted / excited to a higher d–orbital **M3** frequency of light **absorbed** **M4** observed colour is complement of light absorbed	**4**
29(c)(i)	(addition of NH_3) increases $[OH^-]$ (due to ionisation of NH_3 in water) and shifts equilibrium 1 to the right (forming $Ni(OH)_2$)	**1**
29(c)(ii)	(a large excess of NH_3) shifts eqm 2 to the right (forming $[Ni(NH_3)_6]^{2+}$) **AND** the $[Ni^{2+}]/[[Ni(H_2O)_6]^{2+}]$ decreases and eqm 1 shifts to the left (causing the ppt to dissolve)	**1**
29(d)	**M1** two correct structures cis & trans for $[NiBr_2(CN)_2]^{2-}$  **M2** type of stereoisomerism: cis-trans/geometric	**2**

<table>
<tr><td>30(a)(i)</td><td>Kstab = $[(Cu(NH_3)_4)^{2+}] / [(Cu(H_2O)_6)^{2+}] [NH_3]^4$ [1]</td><td>1</td></tr>
<tr><td>30(a)(ii)</td><td>deep / dark / royal blue [1]</td><td>1</td></tr>
<tr><td>30(b)</td><td>[C $_3)_4]^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+ + 2NH_3$ [1]
OR $[Cu(NH_3)_4]^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + 4NH_3$</td><td>1</td></tr>
<tr><td>30(c)</td><td>$Cu(OH)_2 + 4HCl \rightarrow [CuCl_4]^{2-} + 2H_2O + 2H^+$
OR $Cu(OH)_2 + 4Cl^- + 2H^+ \rightarrow [CuCl_4]^{2-} + 2H_2O$

$[CuCl_4]^{2-}$ complex including charge [1]
rest of equation fully correct [1]</td><td>2</td></tr>
<tr><td>30(d)</td><td><table><tr><td></td><td>Y</td><td>Z</td></tr><tr><td>colour of complex</td><td>yellow</td><td>blue / pale blue</td></tr><tr><td>geometry of complex</td><td>tetrahedral</td><td>octahedral</td></tr><tr><td>formula of complex</td><td></td><td>$[Cu(H_2O)_6]^{2+}$</td></tr></table>
one mark for any <u>three</u> cells [1] • • ✓
two marks for all five cells [2] • • ✓ • ✓</td><td>2</td></tr>
<tr><td>30(e)</td><td>M1: d orbitals splits into two sets of energy levels of different energy [1]
M2: wavelength / frequency / light / photon / hν absorbed [1]
M3: electron(s) promoted / excited [1]
M4: colour seen is complementary (to colour absorbed) [1]
M5: d–d energy gap / ΔE is different for Y and Z
AND so different frequency / wavelength of light <u>absorbed</u> • ✓ [1]</td><td>5</td></tr>
</table>

31(a)(i)	(a species) that donates <u>one</u> lone pair [1] to form a dative / coordinate to a central metal atom / metal ion [1]	**2**
31(a)(ii)	$[Ag(S_2O_3)_2]^{3-}$ [1]	**1**
31(b)(i)	$[Ag(S_2O_3)_2]^{3-} + 2CN^- \rightarrow [Ag(CN)_2]^- + 2S_2O_3^{2-}$ [1] **OR** $Ag(S_2O_3)_2]^{3-} + 2NaCN \rightarrow [Ag(CN)_2]^- + Na_2S_2O_3 + S_2O_3^{2-}$	**1**
31(b)(ii)	**Q** is more stable / has a larger K_{stab} than **P** [1]	**1**
31(b)(iii)	**ligand** exchange / displacement / substitution	**1**
31(c)(i)	 both correct [1]	**1**
31(c)(ii)	**square planar** [1]	**1**
31c)(iii)	cis-trans **OR** geometric(al) [1]	**1**

32(a)	(element forming) • one or more stable ions with **AND** • incomplete / partially filled d-orbitals / d-subshell [1]	**1**
32(b)(i)	$(1s^2)\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ (4s^o)$ [1]	**1**
32(b)(ii)	chromium and manganese [1]	**1**
32(c)(i)	 [1] 2– (charge) [1]	**2**
32(c)(ii)	ligand exchange / substitution / replacement / displacement [1]	**1**
32(c)(iii)	**M1** (complexes have two sets of) **d orbital(s)** of different energy **OR d** orbital(s)/d (sub)-shell splits **OR (**inferred from a movement of an electron) from a **lower d** to **higher d orbital** [1] **M2** wavelength / frequency / light / photon / hn **absorbed** **OR** radiation / energy from visible (region) **absorbed** [1] **M3 electron**(s) promoted / excited **OR electron**(s) moves to higher (d-) orbital **OR electron**(s) jumps up (to d-orbital) / jumps to higher (d-orbital) [1] **M4** colour seen is complementary (to colour absorbed) **OR** colour / light not absorbed is transmitted / reflected [1]	**4**
32(c)(iv)	The gap between the d-orbitals / ΔE is different [1] wavelength (**OR** photon**,** frequency) absorbed is different / changed etc 1]	**2**

32(d)(ii)	 [2]	**2**
32(d)(iii)	optical [1]	**1**
32(d)(iv)	six [1]	**1**
32(e)(i)	$[[Hg(CN)_4]^{2-}] / [Hg^{2+}][CN^-]^4$ or $[Hg(CN)_4{}^{2-}] / [Hg^{2+}][CN^-]^4$ [1]	**1**
32(e)(ii)	concentration: highest $[Hg(CN)_4]^{2-}$ lowest $[HgCl_4]^{2-}$ [1] K_{stab} value: highest $[Hg(CN)_4]^{2-}$ lowest $[HgCl_4]^{2-}$ **OR** stability: highest $[Hg(CN)_4]^{2-}$ lowest $[HgCl_4]^{2-}$ [1]	**2**

OR (inferred from a movement of an electron) from a lower d to higher d orbital

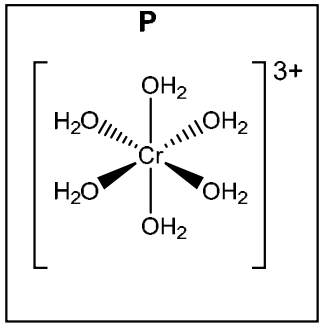
M2: electron(s) promoted / excited
OR electron(s) moves to higher (d–)orbital
OR electron(s) jumps up (to d–orbital) / jumps to higher (d–orbital)

M3: wavelength / frequency / light / photon / hν absorbed
OR radiation / energy from visible (region) absorbed

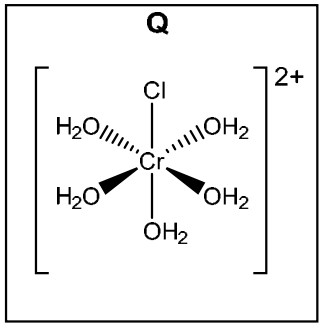
M4: colour seen is complementary (to colour absorbed)
OR wavelength / frequency / colour / light not absorbed is transmitted / reflected / seen

33(b)(i)

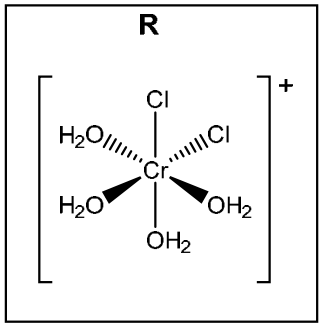
P



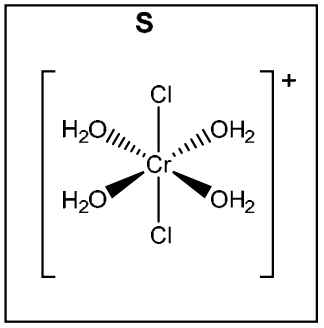
Q



R

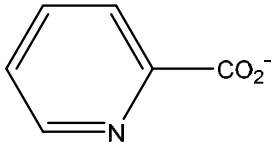


S

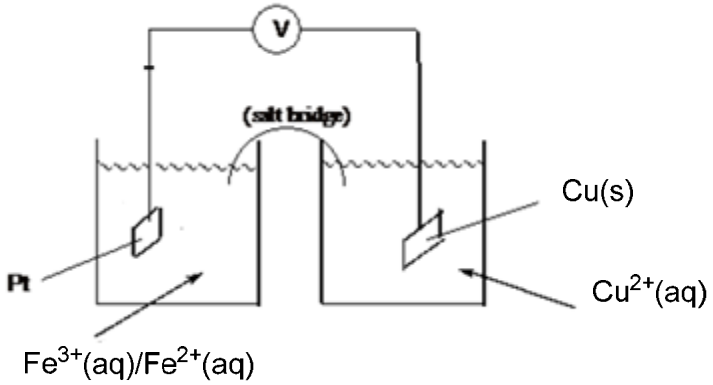


M1: All charges

4

33(b)(ii)	dipoles cancel	**1**
33c)(i)	**M1:** (a species) that donates <u>two</u> lone pairs / forms two coordinate bonds / two dative bonds **M2:** to a metal atom / metal ion	**2**
33(c)(ii)	 structure of the picolinate anion ligand	**1**
33(c)(iii)	(coordination number) six **AND** (geometry around Cr) octahedral	**1**
33(d)(i)	$(NH_4)_2Cr_2O_7$ +6 Cr_2O_3 +3	**1**
33(d)(ii)	$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$	**1**

Question	P41/M/J/21/Q3abcd2	Marks
34(a)(i)	(an element) forming stable ion / ions / compound(s) / oxidation state(s) **AND** with partially filled / incomplete **AND** d orbitals / d subshell / d shell	**1**
34(a)(ii)	(melting point) higher **AND** (density) higher	**1**
34(b)(i)	**M1:** emf / potential difference / difference in electrode potential between two half-cells / two electrodes (in a cell) **M2**	**2**

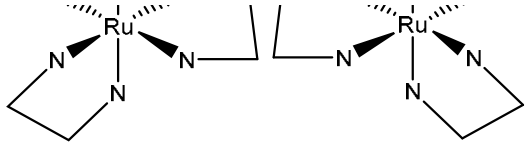
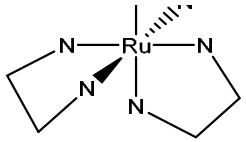
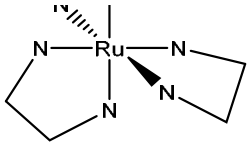
34(b)(ii)	salt bridge, voltmeter, Cu(s), $Cu^{2+}(aq)$, Pt(s), Fe^{2+} and $Fe^{3+}(aq)$ two for one mark, four for two marks, six for three marks  	**3**
34(c)(i)	**M1:** $2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$ **M2:** $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	**2**
34(c)(ii)	**M1:** I_2 / I^- +0.54 V **AND** Fe^{3+} / Fe^{2+} + 0.77 V **AND** $[Fe(CN)_6]^{3-} / [Fe(CN)_6]^{4-}$ +0.36 V **M2:** $E^\ominus$ of I_2 / I^- is more positive / greater than $E^\ominus$ of $[Fe(CN)_6]^{3-} / [Fe(CN)_6]^{4-}$ **OR** $E^\ominus_{cell}$ = –0.18 V so no reaction occurs **OR** $E^\ominus$ of Fe^{3+} / Fe^{2+} is more positive / greater than $E^\ominus$ of I_2 / I^- **OR** $E^\ominus_{cell}$ = 0.23 V so reaction occurs [1]	**2**
34(d)(i)	$S_2O_8^{2-}$ and tartrate ions are both negatively charged / both reactants same charge **AND** so repel each other **OR** have a high E_a	**1**
34(d)(ii)	$C_4H_4O_6^{2-} + 2H_2O \rightleftharpoons 2CO_2 + 2HCO_2^- + 6H^+ + 6e^-$	**1**

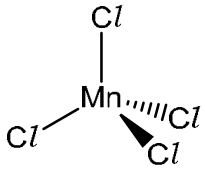
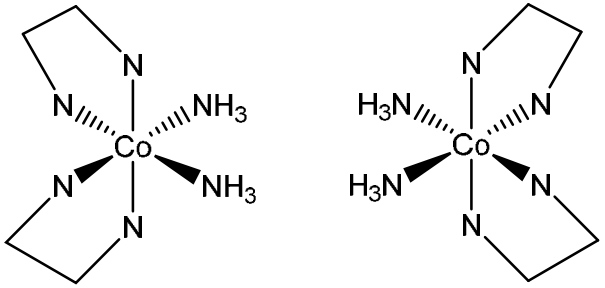
35(a)(i)	**M1:** blue solid / blue ppt **M2:** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ **OR** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ **M3:** precipitation / acid-base	**3**
35(a)(ii)	**M1:** dark blue solution / deep blue solution **M2:** $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ **M3:** ligand exchange / substitution / displacement / replacement	**3**
35(b)	**M1:** **X** $CuSO_4$ and **Y** Cu **M2:** *type of reaction* = redox / disproportionation	**2**

<table>
<tr><td>36(a)(i)</td><td>[1s²] 2s²2p⁶3s²3p⁶3d⁵</td><td>1</td></tr>
<tr><td>36(a)(ii)</td><td>(a molecule or ion formed by a central) metal atom/ion surrounded by / bonded to one or more ligands</td><td>1</td></tr>
<tr><td>36(b)</td><td>
<table>
<tr><th>$[Cr(H_2O)_6]^{3+}$(aq)</th><th>formula of chromium species formed</th><th>type of reaction</th></tr>
<tr><td>+ NaOH(aq)</td><td>$Cr(OH)_3$ or $Cr(OH)_3(H_2O)_3$</td><td>precipitation</td></tr>
<tr><td>+ H_2O_2(aq)</td><td>$Cr_2O_7^{2-}$ / CrO_4^{2-}</td><td>redox / oxidation</td></tr>
<tr><td>+ excess NH_3(aq)</td><td>$Cr(NH_3)_6^{3+}$</td><td>ligand substitution</td></tr>
</table>
chromium species: one mark for each correct species
type of reaction: two correct for one mark and three correct for two marks</td><td>5</td></tr>
<tr><td>36(c)</td><td>M1: ΔE is different OR energy gap between d-orbitals is different

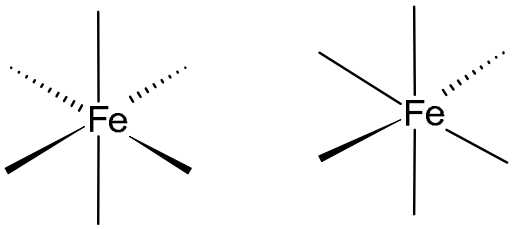
M2: different frequency / wavelength is absorbed
OR different energy / light in visible region is absorbed</td><td>2</td></tr>
<tr><td>36(d)(i)</td><td>ethanoate ions are bidentate whereas as H_2O are monodentate
OR ethanoate ions form two dative bonds whereas H_2O forms one (dative) bond
OR ethanoate ions donate two lone pairs whereas H_2O donates one (lone) pair</td><td>1</td></tr>
<tr><td>36(d)(ii)</td><td>(coordination number) six AND (geometry around Cr) octahedral</td><td>1</td></tr>
<tr><td>36(d)(iii)</td><td>coordinate / (dative) covalent</td><td>1</td></tr>
<tr><td>36(e)(i)</td><td>$4Cr^{2+} + O_2 + 4H^+ \rightarrow 4Cr^{3+} + 2H_2O$ OR $2Cr^{2+} + O_2 + 2H^+ \rightarrow 2Cr^{3+} + H_2O_2$

M1: correct species
M2: balancing</td><td>2</td></tr>
<tr><td>36(e)(ii)</td><td>E°_{cell} = 1.23 – (–0.41) = (+)1.64 V OR E°_{cell} = 0.68 – (–0.41) = (+)1.09 V
value linked to (e)(i)</td><td>1</td></tr>
</table>

	 **OR**   **M1 / M2:** two 3D isomers of $[Ru(en)_3]^{3+}$ **M3:** optical / enantiomerism	
37(b)(i)	$E^{\ominus}_{cell}$ = 1.07 – 0.80 = (+)0.27 V **AND** direction of electron flow = Ag^+ / Ag to Br_2 / Br^-	**1**
37(b)(ii)	**M1:** $E^{\ominus}_{cell}$ 3rd box ticked **M2:** $[Ag^+]$ decreases **AND** so (Ag^+ / Ag) equilibrium shifts to the left **OR** $[Ag^+]$ decreases **AND** E for (Ag^+ / Ag) becomes less positive / more negative	**2**
37c)(i)	(a species) that uses / shares a lone pair of electrons to form a coordinate bond to a metal atom / ion	**1**
37(c)(ii)	$K_c = [Ag(S_2O_3)_2^{3-}]\,[Br^-] / [S_2O_3^{2-}]^2$	**1**
37(c)(iii)	**M1:** $K_c = K_{stab} \times K_{sp}$ = 15.7 **M2:** 1 **OR** none / no units	**2**
37(d)	**M1:** highest $[Ag(CN)_2]^-$ $[Ag(S_2O_3)_2]^{3-}$ $[Ag(NH_3)_2]^+$ lowest **M2:** K_{stab} $[Ag(CN)_2]^-$ is highest / $[Ag(CN)_2]^-$ is the most stable **OR** higher K_{stab} forms the more stable complex	**2**

38(a)(ii)	 [1] bond angle labelled 109.5° [1]	**2**
38(b)(i)	$_2O)_6]^{2+}$ + $2OH^-$ → $Co(H_2O)_4(OH)_2$ + $2H_2O$ **OR** $[Co(H_2O)_6]^{2+}$ + $2OH^-$ → $Co(OH)_2$ + $6H_2O$ [1] **blue** precipitate [1]	**2**
38(b)(ii)	$[Co(H_2O)_6]^{2+}$ + $6NH_3$ → $[Co(NH_3)_6]^{2+}$ + $6H_2O$ [1] yellow / brown / straw solution [1]	**2**
5(b)(iii)	$[Co(H_2O)_6]^{2+}$ + $4Cl^-$ → $[CoCl_4]^{2-}$ + $6H_2O$ [1] blue solution [1]	**2**
38(b)(iv)	**ligand** exchange [1]	**1**
38(c)(i)	(a species) that **donates <u>two</u> lone pairs** to form **<u>two</u> dative bonds** [1] **to** a (transition) **metal atom / metal ion** [1]	**2**
38(c)(ii)		**2**

39(a)	$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ **OR** $2CuSO_4 + 4NaI \rightarrow 2CuI + I_2 + 2Na_2SO_4$ [1]	**1**
39(b)(i)	**d-d orbital** splitting occurs [1] M2: **electron**(s) promoted / excited [1] M3: wavelength / frequency of light is **absorbed** [1] M4: colour seen is complementary **OR** wavelength / frequency of light **not** absorbed is seen [1]	**4**
39(b)(ii)	(for Cu^+) $3d^{10}$ **OR** 3d subshell full [1]	**1**
39(c)	M1: (Cu^{2+} / Cu^+) $E^\ominus = (+)0.15$ V **AND** (I_2 / I^-) $E^\ominus = (+)0.54$ V [1] M2: No, since $(E^\ominus_{cell})$ negative / –0.39 V **OR** No, since (I_2 / I^-) is more positive than (Cu^{2+} / Cu^+) **OR** No, I_2 is more easily reduced **OR** No, I_2 stronger oxidant ORA [1]	**2**
39(d)	Cu^{2+} / Cu^+ E becomes more positive as equilibrium shifts to the right [1] M2: The **new** E for Cu^{2+} / Cu^+ is more positive **than 0.54 / $E^\ominus$ (I_2 / I^-)** [1]	**2**

40(a)(ii)	$Mo(CO)_6$ 0 / no charge / neutral / zero $Fe(CN)_6$ 3– both formulae [1] both charges [1]	**2**
40(a)(iii)	either of these renditions, with a CN on each bond:  **AND** 180° bond angle between two opposite bonds [1]	**1**
40(b)(i)	$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ **OR** $Cu^{2+} + 2H_2O + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}$ [1]	**1**
40(b)(ii)	M1 **d**-orbitals split (could be in diagram) [1] M2 electrons transition to higher orbital / electrons promoted or excited [1] M3 wavelength / frequency / light / photon / hf / hn absorbed [1] M4 colour seen / reflected / transmitted is complement of colour absorbed [1]	**4**

40(c)(i)	$[Cu(NH_3)_4(H_2O)_2]^{2+} + 4HCl \rightarrow CuCl_4^{2-} + 2H_2O + 4NH_4^+$ **OR** $[Cu(NH_3)_4(H_2O)_2]^{2+} + 4Cl^- (+ 4H^+) \rightarrow CuCl_4^{2-} + 2H_2O + 4NH_3 (+ 4H^+)$ M1 formula and charge of $CuCl_4^{2-}$ [1] M2 rest of equation [1]	**2**
40c)(ii)	**ligand** exchange / substitution / replacement / displacement [1]	**1**
40(c)(iii)	tetrahedral [1]	**1**
40(c)(iv)	yellow [1]	**1**
40(c)(v)	**d**-orbital splitting changes / **ΔE** changes [1]	**1**

Question	P42/O/N/21/Q6	Marks
41(a)	red or pink to yellow / straw / brown / orange [1]	**1**
41(b)	[[C $_3)_6]^{2+}$] / $[[Co(H_2O)_6]^{2+}[NH_3]^6$ [1]	**1**
6(c)	C $_3)_6^{2+}$ is more stable (than $Co(H_2O)_6^{2+}$) [1]	**1**
41(d)(i)	E^o_{cell} = + 0.30 [1]	**1**
41(d)(ii)	$4[Co(NH_3)_6]^{2+} + O_2 + 2H_2O \rightleftharpoons 4[Co(NH_3)_6]^{3+} + 4OH^-$ [1]	**1**
41(d)(iii)	M1 No, because 1.82 V **and** 1.23 V [1]	**2**

CAMBRIDGE INTERNATIONAL EXAMINATIONS

A LEVEL CHEMISTRY – 9701

PAPER 4 – STRUCTURED QUESTIONS – PART 2

Topical Past Papers · Question Papers & Marking Schemes

COURSE INSTRUCTOR

FAHAD HAMEED AHMAD

Cambridge Chemistry Specialist · Educator · Content Creator

+92 323 509 4443 ◈ **www.megalecture.com**

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PART 2 · Topics 7 - 14

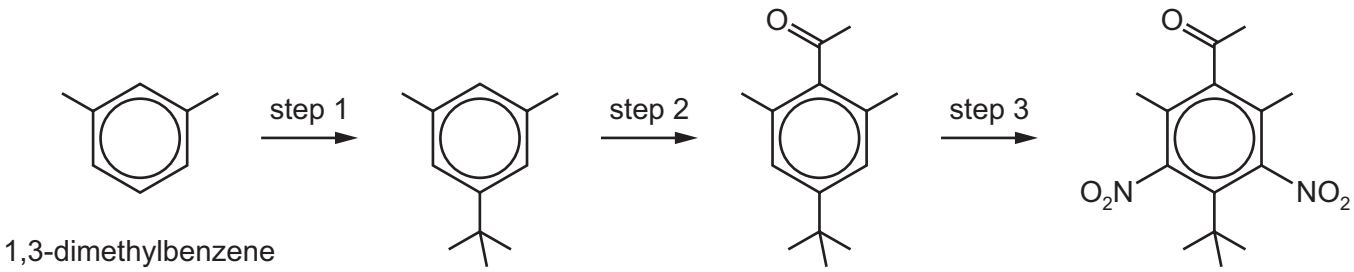
Benzene & Its Compounds · Carboxylic Acids & Derivatives · Organic Nitrogen Compounds · Polymerisation
Analytical Chemistry (NMR/MS/IR) · Organic Synthesis · AS Inorganic & Physical Chemistry · AS Organic Chemistry

Student Name: _____ **Class:** _____

Table of Content

Paper 4
Topic 7
Benzenes And Its Compounds

(a) The artificial 'musk ketone', **A**, is a perfume agent added to many cosmetics and detergents. It is made from 1,3-dimethylbenzene by the following route.



1,3-dimethylbenzene

'musk ketone' **A**

(i) The only by-product of step 2 is HC*l*.

Suggest the reagent that was used in this step.

..... [1]

(ii) Suggest the *type of reaction* that is occurring during both step 2 and step 3.

..... [1]

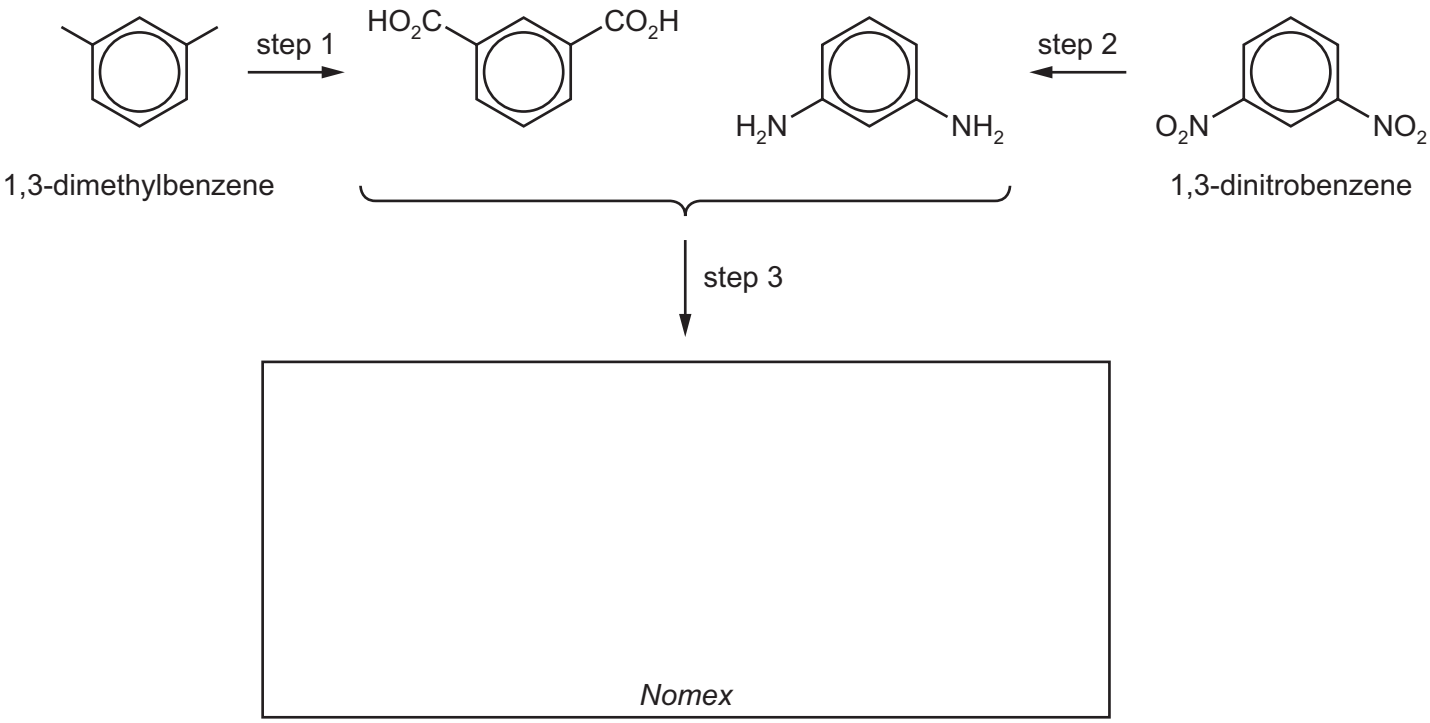
(iii) State the reagents and conditions needed for step 3.

..... [1]

(iv) Suggest the structures of the two products formed when **A** is reacted with alkaline aqueous iodine.

[2]

polymer is made from 1,3-dimethylbenzene and 1,3-dinitrobenzene by the following route.



(i) Draw the structure of one repeat unit of *Nomex* in the box above. [1]

(ii) What *type of polymer* is *Nomex*?

..... [1]

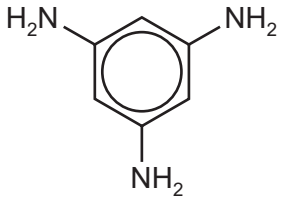
(iii) Suggest the by-product formed during step 3.

..... [1]

(iv) Suggest reagents and conditions for step 2.

..... [1]

(v) Suggest how and why the properties of the polymer might change if some of the diamine monomer were replaced with 1,3,5-triaminobenzene.



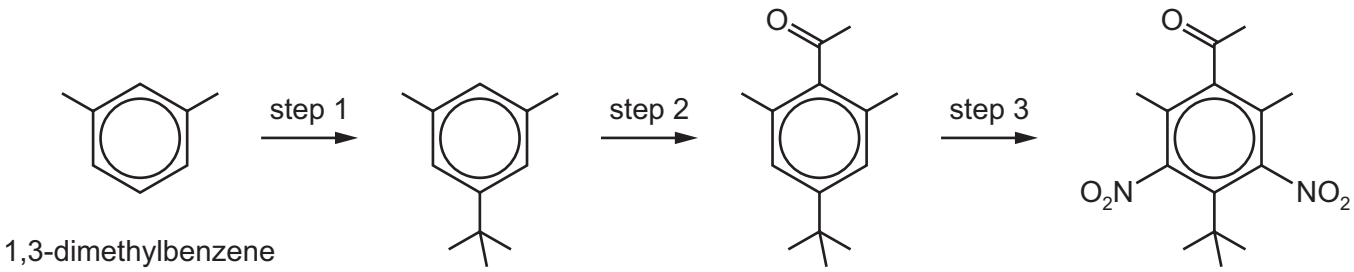
1,3,5-triaminobenzene

.....

..... [1]

[Total: 10]

(a) The artificial 'musk ketone', **A**, is a perfume agent added to many cosmetics and detergents. It is made from 1,3-dimethylbenzene by the following route.



1,3-dimethylbenzene

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Suggest the reagent that was used in this step.

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(ii) Suggest the *type of reaction* that is occurring during both step 2 and step 3.

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..... [1]

(iv) Suggest the structures of the two products formed when **A** is reacted with alkaline aqueous iodine.

[2]

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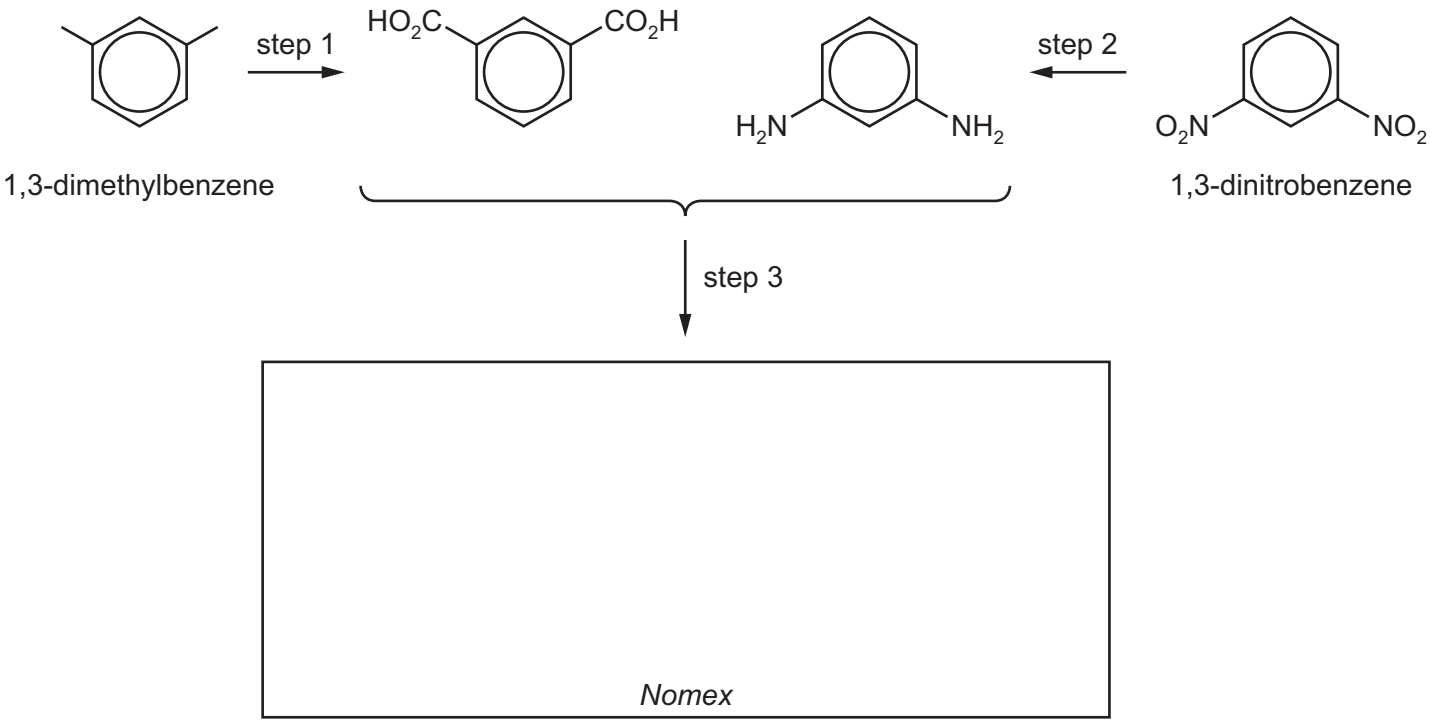

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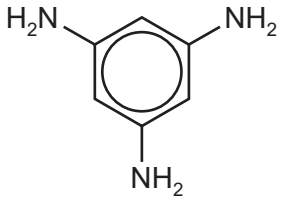
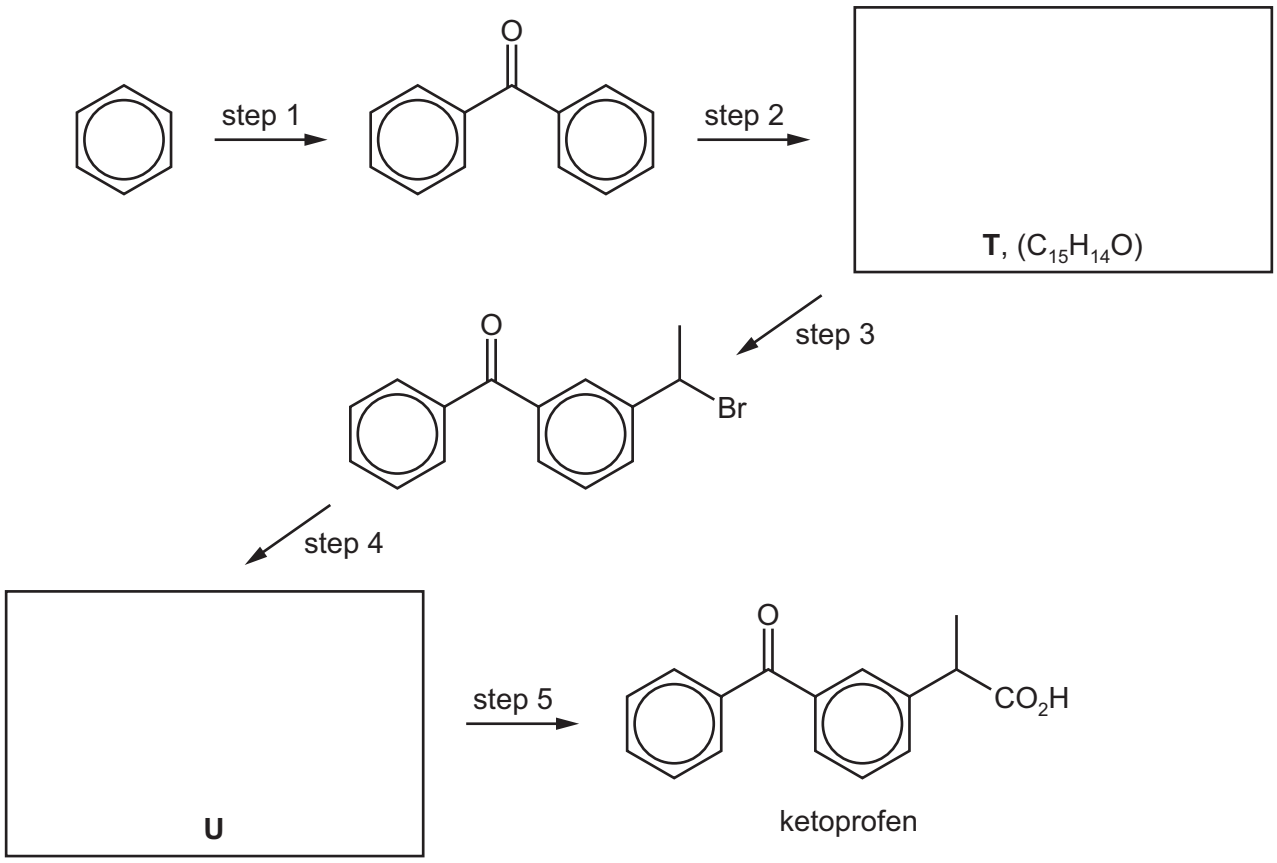


1,3,5-triaminobenzene

.....

..... [1]

[Total: 10]



(a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

[2]

(b) Suggest reagents and conditions for steps 1-5.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

[5]

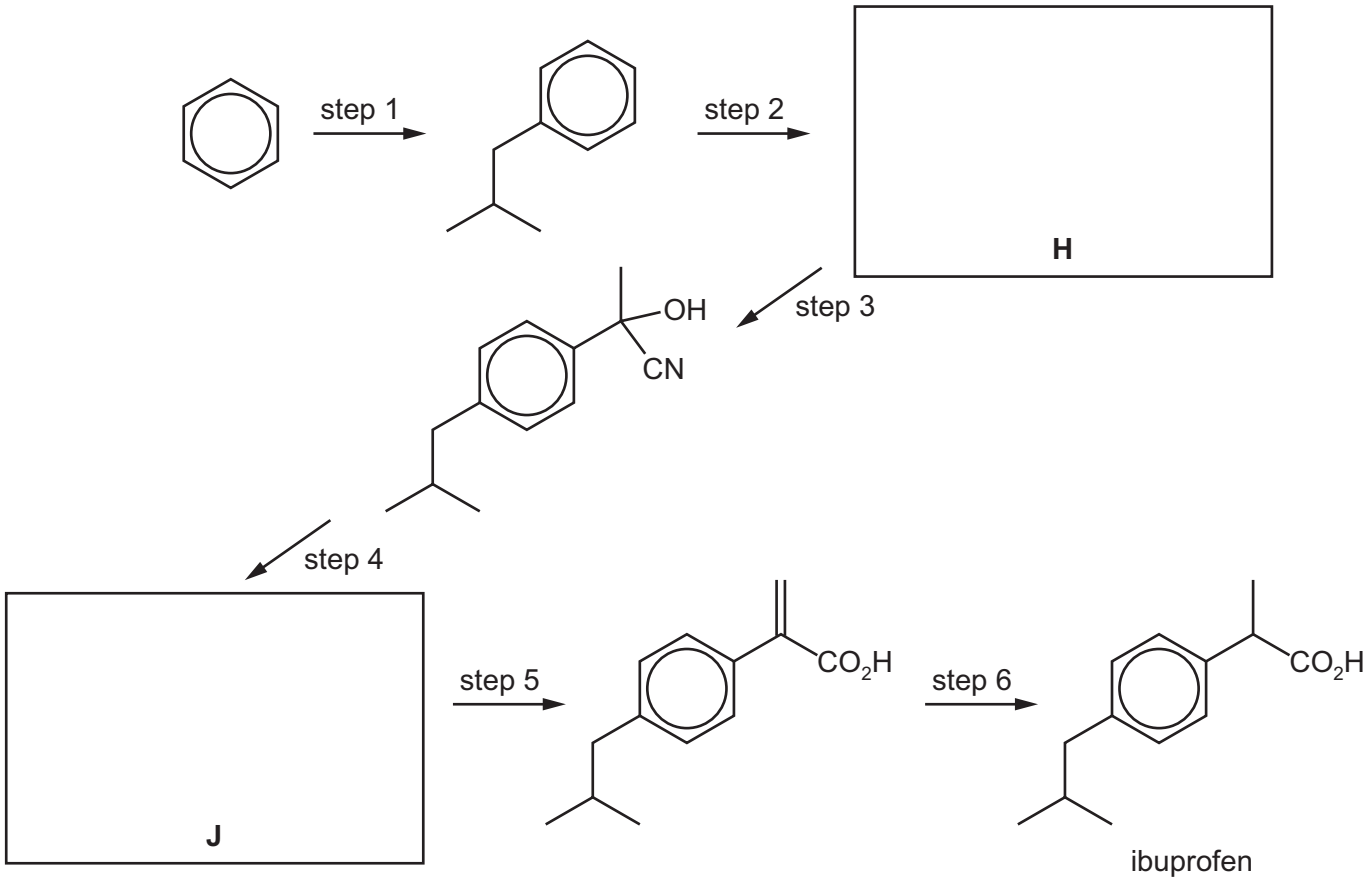
(c) What *types of reaction* are steps 1 and 5?

step 1 .....

step 5 .....

[2]

[Total: 9]



(a) Draw circles around any chiral carbon atoms in the above five formulae. [1]

(b) Suggest the structures of compounds **H** and **J** and draw them in the boxes above. [2]

(c) Suggest reagents and conditions for steps 1-6.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

step 6 .....

[6]

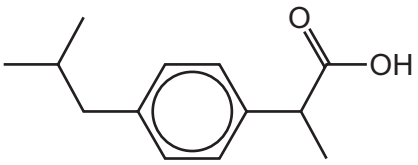
(d) Name the mechanism of step 1 and state the *type of reaction* for step 6.

step 1 .....

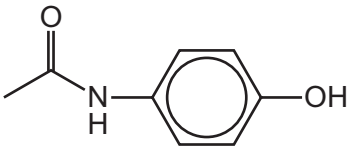
step 6 .....

[2]

[Total: 11]



ibuprofen



paracetamol

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

Name the **other** functional groups present in each molecule.

ibuprofen .....

paracetamol .....

[2]

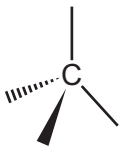
(b) Ibuprofen contains a chiral centre and shows stereoisomerism.

(i) State what is meant by the term *chiral centre*.

.....

..... [1]

(ii) Draw the two stereoisomers of ibuprofen.



[2]

product with ibuprofen

product with paracetamol

[2]

(d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

(i) Suggest a possible identity for each reagent **D** and **E**.

D .....

E .....

[2]

(ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.

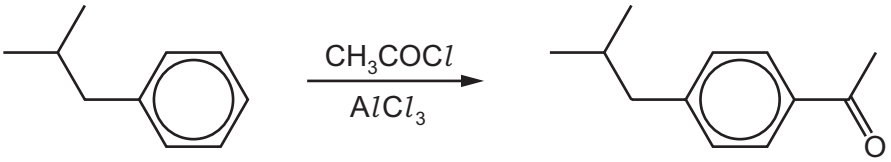
product with ibuprofen

[1]

(iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.

product with paracetamol

[1]

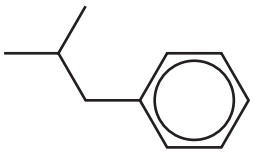


X **Y**

(i) Write an equation for the reaction between CH_3COCl and $AlCl_3$.

..... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



X

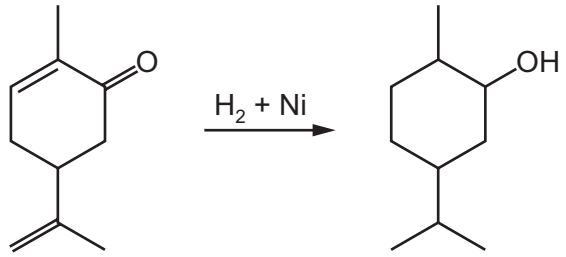
[3]

(iii) Name the mechanism in **(ii)**.

..... [1]

[Total: 16]

formula **X**.



carvone **X**

(a) (i) State the type of stereoisomerism carvone can show. Explain your answer.

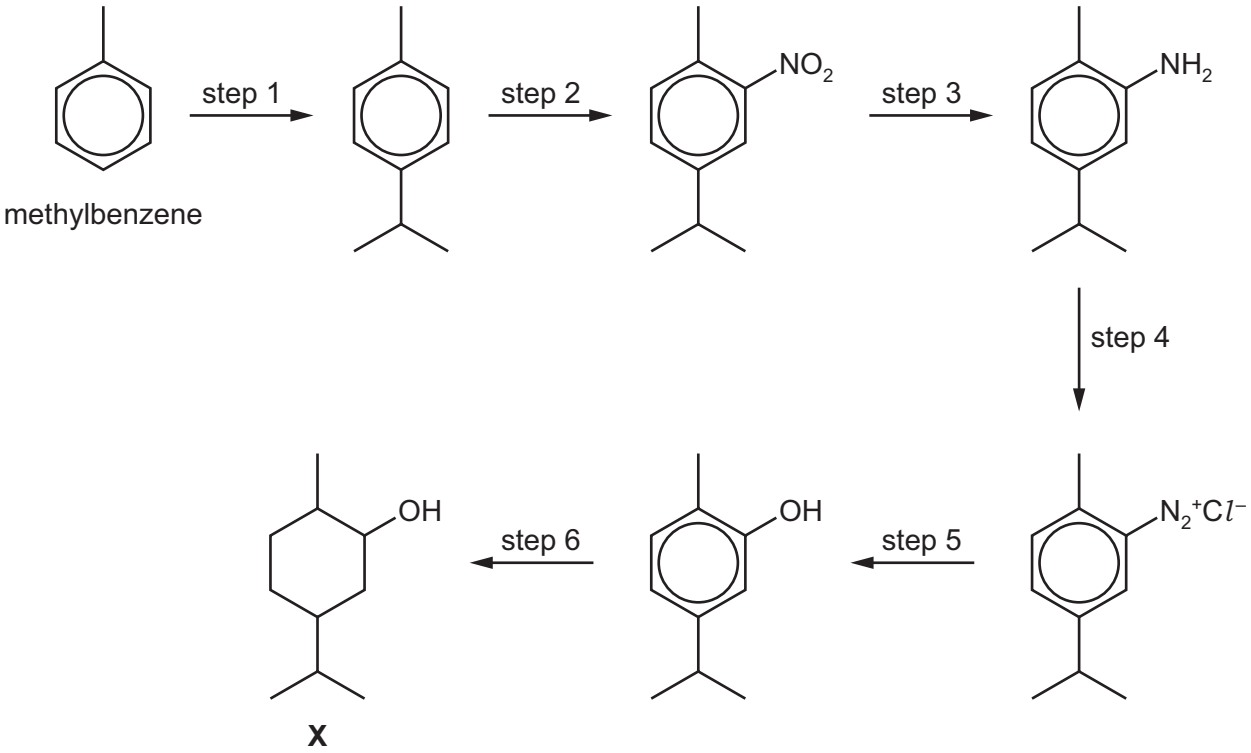
.....

..... [1]

(ii) Write an equation, using molecular formulae, for this conversion of carvone to **X**.

..... [2]

X can be synthesised from methylbenzene by the following route.



methylbenzene

X

..... [1]

(ii) What type of reaction is occuring in the following steps?

step 3 .....

step 5 .....

[2]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

[6]

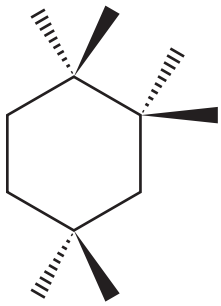
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(i) State the reagents and conditions needed for this reaction.

..... [1]

(ii) Complete the part structure to show the structure of the isomer of **X** that would most likely be obtained during this reaction.

X



[2]

[Total: 15]

Only **one** of the isomers contains a chiral centre.
The results of six tests carried out on **W**, **X**, **Y** and **Z** are shown in the table.

test		observations with each isomer			
		W	**X**	**Y**	**Z**
1	add cold $AgNO_3(aq)$	white ppt. forms immediately	none	white ppt. forms very slowly	none
2	heat with NaOH(aq), then add dilute HNO_3 + $AgNO_3(aq)$	white ppt.	none	white ppt.	none
3	add NaOH(aq) + $I_2(aq)$	none	pale yellow ppt.	none	none
4	warm with Fehling's solution	none	none	red ppt.	none
5	add cold, dilute, acidified $KMnO_4(aq)$	no change	no change	no change	decolourises
6	add $Br_2(aq)$	no change	no change	no change	decolourises and forms white ppt.

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in the four isomers **W**, **X**, **Y** and **Z**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
W	**X**	**Y**	**Z**
.....	.....	.....	.....
.....	.....	.....	.....
.....	.....	.....	.....

[5]

(i) Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes.

W

X

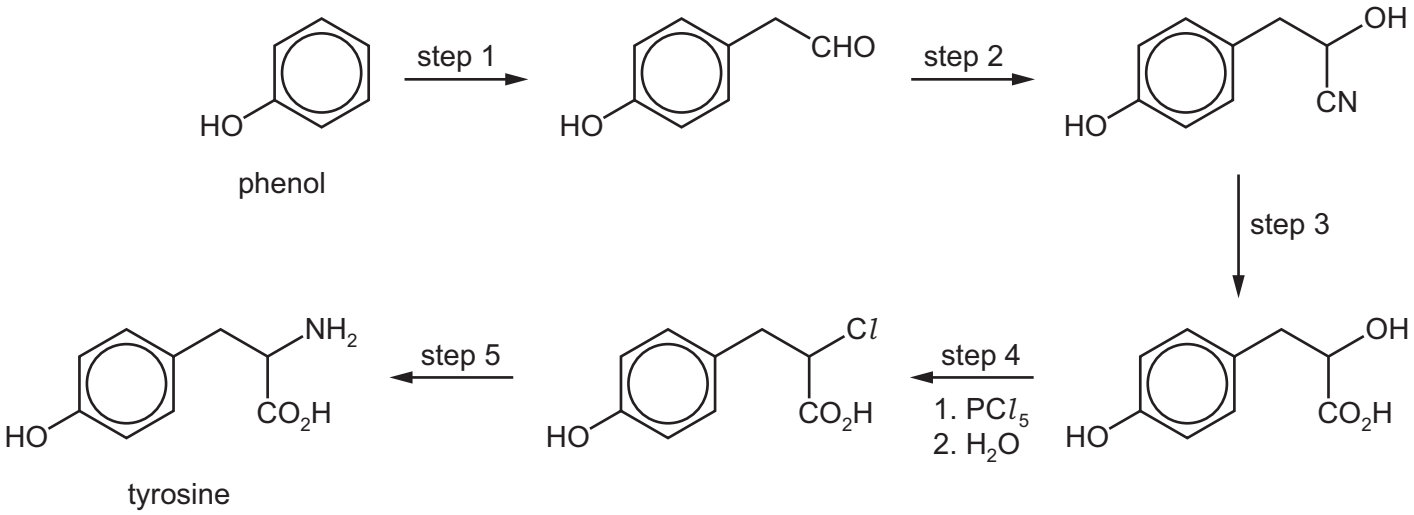
Y

Z

[4]

(ii) Draw a **circle** around the chiral centre in **one** of the above structures. [1]

[Total: 10]



phenol

tyrosine

(i) Name the mechanism occurring in the following steps.

step 1 .....

step 2 .....

[2]

(ii) What *type of reaction* is occurring in step 3?

..... [1]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 .....

step 2 .....

step 3 .....

step 5 .....

[5]

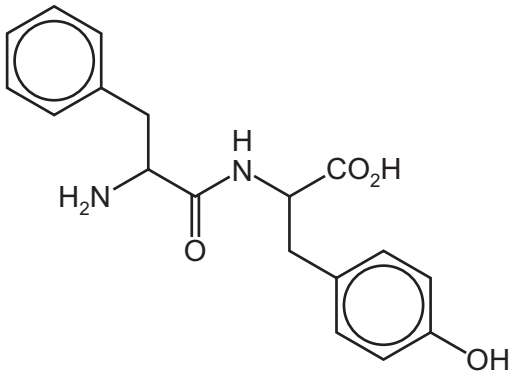
with NaOH(aq)

with HCl(aq)

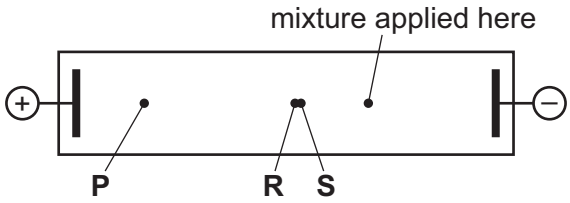
with Br_2(aq)

[4]

Question 8 continues on the next page.



A mixture of this dipeptide (phe-tyr) and its two constituent amino acids (phe and tyr) was subjected to electrophoresis in a buffer at pH 12. At the end of the experiment the following results were seen. Spots **R** and **S** remained very close together.



The three spots are due to the three species phe, tyr and phe-tyr.

(i) Which species is responsible for spot **P**? Explain your answer.

.....

..... [2]

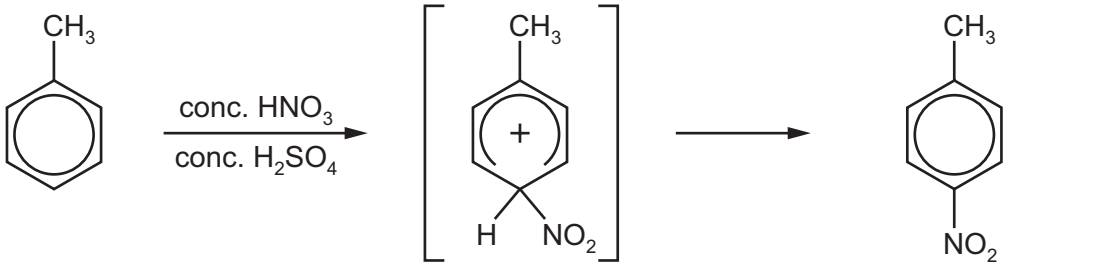
(ii) Suggest why the other two species give spots **R** and **S** that are so close together.

.....

..... [1]

[Total: 15]

9 **(a)** 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown:



methylbenzene | intermediate **T** | 4-nitromethylbenzene

(i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

(ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

..... [1]

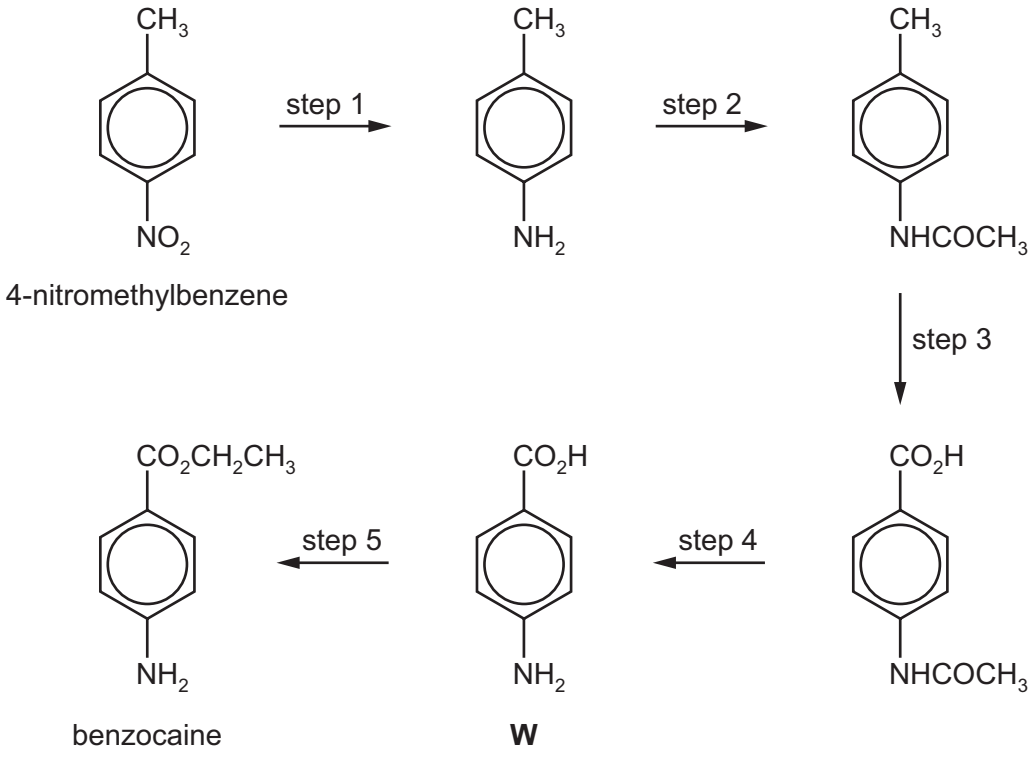
(iii) Describe how the **structure and bonding** of the six-membered ring in intermediate **T** differs from that in methylbenzene.

.....

.....

.....

..... [3]



4-nitromethylbenzene

benzocaine

W

(i) Give the systematic name of compound **W**.

..... [1]

(ii) Suggest the reagents and conditions for steps 1–5.

step 1 .....

step 2 .....

step 3 .....

step 4 .....

step 5 .....

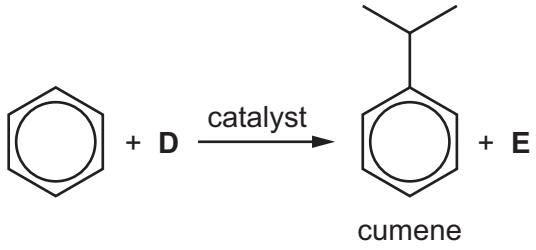
[6]

(c) Suggest how the basicity of benzocaine would compare to that of ethylamine.
Explain your answer.

.....

.....

..... [2]



cumene

(i) Name the reactant **D** and the non-organic product **E**.

D .....

E .....

[2]

(ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

..... [1]

(b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

(i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

..... [1]

(ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

..... [1]

(iv) Draw the structures of **two** isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the side-chain.

[1]

(c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

reagent	structure of organic product
hot $KMnO_4(aq)$	
H_2 + Ni, high pressure	

[2]

Complete the mechanism for this reaction.

- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.

cumene intermediate

[4]

[Total: 13]

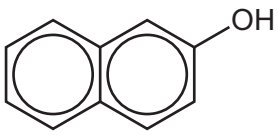
(a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $C_6H_5O^-K^+$. Identify the second product formed in each case.

substance ..... second product .....

substance ..... second product .....

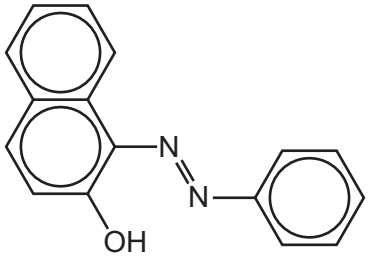
[3]

(b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

(i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]

(ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

.....

.....

.....

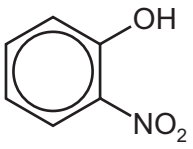
.....

.....

.....

.....

..... [3]



2-nitrophenol

The nitration reaction of phenol to form 2-nitrophenol shows that phenol is more reactive than benzene.

(i) Describe the conditions used for the nitration of phenol.

Explain how these conditions show phenol to be more reactive than benzene.

conditions .....

explanation .....

.....

.....

[2]

(ii) Suggest why phenol is more reactive than benzene.

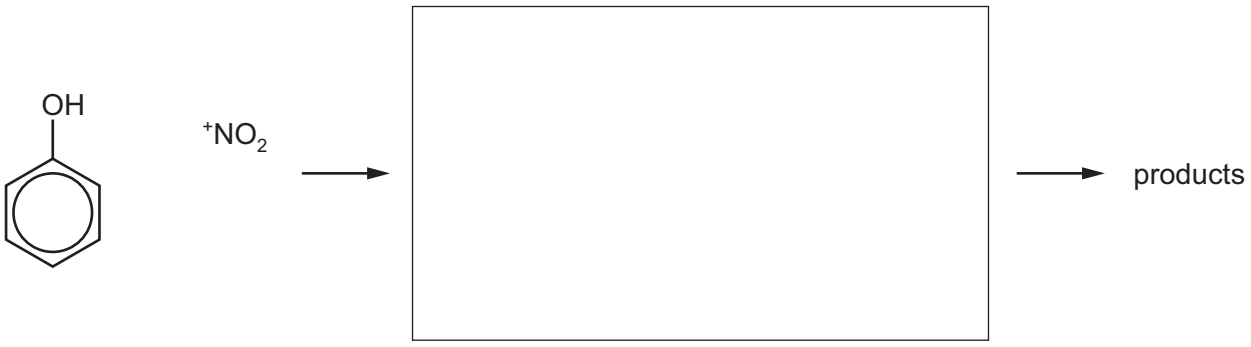
.....

.....

..... [1]

(iii) Complete the mechanism for the nitration of phenol to form 2-nitrophenol. You should assume that the mechanism is the same as that for the nitration of benzene.

- Include all relevant charges and curly arrows to show the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



phenol intermediate

[3]

(iv) Name the isomer of 2-nitrophenol which is also a major product of this reaction.

..... [1]

Explain why.

.....

.....

.....

.....

..... [3]

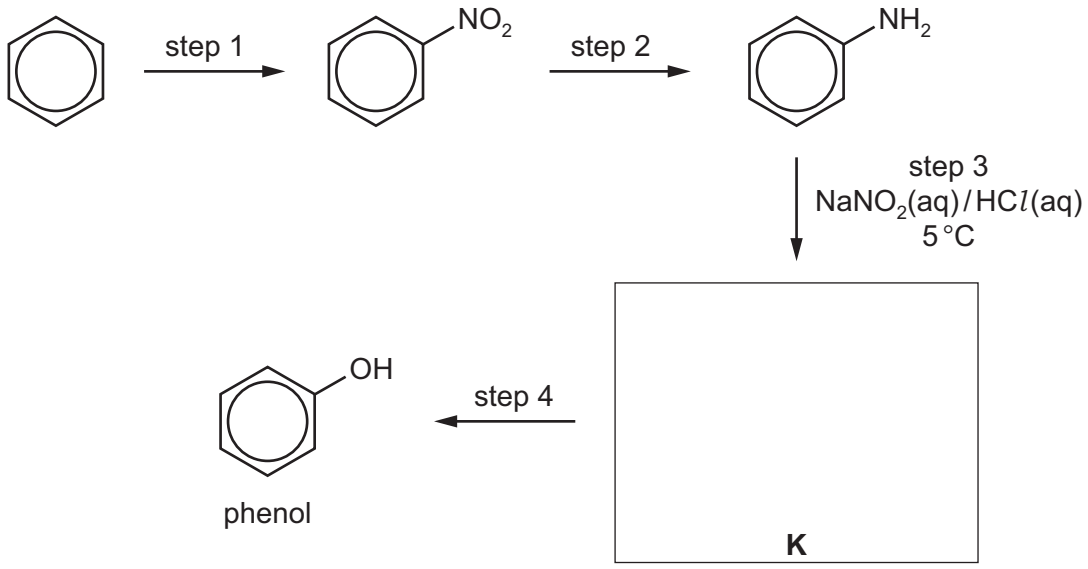
(b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, C_6H_4BrOH, are formed.

Suggest structures for these products. Name each compound.

name: .....

name: .....

[2]



(i) Suggest reagents and conditions for each of the following steps.

step 1 .....

step 2 .....

step 4 .....

[3]

(ii) Deduce the structure for **K** and draw its structural formula in the box. [1]

(iii) Name the mechanism for step 1.

..... [1]

(iv) Write an equation for step 2. Use [H] for the reducing agent in this equation.

[1]

[Total: 11]

(i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction .....

reagent and conditions .....

[2]

(ii) State the bond angles in benzene and cyclohexane.

bond angle in benzene ..... bond angle in cyclohexane .....

Explain your answers.

.....

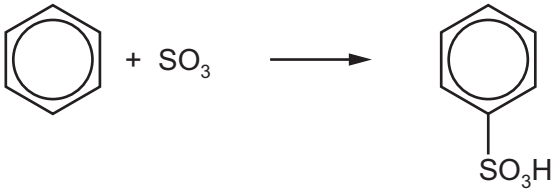
.....

.....

[2]

(b) When benzene reacts with SO_3, benzenesulfonic acid is produced.

benzenesulfonic acid



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.

$$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$$

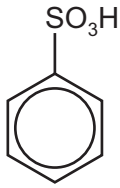
(i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

benzenesulfonic acid

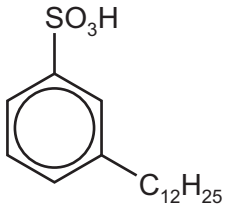
[3]

(ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

benzenesulfonic acid



3-dodecylbenzenesulfonic acid



Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions .....

mechanism .....

[2]

(d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.

stage 1 $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

stage 2 $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_{a2} = 1.0 \times 10^{-2}\,\text{mol dm}^{-3}$

K_{a2} is the acid dissociation constant for stage 2.

(i) Write the expression for the acid dissociation constant K_{a2}.

K_{a2} =

[1]

(ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2}.

..... [1]

(e) Benzoic acid, $C_6H_5CO_2H$, is a weak acid. A solution of $0.0250\,\text{mol dm}^{-3}$ benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

K_a = ... mol dm^{-3}

[2]

.....

.....

.....

.....

.....

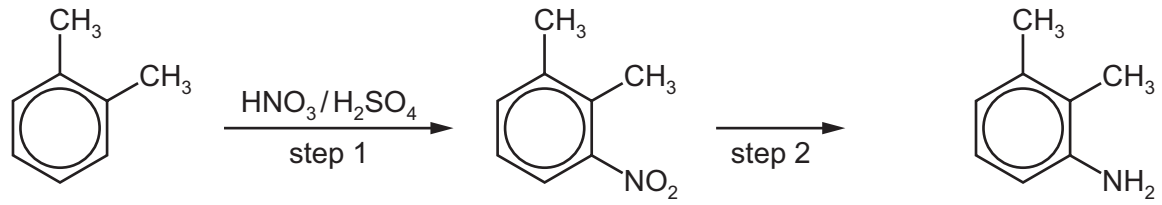
.....

.....

..... [3]

(b) 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

1,2-dimethylbenzene **M** 2,3-dimethylphenylamine

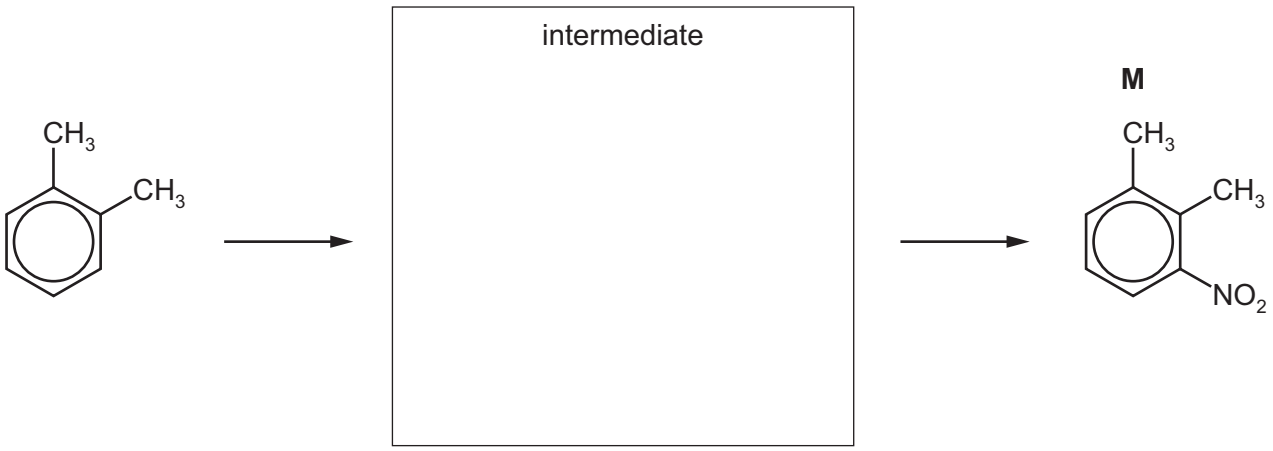


Step 1 is catalysed by H_2SO_4.

(i) Write an equation to show how H_2SO_4 generates the electrophile during step 1.

..... [1]

(ii) Draw the mechanism of the reaction between this electrophile and 1,2-dimethylbenzene to form **M**. Include all relevant curly arrows and charges.



[3]

..... [1]

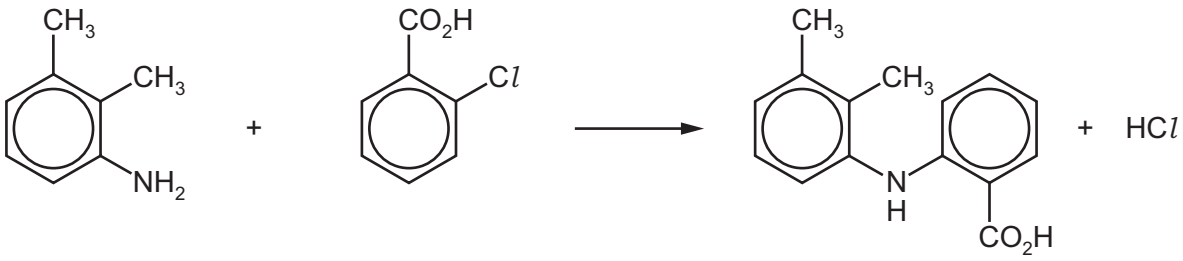
(iv) For step 2, suggest the reagents and conditions and name the *type of reaction*.

- reagents and conditions .....
- type of reaction .....

[2]

(c) The drug mefenamic acid can be made using 2,3-dimethylphenylamine in an excess of 2-chlorobenzoic acid.

2,3-dimethylphenylamine + 2-chlorobenzoic acid → mefenamic acid + HCl



(i) Deduce the molecular formula of mefenamic acid.

..... [1]

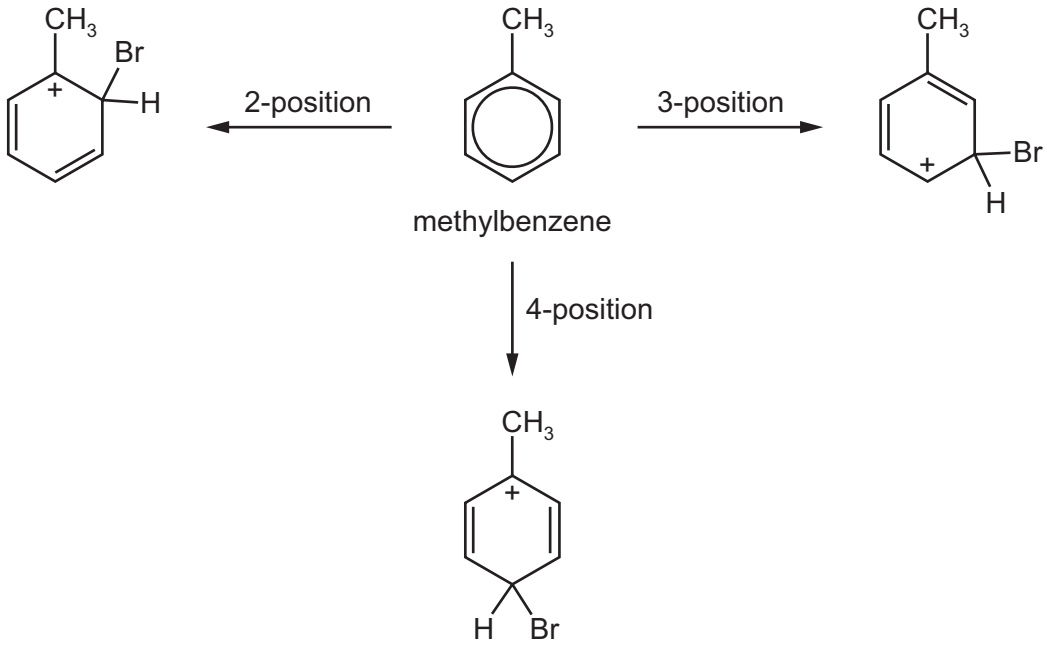
(ii) Name the functional groups, apart from the benzene ring, in mefenamic acid.

..... [1]

(iii) Calculate the maximum mass of mefenamic acid that could be formed from 5.00 g of 2,3-dimethylphenylamine in this reaction. Give your answer to **three** significant figures.

mass of mefenamic acid = ... g [2]

the bromination of methylbenzene.



Use this information and your knowledge about the stability of cations to suggest why the CH_3 group directs incoming electrophiles to the 2- and 4-positions in preference to the 3-position.

.....

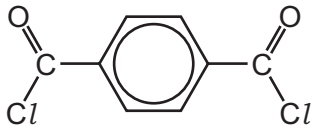
.....

.....

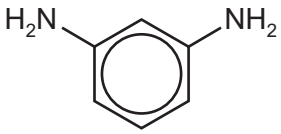
..... [2]

[Total: 16]

benzene-1,4-dioyl chloride



benzene-1,3-diamine



(i) Draw a section of the polymer chain of **P**. Your structure should include two repeat units.

P

[2]

(ii) Place **one** tick in the table to describe polymer **P** and its method of polymerisation.

type of polymer	type of polymerisation	
	addition	condensation
polyalkene		
polyamide		
polyester		

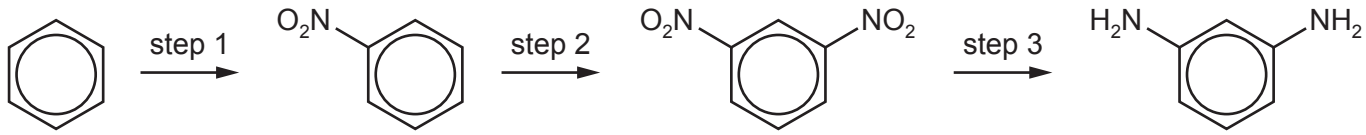
[1]

(iii) State whether or not polymer **P** is biodegradable. Give a reason for your answer.

.....

..... [1]

(iv) State a suitable reagent to produce benzene-1,4-dioyl chloride from benzene-1,4-dicarboxylic acid.



State the reagents used for steps 1 and 3.

step 1 .....

step 3 .....

[2]

(b) Proteins are natural polymers. A protein is said to have a primary, secondary and tertiary structure.

(i) Describe what is meant by each of these terms.

primary structure .....

.....

secondary structure .....

.....

tertiary structure .....

.....

[3]

(ii) Name the forces or bonds responsible for holding together the primary structure of a protein molecule.

..... [1]

(iii) Name the forces or bonds responsible for the stabilisation of the secondary structure of a protein molecule, and identify the groups of atoms within the protein molecule that are held together by these forces or bonds.

.....

..... [2]

[Total: 13]

(i) Explain why no addition reaction takes place.

.....

..... [1]

$Al Br_3$ reacts with bromine to generate an electrophile, Br^+.

(ii) Draw the mechanism of the reaction between benzene and Br^+ ions. Include all relevant arrows and charges.

[3]

(iii) Write an equation to show how the $Al Br_3$ catalyst is reformed.

..... [1]

(b) Suggest why bromination of phenol occurs more readily than bromination of benzene.

.....

.....

.....

.....

..... [2]

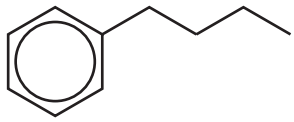
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.
In each reaction an organic compound with formula $C_{10}H_{14}$ is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

[4]

[Total: 14]

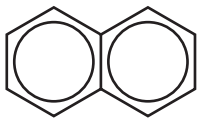
State the shape (geometry) around the substituted carbon atom

- in the benzene molecule, ...
- in the intermediate complex, ...
- in the nitrobenzene product. .....

[2]

(ii) Naphthalene, $C_{10}H_8$, is an arene hydrocarbon.

naphthalene



When naphthalene undergoes nitration, a mixture of two organic compounds is formed. Each compound contains **one** nitro group.

Suggest the structures of these compounds.

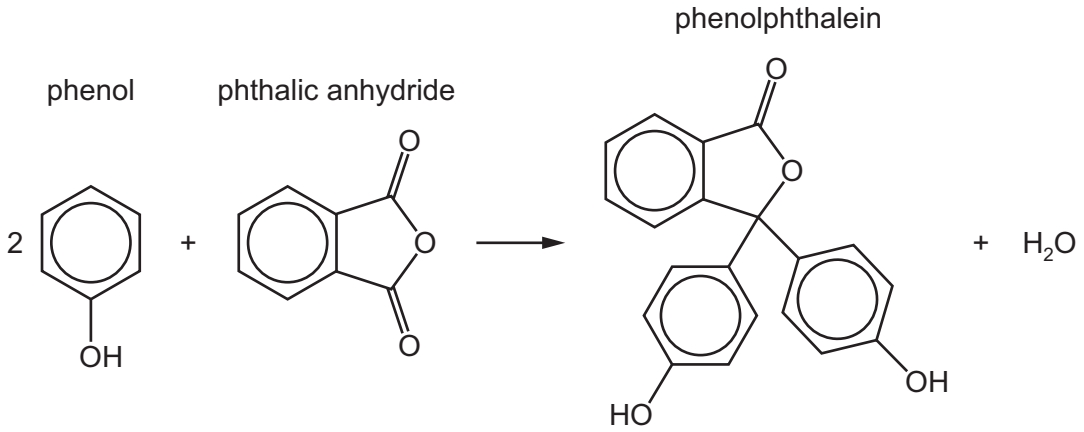
structure 1	structure 2

[1]

(b) Naphthalene can be oxidised under certain conditions to phthalic anhydride, $C_8H_4O_3$, carbon dioxide and water.

Construct an equation for this reaction. Use [O] to represent an atom of oxygen from the oxidising agent.

..... [1]



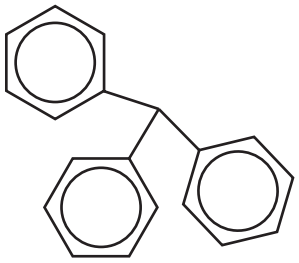
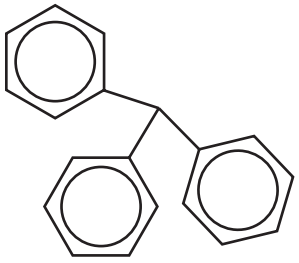
Deduce the *type of reaction* shown by this equation.

..... [1]

..... [1]

(ii) Phenolphthalein reacts separately with the two reagents shown in the table.

Complete the table by:
- drawing the structures of the organic products formed (part of the structure has been given for you)
- stating the types of reaction.

reagent	organic product structure	type of reaction
an **excess** of hot NaOH(aq)		
an **excess** of Br_2(aq)		

[4]

(a) Phenol can be made from phenylamine, $C_6H_5NH_2$.

Give the reagents and conditions for this reaction.

.....

..... [2]

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $C_6H_5NO_3$.

Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.

name .....

name .....

[2]

(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.

name .....

[2]

observation 1 .....

observation 2 .....

[1]

(d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

..... [1]

(e) Water, phenol and ethanol can all behave as acids.

Place these three compounds in order of acidity, starting with the **most** acidic.
Explain your answer.

..... > ..... > .....

most acidic least acidic

.....

.....

.....

.....

.....

.....

[3]

[Total: 11]

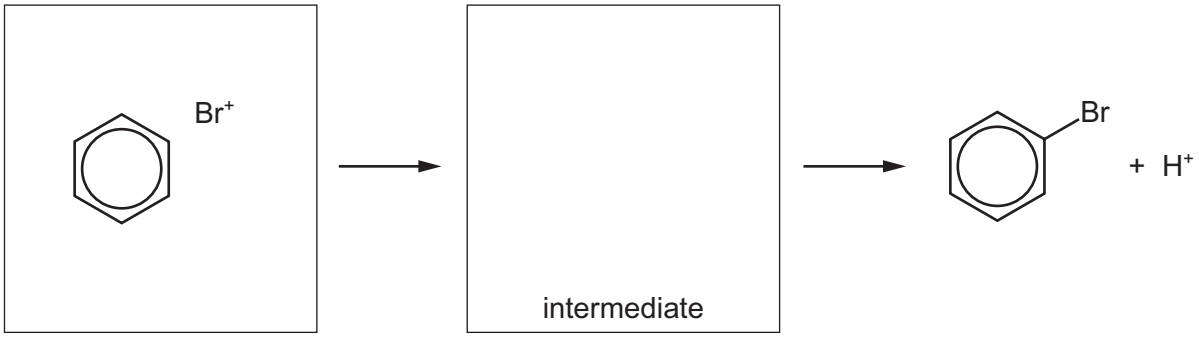
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(i) Give the name or formula of the other product of this reaction.

..... [1]

(ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br^+.

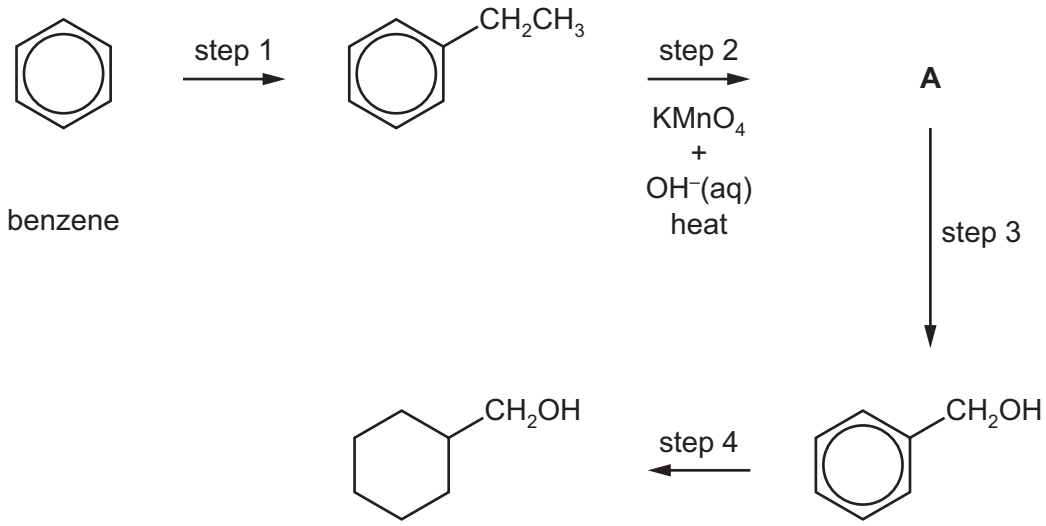
Complete the mechanism by which benzene reacts with Br^+, using curly arrows to show the movement of electron pairs.



[2]

(iii) Name this mechanism.

..... [1]



cyclohexylmethanol

(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent .....

catalyst .....

[2]

(ii) Draw the structure of **A**.

A

[1]

step 3 .....

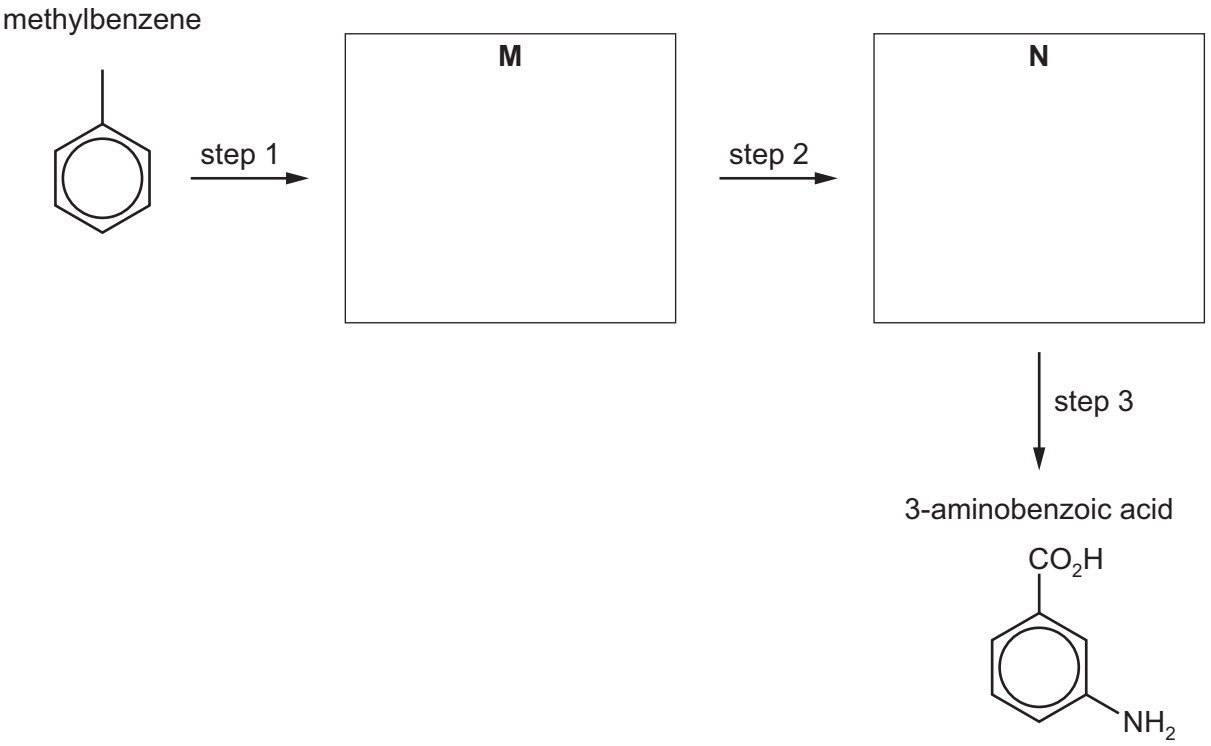
step 4 .....

[2]

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

..... [1]

[Total: 10]



(i) Draw the structures of **M** and **N** in the boxes. [2]

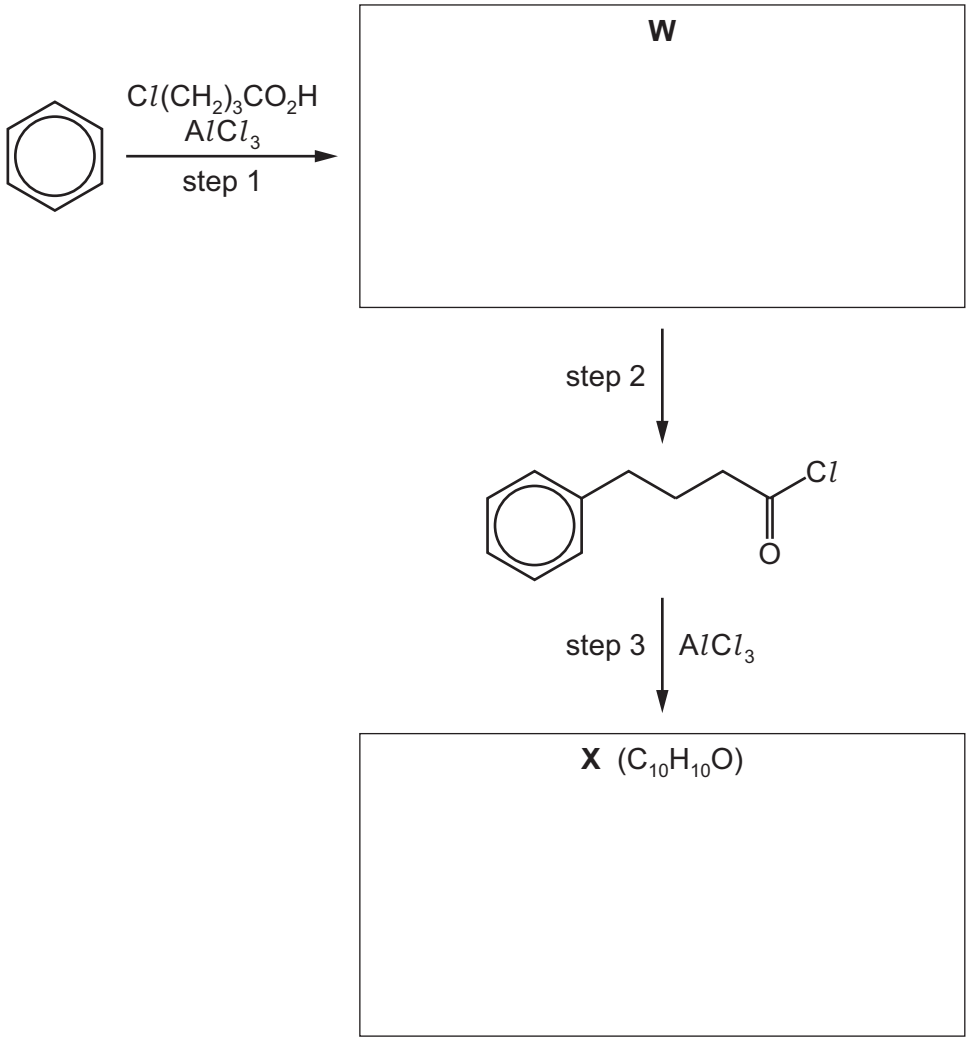
(ii) Suggest reagents and conditions for each step of the synthesis.

step 1 .....

step 2 .....

step 3 .....

[3]



(i) Step 1 is the alkylation of benzene by electrophilic substitution.
Use R–Cl to represent $Cl(CH_2)_3CO_2H$.

Write an equation for the formation of an electrophile from R–Cl and $AlCl_3$.

..... [1]

(ii) Deduce and draw the structures of **W** and **X** in the boxes. [2]

(iii) Suggest the reagents and conditions for step 2.

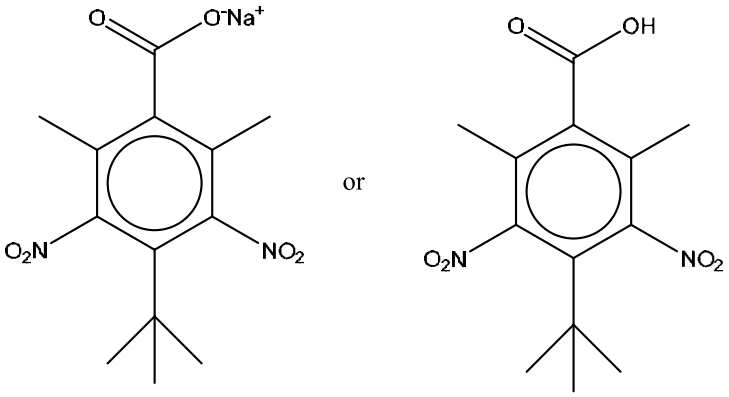
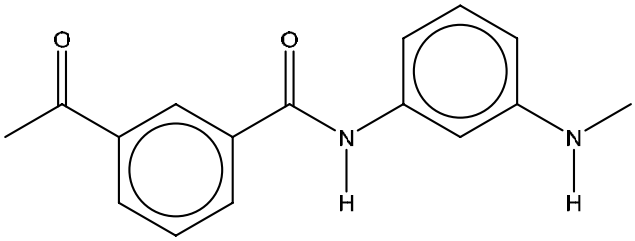
..... [1]

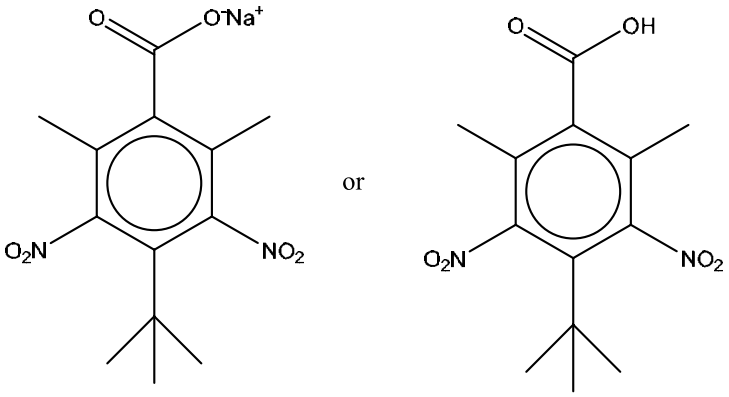
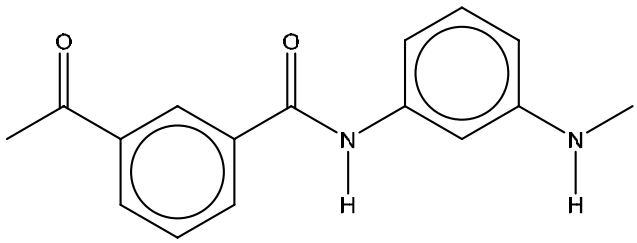
Include all relevant charges and curly arrows showing the movement of electron pairs.

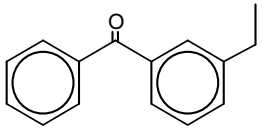
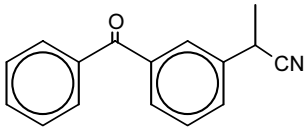
Draw the structure of the intermediate.

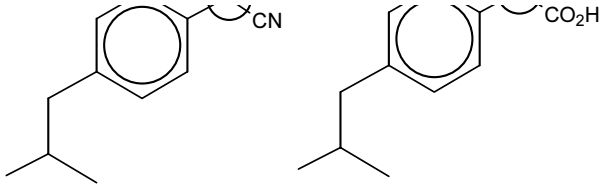
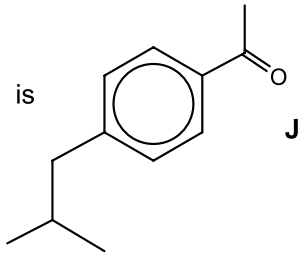
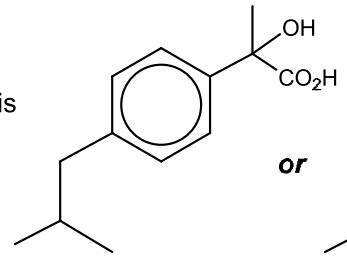
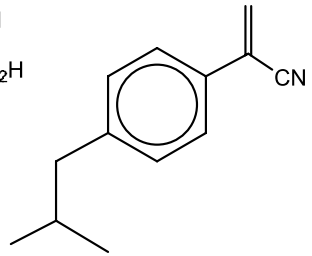
[3]

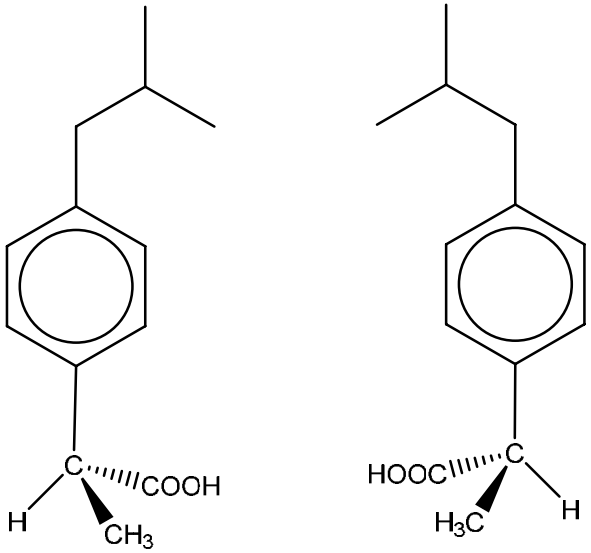
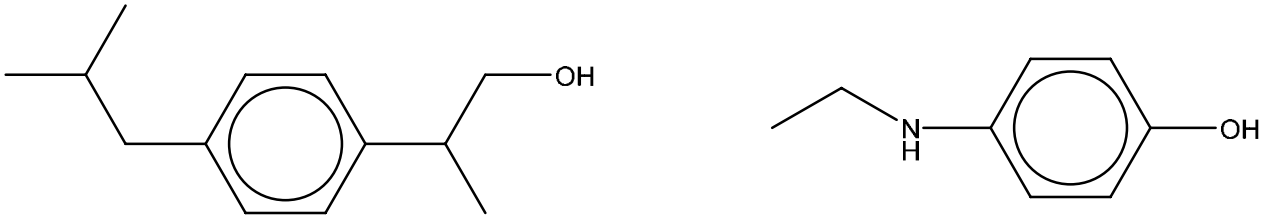
[Total: 11]

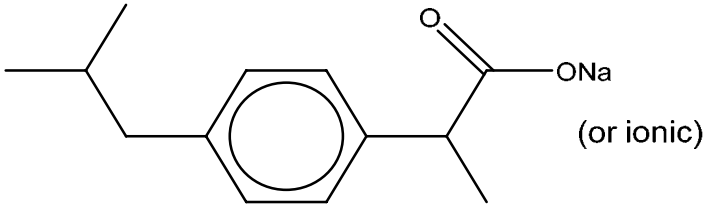
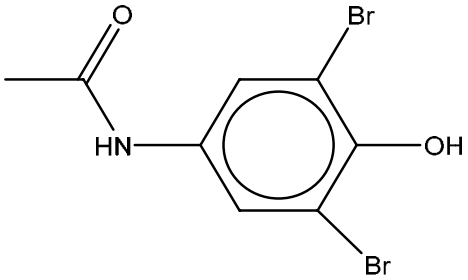
1 (a) (i)	CH_3COCl ***or*** ethanoyl chloride	**1**
(ii)	electrophilic substitution	**1**
(iii)	conc HNO_3 **and** conc H_2SO_4	**1**
(iv)	CHI_3 	**1** **1**
(b) (i)		**1**
(ii)	polyamide ***or*** condensation	**1**
(iii)	H_2O / water	**1**
(iv)	Sn / Fe + HCl + conc / aq / heat/warm	**1**
(v)	harder ***or*** more dense ***or*** stronger ***or*** higher m.pt ***or*** tougher ***or*** more rigid due to cross-linking **or** more H-bonding between the chains	**1**
		[Total: 10]

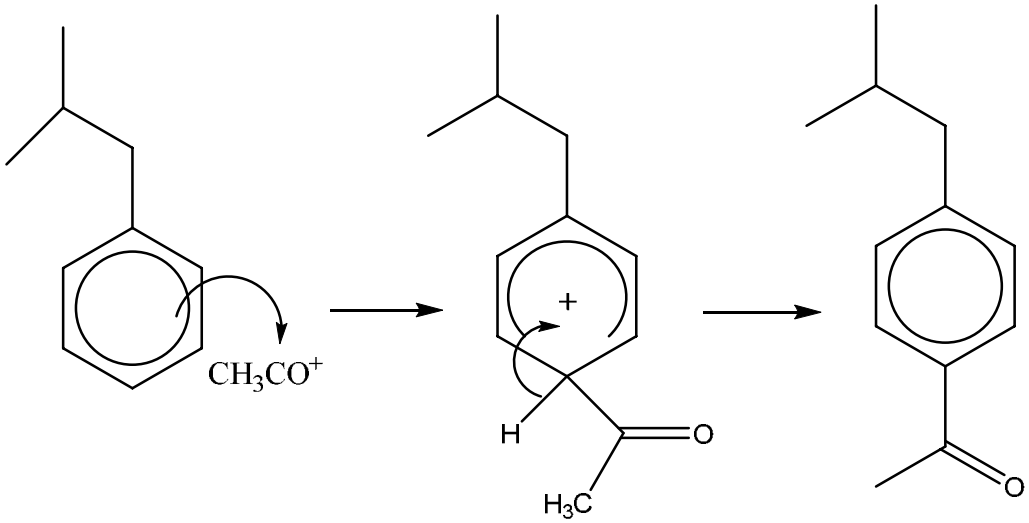
2 (a) (i)	CH_3COCl ***or*** ethanoyl chloride	**1**
(ii)	electrophilic substitution	**1**
(iii)	conc HNO_3 **and** conc H_2SO_4	**1**
(iv)	CHI_3 	**1** **1**
(b) (i)		**1**
(ii)	polyamide ***or*** condensation	**1**
(iii)	H_2O / water	**1**
(iv)	Sn / Fe + HCl + conc / aq / heat/warm	**1**
(v)	harder ***or*** more dense ***or*** stronger ***or*** higher m.pt ***or*** tougher ***or*** more rigid due to cross-linking **or** more H-bonding between the chains	**1**
		[Total: 10]

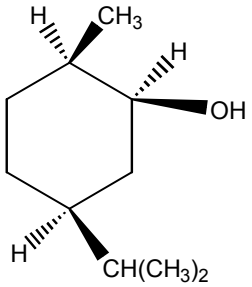
3 **(a)**	**T** is  **U** is 	[1] [1]
(b)	step 1: C_6H_5COCl + $AlCl_3$ (+ heat) step 2: CH_3CH_2Cl + $AlCl_3$ (+ heat) step 3: Br_2 + light (*or* heat) step 4: KCN + heat (in ethanol) step 5: H_3O^+ OR H^+ in H_2O OR HCl (aq) etc AND heat / boil / reflux	[1] [1] [1] [1] [1]
(c)	step 1: electrophilic substitution OR nucleophilic substitution step 5: hydrolysis OR nucleophilic substitution	[1] [1]
		[Total: 9]

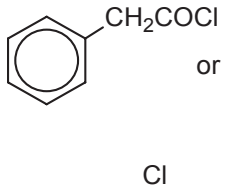
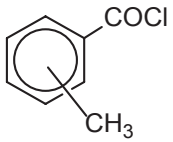
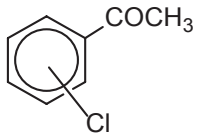
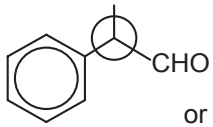
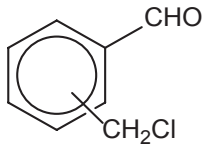
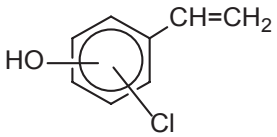
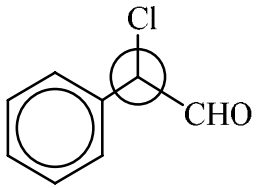
		
(b)	**H** is  **J** is  ***or***  **J1** **J2**	2
(c)	step 1: $(CH_3)_2CHCH_2Cl$ + $AlCl_3$ (+ heat) step 2: CH_3COCl + $AlCl_3$ (+ heat) step 3: HCN + NaCN ***or*** HCN + base ***or*** HCN + CN^- *(steps 4 and 5 could be reversed on J)* ***If J1*** *step 4 then step 5* ***J2*** *step 5 then step 4* step 4: H_3O^+ + heat / aqueous HCl + heat step 5: conc H_2SO_4 + heat / conc H_3PO_4 + heat **or** Al_2O_3 + heat step 6: H_2 + Ni (+ heat)	6
(d)	step 1: electrophilic substitution ***or*** alkylation	2

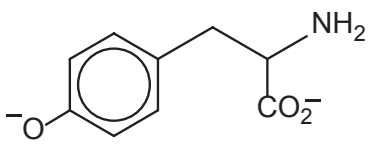
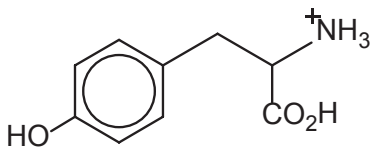
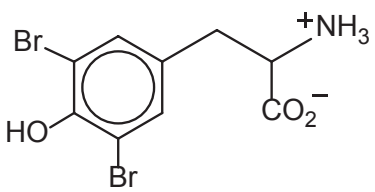
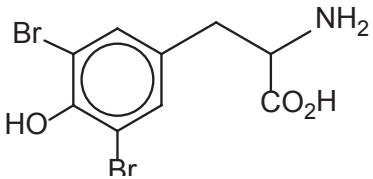
	any two = 1 mark all three = 2 marks	**2**
5(b)(i)	(chiral centre is a) carbon **OR** atom that has four different groups / atoms / species attached to it	1
5(b)(ii)	 one correct isomer second diagram shows second isomer	**1** 1 1 **2**
5(c)		

Question		Mark
5(d)(i)	(reagent **D**) Na_2CO_3 / any carbonate (reagent **E**) Cl_2 / Br_2	1 1 **2**
5(d)(ii)	 (or ionic)	1 **1**
5(d)(iii)		1 **1**
5(e)(i)	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	1 **1**

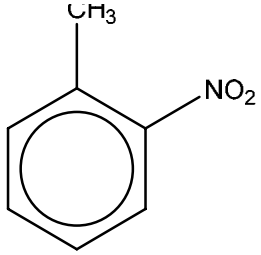
Question	Answer	Mark
5(e)(ii)	 curly arrow from ring system to CH_3CO^+ correct intermediate curly arrow from C–H bond into ring	1 1 1 **3**
5e)(iii)	electrophilic substitution	1 **1**
	Total:	**16**

6(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 **different** groups	1
6(a)(ii)	$C_{10}H_{14}O + 3H_2 \longrightarrow C_{10}H_{20}O$ correct formulae	1
	balancing	1
6(b)(i)	electrophilic substitution	1
6(b)(ii)	step 3 reduction	1
	5step substitution / hydrolysis	1
6(b)(iii)	step 1 $(CH_3)_2CHCl$ + $AlCl_3$ / $AlBr_3$ / $FeCl_3$ / $FeBr_3$	1 + 1
	step 2 HNO_3 + H_2SO_4 conc (T < 55 °C)	1
	step 3 Sn + HCl	1
	step 4 HNO_2 (*or* $NaNO_2$ + HCl) (at T < 10 °C)	1
	the two temperatures for steps 2 and 4	1
6(c)(i)	**H_2** + Pt or **H_2** + Ni + heat or pressure	1
6(c)(ii)	 $(CH_3)_2CH$, CH_3 and OH on the correct ring atoms i.e. structure is correct	1

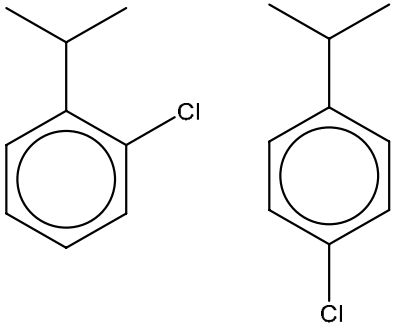
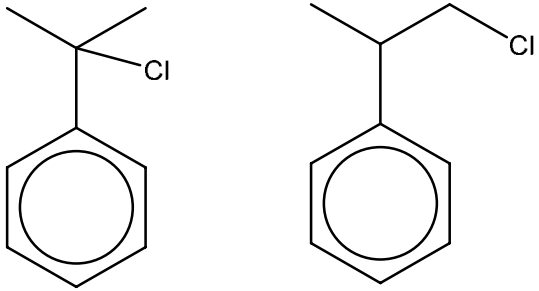
7(a)	<table><tr><th>W</th><th></th><th>Y</th><th>Z</th></tr><tr><td>acyl chloride / COC*l*</td><td>methyl ketone / CH3CO group aryl chloride</td><td>aldehyde / CHO chloro(alkane) / RCl</td><td>Alkene / C=C phenol / C_6H_5OH aryl chloride</td></tr></table> 0–1 [0]; 2 [1]; 3 [2]; 4 [3]; 5 [4]; 6–8 [5]	**5**
7(b)(i)	**W**  or  **X** 	**1 + 1**
	Y  or  **Z** 	**1 + 1**
7(b)(ii)	**Y**  OR any chiral atom correctly labelled	**1**
	Total:	**10**

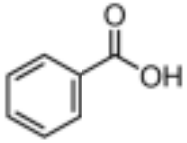
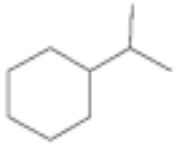
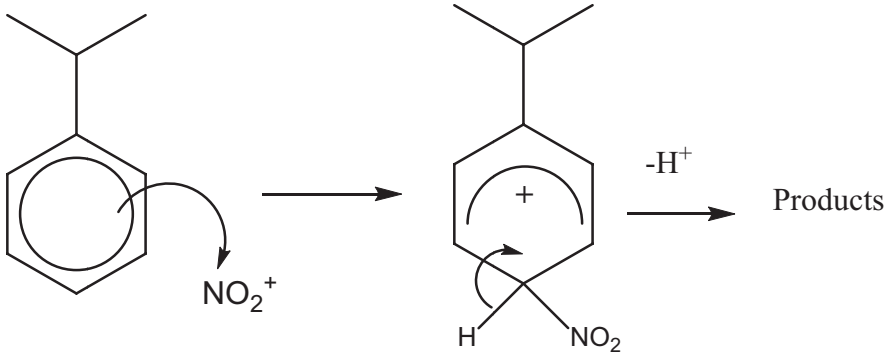
	step 2 nucleophilic addition	**1**
8(a)(ii)	hydrolysis	**1**
8(a)(iii)	step 1 $Cl CH_2CHO$ (**allow** Br, I for Cl)	**1**
	$AlCl_3$	**1**
	step 2 HCN + NaCN	**1**
	step 3 heat in H_3O^+ / heat $H^+(aq)$	**1**
	step 5 NH_3 under pressure (+ heat) **or** heat NH_3 in a sealed tube	**1**
8(a)(iv)	with NaOH(aq)  [2]	**1 + 1**
	with HCl(aq)  [1]	**1**
	with $Br_2(aq)$  or  [1]	**1**

Question	Answer	Marks
8(b)(i)	**P** is tyr	**1**
	tyr is 2– AND it is small / has a small *M*r	**1**
8(b)(ii)	*(dipeptide / phe-tyr)* 2– is about double the M_r / mass of (*phe) 1* OR mass / charge ratios are about the same for each (for dipeptide / phe-tyr and phe)	**1**
	Total:	**15**

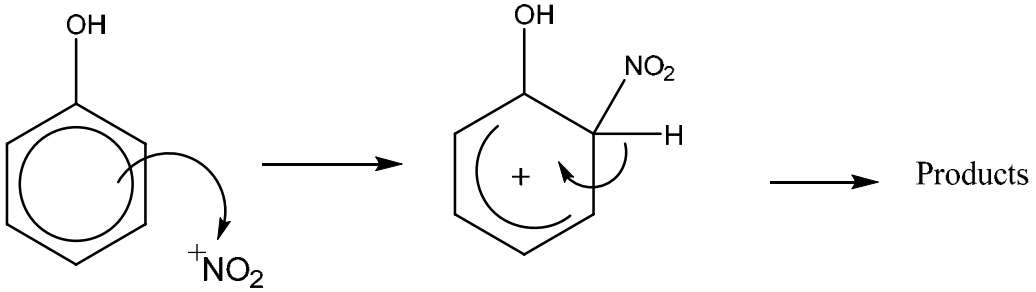
9(a)(i)		1
9(a)(ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	**1**
9(a)(iii)	**any three** from: Point 1: bonds / electrons are **partially** delocalised in **T** **or** delocalised / π system / π bonding extends over only five carbons Point 2: four π-electrons in the (delocalised system of **T**) **or** methylbenzene has (two) more π-electrons / (two) more delocalised electrons Point 3: contains a carbon that is sp^3 hybridised in **T** ***or*** (all the) carbons are sp^2 hybridised in methylbenzene Point 4**:** one carbon has a bond angle of 109.5° / tetrahedral (in **T)** ***or*** (C-C) bond strengths / lengths are not all the same **or** not all the bond angles are 120° (in **T**)	**3**
9(b)(i)	4-aminob acid	**1**
9(b)(ii)	step 1 Sn + HC*l* [1] concentrated / reflux / heat [1] step 2 CH_3COCl [1] step 3 $KMnO_4$ / manganate(VII) / MnO_4^- (acidified / alkaline) **and** heat [1] step 4 aqueous HC*l* **and** heat [1] step 5 ethanol, H_2SO_4, concentrated / reflux / heat [1]	**6**

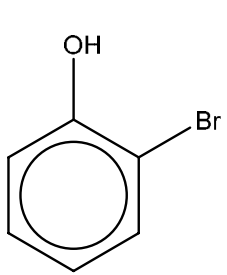
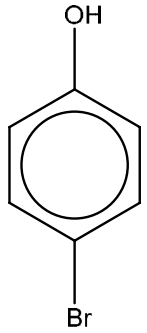
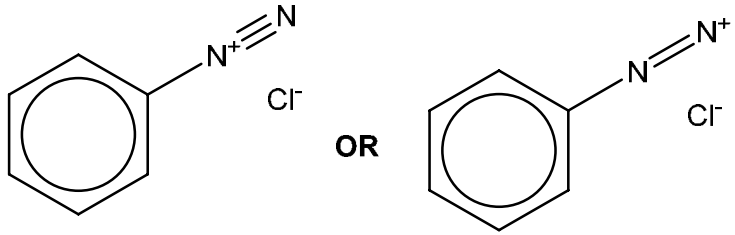
9(c)	(benzocaine) is less (basic than ethylamine) **AND** **lone pair** (on N) is less available to **accept** a proton / H^+ since (lone pair on N) is delocalised over the ring ***or*** phenyl ring is electron withdrawing group **OR** ethylamine is more basic (than benzocaine) **AND** **lone pair** (on N) is more available to **accept** a proton / H^+ since ethyl / alkyl group is electron-donating group	**2**

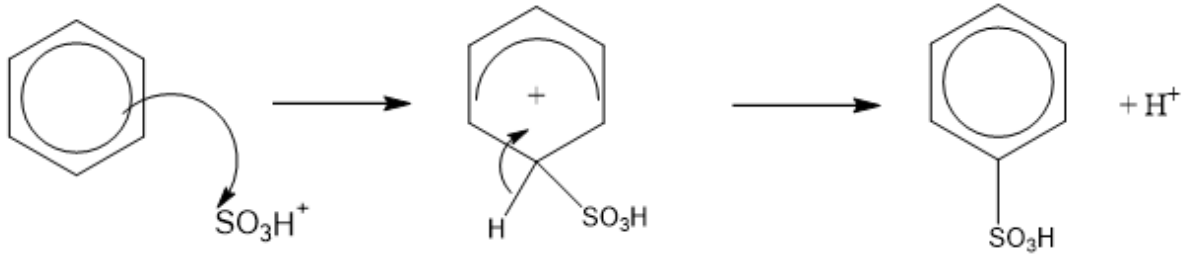
10(a)(i)	**D** 2-chloropropane	**1**
	E hydrogen chloride	**1**
10(a)(ii)	(Friedel-Crafts) alkylation	**1**
10(b)(i)	$AlCl_3$ or $FeCl_3$	**1**
10(b)(ii)		**1**
10(b)(iii)	sunlight or UV **OR** T>100 °C	**1**
10(b)(iv)		**1**

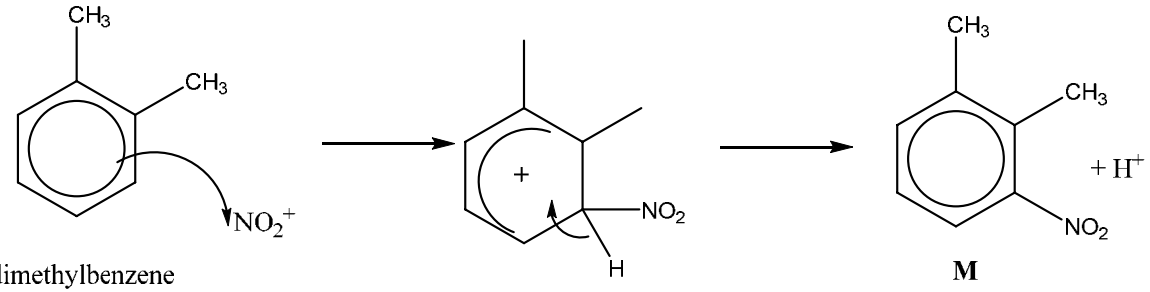
10c)	reaction with hot $KMnO_4(aq)$ 	**1**
	reaction with H_2 + Ni, high pressure 	**1**
10(d)		
	attacking species is NO_2^+	**1**
	curly arrow starting within hexagon and going to NO_2^+	**1**
	correct intermediate	**1**
	2nd curly arrow from C-H bond into ring	**1**

11(a)	<u>any two from</u> K / potassium or KOH / potassium hydroxide or K_2O / potassium oxide	**2**
	correct products: (K) hydrogen, (KOH) water, (K_2O) water	**1**
11(b)(i)	bond circled between N = N	**1**
11(b)(ii)	phenylamine **and** HNO_2	**1**
	T=10 ^oC or below **and** diazonium ion / salt formed or structure of diazonium ion as $[C_6H_5N_2^+]$	**1**
	add 2-naphthol in aqueous NaOH / alkali	**1**
11(c)(i)	/ aqueous nitric acid / $HNO_3(aq)$ (at room temp.)	**1**
	<u>any two from</u> concentrated (acid) needed sulfuric acid / H_2SO_4 needed higher T needed **ora**	**1**
11(c)(ii)	p-orbital(s) / lone pair on oxygen / OH group delocalises into / over ring	**1**

11(c)(iii)		
	first curly arrow	**1**
	structure of intermediate	**1**
	2nd curly arrow	**1**
11(c)(iv)	4-nitrophenol	**1**

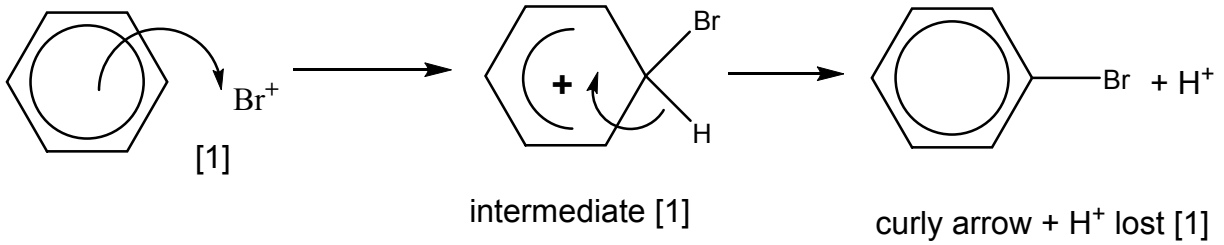
12(a)	**M1** C-X / C-C*l* / C-O bond is strong**er** (in chlorobenzene / phenol) [1] **M2** p-orbital / lone pair on C*l* / O(H) / X (in chlorobenzene / phenol) [1] **M3** electrons of the (C*l* / O / electronegative atom) **AND** overlap / delocalise with π-electron cloud / delocalise into ring [1]	**3**
12(b)	 2-bromophenol  4-bromophenol structure and name correct [1]	**2**
12(c)(i)	step 1 **conc.** HNO_3 + H_2SO_4 (and temperare 50–55 °C) [1] step 2 Sn + HC*l* **AND one** of conc.HC*l* + heat [1] step 4 H_2O warm / heat [1]	**3**
12(c)(ii)		**1**
12(c)(iii)	step 1 electrophilic substitution	**1**
12(c)(iv)	$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$	

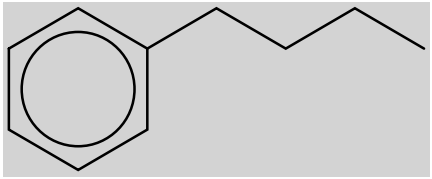
	M2: H_2 + Ni / Pt catalyst	
13(a)(ii)	**M1**: benzene (**120°**) and cyclohexane (**109.5°**) **M2**: as π-bonds are transformed into σ-bonds	**2**
13(b)(i)	 **M1**: first curly arrow to the sulfur atom **M2**: intermediate shown **M3**: 2nd curly arrow and H^+ formed / lost	**3**
13(b)(ii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$	**1**
13(c)	**M1**: $C_{12}H_{25}Br$ **and** halogen carrier e.g. $AlBr_3$ (+ heat) **M2**: electrophilic substitution	**2**
13(d)(i)	$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	**1**
13 d)(ii)	K_a of H_2SO_4 is larger than K_{a2}	**1**
13(e)	**M1**: $[H^+] = 10^{-2.90} = 1.26 \times 10^{-3}$	**2**

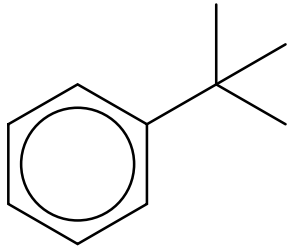
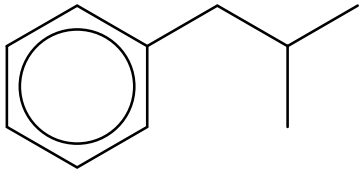
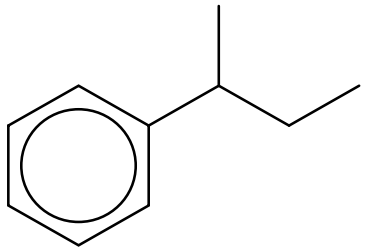
14(a)	any **three** points from: 3 × [1] • bond angle = 120° **and** shape is (hexagonal ring) planar / (trigonal) planar • carbons are sp^2 hybridised • contains <u>delocalised electrons</u> in the π bonds / system • sp^2 orbitals between C-H / C-C overlap to form **σ bonds** • a **p orbital** from each carbon atom overlap sideways with each other above and below the ring forming **π bonds** **ALLOW** labelled diagrams for bullets 1–5	**3**
14(b)(i)	$HNO_3 + H_2SO_4 \rightarrow HSO_4^- + H_2O + NO_2^+$ ***or*** $HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ [1]	**1**
14b)(ii)	 1,2-dimethylbenzene **M** first curly arrow to N of NO_2^+ [1] correct intermediate [1] 2nd curly arrow **and** H^+ formed / lost [1]	**3**
14(b)(iii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$ [1]	**1**
14(b)(iv)	Sn + conc. HC*l* (+ heat) [1] reduction [1] **IGNORE** redox	**2**
14(c)(i)	$_{15}H_{15}NO_2$ [1]	**1**
14(c)(ii)	amine **and** carboxylic <u>acid</u> **both** [1]	**1**

14(c)(iii)	amount of 2,3-dimethylphenylamine = 5.00 / 121 = 0.0413 mol [1] amount of mefenamic acid = 0.0413 mol mass of mefenamic acid = 0.0413 × 241 = **9.96 / 9.95** g 3sf required [1] ECF	**2**
14(d)	**3º** carbocations are more stable than **2º** carbocations [1] due to the methyl group acting as an electron donating group (leading to an increase in electron density on the cation stabilising it) [1]	**2**

Question	P42/ON/19/Q7/	Marks
15(a)(i)	• two or more repeat units • correct orientation of groups on all four rings and rings correct • trailing bonds shown • amide links all correct Award 1 mark for two points, award 2 marks for all four points	**2**
15(a)(ii)	polyamide and condensation	**1**
15(a)(iii)	yes **and** can be hydrolysed	**1**
15(a)(iv)	PCl_3 or PCl_5 or $SOCl_2$	**1**
15(a)(v)	**M1:** conc nitric acid + conc sulfuric acid **M2:** Sn + HCl	**2**
15(b)(i)	**M1:** sequence / order of amino acids **M2:** α-helix **or** β-sheet **M3:** folding of chain **or** 3-D shape	**3**
15(b)(ii)	covalent bonds / peptide bonds / amide bonds	**1**
15(b)(iii)	**M1:** hydrogen bonds **M2:** between C=O and N–H	**2**

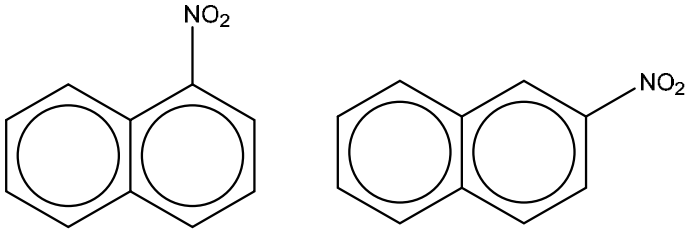
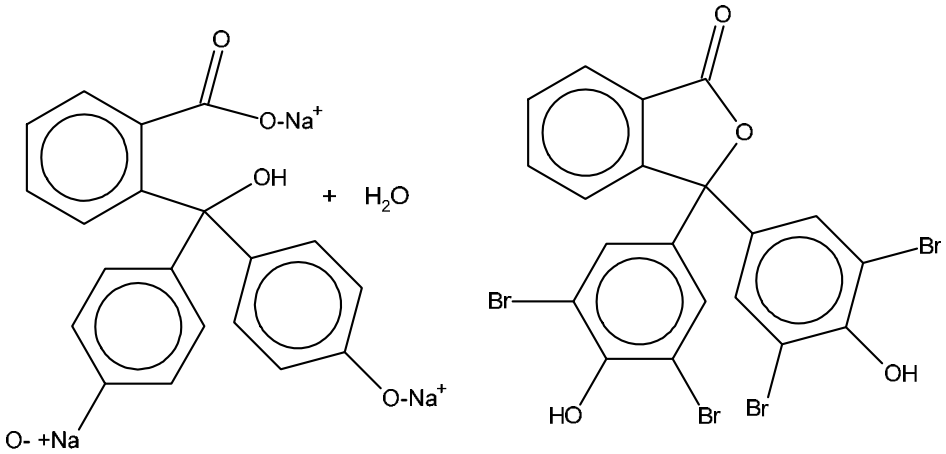
16(a)(i)	The substitution product is stabilised by delocalisation of (6)π-electrons **OR** The addition product is not stabilised by delocalisation of (6)π-electrons [1]	**1**
16(a)(ii)	 [1] intermediate [1] curly arrow + H^+ lost [1] • first curly arrow • intermediate • 2nd curly arrow, product **and** H^+ formed / lost	**3**
16(a)(iii)	$AlBr_4^- + H^+ \rightarrow AlBr_3 + HBr$	**1**
16(b)	lone pair of oxygen is delocalised into the ring <u>any one from:</u> • phenol has a higher electron density in the ring • phenol can polarise/induce a dipole in Br_2	**2**
16(c)(i)	$CH_3CH_2CH^+CH_3$ $(CH_3)_2CHCH_2^+$ $(CH_3)_3C^+$ Each correct structure = 1 mark	**3**

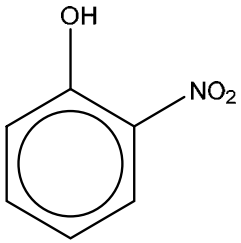
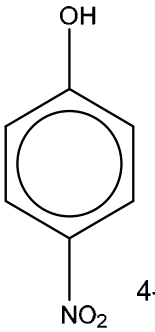
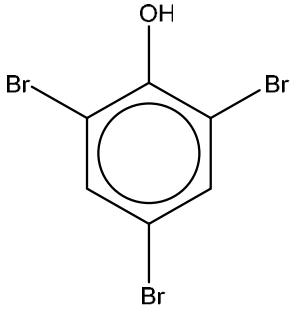
16(c)(ii)	 number of peaks in carbon-13 NMR = 8	**4**

 number of peaks in carbon-13 NMR = 6	
 number of peaks in carbon-13 NMR = 7	 number of peaks in carbon-13 NMR = 8

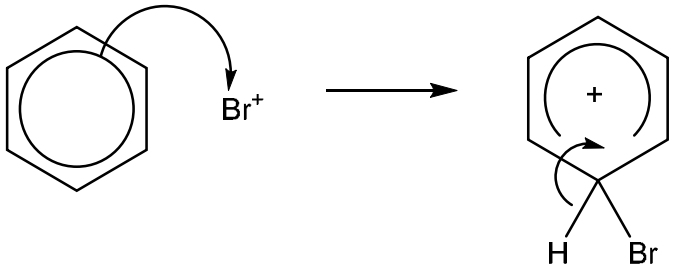
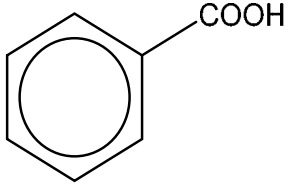
Two correct organic products = 1 mark
three correct organic products = 2 marks

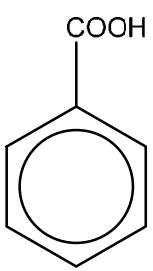
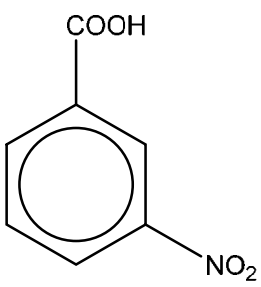
all products linked correctly to NMR = 2 marks

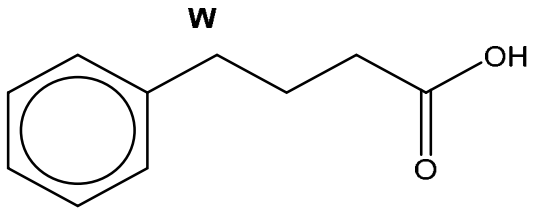
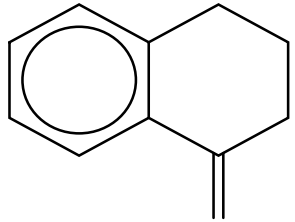
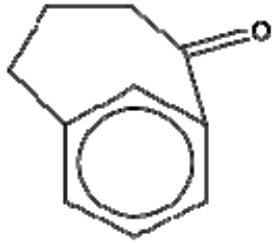
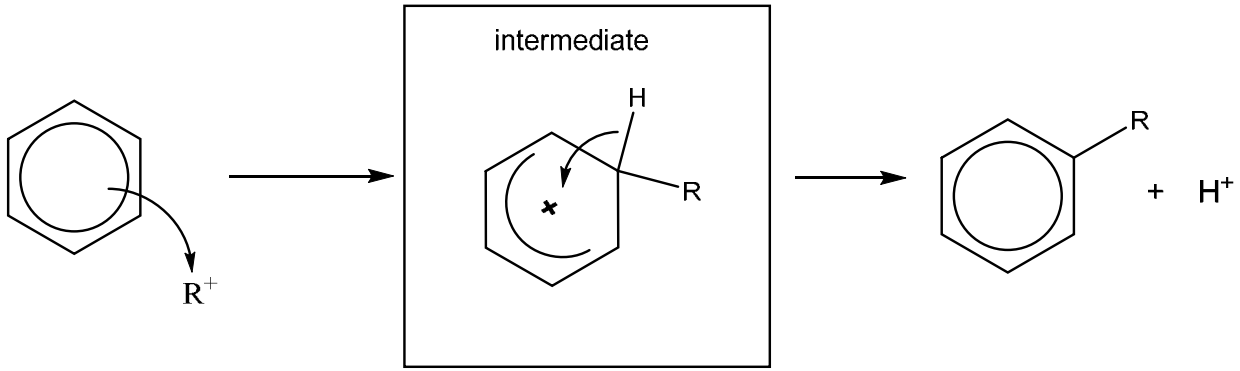
	• trigonal planar Award one mark for two correct statements, award two marks for three correct statements	
17(a)(ii)	 Both structures required	**1**
17(b)	$C_{10}H_8 + 9[O] \rightarrow C_8H_4O_3 + 2CO_2 + 2H_2O$	**1**
17(c)	condensation/ addition-elimination	**1**
17(d)(i)	phenol **AND** ester	**1**
17(d)(ii)	 **M1** correct hydrolysis product of ester **M2** (di)phenoxide salt	**4**

18(a)	**M1:** HNO_2 **OR** $NaNO_2$ + HCl [1] **M2:** T ⩾ 10 °C / warm **AND** water [1]	**2**
18(b)	 2-nitrophenol  4-nitrophenol 2 × [1]	**2**
18(c)(i)	 2,4,6-tribromophenol ✓ ✓ [2]	**2**
18(c)(ii)	bromine is decolourised **AND** white precipitate is formed **BOTH** [1]	**1**
18(d)	$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ [1] **ALLOW** any equation for phenol acting as an acid	**1**

18(e)	phenol>water>ethanol [1] • (phenol:) lone pair on oxygen is delocalised into the benzene ring • (ethanol:) positive inductive effect / electron donating effect of alkyl / ethyl group • correct statement about stabilisation of anion/ conjugate base **OR** weakening of O-H bonds once *in the context of phenol / ethanol* • correct statement about ease of proton/H^+ donation *in the context of phenol / ethanol* [2] Two correct statements = 1 mark	**3**

19(a)(i)	HBr / hydrogen bromide [1]	**1**
19(a)(ii)	 **M1** curly arrow to Br^+ **AND** curly arrow from C–H bond as shown [1] **M2** correct intermediate [1]	**2**
19(a)(iii)	**electrophilic substitution** [1]	**1**
19b)(i)	re chloroethane / bromoethane / iodoethane **OR** formula [1] catalyst: $FeCl_3$ / $AlCl_3$ etc. [1]	**2**
19(b)(ii)	 [1] **ALLOW** C_6H_5COONa	**1**
19(b)(iii)	step 3 = $LiAlH_4$ [1] step 4 = Pt **AND** H_2 [1]	**2**
19(b)(iv)	5 / five [1]	**1**

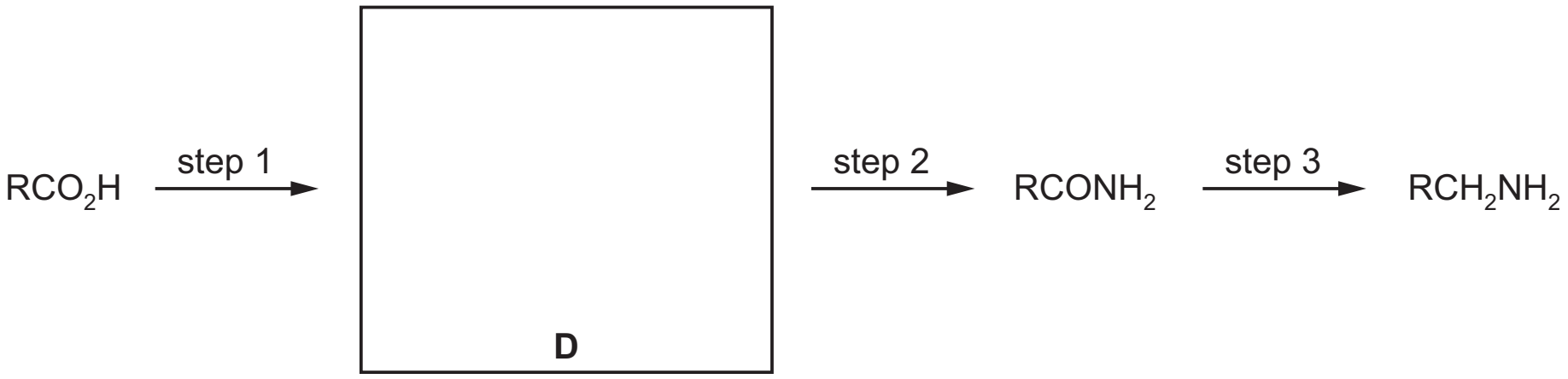
20(a)(i)	**M**  **N** 	**2**
20(a)(ii)	**M1:** step 1 hot $KMnO_4$ / MnO_4^- **M2:** step 2 conc. H_2SO_4 and conc. HNO_3 **M3:** step 3 Sn and conc. HC*l* (heat)	**3**

	OR $Cl(CH_2)_3COOH + AlCl_3 \rightarrow {}^{+}(CH_2)_3COOH + AlCl_4^-$	
21(b)(ii)	**W**  **X** $C_{10}H_{10}O$  **OR** 	**2**
21(b)(iii)	$SOCl_2$ **OR** PCl_5 **ALLOW** PCl_3 **AND** heat	**1**
21(b)(iv)		**3**

M1: arrow to R^+ **OR** arrow to positive carbon of ${}^{+}(CH_2)_3COOH$
M2: correct structure of intermediate
M3: arrow from C-H bond into the ring **AND** H^+

Paper 4
Topic 8
Carboxylic Acid And Their Derivatives

1 **(a)** Carboxylic acids can be converted into primary amines by the following sequence of reactions.



(i) Suggest the identity of intermediate **D** and write its structure in the box above. [1]

(ii) Suggest the reagents for

step 1 .....

step 2 .....

step 3 .....
[2]

(b) Four compounds, **E**, **F**, **G** and **H**, are isomers of each other.
Each compound contains an aromatic ring and **two** functional groups from the following list.

- alcohol
- amide
- amine
- carboxylic acid
- ester
- phenol

(i) Which of these functional groups react readily with cold HCl(aq)?

..... [1]

(ii) Which of these functional groups react readily with cold NaOH(aq)?

..... [1]

The molecular formula of the four isomers, **E**, **F**, **G** and **H**, is $C_8H_9NO_2$. All four compounds are insoluble in water. **Table 1** shows their solubilities in acid or alkali.

compound	solubility in HCl(aq)	solubility in NaOH(aq)
E	insoluble	insoluble
F	soluble	soluble
G	soluble	insoluble
H	insoluble	soluble

Table 1

(iii) Use this information to suggest the **two** functional groups, taken from the list on page 10, that each compound contains.

compound	first functional group	second functional group
E		
F		
G		
H		

[4]

(iv) Suggest a structure for each compound.

E

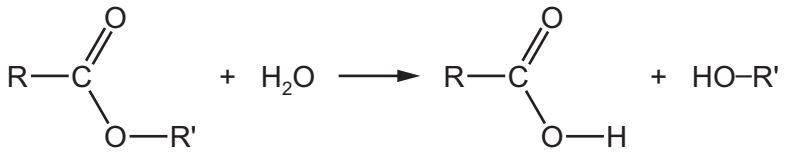
F

G

H

[4]

[Total: 13]



Enzymes can be quite specific in the structures of the substrates they act upon. For example, an esterase isolated from the mould *Aspergillus niger* will hydrolyse phenyl ethanoate, $CH_3CO_2C_6H_5$, but not its isomer methyl benzoate, $C_6H_5CO_2CH_3$.

(a) Outline how enzymes catalyse reactions, and explain their specificity.
Use diagrams in your answer where appropriate.

.....

.....

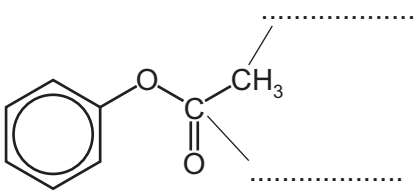
..... [3]

(i) The carbon-13 NMR spectra of isomers **A** and **B** contain the following peaks.

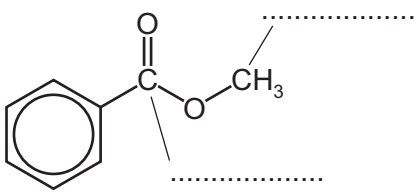
isomer **A**	isomer **B**
δ 52	δ 26
δ 128	δ 122
δ 129	δ 126
δ 130	δ 129
δ 133	δ 151
δ 167	δ 169

The identity of the compound responsible for each spectrum can be deduced by studying the chemical shifts (δ) of the peaks in the spectra.

Use the *Data Booklet* to assign the correct peaks to the labelled carbon atoms in the structures of the isomers below. Write each value next to the relevant carbon atom and hence deduce the identity of each isomer.



phenyl ethanoate is isomer .....



methyl benzoate is isomer .....

[2]

(ii) These two isomers are difficult to distinguish chemically.

Describe a method of converting them to suitable products in step 1 which can then be tested in step 2.
You should state the reagents and conditions for each step, and any observations you would make.

step 1 .....

.....

.....

step 2 .....

.....

.....

[3]

Draw a 'dot-and-cross' diagram of $SOCl_2$. Show the outer shell electrons only.

[2]

(b) When $SOCl_2$ is reacted with a carboxylic acid to produce an acyl chloride, two acidic gases are formed.

$$SOCl_2(l) + RCO_2H(l) \rightarrow RCOCl(l) + SO_2(g) + HCl(g)$$

A 1.00 g sample of a carboxylic acid RCO_2H was treated in this way, and the gases were absorbed in 60.0 cm^3 of 0.500 mol dm^{-3} NaOH(aq), an excess.

(i) Write equations for the reactions between

NaOH and HCl, ...

NaOH and SO_2. .....

[2]

The excess NaOH was titrated with 0.500 mol dm^{-3} $H^+(aq)$. It required 10.8 cm^3 of the $H^+(aq)$ solution to reach the end-point.

(ii) Calculate the total number of moles of NaOH that reacted with the SO_2 and HCl.

moles of NaOH = ... [2]

(iii) Calculate the number of moles of RCO_2H that produced the SO_2 and HCl.

moles of RCO_2H = ... [1]

M_r RCO_2H = ... [1]

(v) The R group contains carbon and hydrogen only.

Suggest the molecular formula of RCO_2H.

..... [1]

(c) The following synthetic route shows how a carboxylic acid can be converted into an amine.

$$CH_3CO_2H \xrightarrow{SOCl_2} CH_3COCl \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow{\text{step 3}} CH_3CH_2NH_2$$

(i) Suggest a reagent for step 3.

..... [1]

Angelic acid, $C_5H_8O_2$, is a natural product isolated from the roots of the angelica plant.

- Angelic acid reacts with H_2 + Ni to form **T**, $C_5H_{10}O_2$.
- **T** undergoes the above synthetic route to form the amine **U**, $C_5H_{13}N$.
- **U** can also be made by reacting 1-bromo-2-methylbutane with ammonia.

Both angelic acid and **T** exist as stereoisomers.

(ii) Suggest structures for angelic acid, **T** and **U**.

angelic acid	**T**	**U**

[3]

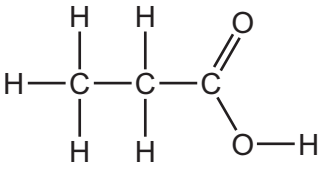
(iii) State the type of stereoisomerism shown by angelic acid and **T**.

angelic acid .....

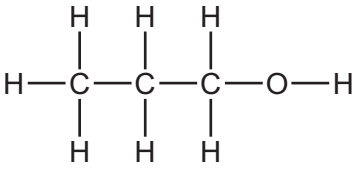
compound **T** .....

[1]

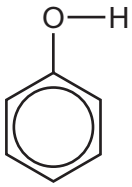
[Total: 14]



propanoic acid



propan-1-ol



phenol

(a) Write an equation for the reaction between propan-1-ol and sodium metal.

..... [1]

(b) **(i)** Give the order of the relative acidities of propanoic acid, propan-1-ol and phenol, stating the most acidic first.

..... [1]

(ii) Explain your answer to **(i)**.

.....

.....

.....

.....

.....

..... [2]

(c) Methanoic acid, HCO_2H, has a similar acid strength to propanoic acid.

Describe a chemical test to distinguish between these two acids. Name the acid which gives a positive result in this test and describe the observations that would be made.

.....

.....

.....

..... [2]

For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

.....

.....

.....

..... [3]

(i) State the reagents and conditions and name the mechanism for this reaction.

reagents and conditions .....

name of mechanism .....
[2]

(ii) State and explain the relative acidities of trichloroethanoic acid, chloroethanoic acid and ethanoic acid.

.....

.....

.....

.....

.....21..... [3]

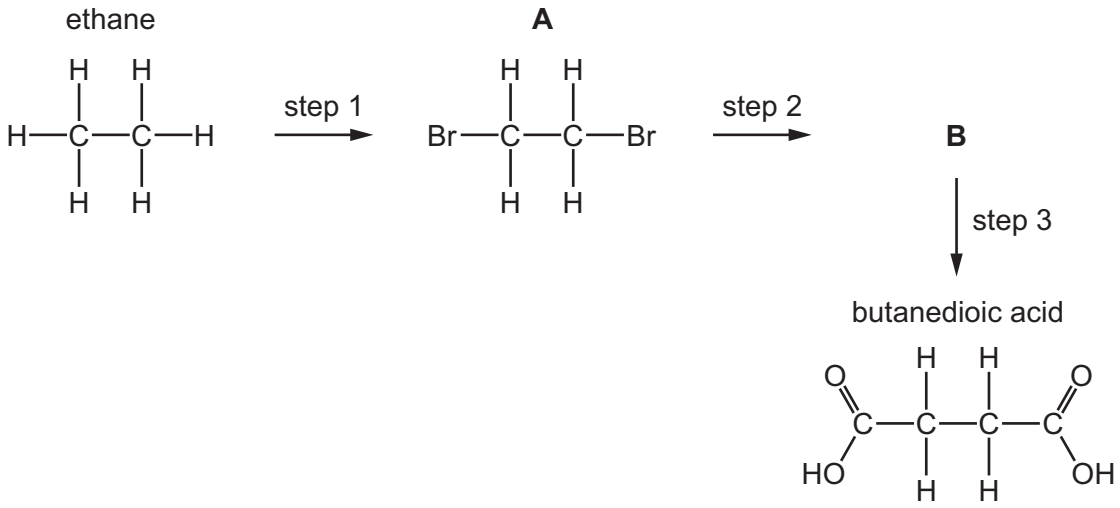
(e) Serine, $HOCH_2CH(NH_2)CO_2H$, can react with alanine, $CH_3CH(NH_2)CO_2H$, to form three different **structural** isomers, each with the molecular formula $C_6H_{12}N_2O_4$.

Draw the structures of these three structural isomers.

isomer 1 ($C_6H_{12}N_2O_4$)

isomer 2 ($C_6H_{12}N_2O_4$)

isomer 3 ($C_6H_{12}N_2O_4$)



(a) Describe the reagents and conditions needed for step 1.

..... [1]

(b) Name the other product also formed in step 1 which is an isomer of **A**.

..... [1]

(c) Give the structural formula of **B**.

[1]

(d) State the reagents and conditions needed for step 2.

..... [2]

(e) Butanedioic acid cannot be oxidised by a warm, aqueous solution of any commonly used oxidising agents but ethanedioic acid can.

(i) Identify the oxidising agent that could be used to oxidise ethanedioic acid.

..... [1]

(ii) State the product(s) of the reaction in **(e)(i)**.

..... [1]

.....

.....

.....

.....

.....

..... [3]

Place these three compounds in order of acidity, starting with the **least** acidic.
Explain your answer.

..... < ..... < .....

least acidic most acidic

.....

.....

.....

.....

.....

[3]

(b) Methanoic acid, HCO_2H, and ethanedioic acid, HO_2CCO_2H, are two other carboxylic acids.

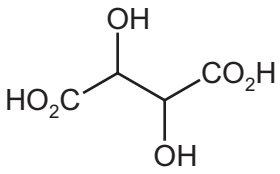
(i) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with Fehling's reagent.

..... [1]

(ii) State which, if any, of ethanoic acid, methanoic acid and ethanedioic acid will react with warm acidified manganate(VII) ions.

..... [1]

tartaric acid



reagent	structure of organic product	type of reaction
an excess of $LiAlH_4$		
an excess of CH_3COCl		

[3]

(ii) Tartaric acid reacts with the amine 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, to form an ionic salt.

Draw the structure of the salt formed in this reaction. Include the charges on the ions.

[1]

[Total: 17]

..... > ..... > ..... > .....

most acidic least acidic

.....

.....

.....

.....

.....

..... [4]

(b) Three carboxylic acids, methanoic acid, HCO_2H, ethanedioic acid, HO_2CCO_2H, and butanedioic acid, $HO_2CCH_2CH_2CO_2H$, are compared. Two tests were carried out on separate samples of each organic acid, as shown.

The following results were obtained. ✓ = observed change ✗ = no observed reaction

test	reagents and conditions	HCO_2H	HO_2CCO_2H	$HO_2CCH_2CH_2CO_2H$	observed change
1		✓	✗	✗	
2		✓	✓	✗	

(i) Complete the table with the reagents and conditions and the observed change for a positive test.
Assume these organic acids all have a similar acid strength. [3]

Complete the table.

compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR
HCO_2H		
HO_2CCO_2H		
$HO_2CCH_2CH_2CO_2H$		

[2]

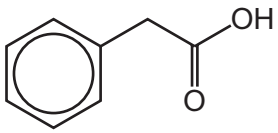
(iii) The proton NMR spectrum of HCO_2H in D_2O is obtained.

Describe and explain the difference observed between this spectrum and the proton NMR spectrum of HCO_2H in **(b)(ii)**.

.....

.....

..... [1]



(a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

(b) Phenylethanoic acid, ethanol and phenol can all behave as acids.

Compare and explain the relative acidities of these three compounds.

..... > ..... > .....
most acidic least acidic

.....

.....

.....

.....

..... [4]

(c) Phenylethanoic acid can be synthesised using benzene as the starting material.

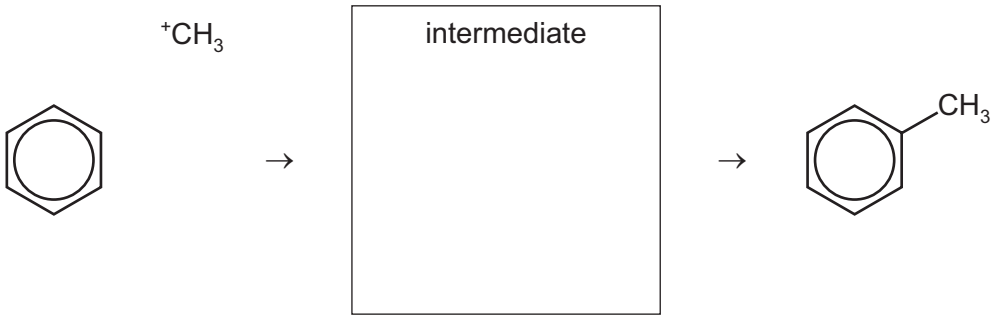
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

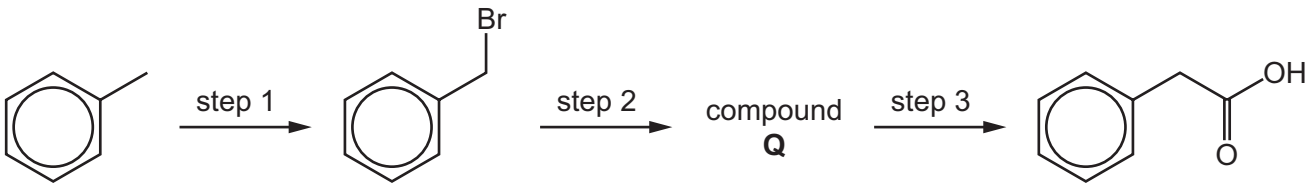
Chloromethane reacts with $AlCl_3$ to form two ions. One of these is the carbocation $^+CH_3$.

(i) Write an equation for the reaction between chloromethane and $AlCl_3$.

..... [1]

(ii) Draw the mechanism of the reaction between benzene and $^+CH_3$. Include all relevant curly arrows, charges and the structure of the intermediate.





(i) State reagents and conditions for step 1.

..... [1]

(ii) Suggest the structure of compound **Q**.

[1]

(iii) State reagents and conditions for steps 2 and 3.

step 2 .....

step 3 .....

[2]

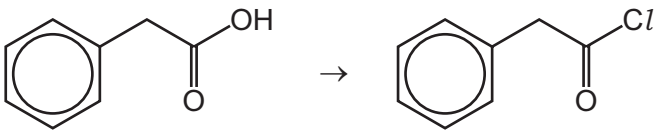
(iv) Draw the structure of an organic by-product that forms in step 1.

[1]

[Total: 14]

(a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.

phenylethanoic acid **R**

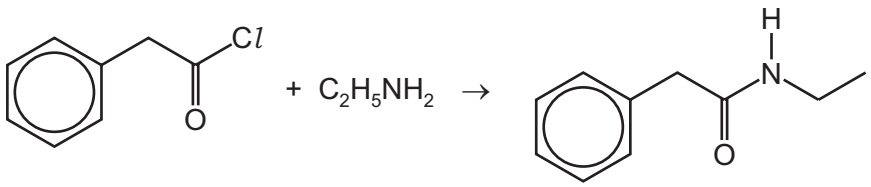
stage 1 

Suggest a suitable reagent for stage 1.

..... [1]

(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

R **S**

stage 2 

(i) Name the functional group formed in stage 2.

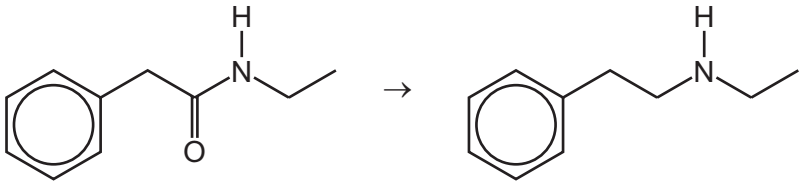
..... [1]

(ii) Identify the other product formed in stage 2.

..... [1]

(c) In stage 3, compound **S** reacts with a suitable reagent to form compound **T**.

S **T**

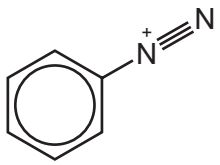
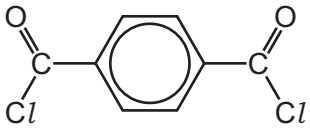
stage 3 

(i) State the formula of a suitable reagent for stage 3.

..... [1]

(ii) Name the type of reaction that occurs in stage 3.

..... [1]

reaction	reaction mixture	structure of organic product
1	phenol + NaOH(aq)	
2	phenol + Na(s)	
3	phenol +  (aq) + NaOH, at 4 °C	
4	an excess of phenol + 	

[4]

(b) Identify **two** reactions from the table in which ethanol would behave in a similar way to phenol.

..... [1]

[Total: 5]

1 (a) There are three acceptable alternatives – follow each column down vertically:

(i) D is	RCOC*l*	$RCOOCH_2CH_3$	$RCO_2^-\ NH_4^+$
(ii) step 1	$SOCl_2$ (*or* PCl_3 *or* PCl_5)	ethanol (e.g.) + conc H_2SO_4	NH_3
(ii) step 2	NH_3 (NaOH negates this mark)		heat
(ii) step 3	$LiAlH_4$ (aq) negates(NOT $NaBH_4$; Sn + HC*l* etc.)		

(b) (i) amine (other groups negate) **[1]**

(ii) phenol **and** carboxylic acid (**both** needed) **[1]**

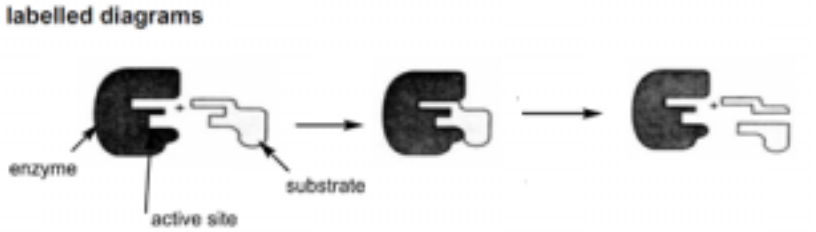
(iii) **[4]**

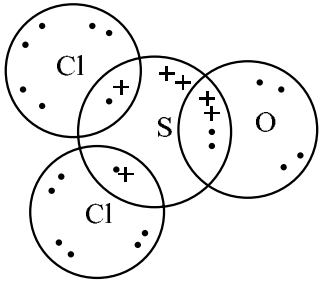
compound	first functional group	second functional group
E	**amide**	**al**
F	**amine**	**carbo** **acid**
G	**amine**	
H	**amide**	**p**

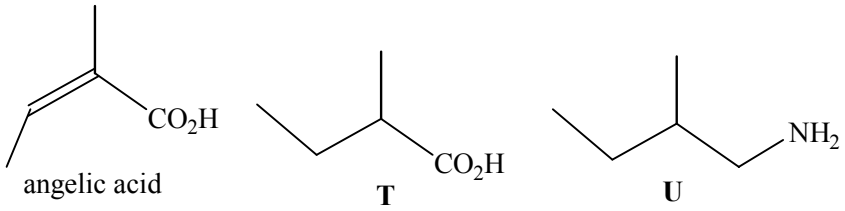
(iv) Mark this in the following way. For each structure of **E**, **F**, **G** and **H**: **[4]**

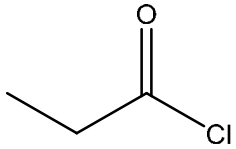
- check whether the structure fits the molecular formula $C_8H_9NO_2$, i.e. that it has: **one** nitrogen, **two** oxygens and **eight** carbons.
- check that it contains the two groups that the candidate's answers to part (ii) says it contains.

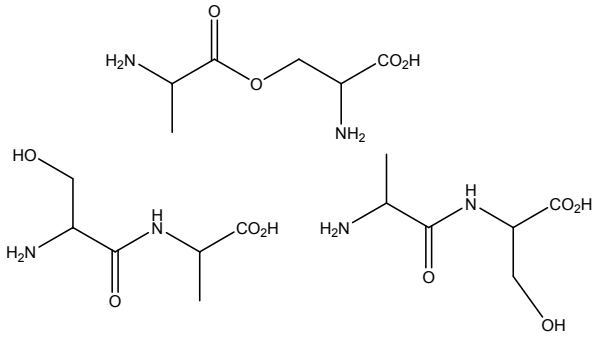
[Total: 13]

Question	Answer	Marks
2 (a)	*essential mark* M1 the reactants / substrate has a **shape** complementary / **specific** to **active site** – can be awarded from a labelled diagram as below **or** diagrams showing this specificity clearly *any two of* M2: reactants / substrate binds to / fits into the active site of the enzyme M3: (Interaction with site) causes a specific bond to be weakened, (which breaks) **or** lowers activation energy M4: forms an E-S complex M5: products released from enzyme / active site labelled diagrams  (products)	3
(b) (i)	δ 26 is **C**H3-CO δ 52 is **C**H3-O δ 169 is CH3**CO** δ 167 is phenyl-**C**O Phenyl ethanoate is **B** methyl benzoate is **A** M1 = any two correct δ linked to phenylethanoate / methyl benzoate M2 = the rest correct	2
(ii)	heat with H_3O^+ (to hydrolyse the ester) then add $Br_2(aq)$ / bromine water decolourises/gives white ppt (with phenol from **B**)	3

3(a)		
	four shared pairs: S=O and 2 × S-C*l*	**1**
	all (9) lone pairs	**1**
3(b)(i)	$NaOH + HCl \longrightarrow NaCl + H_2O$	**1**
	$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$	**1**

3(b)(ii)	moles (at start) = $0.5 \times 60 / 1000 = 3 \times 10^{-2}$ AND moles (at end) = $0.5 \times 10.8 / 1000 = 5.4 \times 10^{-3}$	**1**
	moles reacted (= $(30–5.4) \times 10^{-3}$ =) **2.5×10^{-2}** correct ans. scores [2]	**1**
3(b)(iii)	moles of $RCO_2H = 2.46 \times 10^{-2}/3 = 8.2–8.3 \times 10^{-3}$ mole	**1**
3(b)(iv)	$M_r = 1.00 / (8.2 \times 10^{-3}) = 121.95$ (=122)	**1**
3(b)(v)	$C_7H_6O_2$ OR $C_6H_5CO_2H$	**1**
3(c)(i)	$LiAlH_4$	**1**
3(c)(ii)		**3**
3(c)(iii)	angelic acid: geometrical OR cis-trans compound **T**: optical	**1**
	Total:	**14**

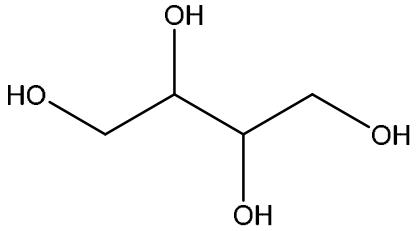
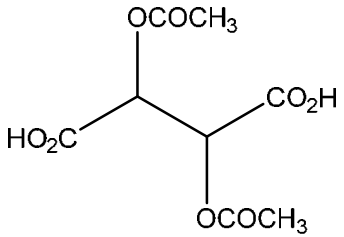
4(a)	$2C_3H_7OH + 2Na \rightarrow 2C_3H_7ONa + H_2$	**1**
4(b)(i)	propanoic acid, phenol, propan-1-ol	**1**
4(b)(ii)	• propan-1-ol: O-H bond strengthened by positive inductive effect of alkyl group **OR** propoxide ion is destabilised by positive inductive effect of alkyl group • phenol: O-H bond weakened by negative inductive effect of ring **OR** phenoxide ion is stabilised by delocalisation of oxygen lone pair into ring • propanoic acid: O-H bond weakened by negative inductive effect of C=O **OR** propanoate ion is stabilised by delocalisation of minus charge by C=O 1 mark for a correct explanation, max 2 marks	**2**
4(c)	Tolle reagent **or** Fehling's reagent	**1**
	methanoic acid gives a silver mirror/solid with Tollen's reagent **OR** red / orange ppt / solid with Fehlings' reagent	**1**
4(d)	PCl_5 or PCl_3 (+heat) or $SOCl_2$ (added to propanoic acid)	**1**
	product of first step: 	**1**
	add product of first step to phenol in NaOH	**1**

5(d)(i)	$_3$ (in ethanol) heat in a sealed tube [1] nucleophilic substitution [1]	**2**
5(d)(ii)	acidity of Cl_3CCO_2H > $ClCH_2CO_2H$ > CH_3CO_2H [1] **any two of:** C*l* is electronegative / electron withdrawing group **AND** Cl_3CCO_2H has more / 3 C*l* groups [1] weakens O-H bond **so** more likely to ionise / dissociate **OR negative** charge on anion is more stabilised **OR** charge / electron density on COO^- decreases so anion is (more) stabilised [1] CH_3 is electron donating **so** O-H bond is stronger so less likely to ionise in CH_3CO_2H **OR** CH_3CO_2H has no -I group **so** O-H bond is stronger and less likely to ionise [1]	**3**
5(e)	 One mark for each structure. [1] [1] [1]	**3**

6(a)	bromine / Br_2 **and** uv / light / heat	**1**
6(b)	1,1-dibromoethane	**1**
6(c)	$NCCH_2CH_2CN$ / CH_2CNCH_2CN	**1**
6(d)	**M1:** KCN / NaCN / CN^- **M2:** boil/heat/reflux **and** ethanol as solvent	**2**
6 (e)(i)	acidified manganate(VII) or dichromate(VI)	**1**
6(e)(ii)	carbon dioxide and water	**1**
6(f)	**M1:** most acidic: hexanoic acid > phenol > hexan-1-ol :least acidic • the other O atom in CO_2H group of hexanoic acid **either** – withdraws charge from OH group **or** is electronegative **and** weakens O–H bond **or** – stabilises resultant anion/negative ion / $–CO_2^-$ group/carboxylate ion • benzene / aromatic / C_6H_5 ring in phenol <u>delocalises</u> **either** – lone pair on O atom **and** weakens O–H bond **or** – lone pair on resultant anion/negative ion / phenoxide ion this stabilises resultant anion negative ion / $–CO_2^-$ group/carboxylate ion • the alkyl group in hexan-1-ol donates electrons this strengthens O–H bond Award 1 mark for each bullet point identified.	**3**

Question	Answer	Marks
7(a)	ethanamide – ethanoic acid – trichloroethanoic acid [1] • ethanamide is neutral / not a proton donor • chlorine is electronegative / electron withdrawing [1] • O–H bond weakened / anion stabilised • correct statement linking acid strength to H^+ donation [1]	**3**
7(b)(i)	methanoic acid [1]	**1**
7(b)(ii)	methanoic and ethanedioic acids [1]	**1**

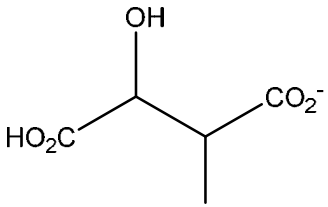
8(e)(i)

reagent	structure of organic product	type of reaction
an excess of LiA/H_4		reduction
an excess of CH_3COCl		condensation

M1: product with LiA/H_4
M2: product with CH_3COCl
M3: both types of reaction

3

8(e)(ii)



$C_6H_5CH(NH_3^+)CH_3$

OR dianion of tartrate with two cations present

1

<table>
<tr>
<td>9(a)</td>
<td>M1: ethanoic acid > butanoic acid > water > ethanol

M2: a reason given in terms of an electron donating or an electron withdrawing group for one of:
strengthening of O–H bond OR weakening of O–H bond OR stability of anion

Two out of the three alternatives M3, M4 and M5:

M3: <u>ethanol</u>: positive inductive effect / electron donating effect of ethyl / alkyl / R group

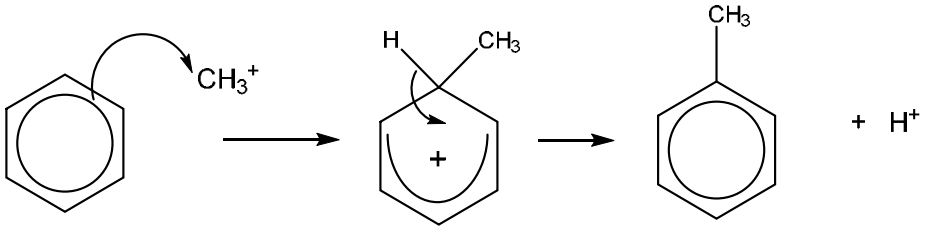
M4: <u>butanoic acid</u>: positive inductive effect / electron donating effect of propyl / alkyl / R group

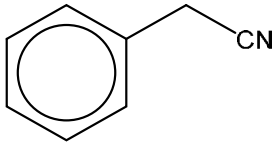
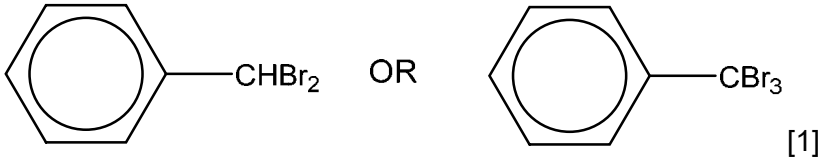
M5: (either ethanoic or butanoic) <u>acid</u>: negative inductive effect of either C=O or carbonyl OR negative charge delocalised over COO^-</td>
<td>4</td>
</tr>
<tr>
<td>9(b)(i)</td>
<td>
<table>
<tr><th></th><th>reagents and conditions</th><th>observed change</th></tr>
<tr><td>test 1</td><td>Tollen’s reagent, warm
OR
Fehling’s solution, warm</td><td>silver mirror

(brick) red ppt / solid</td></tr>
<tr><td>test 2</td><td>acidified MnO_4^-, warm</td><td>decolourises OR bubbles</td></tr>
</table>
M1 / M2: reagents and conditions × 2

M3: observations both correct
</td>
<td>3</td>
</tr>
</table>

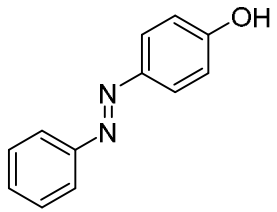
9(b)(ii)	<table><tr><th>compound</th><th>number of peaks in proton NMR</th><th>number of peaks in carbon-13 NMR</th></tr><tr><td>HCO_2H</td><td></td><td>1</td></tr><tr><td>HO_2CCO_2H</td><td></td><td>1</td></tr><tr><td>$HO_2CCH_2CH_2CO_2H$</td><td></td><td>2</td></tr></table> one mark for three, four or five correct two marks for six correct	**2**
9(b)(iii)	OH peak disappears **AND** proton / H exchanges with deuterium	**1**

10(a)	[1]	**1**
10(b)	M1: trend phenylethanoic acid > phenol > ethanol [1] M2: *why phenylethanoic acid is the strongest* • negative inductive electron withdrawing effect of C=O which weakens O-H bond / stabilises anion [1] M3: *why phenol is stronger than ethanol / weaker than phenylethanoic acid* • oxygen lone pair is delocalised into the ring system which weakens O-H bond / stabilises anion [1] M4: *why ethanol is the weakest* • electron donating alkyl / ethyl group which strengthens O-H bond / destabilises anion [1]	**4**
10(c)(i)	$CH_3Cl + AlCl_3 \rightarrow {}^{+}CH_3 + AlCl_4^-$ [1]	**1**
10(c)(ii)	 M1: arrow to CH_3^+ (arrow must come from inside the hexagon) [1] M2: correct structure of intermediate [1] M3: arrow <u>from</u> C-H bond into the ring **AND** H^+ seen [1]	**3**
10(d)(i)	Br_2 + UV light [1]	**1**

10(d)(ii)	 [1]	**1**
10(d)(iii)	**CHECK Q** is correct step 2 – KCN in ethanol + heat [1] step 3 – HC*l*(aq) + heat/reflux/boil [1]	**2**
10(d)(iv)	 [1] **ALLOW** any viable organic by-product from this radical substitution reaction, e.g. $C_6H_5CH_2CH_2C_6H_5$	**1**

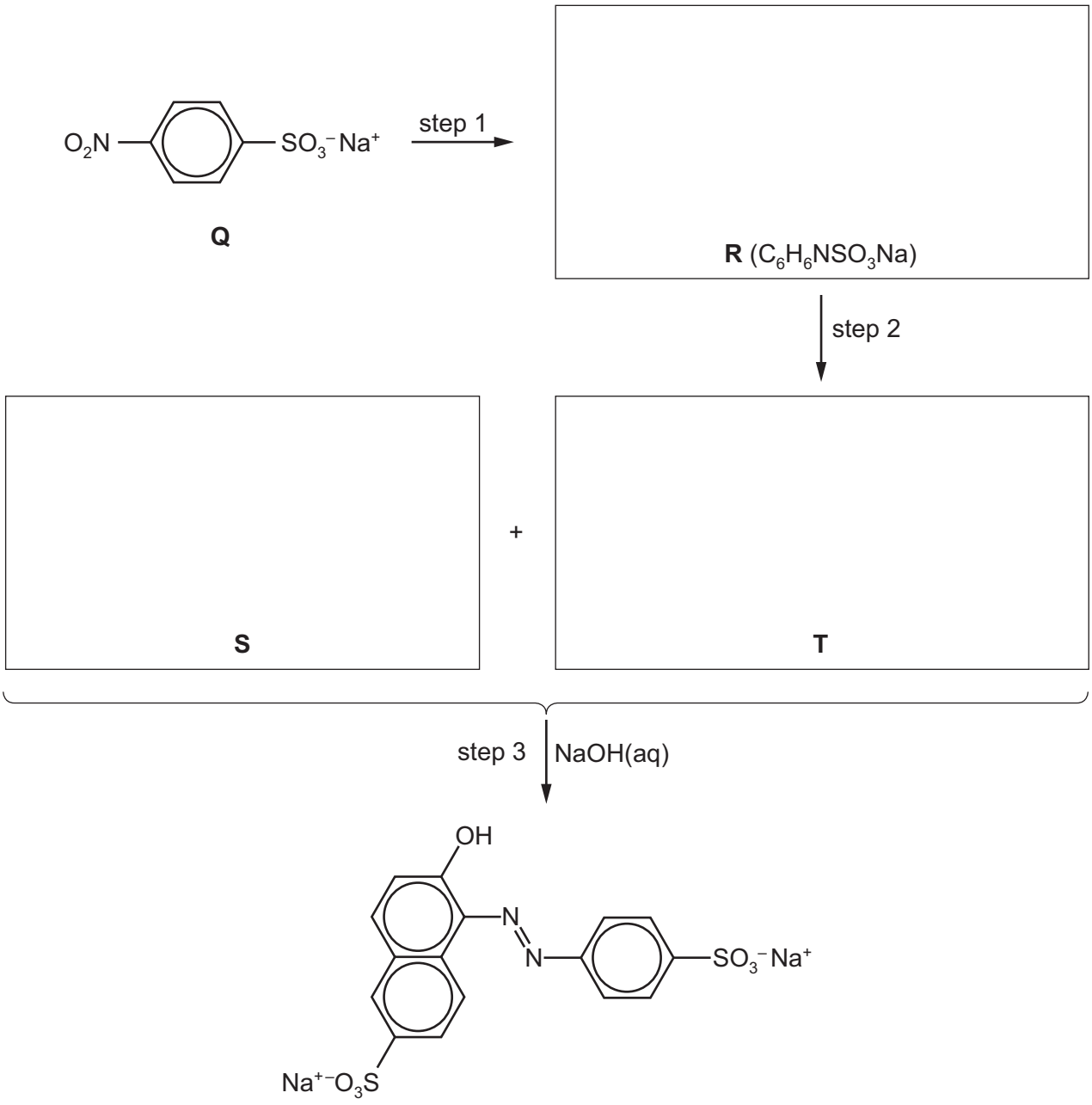
P41/O/N/21/Q9abc

Question	Answer	Marks
11(a)	PCl_5 **OR** PCl_3 **OR** $SOCl_2$ [1]	**1**
11(b)(i)	amide [1]	**1**
11(b)(ii)	HC*l*/ hydrogen chloride **OR** $C_2H_5NH_3Cl$/ ethylammonium chloride [1]	**1**
11(c)(i)	$LiAlH_4$ [1]	**1**
11(c)(ii)	reduction [1]	**1**

12(a)	$C_6H_5O^-$ / $C_6H_5O^-Na^+$ / C_6H_5ONa [1] $C_6H_5N_2C_6H_4O^-$ or $C_6H_5N_2C_6H_4OH$ or  [1] $C_6H_5OCOC_6H_4CO_2C_6H_5$ [1]	
12(b)	2 and 4 [1]	**1**

Paper 4
Topic 9
Organic Nitrogen Compunds And Proteins

In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
Assume that the $–SO_3^-Na^+$ group does not react.



Sunset Yellow

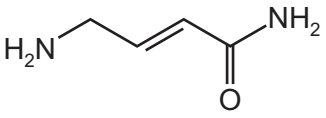
(i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]

(ii) Suggest reagents and conditions for

step 1, ...

step 2. .....
[3]

(iii) What type of organic salt is formed in step 2?



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds ..... π bonds ..... [2]

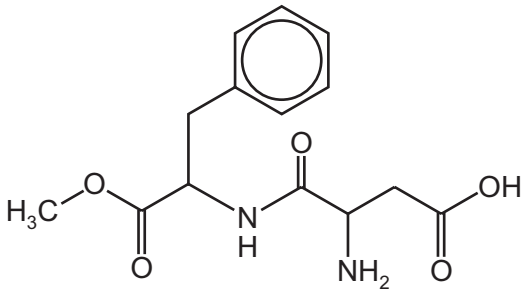
(ii) The products of the reactions of **W** with cold HC*l* and with CH_3CH_2Br are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

reagent	structure of product (molecular formula given)	type of reaction
HC*l*	($C_4H_9N_2OCl$)	
CH_3CH_2Br	($C_6H_{13}N_2BrO$)	

[3]

[Total: 12]



aspartame

(i) Draw a circle around each chiral centre in aspartame. [1]

In the stomach, aspartame is hydrolysed by acid to form three organic products.

(ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]

(iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.

[3]

By referring to the structure of aspartame, explain why it is soluble in water.

.....

.....

..... [2]

(c) Recently, nanotechnology has been involved in the development of a new natural sweetener, *Nano Sugar*, extracted from sugar cane.

What is the approximate width of a nanoparticle?

..... [1]

[Total: 9]

(a) **(i)** Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$$C_6H_5NO_2 + ...e^- + ...H^+ \rightarrow C_6H_5NH_2 + ...H_2O$$ [1]

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

$$.....C_6H_5NO_2 + ...HCl + ...Sn \rightarrow .....C_6H_5NH_3Cl + ...SnCl_4 + ...H_2O$$ [2]

(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $C_6H_5NH_3Cl$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

(c) Following the reaction in **(b)**, an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

(i) Calculate the mass of phenylamine, $C_6H_5NH_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of NaOH(aq).

mass of phenylamine = ... g [1]

The final volume of the alkaline solution of phenylamine in **(i)** was 25.0 cm^3. The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

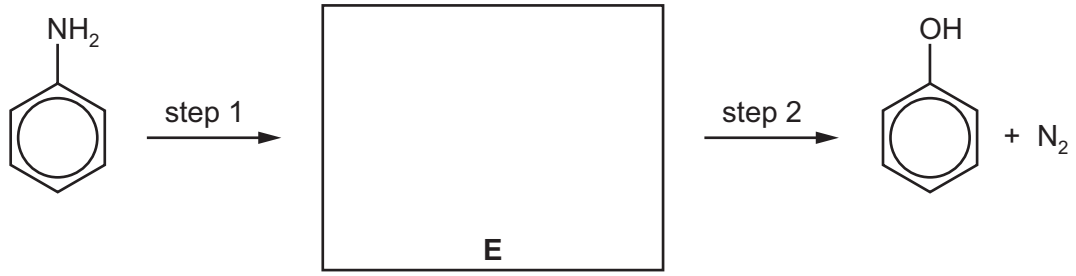
(ii) Use the data to calculate the partition coefficient, $K_{partition}$, of phenylamine between dichloromethane and water.

.....

.....

..... [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1 .....

step 2 .....

[2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

[Total: 13]

Ala-Ser-Gly

[2]

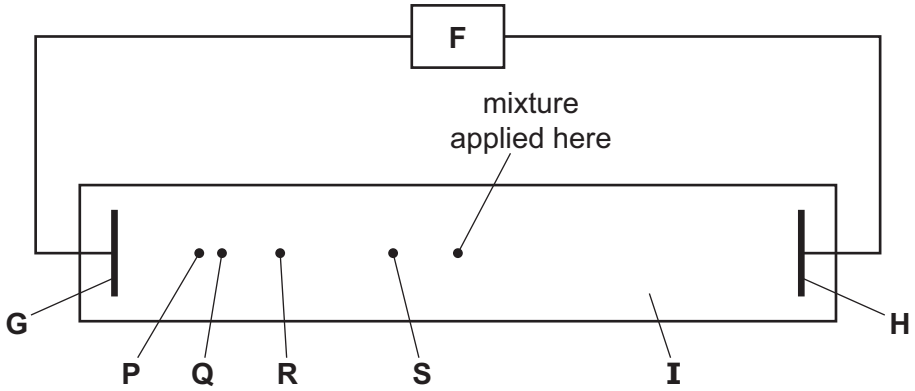
(ii) Calculate the relative molecular mass, M_r, of Ala-Ser-Gly.

M_r = ... [1]

(b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

(i) Draw the structure of serine at pH 11.

[1]



(ii) Identify the components labelled **F**-**I** in the above diagram.

F .....

G .....

H .....

I .....

[4]

(iii) Suggest the identities of the species responsible for

spot **P**, ...

spot **S**. .....

Explain your answers.

.....

..... [3]

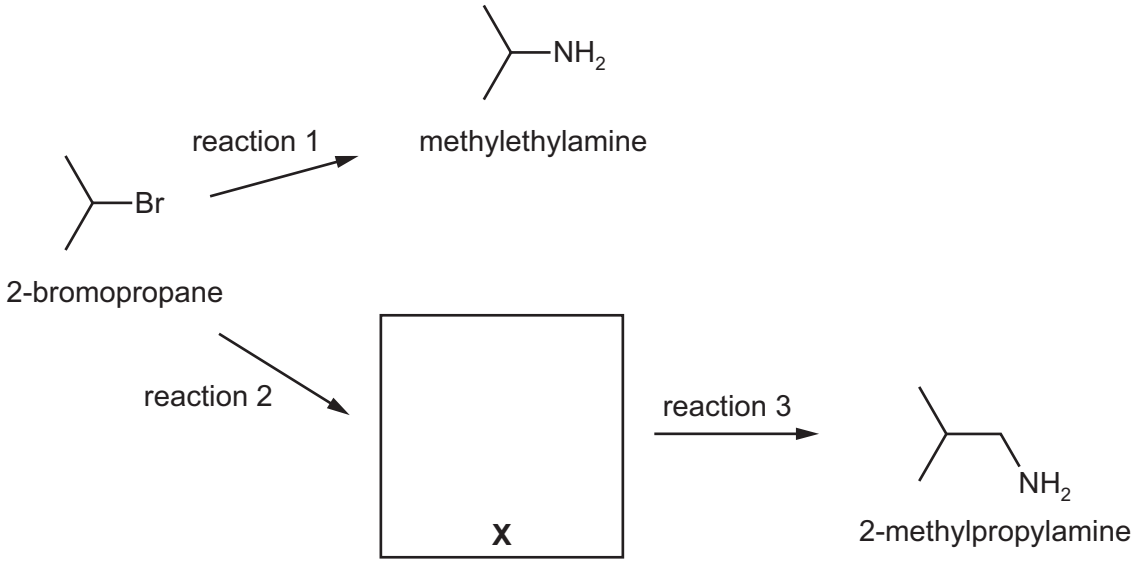
(c) (i) State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

..... [1]

(ii) Name the *type of reaction* in **(i)**.

..... [1]

[Total: 13]



(i) Draw the structure of the intermediate **X** in the box above. [1]

(ii) Suggest reagents and conditions for

- reaction 1, ...
- reaction 2, ...
- reaction 3. .....

[3]

(b) (i) Write an equation showing why aqueous solutions of ethylamine are alkaline.

..... [1]

(ii) Compare the basicities of ethylamine and ammonia. Explain your answer.

.....

.....

.....

..... [2]

(i) Explain what is meant by the term *buffer solution*.

.....

..... [1]

(ii) Write two equations to show how a solution containing a mixture of CH_3NH_2 and CH_3NH_3Cl acts as a buffer.

.....

..... [2]

[Total: 10]

(i) Draw a labelled diagram of the apparatus used to separate a mixture by electrophoresis.

[3]

(ii) Explain the principles of the separation of amino acids by electrophoresis.

.....

.....

..... [2]

(b) Electrophoresis is usually carried out in a buffer solution.

Given three buffers, with pH values of 2.0, 7.0 and 12.0, suggest, with a reason, which buffer would be the most suitable for the separation of the following amino acid mixtures.
Your reasons should refer to the structure of each molecule.
(The structures of these amino acids are given in the *Data Booklet*.)

(i) Asp and Val

buffer pH .....

reason .....

.....

(ii) Lys and Ser

buffer pH .....

reason .....

.....

(iii) Tyr and Phe

buffer pH .....

reason .....

.....

Two of the isomers contain a chiral centre.
The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

test		observations with each isomer			
		J	**K**	**L**	**M**
1	add cold HC*l*(aq)	soluble	soluble	soluble	insoluble
2	add 2,4-DNPH reagent	orange ppt.	orange ppt.	orange ppt.	no reaction
3	add NaOH(aq) + I_2(aq)	pale yellow ppt.	no reaction	pale yellow ppt.	no reaction
4	warm with Fehling's solution	no reaction	red ppt.	no reaction	no reaction
5	heat with NaOH(aq)	no reaction	no reaction	no reaction	**P**(C_6H_7N) and **Q**($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced	no dye produced	no dye produced

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
J	**K**	**L**	**M**
.....	.....	.....	.....
.....	.....	.....	.....
.....	.....	.....	.....

[5]

..... [1]

(ii) Suggest structures for compounds **P** and **Q**.

P (C_6H_7N)

Q ($C_3H_5O_2Na$)

[2]

(c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $C_9H_{11}NO$.

Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.

J

K

L

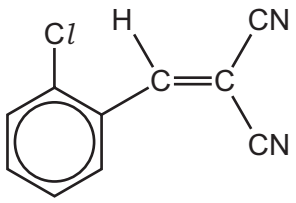
M

[5]

(d) Compound **N** is another isomer which has the same molecular formula $C_9H_{11}NO$ and also contains a benzene ring.
N contains the same functional group as **M**.
When heated with NaOH(aq), **N** produces ethylamine and a sodium salt **W**.
Suggest the structure of **W**.

W

[1]



P

(a) Name the functional groups present in **P**.

.....

..... [2]

(b) Compound **P** can be polymerised.

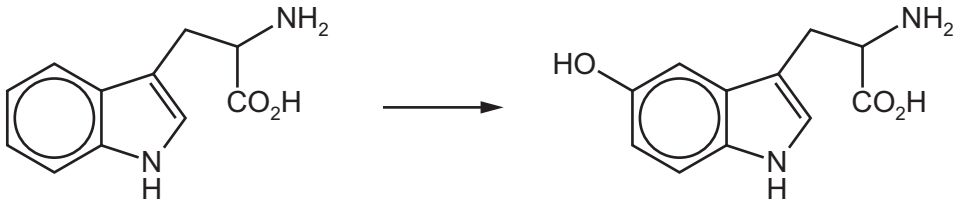
Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

type of polymerisation .....
[2]

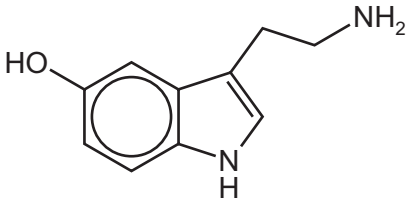
reagent	structure(s) of product(s)		*type of organic reaction*
excess $Br_2(aq)$			
excess hot, concentrated, acidified $MnO_4^-(aq)$			
excess hot $HCl(aq)$			
excess H_2 / Pt catalyst			

[8]

[Total: 12]



tryptophan



serotonin

(a) (i) In a buffer solution at pH 5.9, a sample of tryptophan does **not** move during electrophoresis.

Draw the structures of the ions formed by tryptophan at pH 1.0 and pH 5.9.

pH 1.0

pH 5.9

[2]

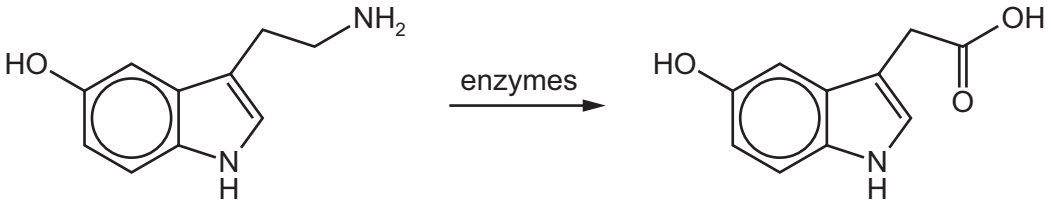
(ii) Tryptophan can combine with valine to form a dipeptide.

Use the *Data Booklet* to draw the structure of this dipeptide.

[2]

reagent	structure of product	*type of reaction*
Na		
excess $Br_2(aq)$		
excess CH_3COCl		
excess H_2 / Pt catalyst		

[8]



serotonin **M**

(i) By reference to the *Data Booklet*, suggest how the infra-red spectrum of **M** would differ from that of serotonin.

.....

..... [1]

(ii) The proton NMR spectrum of **M** dissolved in $CDCl_3$ shows eight peaks due to the eight different types of proton present in the molecule.

The proton NMR spectrum of **M** dissolved in D_2O was recorded.

Predict the number of peaks that would be seen in the proton NMR spectrum of **M** in D_2O. Explain your answer.

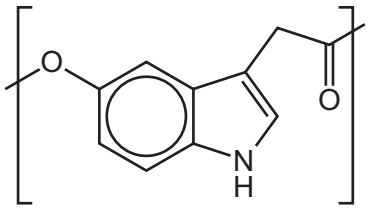
number of peaks .....

explanation .....

.....

[2]

(d) Compound **M** can be polymerised under certain conditions to form polymer **N**, shown.



N

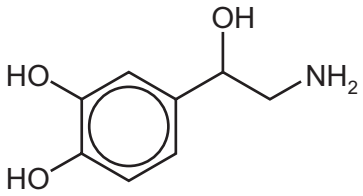
Polymer **N** is biodegradable, unlike polyethene which is not.

Explain why **N** is biodegradable.

.....

..... [1]

[Total: 16]



noradrenaline

(a) Give the molecular formula of noradrenaline.

..... [1]

(b) State whether or not noradrenaline shows stereoisomerism. Explain your answer.

.....

..... [1]

(c) HNO_2(aq) is reacted at 5 °C with separate samples of noradrenaline and phenylamine.
The reaction with phenylamine produces a stable diazonium ion.
The reaction with noradrenaline produces an unstable diazonium ion.

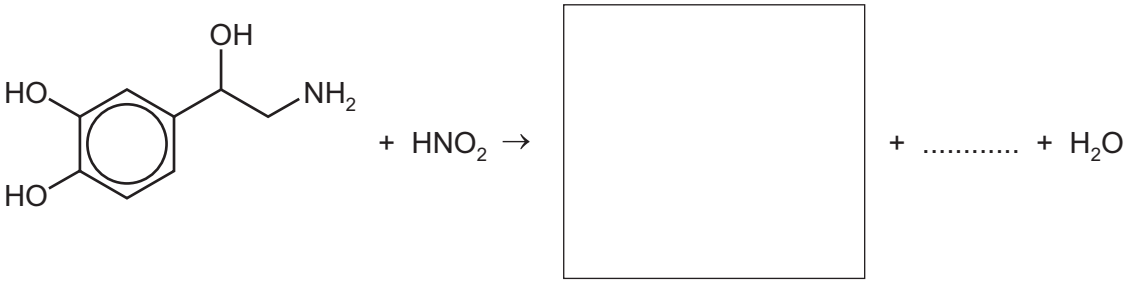
(i) Suggest why the diazonium ion produced with phenylamine is stable.

.....

..... [1]

(ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



[2]

[Total: 5]

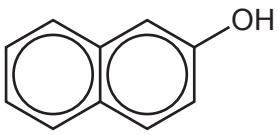
(a) Suggest **two** different substances that react with phenol to produce potassium phenoxide, $C_6H_5O^-K^+$. Identify the second product formed in each case.

substance ..... second product .....

substance ..... second product .....

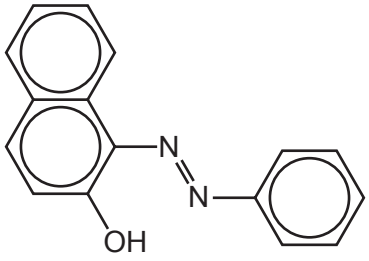
[3]

(b)



2-naphthol

2-naphthol can show similar properties to phenol. It can be used to produce Sudan I, an orange coloured dyestuff.



Sudan I

(i) On the diagram of Sudan I above **circle** the bond or bonds that make this substance a dyestuff. [1]

(ii) Describe how Sudan I can be made using phenylamine and 2-naphthol as the organic starting materials.

.....

.....

.....

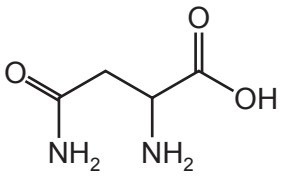
.....

.....

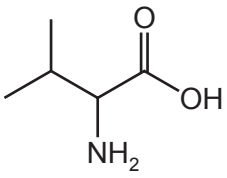
.....

.....

..... [3]



asparagine



valine

(a) Give the molecular formula of asparagine.

..... [1]

(b) Name **all** of the functional groups in an asparagine molecule.

..... [2]

(c) Draw the structure of the dipeptide formed by valine and asparagine.

The peptide bond should be shown displayed and should be clearly labelled.

[2]

(d) A solution of valine in water acts as a buffer solution.

(i) Explain what is meant by a *buffer solution*.

.....

.....

..... [2]

(ii) Write **two** equations to explain how valine can act as a buffer. Use the formula $H_2NCHRCO_2H$ for valine in your equations.

.....

.....

[2]

Draw three-dimensional diagrams to show the two optical isomers of valine.
The $(CH_3)_2CH$ group can be represented as R.

[2]

(f) Asparagine is hydrolysed when heated with aqueous sulfuric acid.

Write an equation for this reaction.

..... [2]

[Total: 13]

.....

.....

.....

.....

.....

.....

.....

..... [4]

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

State and explain the relative rates of hydrolysis of the following compounds.

CH_3CH_2Cl CH_3COCl C_6H_5Cl

.....

.....

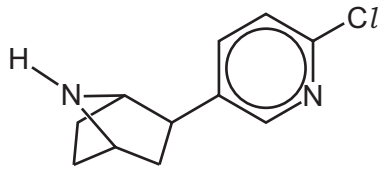
.....

.....

..... [3]

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



(i) Epibatidine is a weak base.

State what is meant by the term *weak base*.

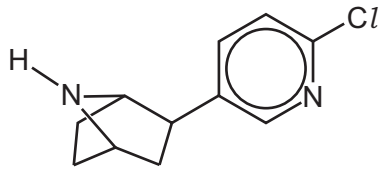
.....

..... [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

(ii) Epibatidine reacts with HCl(aq).

Complete the structure to suggest the product formed in this reaction.



[1]

(15b) Glycine, $H_2NCH_2CO_2H$, is the simplest amino acid.

(i) Complete the equations to show the acid-base properties of glycine.

$H_2NCH_2CO_2H(aq) + HCl(aq) \rightarrow$ .....

$H_2NCH_2CO_2H(aq) + NaOH(aq) \rightarrow$ .....

[2]

(ii) In aqueous solution, amino acids exist as zwitterions.

Draw the zwitterionic structure of glycine. Explain how the zwitterion for glycine is formed.

.....

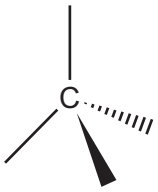
.....

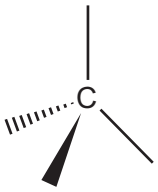
.....

[2]

(c) Apart from glycine, all naturally occurring amino acids have a chiral centre and exhibit stereoisomerism.

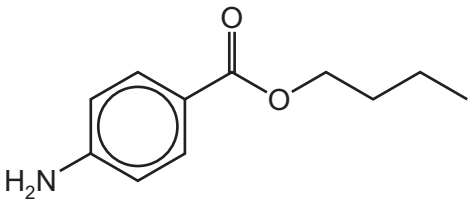
Draw the two stereoisomers of alanine, $CH_3CH(NH_2)CO_2H$.





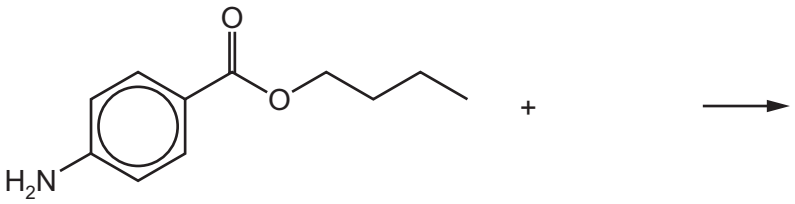
[1]

butamben



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



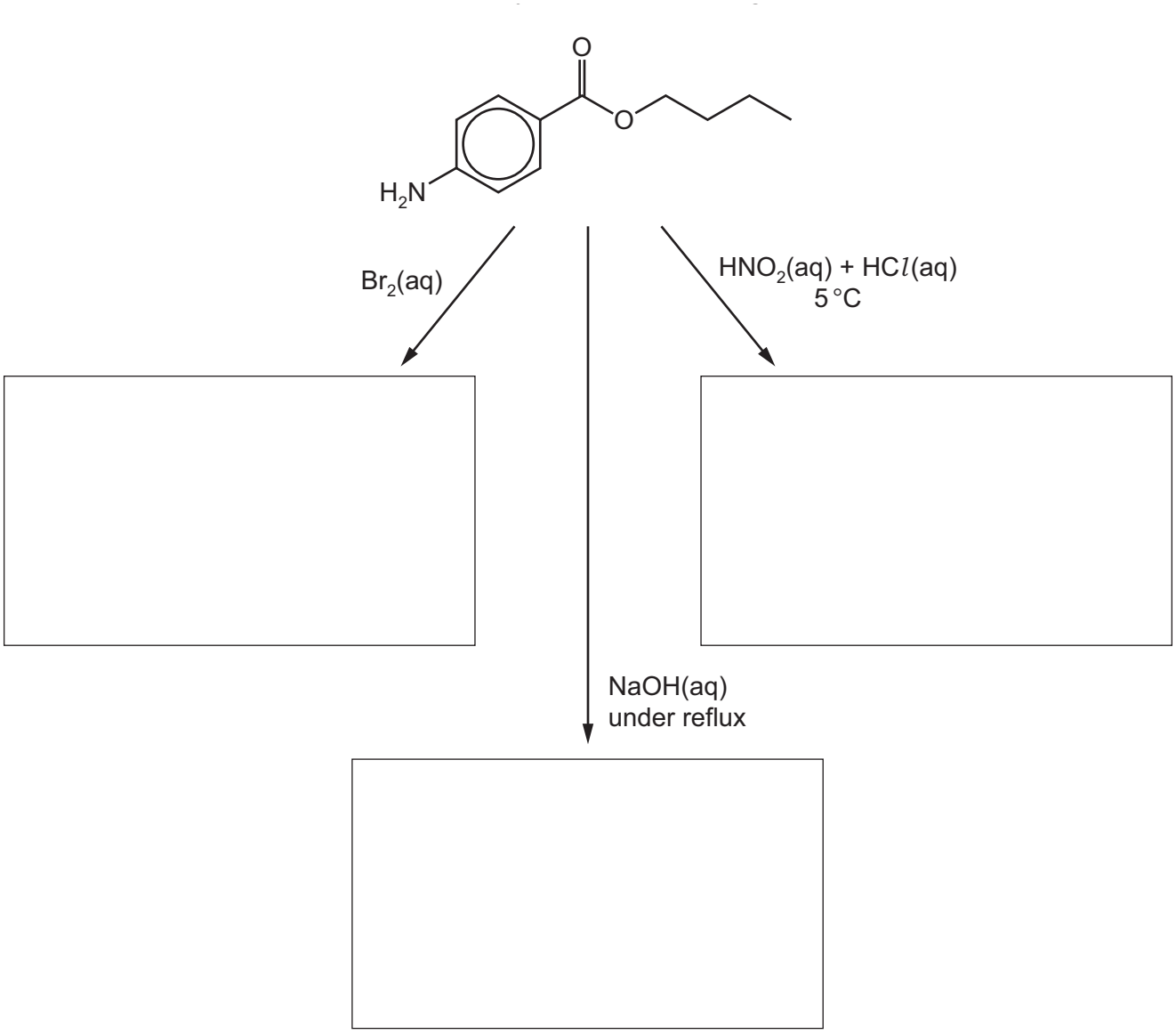
[1]

(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

.....

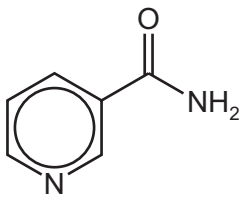
.....

..... [1]



[3]

nicotinamide



(a) The nitrogen atom in the six-membered ring has one electron in an unhybridised p-orbital. This electron becomes delocalised, becoming part of a single delocalised system of electrons. This delocalised system also includes:

- electrons from the carbon atoms in the six-membered ring
- the two electrons in the π bond of the C=O group
- the two electrons in the lone pair on the nitrogen atom of the amide group.

(i) State the number of delocalised electrons in one nicotinamide molecule.

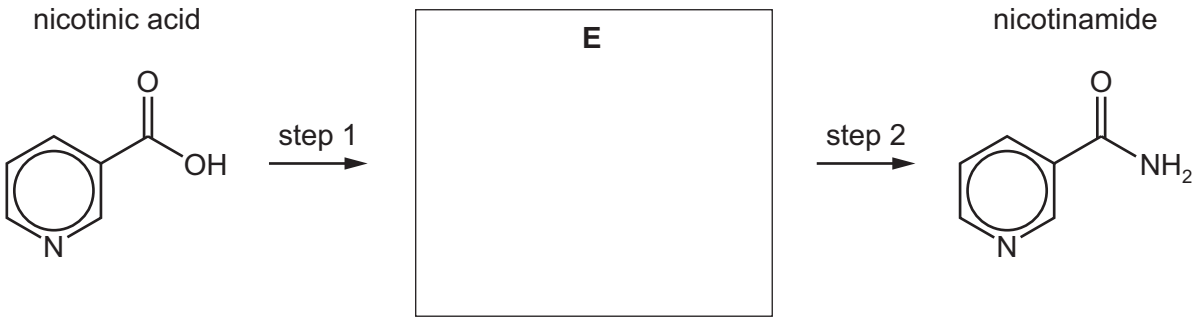
..... [1]

(ii) Predict the H–N–H bond angle in the NH_2 group in nicotinamide.

..... [1]

(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.

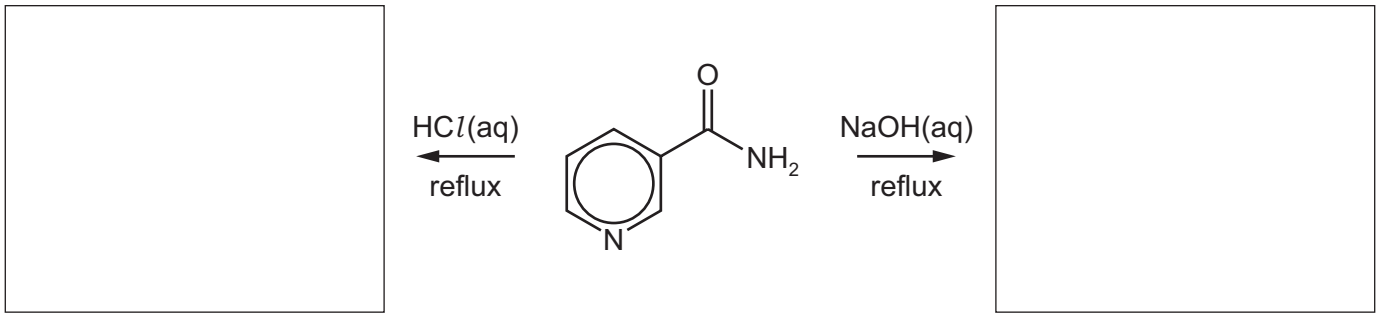


(i) Draw the structural formula of **E** in the box. [1]

(ii) Give the name or formula of a suitable reagent for step 2.

..... [1]

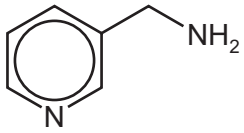
Complete the reaction scheme below to give the structural formula of the organic product of each reaction.



[2]

(d) Nicotinamide can be reduced to compound **X**.

X



(i) Identify a suitable reducing agent for this reaction.

..... [1]

(ii) Predict and explain the relative basicities of the NH_2 groups in phenylamine, $C_6H_5NH_2$, nicotinamide and compound **X**.

.....

.....

.....

..... [3]

S $C_6H_5CONH_2$

T $C_6H_5NH_2$

U $C_6H_5CH_2NH_2$

Describe and explain the relative basicities of **S**, **T** and **U**.

..... > ..... > .....
most basic least basic

.....

.....

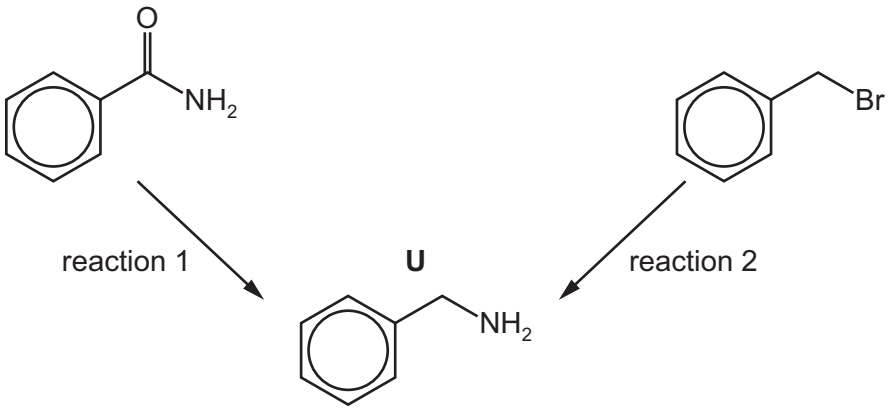
.....

.....

.....

.....
[3]

(b) Compound **U** can be prepared by two different methods as shown.



(i) Suggest reagents and conditions for reaction 1 and for reaction 2.

reaction 1 .....

reaction 2 .....
[2]

(ii) State the type of reaction in reaction 1 and name the mechanism in reaction 2.

type of reaction in reaction 1 .....

mechanism of reaction 2 .....
[2]

(i) Draw the structures of the two structural isomers with the molecular formula $C_6H_{12}N_2O_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.

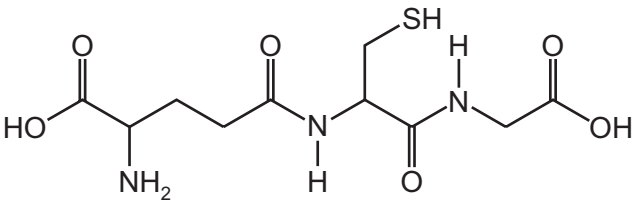
[3]

(ii) Predict the number of different structural isomers with the molecular formula $C_9H_{19}N_3O_4$ that could be present in the product mixture.

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	

[1]

glutathione



(i) On the diagram of glutathione, label each chiral centre with an asterisk (*). [1]

(ii) Draw the structures of the three products formed after complete acid hydrolysis of glutathione. Assume the thiol group, –SH, does not react.

[2]

(iii) Glutathione is soluble in water.

By referring to the structure of glutathione, explain why glutathione is soluble in water.

.....

.....

..... [1]

..... > ..... > .....

most basic least basic

.....

.....

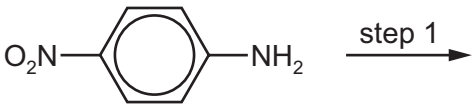
.....

.....

..... [4]

(b) The dye **R** can be synthesised from 4-nitrophenylamine in two steps.

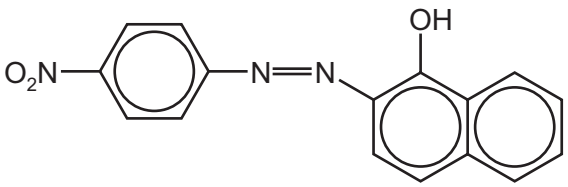
4-nitrophenylamine



Q

step 2

R



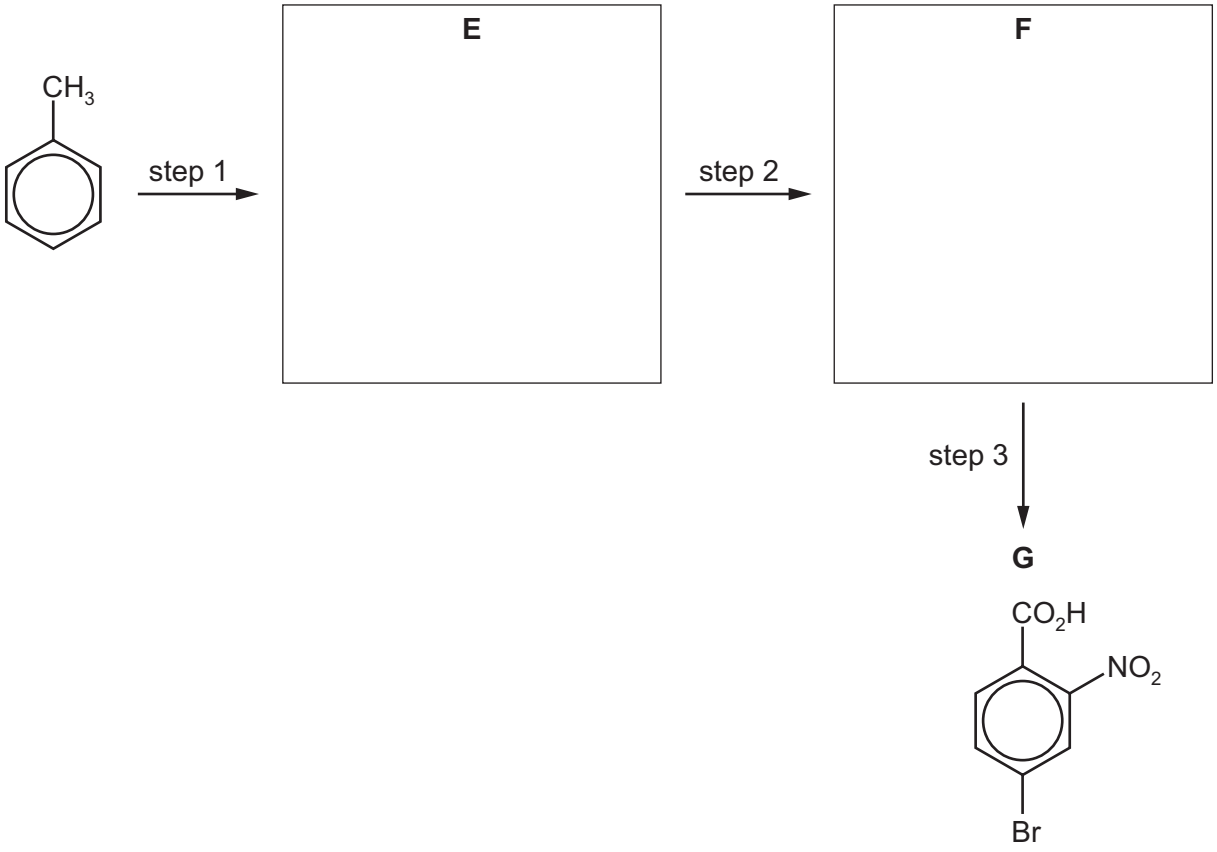
(i) Deduce and draw the structure of the organic salt **Q** in the box. [1]

(ii) Suggest reagents and conditions for step 1 and 2 in **(b)**.

step 1 .....

step 2 .....

[2]



(i) Give the systematic name of compound **G**.

..... [1]

(ii) Deduce the identities of **E** and **F** and draw their structures in the boxes. [2]

(iii) Suggest reagents and conditions for each of steps 1 to 3 in **(c)**.

step 1 .....

step 2 .....

step 3 .....

[3]

[Total: 13]

(a) State what is seen when aqueous bromine is added to phenylamine.

.....

..... [2]

(b) Suggest what is seen when aqueous bromine is added to ethylamine.

..... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

(d) Name the product you have drawn in **(c)**.

..... [1]

[Total: 5]

(a) Complete the table to describe three different syntheses.

- One of the three syntheses should involve a nucleophilic substitution reaction.
- The starting organic compound for each synthesis should contain a different functional group.
- A different reagent should be used for each synthesis.

starting organic compound	reagent and conditions

[6]

(b) Compare and explain the relative basicities of ammonia, butylamine and phenylamine.

..... > ..... > .....
most basic least basic

.....

.....

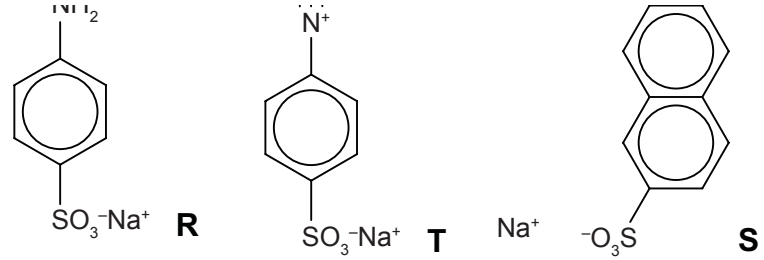
.....

.....

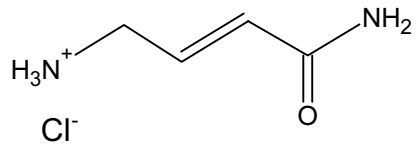
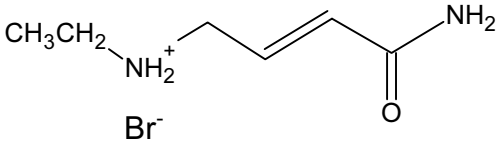
.....

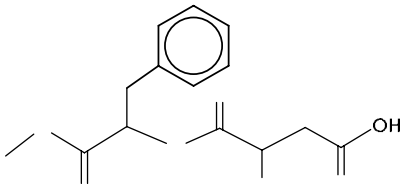
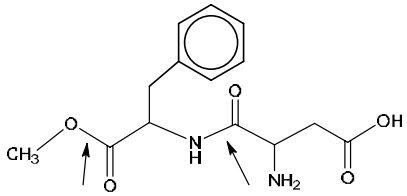
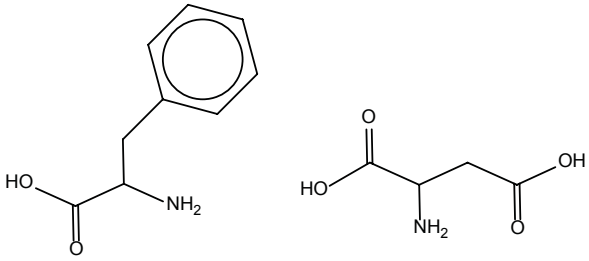
..... [4]

[Total: 10]

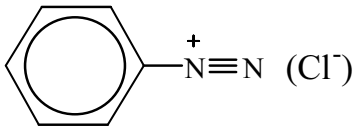


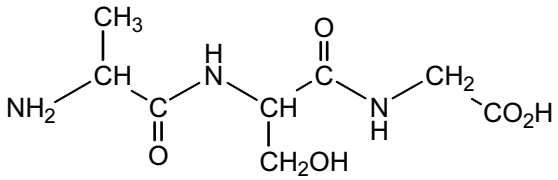
(ii)	Sn + HCl HNO_2 or $NaNO_2$ + HCl step 1 (linked to a reduction) reflux / heat / >50 °C **or** conc / 6M (HCl) **and** step 2 ⩽10 °C	**3**
(iii)	diazonium (group)	**1**
(b) (i)	σ-bonds = 14 π-bonds = 2	**2**
1		**3**

reagent	structure of product	type of reaction
HCl		acid-base **or** neutralisation
CH_3CH_2Br		(nucleophilic) substitution

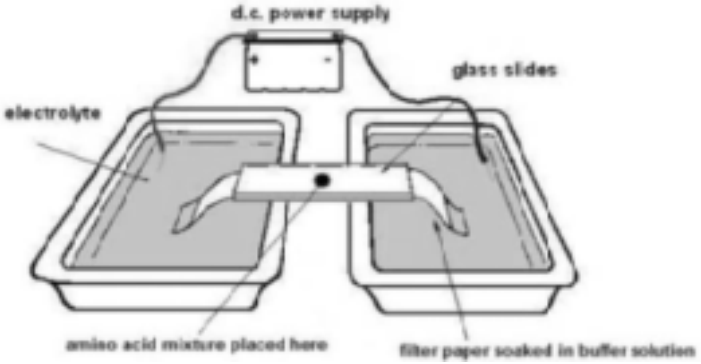
2 (a) (i)		**1**
(ii)		**2**
(iii)		**3**
(b)	M1: hydrogen bonding M2: between the NH_2 groups and water **or** CO_2 / C=O / –OH groups and water (allow names) **or** lone pair on N/O with water	**2**
(c)	allow range 1–200 nm or 1–200 × 10^{-9} m	**1**
		9

P41/M/J/16/Q6

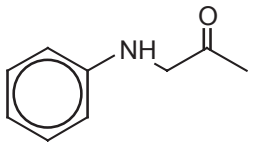
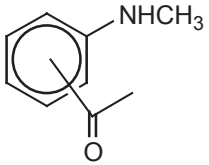
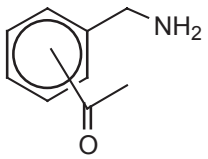
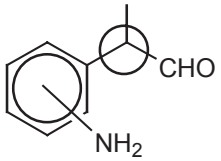
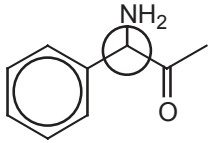
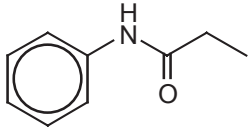
3 (a) (i)	$C_6H_5NO_2$ + **6**e^- + **6**H^+ $\longrightarrow$ $C_6H_5NH_2$ + **2**H_2O	[1]
(ii)	**2**$C_6H_5NO_2$ + **14**HCl + **3**Sn $\rightarrow$ **2**$C_6H_5NH_3Cl$ + **3**$SnCl_4$ + **4**H_2O	[2]
(b)	(M_r values: $C_6H_5NO_2$ = 123 $C_6H_5NH_3Cl$ = 129.5) theoretical yield = 5.0 × 129.5/123 = 5.26 g percentage yield = 100 × 4.2/5.26 = 79.8% (80%)	[1] [1]
(c) (i)	$C_6H_5NH_2$ = 93 yield of phenylamine = 4.2 × 93/129.5 = 3.016 g	[1]
(ii)	mass left in water = 3.016 – 2.68 = 0.336 g K_{part} = (2.68/50) / (0.336/25) = 3.99	[1] [1]
(d)	phenylamine is less basic that ethylamine the lone pair on N is delocalised over the ring… …making it less available for reaction with a proton / δ+ H	[2]
(e) (i)	step 1: HNO_2 OR ($NaNO_2$ + HCl) at $T \leqslant 10\,°C$ step 2: boil / heat in water	[1] [1]
(ii)	**E** is 	[1]
		[Total: 13]

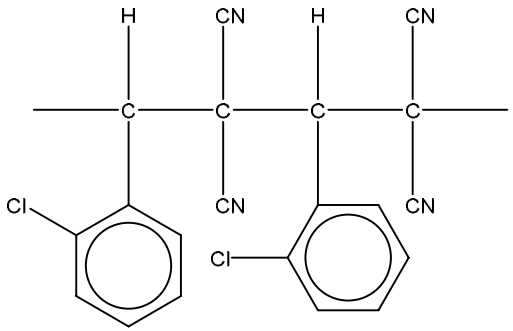
Question	Answer	Marks
4 (a) (i)		[2]
(ii)	M_r = 233	[1]
(b) (i)	$NH_2CH(CH_2OH)CO_2^-$	[1]
(ii)	**F** is a DC power supply **G** is the anode OR positive electrode **I** is the cathode OR negative electrode **H** is filter paper (OR gel) soaked in **buffer** solution	[4]
(iii)	**P** is $NH_2CH_2CO_2^-$ *or* $NH_2CH_2CO_2H$ *or* glycine **S** is [ala–ser–gly]$^{(-)}$ glycine is the smallest, so travels fastest; tripeptide is the largest, so travels slowest	[1] [1] [1]
(c) (i)	heat with H_3O^+ OR heat with OH^-(aq)	[1]
(ii)	hydrolysis	[1]
		[Total: 13]

(ii)	reaction 1: NH_3 (in ethanol) under pressure (+ heat) or heat NH_3 in a sealed tube reaction 2: KCN / NaCN **and** heat / reflux (in ethanol) reaction 3: H_2 + Ni *or* $LiAlH_4$	3
(b) (i)	$CH_3CH_2NH_2 + H_2O \rightarrow CH_3CH_2NH_3^+ (+) OH^-$	1
(ii)	ethylamine is **more basic** than ammonia… because of electron-donating (alkyl / ethyl / R) group (in ethylamine) which makes the lone pair (on N) more available for donation **or** the lone pair (on N) more available for a proton / H^+	2
(c) (i)	A solution which resists / minimises / roughly maintains changes in pH when (small amounts of) H^+ or OH^- are added	1
(ii)	$CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$ $CH_3NH_3Cl + OH \rightarrow CH_3NH_2 + H_2O + Cl$	2
		[Total: 10]

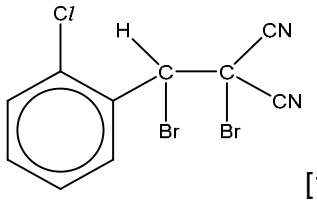
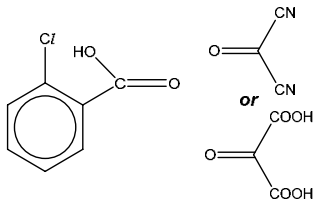
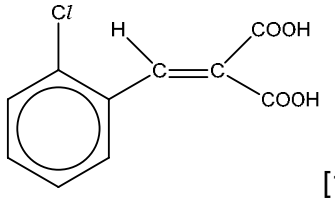
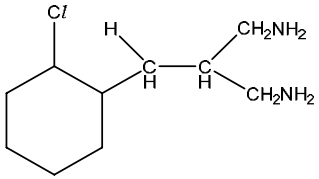
	labelled with: M1: DC power supply + and – / battery / cell / + and – sign (on cell / electrodes) with a complete circuit M2: buffer solution / electrolyte labelled M3: (amino acid) mixture / **x** on (filter) paper / gel / agarose  	
(ii)	direction of movement related to charge (of amino acids) distance travelled depends on charge / M_r (of amino acids)	2
(b) (i)	Asp + Val: **pH 12** because Asp will be $–CH_2COO^-$ (R-group) moves further (to positive electrode than Val) ***or* pH 12** Asp more negative so moves further (to positive electrode) **or pH 12** because Asp has a charge of 2– but Val has a charge of 1– ***or*** best at **pH 7** because Asp will be negatively charged (anionic) but Val neutral	1
(ii)	Lys + Ser: **pH 2** because Lys will be $(CH_2)_4NH_3^+$ (R-group) moves further (to negative electrode than Ser) ***or* pH 2** Lys more positive so moves further (to negative electrode) **or pH 2** because Lys has a charge of 2+ and Ser has a charge of 1+ ***or* pH 7** because Lys is positively charged (cationic) but Ser neutral / zwitterionic	1
(iii)	Tyr + Phe:	1

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td rowspan="4">7(a)</td><td><table>
<tr><th>J</th><th></th><th>L</th><th>M</th></tr>
<tr><td>amine
methyl ketone</td><td>aromatic amine
aldehyde</td><td>amine
methyl ketone</td><td>amide</td></tr>
</table></td><td></td></tr>
<tr><td>J and L correct</td><td>1 + 1</td></tr>
<tr><td>K correct</td><td>1 + 1</td></tr>
<tr><td>M correct</td><td>1</td></tr>
<tr><td>7(b)(i)</td><td>hydrolysis</td><td>1</td></tr>
<tr><td rowspan="2">7(b)(ii)</td><td>P is $C_6H_5NH_2$</td><td>1</td></tr>
<tr><td>Q is $CH_3CH_2CO_2Na$</td><td>1</td></tr>
</table>

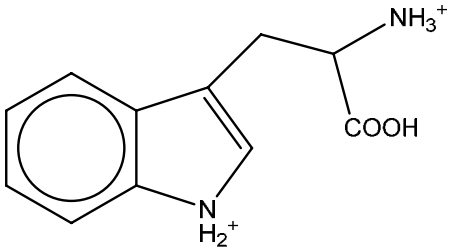
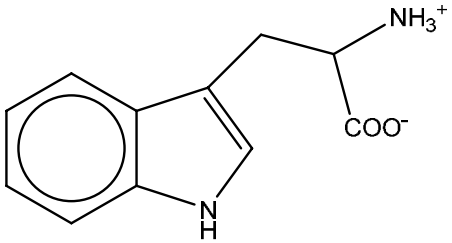
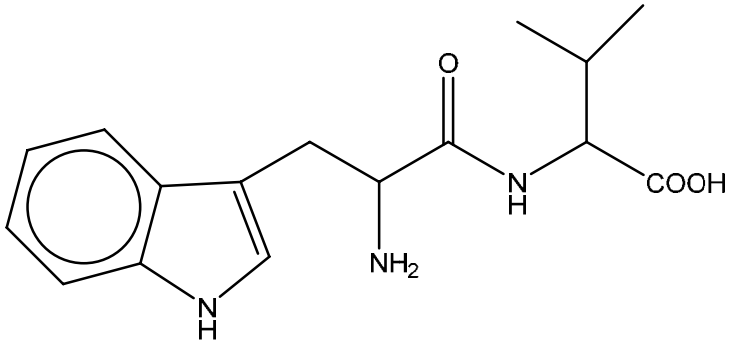
7(c)	**J** is  *or*  *or* 	**1**
	K is 	**1**
	L is 	**1**
	M is 	**1**
	K&L only: two chiral atoms shown	**1**
7(d)	**W** is $C_6H_5CO_2Na$	**1**
	Total:	**14**

8(a)	nitrile; alkene; chloro; benzene / arene	**2**
8(b)		**1**
	addition (polymerisation)	**1**

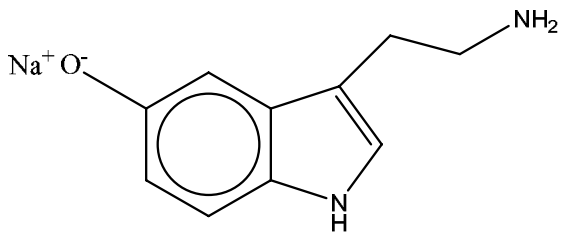
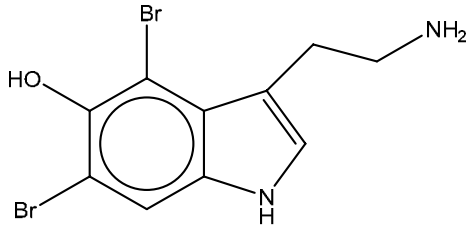
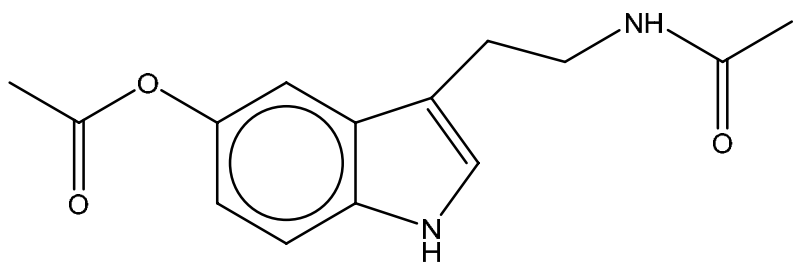
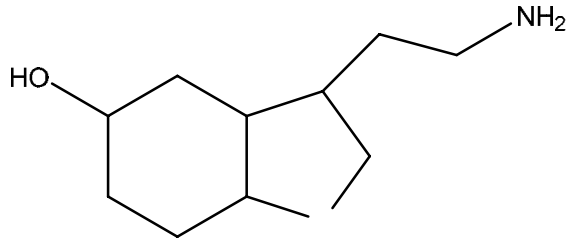
8(c)

reagent	structure of product	type of organic reaction
excess $Br_2(aq)$	 [1]	(electrophilic) addition
excess hot, conc. $MnO_4^-(aq)$	 [1] + [1]	oxidation
excess hot, aqueous HCl	 [1]	hydrolysis
excess H_2 / Pt catalyst	 both CH_2NH_2 formed [1] both arene and alkene reduced [1]	reduction / hydrogenation
	structures [6]	2 correct for 1 mark total [2]

8

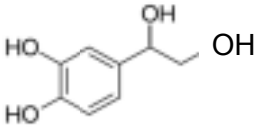
9(a)(i)	 pH 1  pH 5.9	**2**
9(a)(ii)	 peptide link [1] rest of the structure [1]	**2**

9(b)

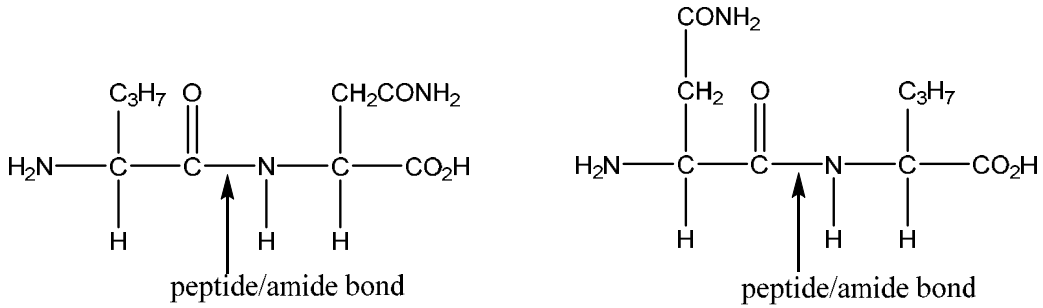
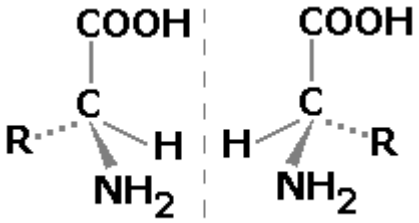
reagent	structure of product	type of organic reaction
Na	 [1]	redox or reduction
excess $Br_2(aq)$	 [1]	(electrophilic) substitution
excess CH_3COCl	 acylated OH [1] acylated $NH_{(2)}$ [1]	condensation (or addition + elimination)
excess H_2 / Pt catalyst	 [1]	reduction or hydrogenation or addition

8

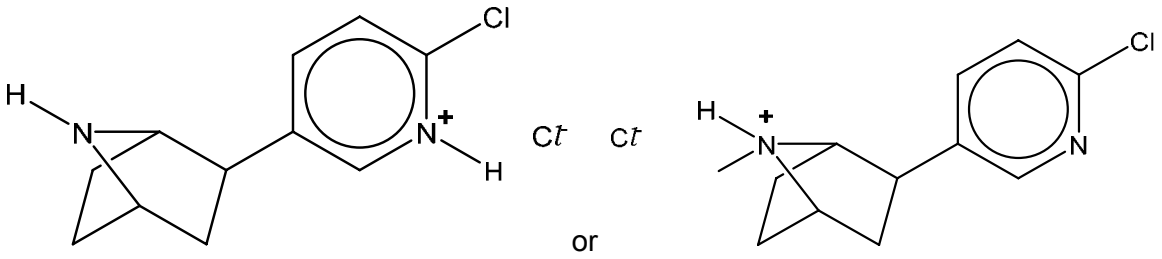
9(c)(i)	(spectrum of M) contains a broad peak (for O–H) at 2500–3000 cm^{-1} ***or*** (spectrum of M) contains peak (for C=O) at 1640–1750 cm^{-1} ***or*** (spectrum of M) lacks (NH_2 peak) at 3300–3500 cm^{-1}	**1**
9(c)(ii)	5 or 6 peaks	**1**
	OH/NH protons exchange with deuterium ***or*** –OH / –NH + D_2O → –OD / –ND + DHO	**1**
9(d)	ester **and** hydrolysed	**1**

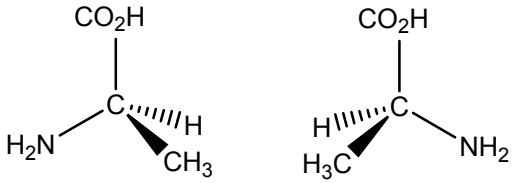
10(a)	$_8H_{11}O_3N$	**1**
10(b)	ye as it has a chiral C atom	**1**
10(c)(i)	yldiazonium ion is stabilised because) positive charge is delocalised by ring / positive charge is spread over ring	**1**
10(c)(ii)		**1**
	N_2	**1**

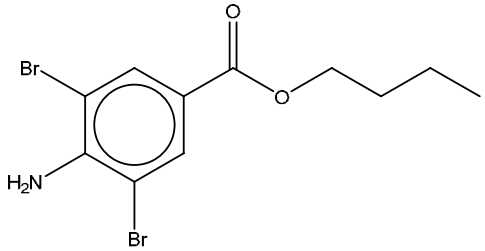
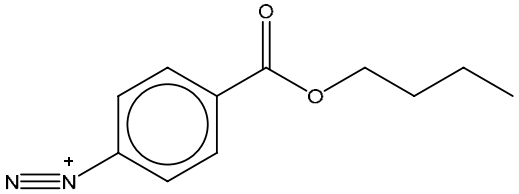
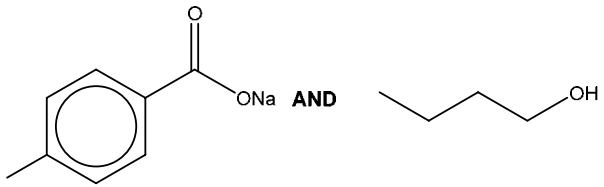
11(a)	<u>any two from</u> K / potassium or KOH / potassium hydroxide or K_2O / potassium oxide	**2**
	correct products: (K) hydrogen, (KOH) water, (K_2O) water	**1**
11(b)(i)	bond circled between N = N	**1**
11(b)(ii)	phenylamine **and** HNO_2	**1**
	T=10 ^oC or below **and** diazonium ion / salt formed or structure of diazonium ion as $[C_6H_5N_2^+]$	**1**
	add 2-naphthol in aqueous NaOH / alkali	**1**

12(b)	amide, amine, carboxylic acid 2 correct = 1 mark 3 correct = 2 marks	**2**
12(c)		
	peptide / amide bond / unit labelled or circled	**1**
	(val-asp or asp-val) rest of the dipeptide structure is correct	**1**
12(d)(i)	resists change in pH / pH kept within a small range	**1**
	when small amount of acid or alkali / base is added	**1**
12(d)(ii)	$H_2NCHRCO_2H + H^+ \rightarrow H_3N^+CHRCO_2H$	**1**
	$H_2NCHRCO_2H + OH^- \rightarrow H_2NCHRCO_2^- + H_2O$	**1**
12(e)	 each structure [1]	**2**

13(d)	ethylamine > ammonia > phenylamine [1] ethyl group is electron donating group [1] p-orbital from N in phenylamine overlaps with π-ring system **OR** lone pair on N is delocalised into benzene ring [1] basicity linked to ability of N to accept a proton [1]	**4**

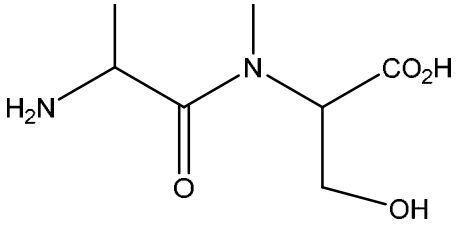
14(a)	**M1**: CH_3COCl > CH_3CH_2Cl > C_6H_5Cl **M2 & M3 any two from:** • in C_6H_5Cl (no hydrolysis) C-Cl bond is part of delocalised system **OR** p-orbital on Cl overlaps with π system **OR** electrons from Cl overlap with π system • CH_3COCl carbon in C-Cl bond is more electron deficient since it is also attached to an oxygen atom (ora) **or** C-Cl bond strength is weakest in CH_3COCl (ora) • CH_3CH_2Cl carbon in C-Cl bond strengthened by positive inductive effect of alkyl group	**3**
14(b)(i)	partially ionised **and** proton acceptor	**1**
14(b)(ii)		**1**

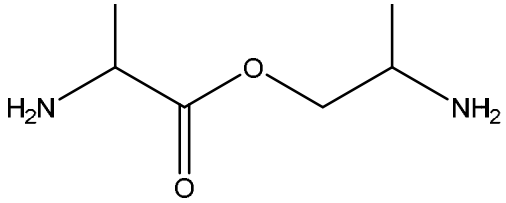
15(b)(i)	$H_2NCH_2CO_2H + HCl \rightarrow Cl^-H_3N^+CH_2CO_2H$ [1] $H_2NCH_2CO_2H + NaOH \rightarrow H_2NCH_2CO_2^-Na^+ + H_2O$ [1]	**2**
15(b)(ii)	$H_3N^+CH_2CO_2^-$ [1] Proton is transferred from the CO_2H group to the NH_2 group [1]	**2**
15(c)	 two non-superimposable mirror images for alanine drawn [1]	**1**

Question	Answer	Marks
16(a)(i)	$RNH_2 + H^+ \rightarrow RNH_3^+$ **OR** $RNH_2 + HCl \rightarrow RNH_3Cl$ [1]	**1**
16(a)(ii)	weaker **AND** lone pair of N delocalised into benzene ring [1]	**1**
16(b)	 [1]  [1]  **AND**	**3**

Question	Answer	Marks
17(a)(i)	10	**1**
17(a)(ii)	120	**1**
17(b)(i)	correct acid chloride	**1**
17(b)(ii)	NH_3 or ammonia	**1**
17(c)	**M1:** $(C_5NH_4)COOH$ or $(C_5NH_5)^+COOH$ **M2:** $(C_5NH_4)COO^-(Na^+)$ or $(C_5NH_4)COONa$	**2**
17(d)(i)	$LiAlH_4$	**1**
17(d)(ii)	**M1:** most basic: X > phenylamine > nicotinamide :least basic **M2:** LP in X cannot be delocalised **M3:** LP in phenylamine delocalised over the benzene ring **or** LP in amide delocalised (more effectively) by C=O	**3**

Question	Answer	Marks
18(a)	**M1** phenylmethanamine / **U** > phenylamine / **T** > benzamide / **S** [1] any two from: • alkyl group is electron donating so lone pair more able to accept a proton • lone pair on N overlaps with delocalised system so less able to accept a proton • presence of electron-withdrawing oxygen / carbonyl group means lone pair is not available to accept a proton **OR** amides are neutral	**3**
18(b)(i)	reaction 1 $LiAlH_4$ reaction 2 heat NH_3 under pressure/ heat NH_3 in a sealed tube	**2**
18(b)(ii)	reaction 1 reduction reaction 2 nucleophilic substitution	**2**





M1 / M2: each structure

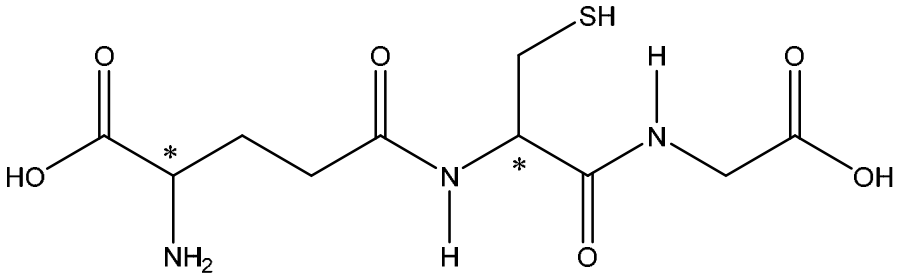
M3: both displayed linkage

19(b)(ii)

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	4

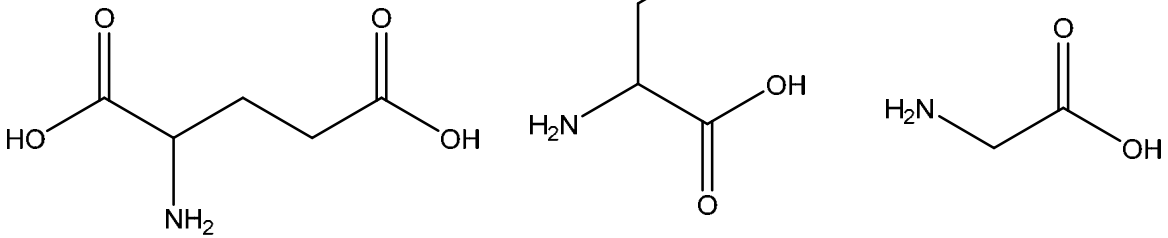
1

19(c)(i)



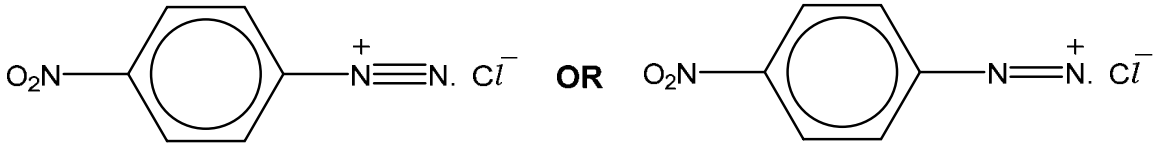
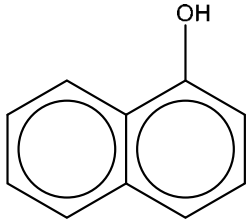
1

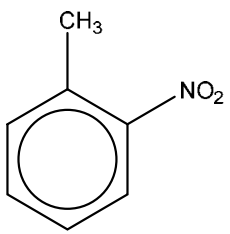
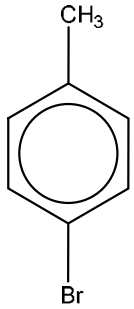
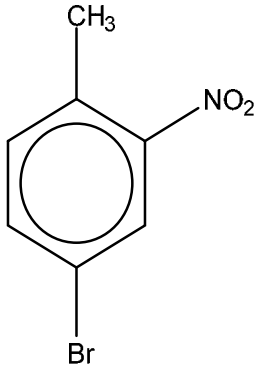
19(c)(ii)

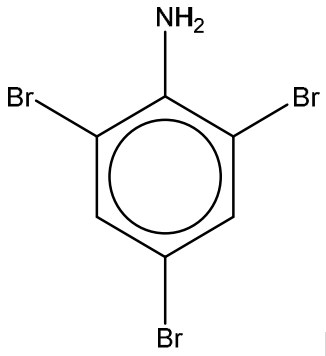


one mark for two correct

2

20(a)	**M1:** ethylamine phenylamine 4-nitrophenylamine most basic least basic **M2 / 3 / 4:** *explanation two correct for one mark, three correct for two marks, four correct for three marks* • (basicity linked to) lone pair / p orbital on N **AND** being able accept / donate to / coordinate to a proton / H^+ • ethyl / alkyl group is electron donating / has a positive inductive effect (so lone pair on N is more able to accept a proton) • (phenylamines are less basic than ethylamine as) p orbital / lone pair on N is delocalised (into the ring so less able to accept a proton) • (4-nitrophenylamine is less basic than phenylamine as) nitro / NO_2 group is electron withdrawing (so lone pair on N is less able to accept a proton)	**4**
20(b)(i)	 **OR**	**1**
20(b)(ii)	**M1:** step 1: HNO_2, ⩽ 10°C **OR** $NaNO_2$, HC*l*(aq), ⩽ 10°C **M2:** step 2: NaOH / alkaline **AND** 1-naphthol / α-naphthol / structure below 	**2**

20(c)(ii)	**E =**  **OR**  **F =** 	**2**
20(c)(iii)	**M1:** step 1 conc. H_2SO_4 and conc. HNO_3 **M2:** step 2 Br_2 and A*l*Br_3 **M3:** step 3 hot (alkaline / acidified) MnO_4^- / $KMnO_4$	**3**

Question	Answer	Marks
21(a)	bromine decolourised **OR** orange / brown to colourless [1] white precipitate [1]	**2**
21(b)	no change [1]	**1**
21(c)	 [1]	**1**
21(d)	2,4,6-tribromophenylamine [1] **ECF** 8(c) for a bromophenylamine	**1**

22(a)

organic starting material	reagent and conditions	
1-butyl halide, e.g. $CH_3CH_2CH_2CH_2Br$	NH_3 under pressure or heated in sealed tube	[1] + [1]
butanenitrile $CH_3CH_2CH_2CN$	H_2 and Ni or Pt / LiA/H_4 / Na + ethanol	[1] + [1]
butanamide $CH_3CH_2CH_2CONH_2$	LiA/H_4 / Na + ethanol	[1] + [1]

6

22(b)

M1 butylamine > ammonia > phenylamine [1]

M2 basicity related to ability of **lp** to accept proton / H^+ [1]

M3 butylamine is stronger because of positive inductive effect of **alkyl** group / C_4H_9 [1]

M4 phenylamine is weaker because **lp on N** is delocalised into ring [1]

4

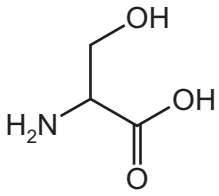
Paper 4
Topic 10
Polymerisation

1 Proteins are formed by the polymerisation of amino acids.

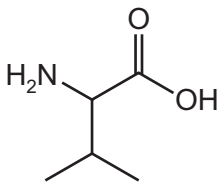
(a) (i) State the type of chemical reaction used to form these polymer chains.

..... [1]

(ii) The amino acids serine and valine can combine together to form a dipeptide.



serine, *ser*



valine, *val*

Draw the skeletal structure of the dipeptide 'ser-val'.

[2]

(iii) Suggest how the type of amino acids in a protein determines its three-dimensional structure.

.....

.....

.....

..... [2]

(i) why a particular enzyme may only catalyse a specific reaction on a specific substrate,

.....

.....

.....

..... [2]

(ii) how *non-competitive* inhibition of an enzyme-catalysed reaction can occur.

.....

.....

.....

..... [3]

[Total: 10]

P43/O/N/15/Q7ab

2 DNA is an important biochemical molecule.

(a) DNA has a double helical structure that consists of two strands linked together.

Draw a **block diagram** of DNA showing **two** repeat units in each strand.
Label all the components, showing and labelling the bonds between the strands.

[5]

(b) Genetic information is stored in DNA.

Outline the main steps in the replication of DNA.

.....

.....

.....

..... [2]

(3b) Ethyne is the simplest member of the alkyne homologous series.

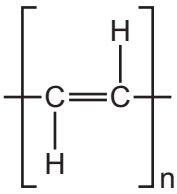
ethyne

Propyne, C_3H_4, and butyne, C_4H_6, are the next two members of the series.

Deduce the general formula for the alkynes.

..... [1]

(c) Ethyne can be polymerised into poly(acetylene), which is a conducting polymer.



poly(acetylene)

(i) Suggest why this polymer conducts electricity.

.....

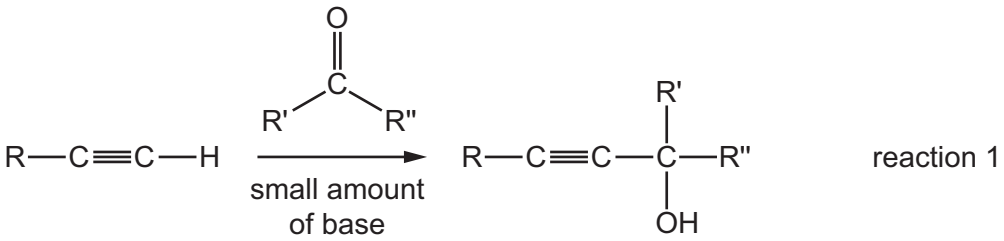
..... [1]

(ii) State the empirical formula of poly(acetylene).

..... [1]

(iii) By reference to a physical or chemical property, suggest **one** advantage of a conducting polymer when compared with metals.

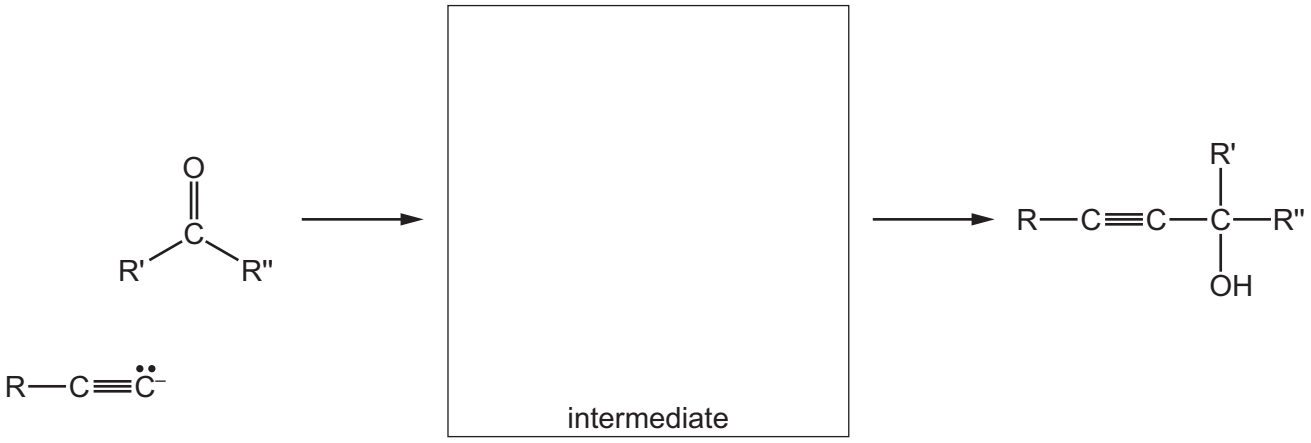
..... [1]



reaction 1

(i) The first step of the mechanism of reaction 1 involves the alkyne anion reacting with the carbonyl compound.

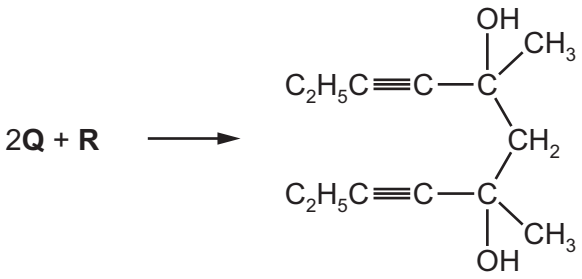
Complete the first step of the mechanism and draw the intermediate for this reaction. Include all relevant dipoles, charges and curly arrows.



[3]

(ii) Suggest the name of the mechanism in reaction 1.

..... [1]



P

Use reaction 1 to suggest the structures of **Q** and **R**.

Q

R

[2]

(e) A series of twelve separate experiments is carried out as shown in the table.

Complete the table by writing in **each** box a tick (✓) if a reaction occurs, or a cross (✗) if no reaction occurs.

	CH_3CHO	HCO_2H	CH_3COCH_3	HO_2CCO_2H
hot, acidified $MnO_4^-(aq)$				
alkaline $I_2(aq)$				
warm Tollens' reagent				

[4]

[Total: 16]

- homopolymer - a polymer made up of the same monomer unit
- copolymer - a polymer made up of two or more different monomer units

The reaction of propene, $CH_3CH=CH_2$, with phenylethene, $C_6H_5CH=CH_2$, gives a copolymer.

Draw a length of the chain of this copolymer that contains one molecule of **each** monomer.

[2]

(d) (i) Polyalkenes biodegrade very slowly.

Explain why by referring to the structures of the polymers.

.....

.....

..... [1]

(ii) Some polymers will degrade in the environment.

Describe **two** processes by which this occurs.

1 .....

2 .....

[2]

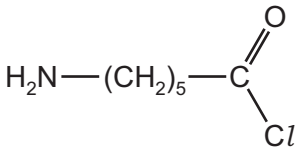
[Total: 11]

(5c) Compound **R** can be polymerised.

Draw a section of this polymer showing **two** repeat units.

[2]

nylon-6 monomer



(i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

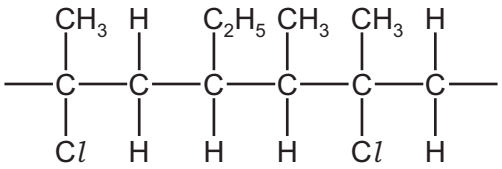
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

(ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

(d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



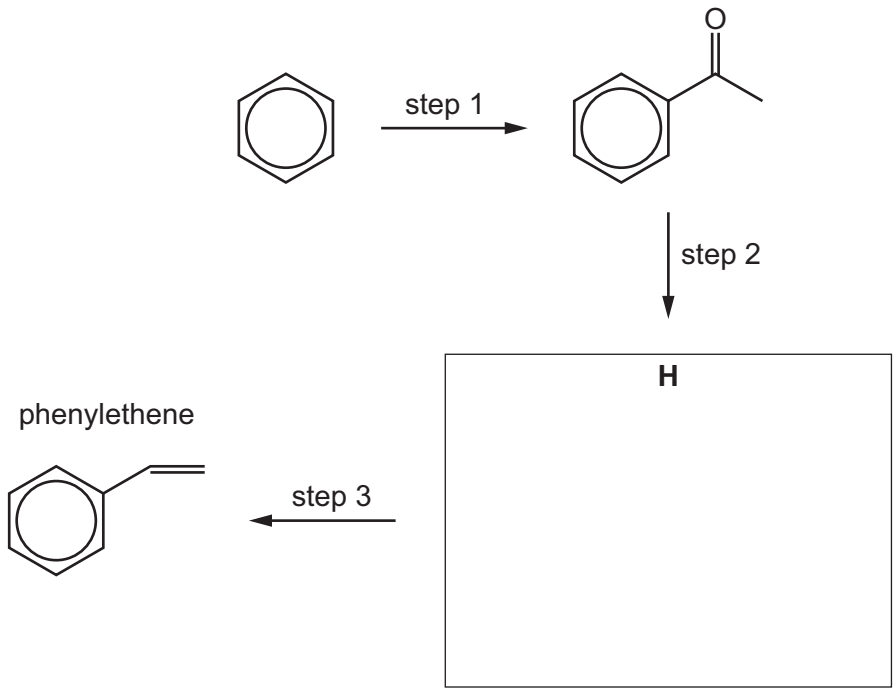
Draw the structure of the **two** alkene monomers which produce this co-polymer.

[2]

.....

..... [1]

(f) The alkene phenylethene can be prepared from benzene in three steps.



(i) Deduce the identity of compound **H** and draw its structure in the box. [1]

(ii) Suggest reagents and conditions for each of the steps 1–3.

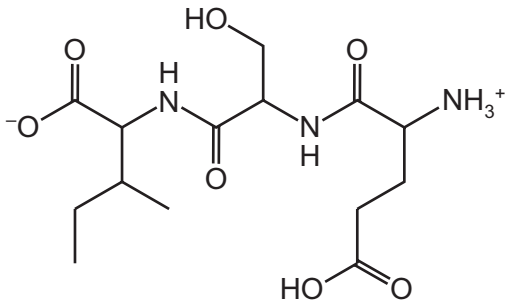
step 1 .....

step 2 .....

step 3 .....

[3]

tripeptide **E**



(a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

..... [1]

(ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

The three amino acids should be shown in the correct form for the conditions you have chosen in **(a)(i)**.

[2]

(b) If a pure sample of **E** is obtained in aqueous solution, several different types of intermolecular forces are possible between pairs of **E** molecules.

Name three different types of intermolecular force that exist between pairs of **E** molecules, stating the groups on the molecules where the forces are acting.

type of force/bond	pair of groups responsible

(i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.

[1]

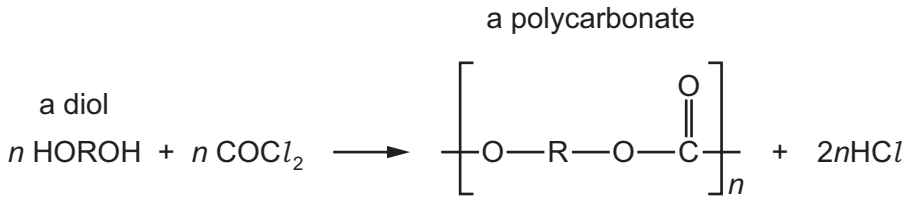
(ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.

name .....

name .....

[4]

[Total: 11]

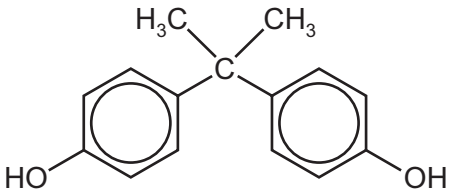


(a) (i) Deduce the *type of polymerisation* shown here.

..... [1]

Nalgene® is a polycarbonate formed from the diol **P** and $COCl_2$.

P



(ii) Draw **one** repeat unit of Nalgene®.

[1]

(iii) Nalgene® is a strong and tough polymer.

Identify **two** types of intermolecular force that are responsible for these properties of Nalgene®.

1 .....

2 .....

[1]

(b) Proteins are polymers of amino acids.

Complete the table to show how the secondary and tertiary structures of proteins are stabilised.

	one intermolecular force responsible	groups involved
secondary structure		
tertiary structure		

.....

.....

..... [2]

(d) Many polymers are degradable.

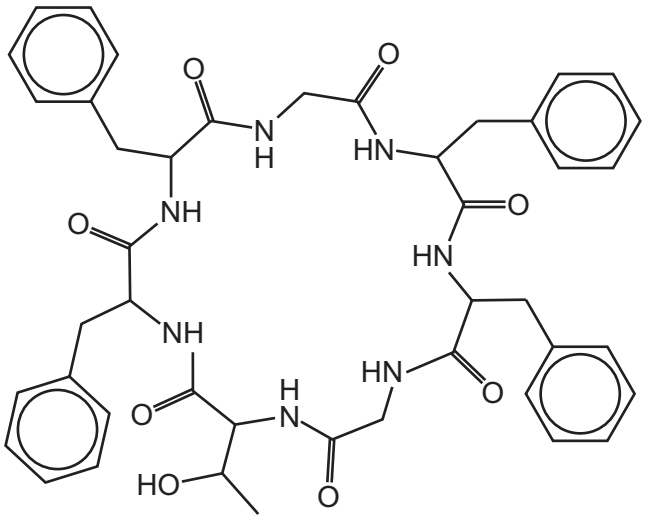
State **two** different processes by which some polymers can be degraded.

.....

..... [1]

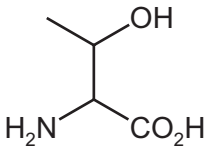
(e) The cyclic peptide **B** is shown.

B



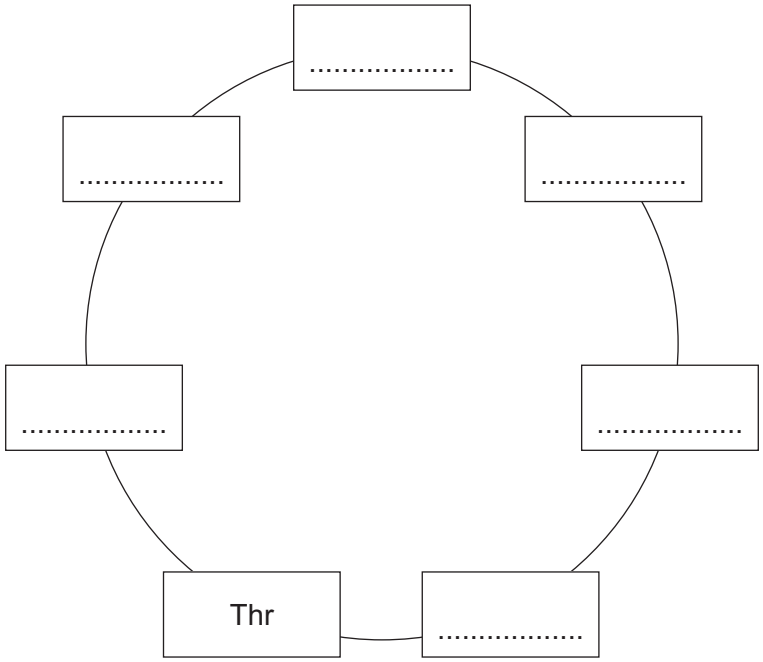
Cyclic peptide **B** is broken into its monomers by heating under reflux with dilute hydrochloric acid. The amino acid threonine, Thr, and two other organic products are formed.

threonine



[2]

(ii) Using the 3-letter abbreviations for the amino acids as given in the *Data Booklet*, complete the sequence for the cyclic peptide, **B**.



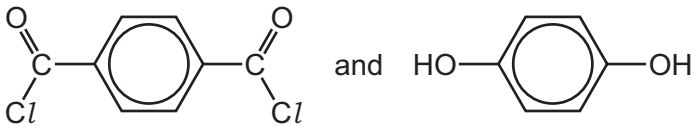
[1]

(iii) Name **two** analytical techniques that could be used to separate these amino acids.

..... and ..... [1]

[Total: 12]

Complete the table by identifying each type of polymerisation.

pair of monomers	type of polymerisation
$HOCH_2CH_2OH$ and $HO_2CCH_2CO_2H$	
	
CH_3CHCF_2 and CH_3CHCH_2	

[1]

(b) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

(i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

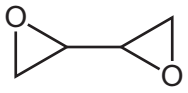
[3]

(ii) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism .....

[2]



When **W** is mixed with a second compound, called a hardener, a polymerisation reaction occurs, producing a non-solvent-based adhesive.

(i) Give the name of this type of non-solvent-based adhesive.

..... [1]

(ii) The hardener is a diamine. A diamine has an alkyl chain with two amine groups which are not bonded to the same carbon atom.

Draw the structural formula of a compound that would make a suitable hardener.

[1]

(i) Identify **one** compound that would react with 1,3-diaminopropane to form a polyamide.

..... [1]

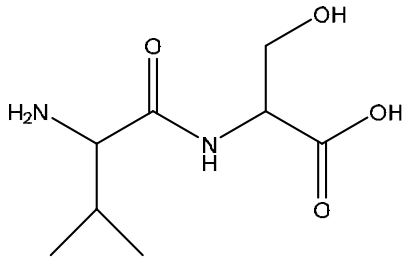
(ii) Draw a section of the polymer chain formed from 1,3-diaminopropane and the compound you chose in **(e)(i)**.

Your answer should:
- include four monomer residues (two of each type of monomer)
- show the amide link fully displayed
- clearly identify **one** repeat unit of this polymer.

[2]

[Total: 20]

(ii)



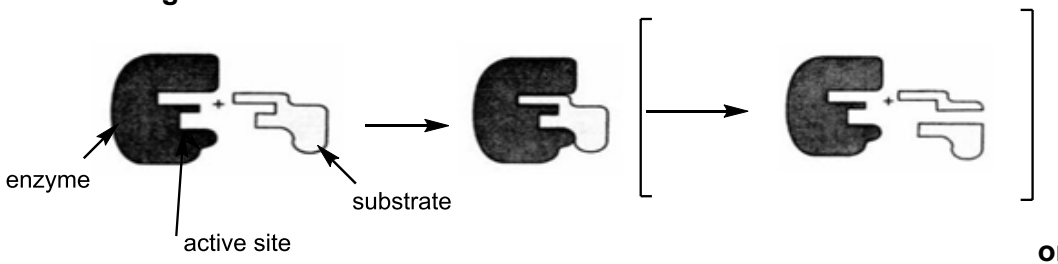
2

(iii) any **two** side-chain interactions mentioned with group

Ionic attractions / bonds	between $–CO_2^-$ and $–NH_3^+$
van der Waals	between alkyl / aryl / non-polar groups ***or*** valine
hydrogen(H) bonding	between –OH, $–NH_2$, COOH, –NH ***or*** serine
–S–S– ***or*** disulfide bonds ***or*** disulfur bond / bridge	between –SH groups or cysteine

2

(b) (i) **labelled diagrams**

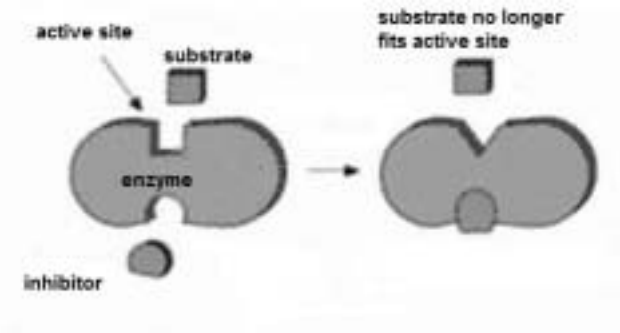


or

in words

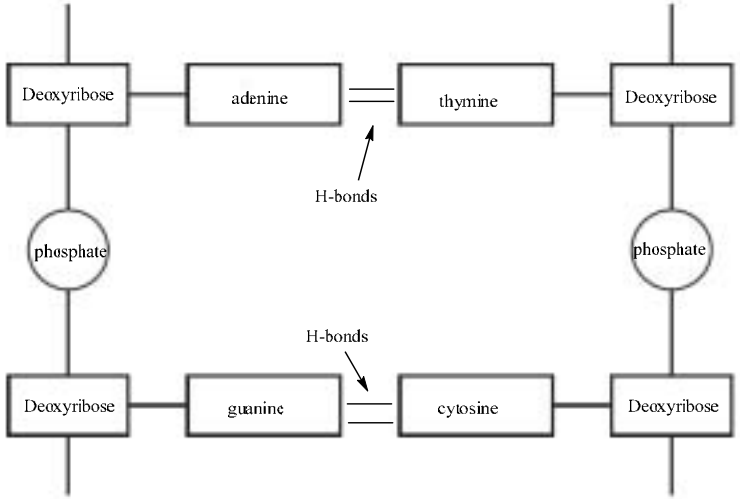
- the enzyme has a specific shape **or** substrate shape is complementary to active site **1**
- the substrate bonds / binds / fits to the active site ***or*** other substrates do not fit into active site **1**

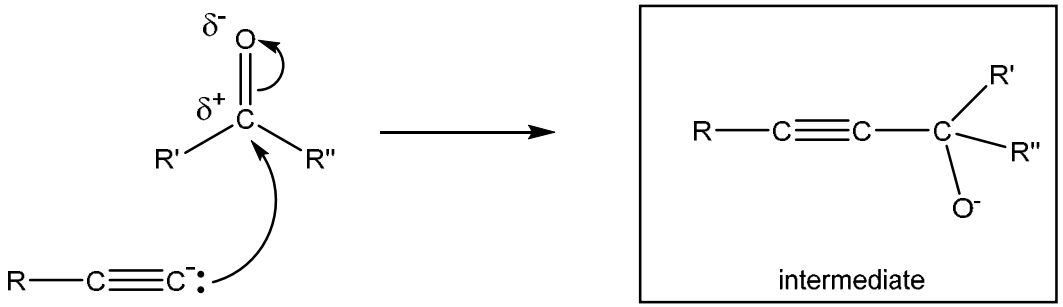
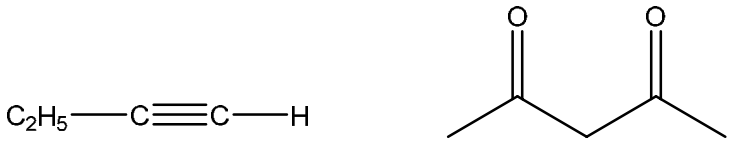
(ii) **labelled diagrams**



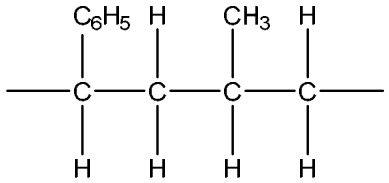
or in words

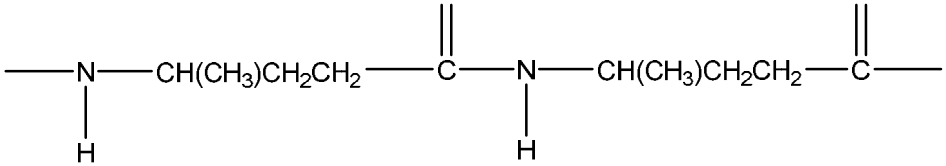
- inhibitor binds to enzyme away from the active site ***or*** inhibitor binds to allosteric site **1**
- this changes the **shape (or structure)** of the **active site** **1**

2 (a)	backbone of sugar phosphate sugar phosphate • base bonded to sugar • deoxyribose correct label • two complementary base pairings e.g A–T or C–G • hydrogen bonding / H–bonding between bases, labelled  		
(b)	any **two** of • DNA uncoils or unzips • hydrogen bonds break or weaken • complementary bases join to form a new strand of DNA	**2**	

3(c)(i)	delocalised electrons	**1**
3(c)(ii)	CH	**1**
3(c)(iii)	less dense	**1**
3(d)(i)	 2 curly arrows [1] dipole [1] intermediate [1]	**3**
3(d)(ii)	nucleophilic addition	**1**
3(d)(iii)	 [1] **Q** [1] **R**	**2**
3(e)		**4**

	CH_3CHO	HCO_2H	H_3COCH_3	HO_2CCO_2H
hot acidified MnO_4^-(aq)	✓	✓	×	✓

4(c)	 **M1** length of chain with both monomers [1] **M2** continuation bonds [1]	**2**
4(d)(i)	C-C bonds are non-polar / have no dipole so cannot be hydrolysed [1]	**1**
4(d)(ii)	**M1** Hydrolysis using acid / base / alkali / enzymes [1] **M2** action of UV light [1]	**2**

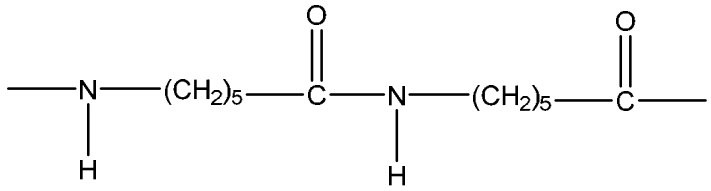
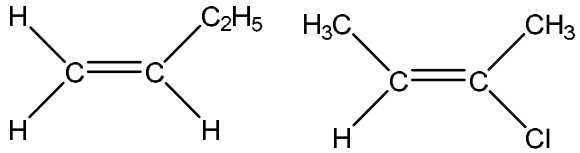
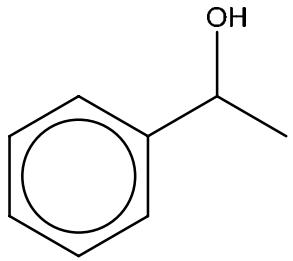


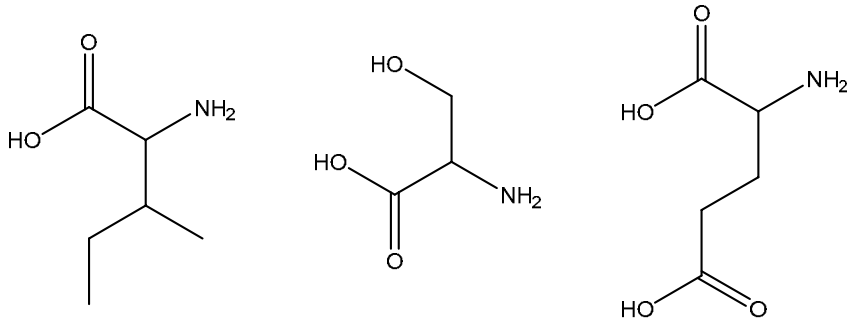
- amide bond (CO-NH)
- structure of polymer with exactly two repeat units
- continuation bonds
- hydrocarbon portions correct

two points = [1]
four points = [1]

	bonds formed	✓

Both ticks correct

6(c)(ii)	 **M1**: amide link **M2**: rest of the structure	**2**
6(d)	 **or** $CH_3CCl{=}CH_2$ and $C_2H_5CH{=}CHCH_3$ each correct structure scores one mark	**2**
6(e)	C-C bonds are non-polar / polyalkenes cannot be hydrolysed **and** polyamides can be broken down by hydrolysis	**1**
6(f)(i)		**1**
6(f)(ii)	**M1**: step 1: CH_3COCl + $AlCl_3$ [1]	**3**

	• protease or named protease; water; T = 30° – 40°C all three points in each bullet [1]	
7(a)(ii)	 M1: three amino acids in any ionic / non-ionic states [1] M2: three amino acids in the correct ionic state for their conditions [1]	**2**
7(b)	• permanent dipole-dipole • one group that will have a δ^+ and another with δ^- e.g. CO, NH, COOH, OH **BOTH** [1] • hydrogen bonds • one group that will have a $H^{\delta+}$, e.g. NH, OH and another with lone pair, e.g. NH, COOH, OH, $CONH_2$ **BOTH** [1] • ionic bonding • NH_3^+ **and** COO^- **BOTH** [1] **ALLOW** • London forces • C_4H_9 groups or parts of these alkyl groups	**3**
7(c)(i)	any structure containing one COOH / COCl **and** NH_2 groups in the same molecule [1]	**1**
7(c)(ii)	$HOCH_2CH_2OH$ [1]	**4**

8(a)	**M1** 2-chloropropanoic acid > 3-chloropropanoic acid > propanoic acid [1] **M2** $CH_3CHClCO_2H$ / $ClCH_2CH_2CO_2H$ (are more acidic) as they contain an electronegative Cl atom so weaken O-H bond / stabilise carboxylate anion [1] **M3** $CH_3CHClCO_2H$ (is more acidic than $ClCH_2CH_2CO_2H$) as the Cl atom is closer to CO_2H so weaken O-H bond more / stabilise carboxylate anion more [1]	**3**
8(b)(i)	K_{eq} = 4.07x10^{-3}/1.78x10^{-4} = **22.9**	**1**
8(b)(ii)	3rd box ticked [to the right] **AND** as the K_{eq} is greater than one ecf on K_{eq}	**1**
8(b)(iii)	pK_a 1.23 $HO_2CCO_2H + H_2O \rightleftharpoons HO_2CCO_2^- + H_3O^+$ **OR** $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$ pK_a 4.19 $HO_2CCO_2^- + H_2O \rightleftharpoons {}^-O_2CCO_2^- + H_3O^+$ **OR** $HO_2CCO_2^- \rightleftharpoons {}^-O_2CCO_2^- + H^+$	**2**
8(b)(iv)	pK_a = – logK_a	**1**
8(c)	<table><tr><th></th><th>reagents and conditions</th><th>observed change</th></tr><tr><td>test 1</td><td>**M1** Tollen's reagent, warm **OR** Fehling's solution, warm</td><td>silver mirror (brick)-red ppt.</td></tr><tr><td>test 2</td><td>**M2** aqueous alkaline iodine **OR** 2,4-DNPH</td><td>yellow ppt. orange ppt.</td></tr><tr><td>test 3</td><td>**M3** acidified MnO_4^- , warm</td><td>decolourises (and bubbles)</td></tr></table> Two correct observations = 1 mark	**5**

8(d)

chemical shift (δ)	environment of the carbon atom	hybridisation of the carbon atom
27	**C**H_3 circled	sp^3
163	**C**OOH circled	sp^2
192	**C**=O(COOH) circled	sp^2

Award one mark for each correct column

2

8(e)

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3	alk / CH / CH_3	triplet	3
2.2	CH_3CO **or** alkyl / CH next to C=O	singlet	3
4.0	CH_2O **or** alkyl / CH next to electronegative atom / C=O	quartet / quadruplet	2

Award one mark for every three correct responses.

3

8(f)

AND CH_3 **circled**

these protons do not exchange with D_2O
OR OH and NH protons exchange with D_2O

2

8(g)(i)

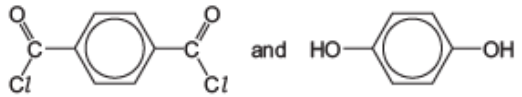
$K_w = [D^+][DO^-]$

1

8(g)(ii)

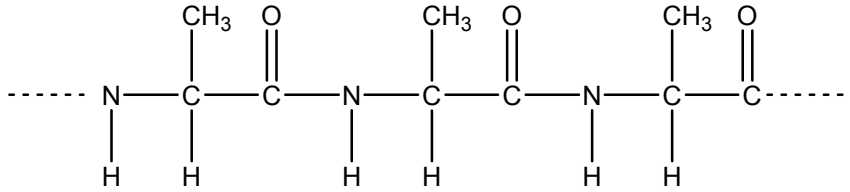
M1 $[D^+] = \sqrt{1.35 \times 10^{-15}} = 3.67 \times 10^{-8}$

2

pair of monomers	type of polymerisation
$HOCH_2CH_2OH$ and $HO_2CCH_2CO_2H$	condensation
	condensation
CH_3CHCF_2 and CH_3CHCH_2	addition

ALL correct [1]

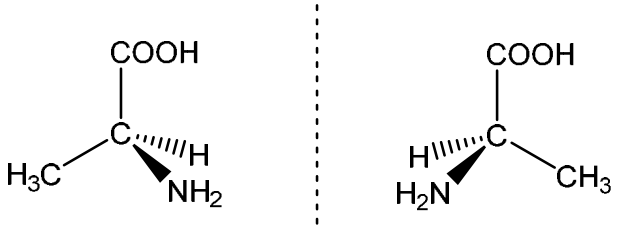
9(b)(i)



- amide links displayed correct (NHCO **OR** CONH)
- three monomers of Ala only
- one repeat unit correctly identified
- continuation bonds (with a polypeptide involving Ala only)
  mark as • ✓ ✓ ✓ [3]

3

9(b)(ii)



3D, tetrahedral, both isomers of 2-aminopropanoic acid [1]

optical [1]

2

9(c)(i) **epoxy resin** [1] **ALLOW** Super Glues

1

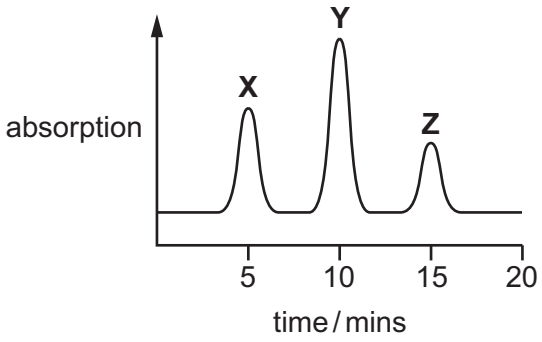
P42/O/N/20/Q7e

10(e)(i)	either a dioic acid or a dioyl chloride [1]	**1**
10(e)(ii)	• trailing bonds • two of each monomer residue, consistent with ei [1] • repeat unit identified • amide link showing C=O [1]	**2**

Paper 4

Topic 11 Analytical Chemistry NMR+MS+IR

known values.
A gas chromatogram is shown.



(i) Suggest what is meant by the term *retention time*.

.....

..... [1]

(ii) Give an example of a carrier gas used in gas chromatography.

..... [1]

(iii) **Z** spends the longest time in the chromatography column.

Suggest why this might be the case.

.....

..... [1]

(iv) Explain a possible limitation of gas / liquid chromatography in separating two esters such as ethyl methanoate, $HCO_2CH_2CH_3$, and methyl ethanoate, $CH_3CO_2CH_3$.

.....

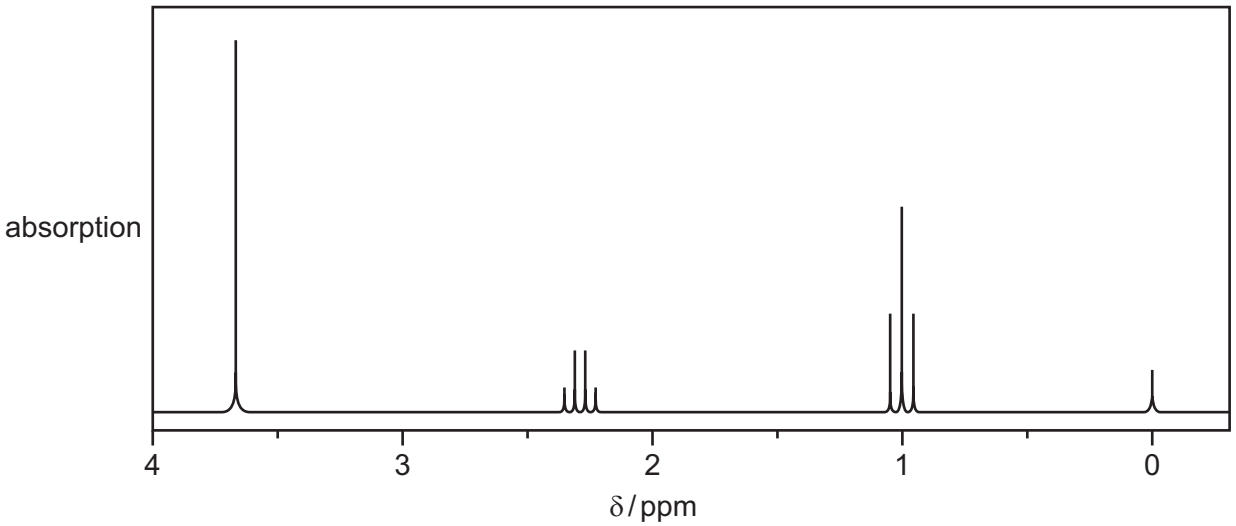
..... [1]

(v) A student works out the areas underneath the three peaks in the chromatogram.

peak	**X**	**Y**	**Z**
area / mm^2	22	38	16

Assuming the areas underneath the peaks are proportional to the masses of the respective components, what percentage of the original mixture was made up of the organic compound, **X**?

% of **X** = [1]



(i) What compound is responsible for the absorption at $\delta = 0$?

..... [1]

(ii) Compound **Y** is an ester with the molecular formula $C_4H_8O_2$.

Complete the table for the NMR spectrum of **Y**.
The actual chemical shifts for three absorptions in **Y** and the splitting pattern for the resonance at $\delta = 3.7$ ppm have been given for you.
Use of the *Data Booklet* may be helpful.

chemical shift δ / ppm	type of proton(s)	number of protons	splitting pattern
1.0			
2.3			
3.7			singlet

[4]

(iii) Use your conclusions to suggest a structure for the ester **Y**.

[1]

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with 0.0200 mol dm^{-3} $KMnO_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.

$$2MnO_4^- + 6H^+ + 5C_2O_4H_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the titration, 15.20 cm^3 of $KMnO_4$ was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

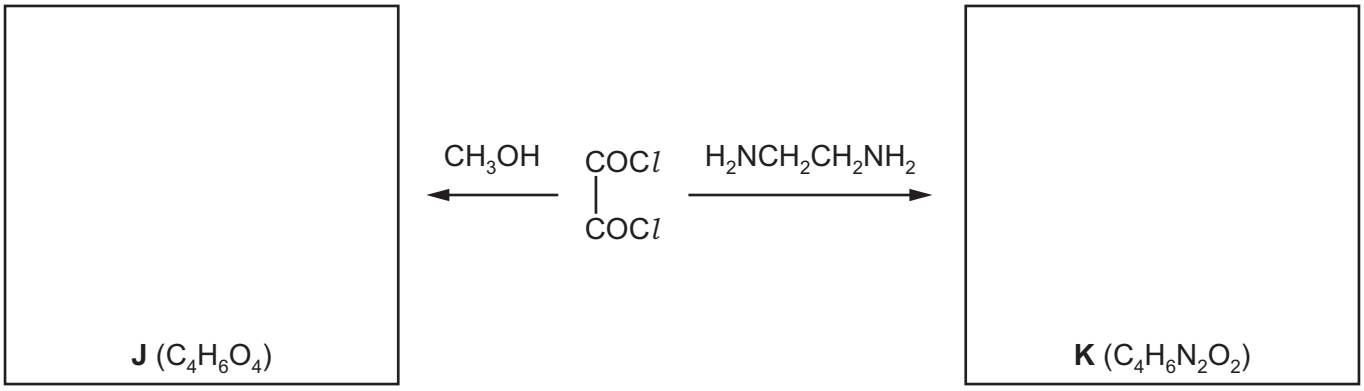
percentage of ethanedioic acid = ... % [3]

$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(i) State a suitable reagent for this reaction.

..... [1]

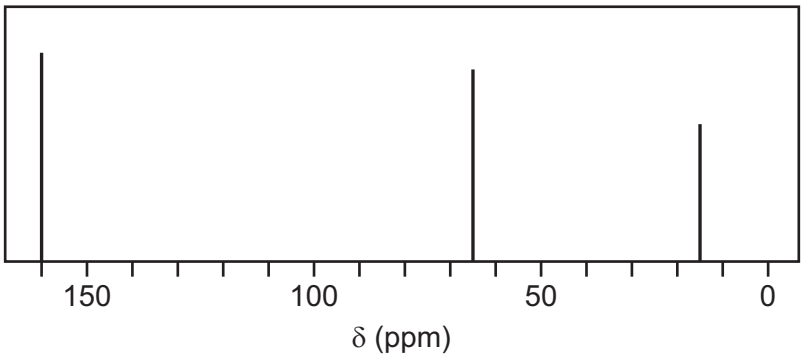
(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.



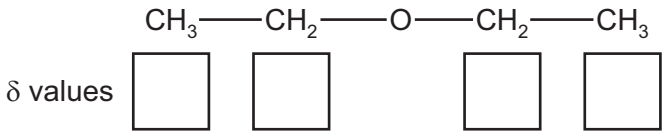
[2]

(c) When ethanedioyl chloride is reacted with silver ethanedioate, AgO_2CCO_2Ag, in ethoxyethane at –30 °C, an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6.

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $CH_3CH_2OCH_2CH_3$, is shown below.

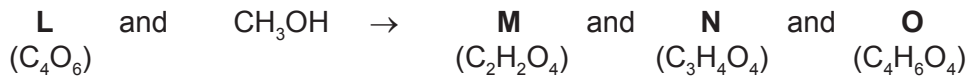


(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.



[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.



M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.

M, $(C_2H_2O_4)$

N, $(C_3H_4O_4)$

O, $(C_4H_6O_4)$

[3]

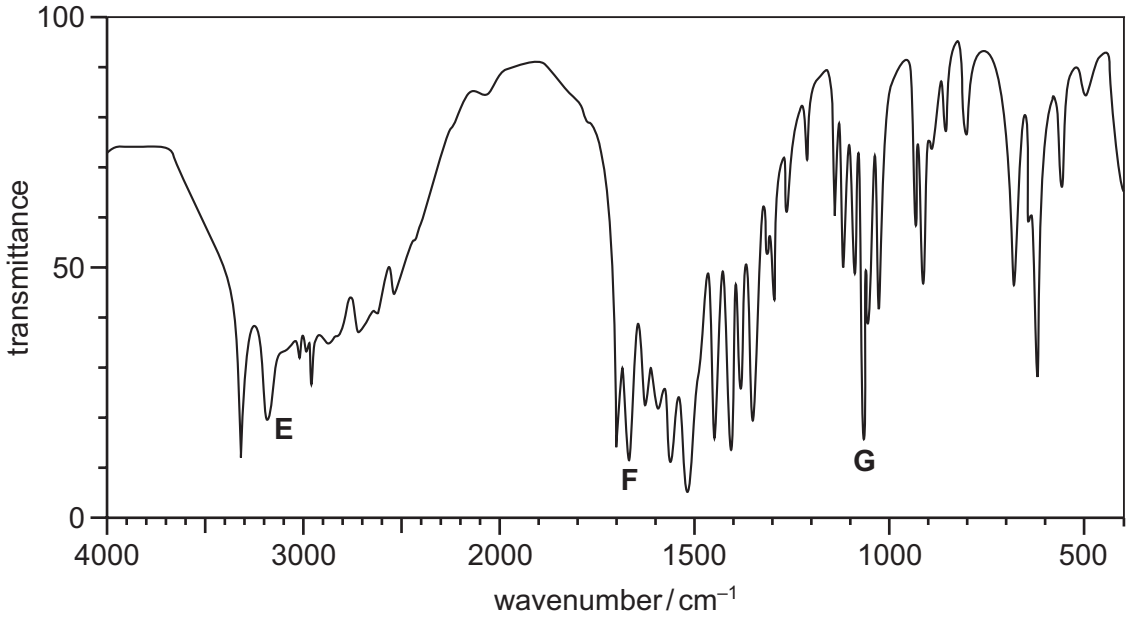
(ii) Suggest a structure for **L** that fits all the data given in **(c)** and **(d)**.

L, (C_4O_6)

[1]

[2]

The infra-red spectrum of Gly-Ser is shown below.



(ii) Use the *Data Booklet* to identify the bond in the molecule of Gly-Ser that is responsible for each of the peaks indicated on the above infra-red spectrum.

E .....

F .....

G .....

[2]

[Total: 12]

NMR spectroscopy.

(a) The mass spectrum shows that the *m* / *e* value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

(i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

number of carbon atoms = ... [2]

(ii) Suggest the molecular formula of **F**.

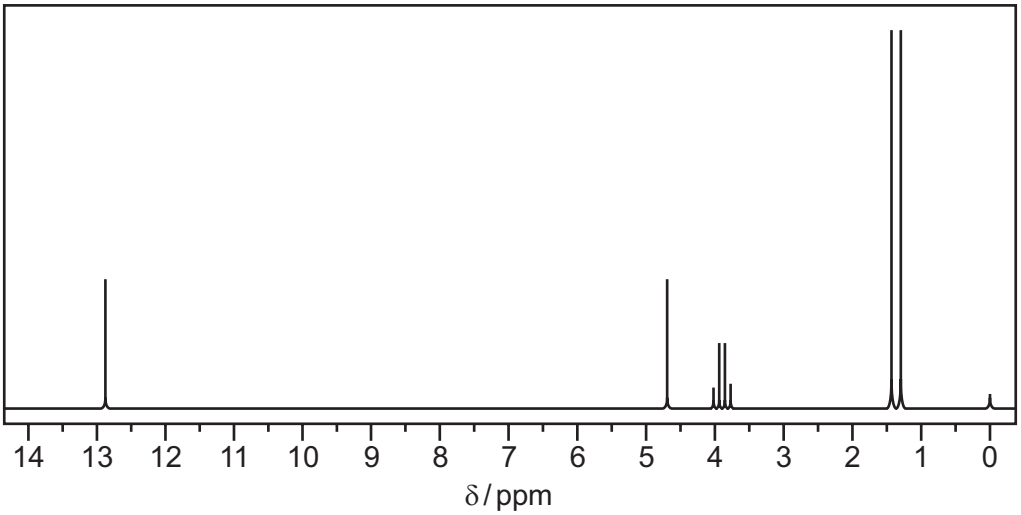
molecular formula = C H O [1]

(b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption / cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong		
2680	very broad and strong		
1725	strong		

[2]



(i) Use the *Data Booklet* and your answer to **(a)(ii)** to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ / ppm	type of proton	relative peak area
1.4		
3.9		
4.7		
12.9		

[4]

(ii) Describe and explain the splitting pattern for the absorption at δ = 1.4.

.....

..... [1]

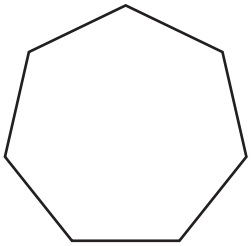
(iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained.
Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

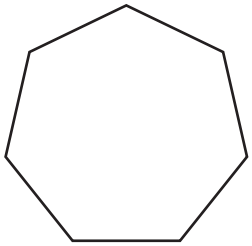
..... and ..... [1]

(iv) Suggest the structure of **F**.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.



P



Q

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

isomer	number of peaks
P	
Q	

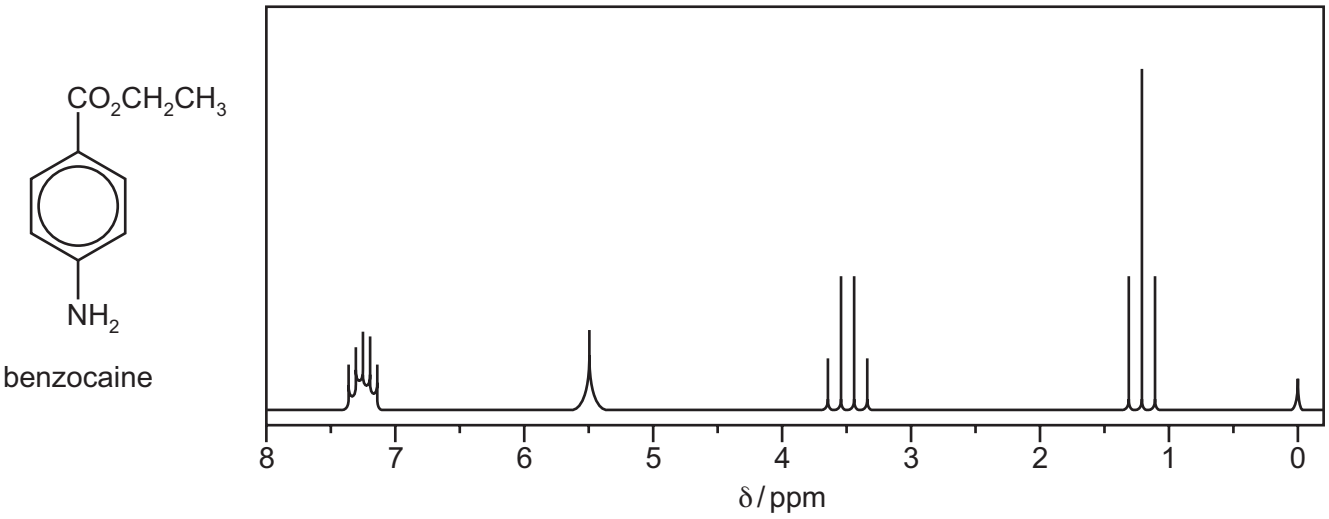
[2]

[Total: 15]

(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

..... [1]

(ii) Benzocaine was dissolved in $CDCl_3$ and the proton NMR spectrum of this solution was recorded.



benzocaine

Suggest why $CDCl_3$ and not $CHCl_3$ is used as the solvent when obtaining a proton NMR spectrum.

.....

..... [1]

(iii) Use the *Data Booklet* and the spectrum in **(d)(ii)** to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ, for the four absorptions have been added.

δ / ppm	group responsible for the peak	number of ^1H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at δ1.2 ppm.

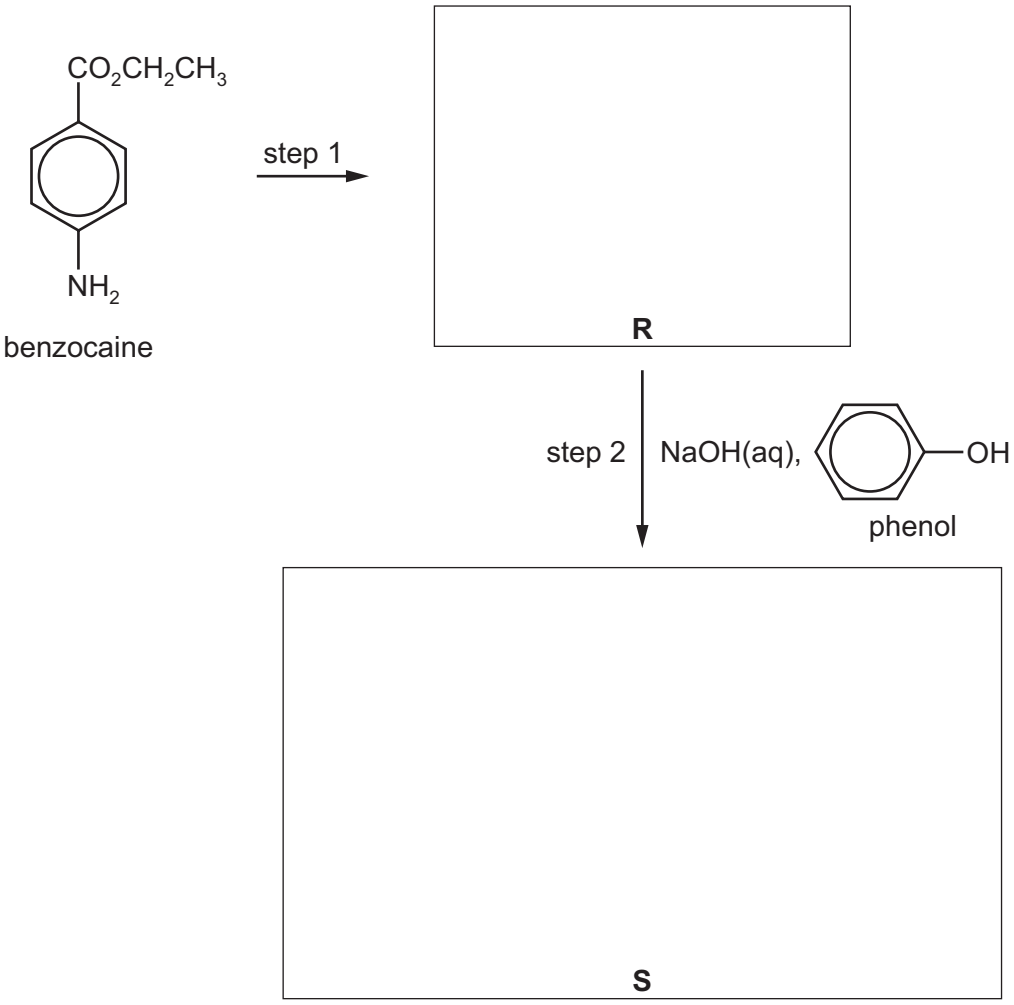
.....

Suggest how this spectrum would differ from the spectrum in **(d)(ii)**.
Explain your answer.

.....

..... [1]

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



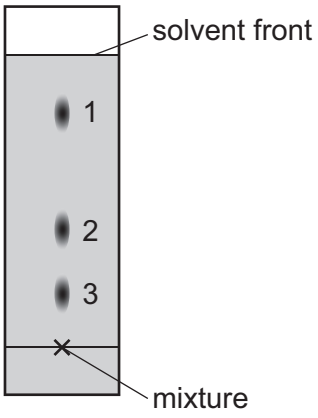
(i) Suggest the reagents used for step 1.

..... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

[Total: 25]

similar molecular masses. The resulting chromatogram is shown.



(i) Identify which spot corresponds to each compound.

compound	spot
J CH_3COCO_2H	
K HO_2CCO_2H	
L $CH_3CH_2COCH_2CH_3$	

[1]

(ii) Explain your answers to **(b)(i)**.

.....

..... [1]

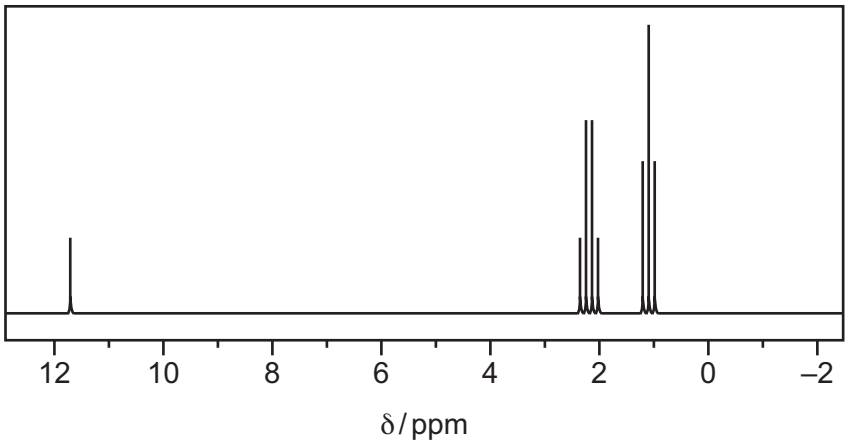
(iii) What is meant by the term R_f *value*?

.....

..... [1]

[Total: 10]

spectrum of **Z** dissolved in $CDCl_3$ is shown.



(i) From the proton NMR spectrum, identify **Z**.

..... [1]

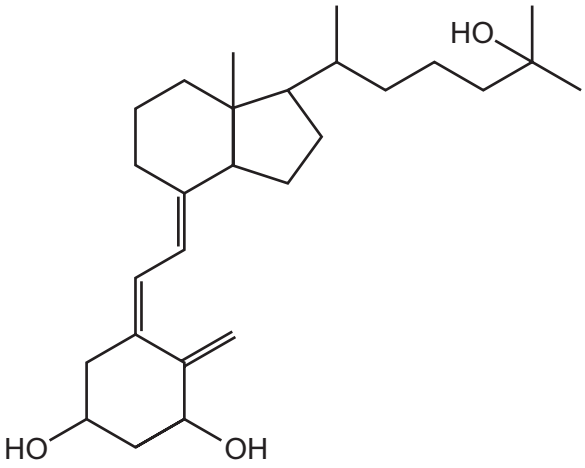
(ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

.....

.....

.....

..... [2]



calcitriol

(a) Give the number of primary, secondary and tertiary alcohol groups in one molecule of calcitriol.

primary ..... secondary ..... tertiary .....
[1]

(b) Give the number of chiral carbon atoms in one molecule of calcitriol.

..... [1]

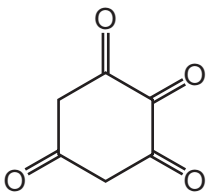
(c) Calcitriol shows geometrical isomerism.

Give the number of geometrical isomers of calcitriol, including calcitriol.

..... [1]

(d) A sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII). There are three different carbon-containing products of this reaction.

One of these three products, **X**, is shown.



X

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **X**.

..... [1]

.....

.....

.....

..... [3]

(iii) Predict the number of peaks this compound would show in its proton NMR spectrum.

..... [1]

(iv) For each of the peaks in the proton NMR spectrum you have identified in **(iii)** give the expected splitting pattern. Explain your reasoning.

.....

.....

..... [2]

(e) In addition to the product shown in **(d)**, two other carbon-containing products are formed when a sample of calcitriol is treated with an excess of hot, concentrated, acidified potassium manganate(VII).

(i) Of these two other carbon-containing products, identify the product with the **smaller** molecular mass. Explain how this product is formed.

.....

.....

.....

..... [2]

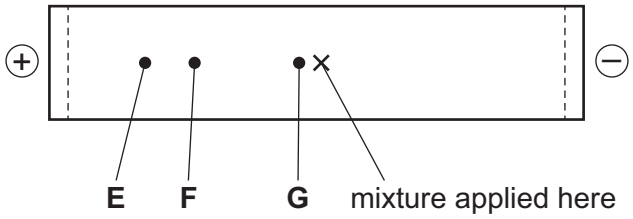
(ii) Of these two other carbon-containing products, identify the product with the **larger** molecular mass by drawing its skeletal formula in the space below.

[1]

[2]

The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of glutamic acid is 3.2 and of cysteine is 5.0.

A mixture of the dipeptide glu-cys and its two constituent amino acids, glutamic acid and cysteine, was analysed by electrophoresis using a buffer at pH 5.2. The results obtained are shown.



(b) Suggest identities for the species responsible for spots **E**, **F** and **G**. Explain your answers.

spot	identity
E	
F	
G	

explanation .....

.....

.....

[3]

[Total: 5]

The peak heights of the M and M+1 peaks are 22.65 and 1.25 respectively.

(i) Use these data to show that there are fiv carbon atoms present in one molecule of **X**.

Show your working.

[1]

(ii) The mass spectrum has a peak at *m*/*e* = 57.

Complete the equation to show the fragmentation of **X** to produce this peak.

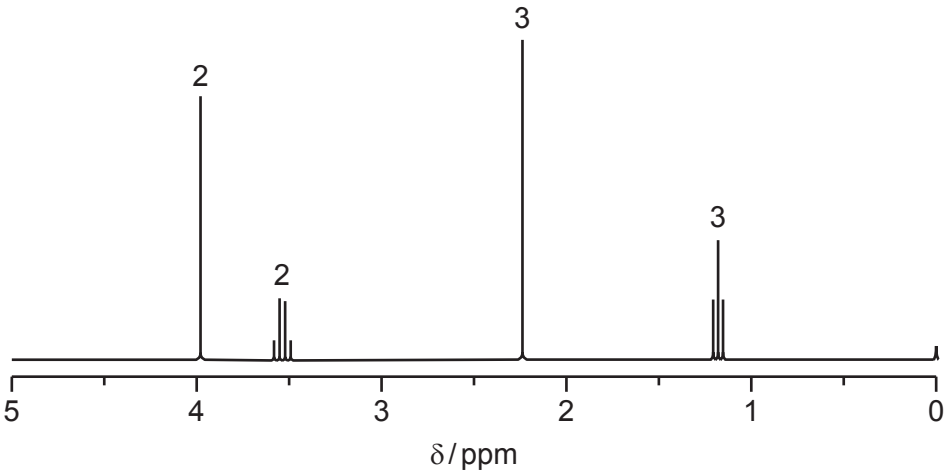
$[C_5H_{10}O_2]^+ \rightarrow$ ..... + ...

[2]

(b) State the use of TMS and $CDCl_3$ in NMR spectroscopy.

- TMS .....
- $CDCl_3$ .....

[1]



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at δ2.2,

.....

- deduce the part of the molecule that produces the peaks at δ1.2 and δ3.5,

.....

- deduce the part of the molecule that produces the peak at δ4.0.

.....

[3]

(ii) When reacted with aqueous alkaline iodine, **X** produces a yellow precipitate.

Use this information and your answers to **(c)(i)** to suggest a structure for **X**.

[1]

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

Suggest a structure for this ester, **W**.

[1]

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

.....

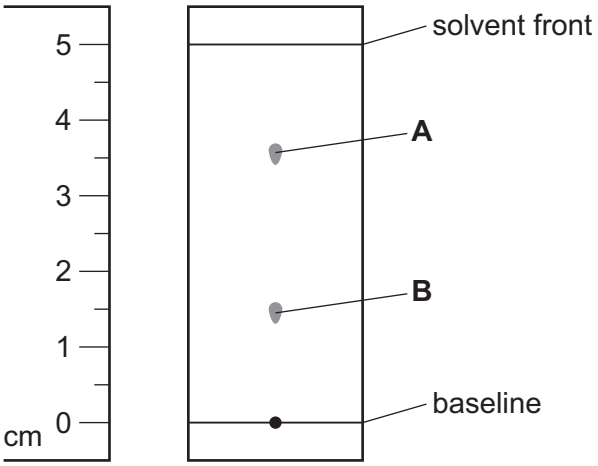
..... [1]

(ii) Suggest a structure for **V**.

[1]

[Total: 11]

The chromatogram obtained is shown, drawn to scale. The table shows some R_f values for different amino acids in the solvent used.



amino acid	R_f value
alanine	0.40
glutamic acid	0.29
leucine	0.71
valine	0.61

(i) Use the chromatogram and the R_f values to deduce the amino acid responsible for spot **A** and spot **B**.

amino acid responsible for spot **A** .....

amino acid responsible for spot **B** .....
[1]

(ii) A second chromatogram of the same mixture is taken using a **more polar** solvent.

Predict the effect on the R_f values of the amino acids. Explain your reasoning.

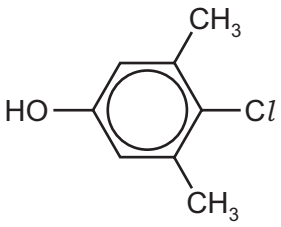
.....

.....

.....

..... [1]

R



(a) State the systematic name of compound **R**.

..... [1]

(b) (i) **R** is dissolved in $CDCl_3$ and analysed using carbon-13 and proton NMR spectroscopy.

- Predict the number of peaks that are seen in the carbon-13 NMR spectrum of **R**.

.....

- Predict the number of peaks that are seen in the proton NMR spectrum of **R**.

.....
[2]

(ii) A separate sample of **R** is dissolved in D_2O. The proton NMR spectrum of this solution shows **one less** peak than is obtained in $CDCl_3$.

Explain why.

.....

..... [1]

..... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

.....

.....

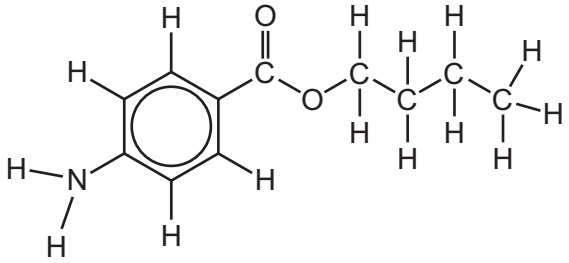
..... [2]

[Total: 18]

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

..... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in **(c)(i)**.



[1]

(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in $CDCl_3$.

.....

..... [2]

(d) The mass spectrum of butamben includes peaks at *m*/*e* 92 and 57.

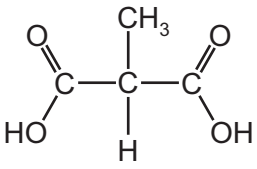
Identify the fragments responsible for these peaks.

m/*e* 92 = ...

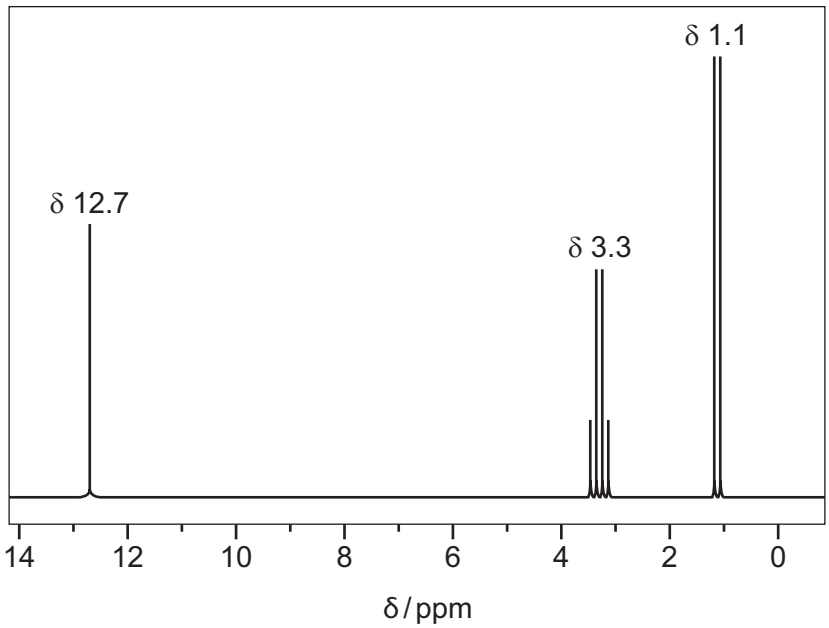
m/*e* 57 = ...

[1]

[Total: 10]



The proton NMR spectrum of methylpropanedioic acid in CCl_4 is shown.



(i) Identify the protons in the methylpropanedioic acid molecule that are responsible for each area of the proton NMR spectrum.

δ 12.7 .....

δ 3.3 .....

δ 1.1 .....

[2]

(ii) Name the splitting pattern shown at δ 3.3 and explain how it arises.

.....

..... [1]

The carbon-13 NMR spectra of butanedioic acid, $HO_2CCH_2CH_2CO_2H$, and methylpropanedioic acid, $HO_2CCH(CH_3)CO_2H$ are different.

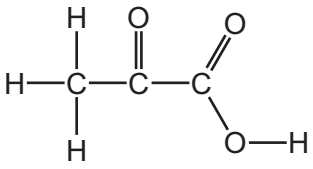
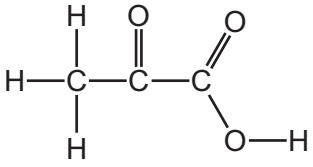
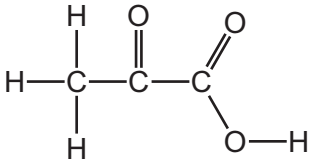
(iii) State the number of peaks

- in the carbon-13 NMR spectrum of butanedioic acid

.....

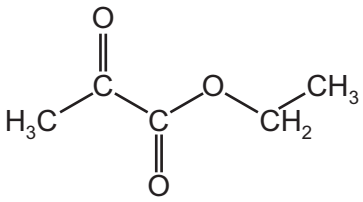
Complete the table by:

- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

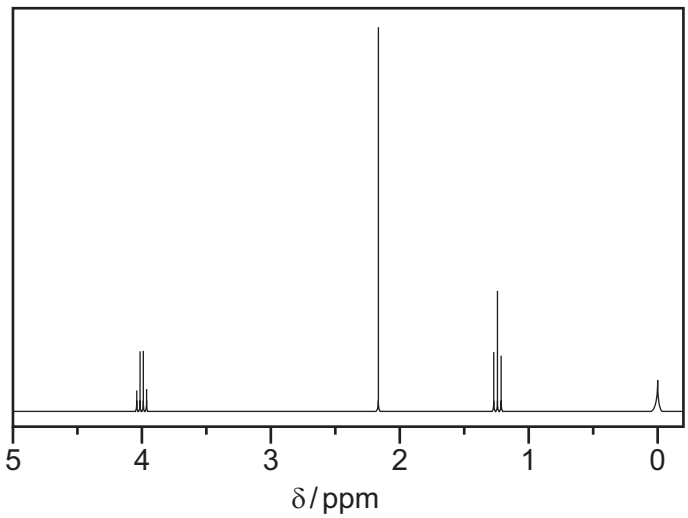
chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

[2]

F



The proton NMR spectrum of **F** is shown.



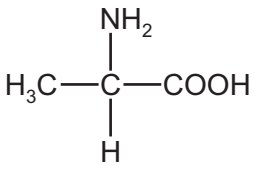
Use the proton NMR spectrum of **F** to complete the table.

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^{1}H atoms responsible for the peak
1.3			
2.2			
4.0			

[3]

The proton NMR spectrum of alanine in D_2O has 2 peaks.

alanine



On the diagram of alanine, circle the protons that show peaks in **both** NMR spectra.
Explain your answer.

.....

.....

..... [2]

(g) The ionic product, K_w, for D_2O has a value of $1.35 \times 10^{-15}\,mol^2\,dm^{-6}$ at 298 K.

(i) Write the expression for the K_w of D_2O.

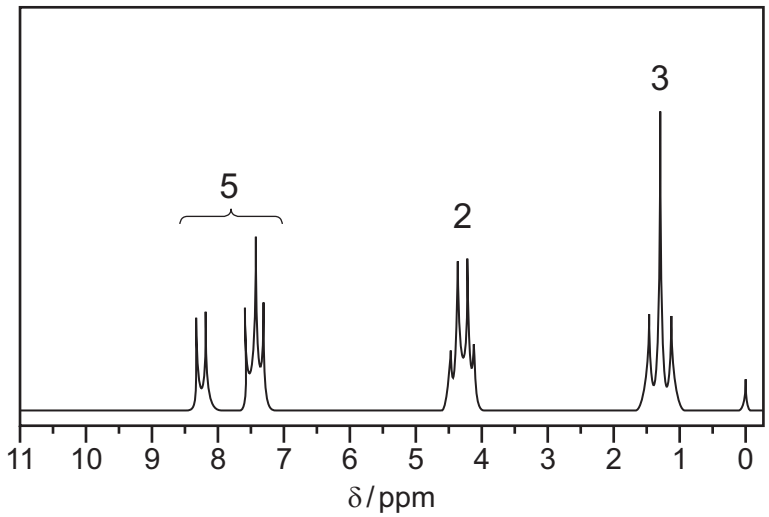
K_w =

[1]

(ii) Calculate the pH of pure, neutral D_2O at 298 K.
Assume $[D^+]$ is equivalent to $[H^+]$ for pH calculations.

pH = ... [2]

[Total: 23]



(a) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

..... [1]

(b) Explain why TMS is added to give the small peak at chemical shift $\delta = 0$.

..... [1]

(c) Compound **E** is hydrolysed by hot NaOH(aq), giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq).

..... [1]

(d) (i) Describe and explain the splitting patterns of the peaks at $\delta = 1.4$ and $\delta = 4.3$.

splitting pattern at $\delta = 1.4$ .....

reason for splitting pattern at $\delta = 1.4$ .....

splitting pattern at $\delta = 4.3$ .....

reason for splitting pattern at $\delta = 4.3$ .....
[2]

(ii) Each molecule of compound **E** contains five protons which give rise to the peaks between $\delta = 7.0$ and $\delta = 8.5$.

Identify the functional group in compound **E** which contains these protons.

..... [1]

[1]

(e) The mass spectrum of compound **E** includes fragment ions with *m*/*e* values of 29 and 77.

Give the formulae of these fragment ions.

fragment ion with *m*/*e* = 29 .....

fragment ion with *m*/*e* = 77 .....

[2]

[Total: 9]

(18c) Ethanamide can be made from ethanoic acid in a two-step synthesis.

$$\text{ethanoic acid} \xrightarrow{\text{step 1}} \mathbf{A} \xrightarrow{\text{step 2}} \text{ethanamide}$$

(i) Compound **A** contains chlorine.

Give the structural formula and name of **A**.

structural formula .....

name .....

[2]

(ii) Suggest suitable reagents for steps 1 and 2.

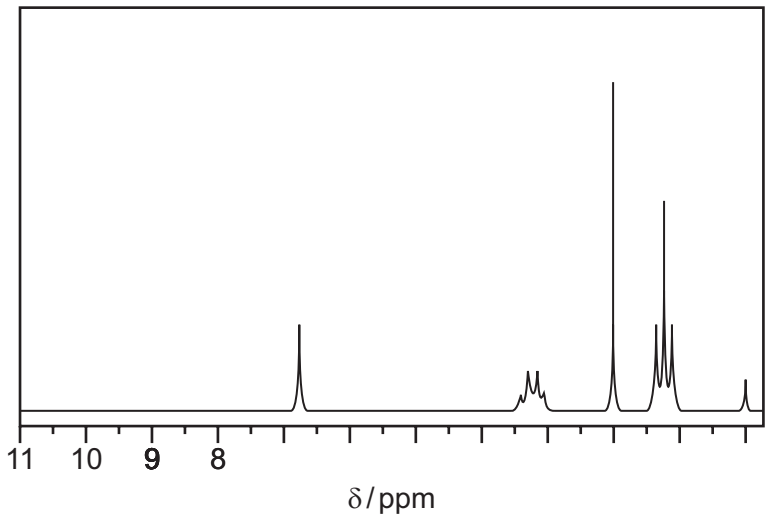
step 1 .....

step 2 .....

[2]

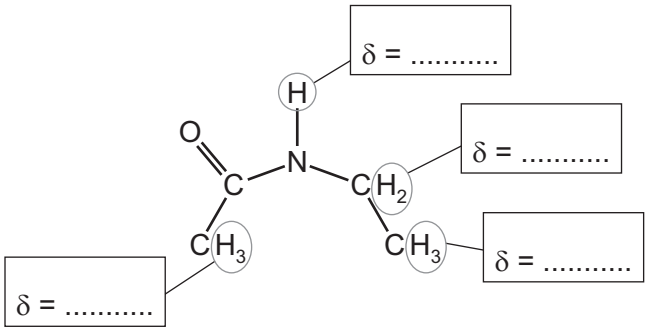
(d) Compound **A** can also be used to make the amide $CH_3CONHC_2H_5$.

The proton NMR spectrum of the amide $CH_3CONHC_2H_5$ in the solvent $CDCl_3$ is shown.



(i) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

..... [1]



[2]

(iii) State and explain how the proton NMR spectrum of the amide $CH_3CONHC_2H_5$ differs when dissolved in D_2O rather than $CDCl_3$.

.....

.....

..... [2]

(e) The mass spectrum of the amide $CH_3CONHC_2H_5$ includes a fragment ion with *m*/*e* value of 58.

Give the molecular formula of this fragment ion.

fragment ion with *m*/*e* value of 58 is ..... [1]

(f) The amide undergoes the following reaction to produce diethylamine.

$$CH_3CONHC_2H_5 \xrightarrow{\text{reagent } \mathbf{B}} C_2H_5NHC_2H_5$$

diethylamine

(i) Identify reagent **B**.

..... [1]

(ii) State the number of different absorptions in the carbon-13 NMR spectrum of diethylamine.

..... [1]

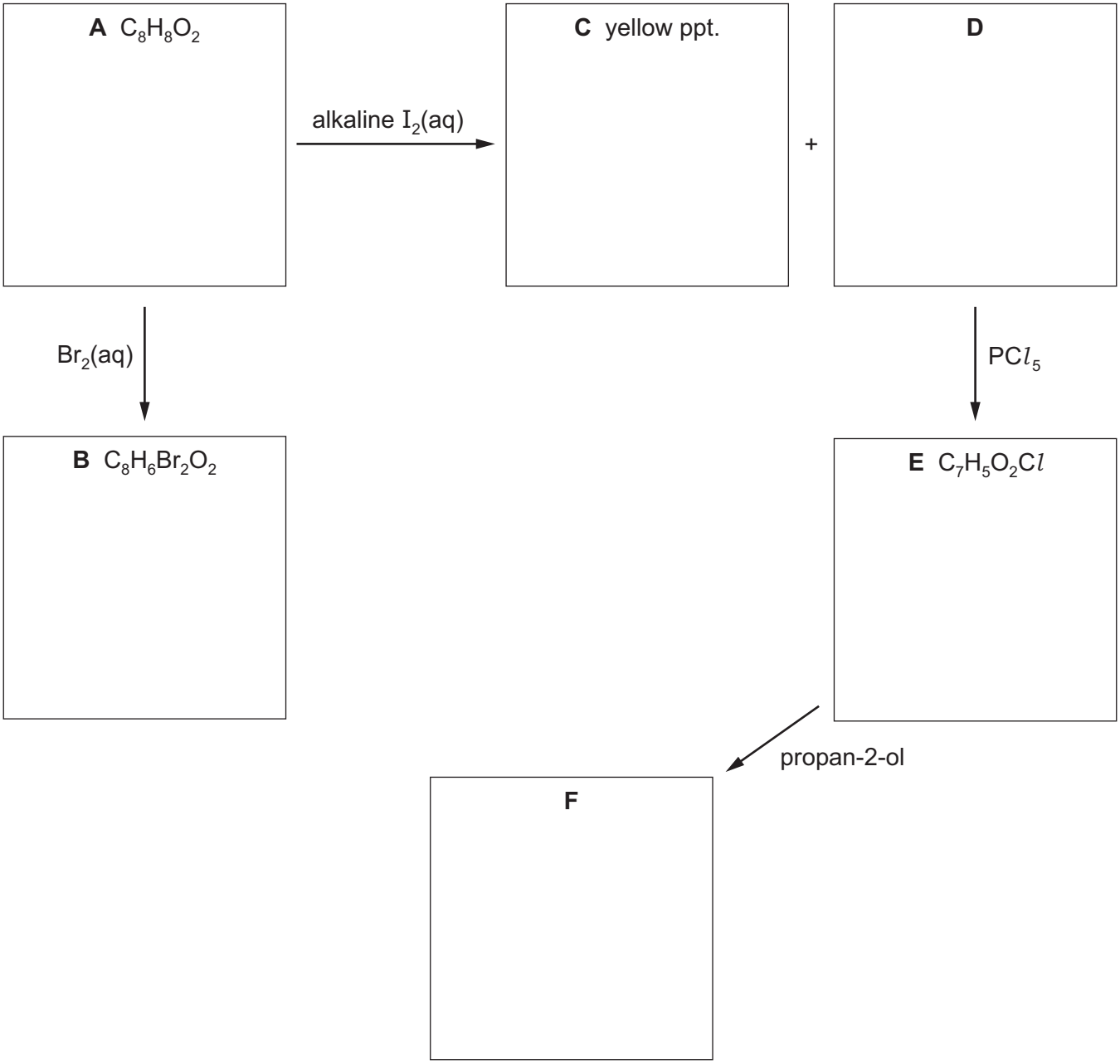
Compound **A** reacts with an excess of bromine water to give compound **B**, $C_8H_6Br_2O_2$.

Compound **A** reacts with alkaline aqueous iodine to form a yellow precipitate **C** and compound **D**.

Compound **D** reacts with PCl_5 to form compound **E**, $C_7H_5O_2Cl$.

Compound **E** reacts with propan-2-ol to form compound **F**.

Draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F** in the boxes.

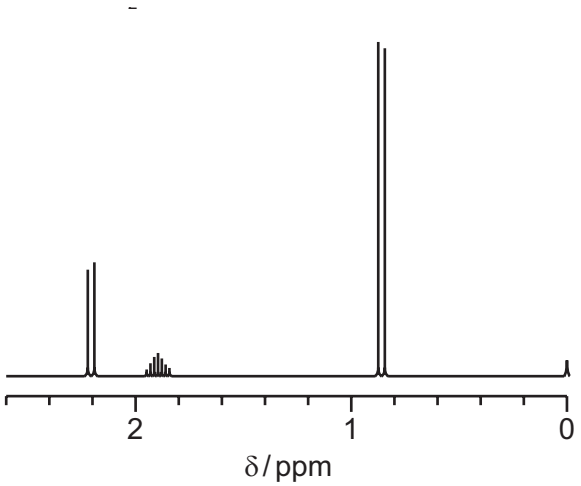


[6]

Draw the **skeletal** formulae of the four structural isomers in the appropriate boxes. The number of peaks observed in the carbon-13 (^{13}C) NMR spectrum of each compound is given.

isomer 1	isomer 2
three peaks in ^{13}C NMR	four peaks in ^{13}C NMR
isomer 3	**isomer 4**
five peaks in ^{13}C NMR	six peaks in ^{13}C NMR

[4]



(i) Use this information to suggest a structure for **Y**.

[1]

(ii) Use the *Data Booklet*, the proton (^{1}H) NMR spectrum and your answer to **(c)(i)** to complete the table.

chemical shift (δ)	environment of proton	splitting pattern	number of ^{1}H atoms responsible for the peak
0.95			
1.90			
2.20			

[3]

[Total: 10]

(i) Calculate the relative abundance of the M+1 peak in the mass spectrum of ethylamine.

relative abundance = ... [1]

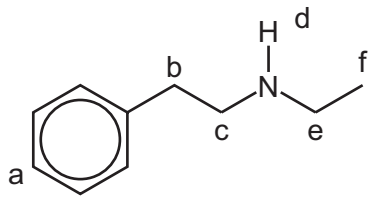
(ii) The mass spectrum of compound **T** contains several fragments. The *m*/*e* values of two of these fragments are 29 and 91.

Draw the structures of the ions responsible for these peaks.

m/*e*	structure of ion
29	
91	

[2]

(e) The proton (^{1}H) NMR spectrum of compound **T** shows hydrogen atoms in different environments. Six of these environments are shown on the structure using letters a, b, c, d, e and f.



Use the letters a, b, c, d, e and f to answer the questions that follow. The questions relate to the proton (^{1}H) NMR spectrum of **T**.

Proton d does not cause splitting of the peaks for protons c or e under the conditions used.

Each answer may be one, or more than one, of the letters a, b, c, d, e and f.

(i) Identify the proton or protons with a chemical shift (δ) in the range 6.0 to 9.0.

..... [1]

(ii) Identify the proton or protons whose peak will disappear if D_2O is added.

..... [1]

..... [1]

(iv) Identify the proton or protons with the lowest chemical shift (δ).

..... [1]

[Total: 12]

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion. The isoelectric point of valine is 6.0. The isoelectric point of lysine is 9.7.

(a) Draw the structure of valine at pH 6.0.

[1]

(b) A solution of lysine is produced with pH 9.7. Dilute sulfuric acid is added slowly until the pH of the solution is 1.0. The sulfuric acid reacts with lysine to produce different organic ions that are not present in significant concentrations at pH 9.7.

Draw the structures of three of the organic ions that form during the addition of sulfuric acid in the boxes. Draw the organic ion present at pH 1.0 in box C.

A	B	C (pH 1.0)

[3]

(c) Draw the structure of the dipeptide Val-Lys. The peptide bond should be shown fully displayed.

[2]

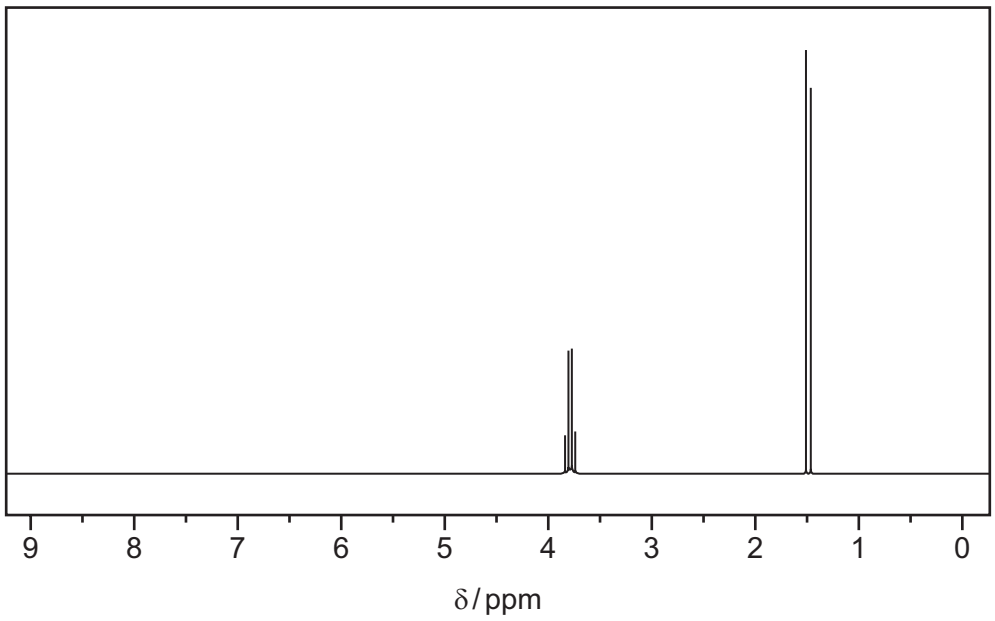
[Total: 6]

(a) $H_2NCH(CH_3)CO_2H$ exists as two optical isomers.

Draw three-dimensional structures of these two optical isomers.

[2]

(b) The proton (^1H) NMR spectrum of **either** alanine in D_2O or glutamic acid in D_2O is shown.



State whether this is the spectrum of alanine in D_2O or the spectrum of glutamic acid in D_2O. Explain your answer by reference to the number of peaks and splitting patterns.

.....

.....

.....

..... [3]

(i) State the *m*/*e* value of the molecular ion peak in this spectrum.

..... [1]

(ii) The spectrum has peaks with *m*/*e* values of 88 and 131.

Draw the structures of the ions responsible for these peaks.

m/*e*	structure of ion
88	
131	

[2]

(d) At pH 11 alanine exists as $H_2NCH(CH_3)CO_2^-$ ions and glutamic acid exists as $H_2NCH(CH_2CH_2CO_2^-)CO_2^-$ ions. A mixture of alanine and glutamic acid at pH 11 is subjected to electrophoresis.

(i) State how the mixture can be maintained at pH 11 during electrophoresis.

..... [1]

(ii) Draw a fully labelled diagram for the apparatus that would be used to carry out this electrophoresis. Your diagram should include the position of the mixture of alanine and glutamic acid at the start of the electrophoresis experiment.

[2]

alanine .....

glutamic acid .....
[1]

(iv) In a particular electrophoresis experiment at pH 11, the glutamic acid travels 3.4 cm. Alanine travels a shorter distance.

Explain the factors that account for the difference in the distances travelled.

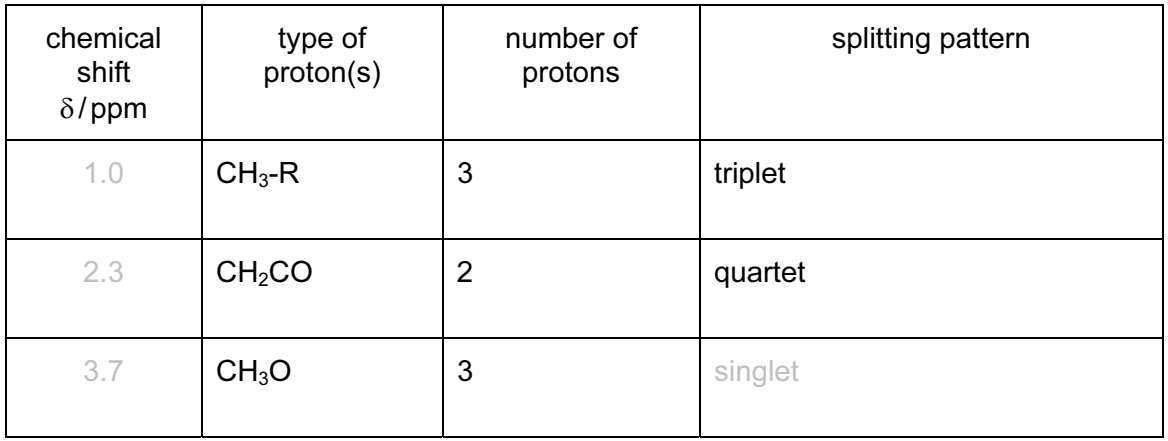
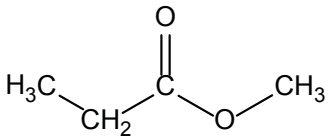
.....

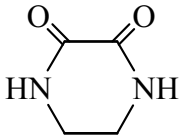
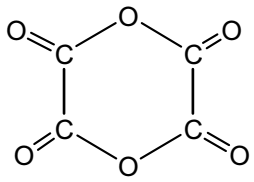
.....

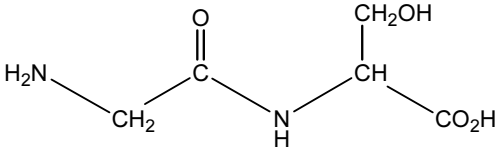
.....

..... [2]

[Total: 14]

(ii)	hydrogen **or** helium **or** nitrogen	**1**	
(iii)	it is more soluble in the stationary phase	**1**	
(iv)	same functional group **or** same IMF with stationary phase or same polarity	**1**	
(v)	% X (= 100 × 22 / 76) **= 29** (28.9)	**1**	
(b) (i)	TMS or tetramethylsilane or $Si(CH_3)_4$	**1**	
(ii)		**4**	
(iii)	structure / name of methyl propanoate 	**1**	
			[Total: 11]

	n($C_2O_4H_2$) = $3.04 \times 10^{-4} \times 372$ = 7.6×10^{-2} (in 25 cm^3) = 3.04×10^{-3} mol in 100 cm^3 M_r = 24 + 64 + 2 = 90 mass of $C_2O_4H_2$ = $3.04 \times 10^{-3} \times 90$ = 0.2736 g (0.274) percentage = 0.2736 × 100/40 = 0.68%	[1] [1] [1]
(b) (i)	$SOCl_2$ *or* PCl_5 *or* PCl_3	[1]
(ii)	**J** is $CH_3OCO–COOCH_3$ **K** is 	[1] [1]
(c) (i)	CH_3 at δ 15 CH_2O at δ 65	[1] [1]
(ii)	Only one peak, so only one type / environment of C atom	[1]
(d) (i)	**M** is $HO_2C–CO_2H$ **N** is $CH_3OCO–CO_2H$ **O** is $CH_3OCO–COOCH_3$	[3]
(ii)	**L** is 	[1]
		[Total: 13]

3(c) (i)	 M1: for –CONH– as shown above M2: for rest of molecule **and** correct connectivity of the bonds	2
(ii)	*from the IR spectrum* • **E** is O-H *or* N-H (allow NH_2) • **F** is C=O • **G** is C-O	2

4(a)(i)

$(100/22.1)\times(0.7/1.1)$ or $\frac{100\times0.7}{22.1\times1.1}$ or 2.87 / 2.88 / 2.9 — 1

3 carbon atoms — 1

2

4(a)(ii)

$_3H_6O_3$ — 1

1

4(b)

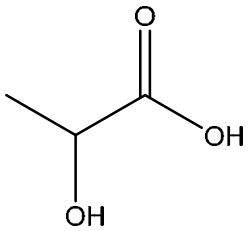
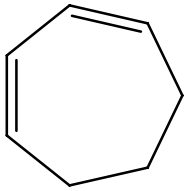
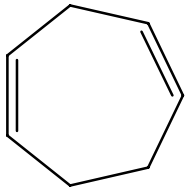
absorption / cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong	OH or O–H	alcohol / ROH
2680	very broad and strong	OH or O–H	(carboxylic) acid / CO_2H
1725	st	C = O	(carboxylic) acid / CO_2H

2

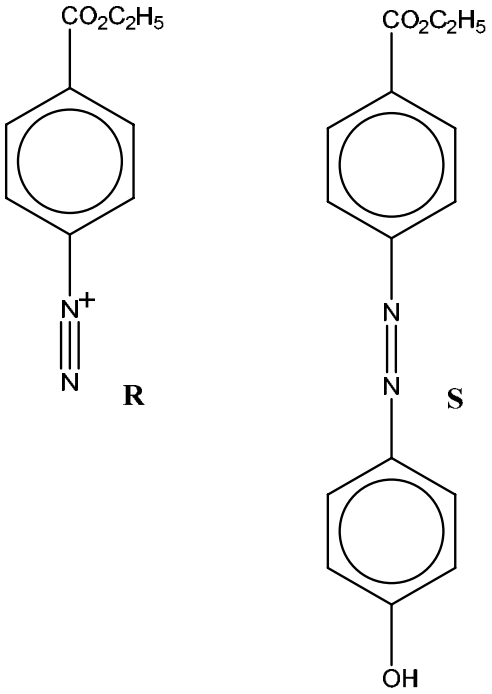
4(c)(i)

δ/ppm	type of proton	relative peak area
1.4	$_3$ or $–CH_2$ or –CH or alkane	3
3.9	–OCH or $–OCH_2$ or $–OCH_3$ or CH or alkyl next to electronegative atom / oxygen	1
4.7	–OH or alcoho	1
12.9	–OH or $–CO_2H$ or carboxylic acid	1

4

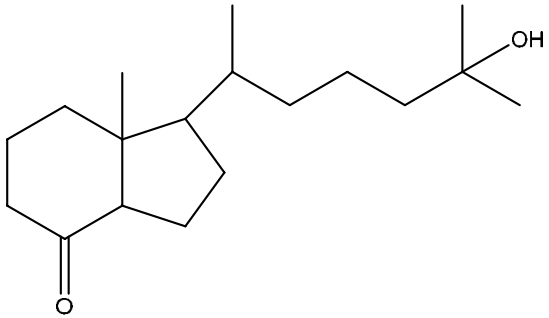
4(c)(iii)		**1**
4(c)(iv)		1 **1**
4(d)(i)	  both required for 1 mark	1 **1**
4(d)(ii)	isomer / number of peaks **P** / 4 **Q** / 4	1 1 **2**
	Total:	**15**

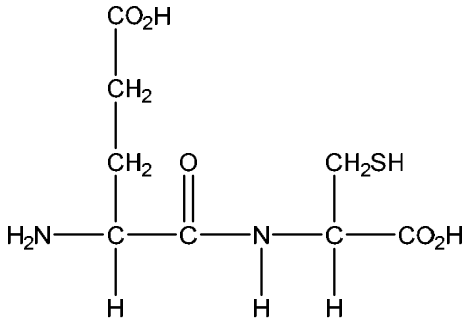
<table>
<tr><td>5(d)(ii)</td><td>CDCl_3 will produce no signal in the spectrum
or CHCl_3 would produce a signal / would be detected</td><td>1</td></tr>
<tr><td>5(d)(iii)</td><td>
<table>
<tr><th>δ/ppm</th><th>group responsible for the peak</th><th>number of H atoms responsible for the peak</th><th>splitting pattern</th></tr>
<tr><td>1.2</td><td>$CH_{(3)}$</td><td>3</td><td>triplet</td></tr>
<tr><td>3.5</td><td>$CH_{(2)}O$</td><td>2</td><td>quartet</td></tr>
<tr><td>5.5</td><td>NH_2</td><td>2</td><td>singlet (broad)</td></tr>
<tr><td>7.1–7.4</td><td>H attached to aromatic / benzene ring</td><td>4</td><td>multiplet</td></tr>
</table>
</td><td>4</td></tr>
<tr><td>5(d)(iv)</td><td>neighbouring / adjacent carbon atom has two protons / H (attached to it)
or there is an adjacent $CH_2(O)$ group</td><td>1</td></tr>
<tr><td>5(d)(v)</td><td>peak at 5.5 / NH_2 peak will disappear
and
NH_2 / protons exchange / swap with deuterium</td><td>1</td></tr>
</table>

5(e)(i)	$NaNO_2 + HCl$ ***or*** HNO_2	**1**
5(e)(ii)		
	structure of diazonium salt **R**	**1**
	structure of azo dye **S**	**1**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>6(b)(i)</td><td><table><tr><th>compound</th><th>spot</th></tr><tr><td>J</td><td>2</td></tr><tr><td>K</td><td>3</td></tr><tr><td>L</td><td>1</td></tr></table></td><td>1</td></tr>
<tr><td>6(b)(ii)</td><td>The more polar the compound and stronger attractive forces to the (polar) stationary phase
ora: less polar compound and weaker attractive forces to the (polar) stationary phase</td><td>1</td></tr>
<tr><td>6(b)(iii)</td><td>R_f = retardation factor or retention factor or
R_f =distance moved by compound from baseline over distance travelled by solvent front</td><td>1</td></tr>
</table>

7(e)(i)	propanoic acid	**1**
7(e)(ii)	propan-1-ol would have peak at 0.5–6.0 because of OH group	**1**
	propanal would have peak at 9.3–10.5 because of CHO / aldehyde	**1**

8(b)	6	**1**
8(c)	4	**1**
8(d)(i)	4	**1**
8(d)(ii)	range δ 25–5	**1**
	range δ 190–220	**1**
	one peak in first range and three peaks in second range	**1**
8(d)(iii)	1	**1**
8(d)(iv)	singlet	**1**
	neighbouring / adjacent (carbon) atom has no protons / H	**1**
8(e)(i)	CO_2	**1**
	(further) oxidation / oxidative cleavage	**1**
8(e)(ii)		**1**

<table>
<tr><th>Question</th><th>Answer</th><th>Marks</th></tr>
<tr><td>9(a)</td><td> 

M1 peptide link [1]
M2 rest of the structure [1]</td><td>2</td></tr>
<tr><td>9(b)</td><td><table>
<tr><td>spot</td><td>iden</td></tr>
<tr><td>E</td><td>Glu</td></tr>
<tr><td>F</td><td>Glu-Cys</td></tr>
<tr><td>G</td><td>Cys</td></tr>
</table>
M1 correct table [1]
M2 Explanation of why Cys moves the least – because it exists as a zwitterion / it is almost neutral [1]
M3 Explanation of why Glu-Cys moves a smaller distance than Glu – a comparitive statement that Glu-Cys has a greater M_r than Glu [1]</td><td>3</td></tr>
</table>

10(a)(i)	no. of carbons = 100 × 1.25 / (22.65 × 1.1) (= **5.02)**	**1**
10(a)(ii)	M1: C_2H_5O M2: $C_3H_5O^+$ (positive sign required for m / e = 57 fragment)	**2**
10(b)	TMS: Reference $CDCl_3$: Solvent	**1**
10(c)(i)	**M1**: CH_3CO **M2**: CH_3CH_2O **M3**: $(CO)CH_2O$	**3**
10(c)(ii)	$CH_3COCH_2OCH_2CH_3$	**1**
10(d)	$HCO_2C(CH_3)_3$	**1**
10(e)(i)	this is a (carbon) atom which has four different atoms or groups attached to it	**1**
10(e)(ii)	$CH_3CH_2CH(CH_3)COOH$	**1**

11(a)(i)	leucine B= glutamic acid **both** [1]	**1**
11(a)(ii)	greater **and** more soluble in the solvent / mobile phase **OR** greater **and** form more H-bonds with the solvent [1]	**1**

P42/M/J/19/Q8ab

Question	Answer	Marks
12(a)	4-chloro-3,5-dimethylphenol **OR** 3,5-dimethyl-4-chlorophenol [1] **ALLOW** 2,6-dimethyl-4-hydroxychlorobenzene and 2-chloro-5-hydroxy-1,3-dimethylbenzene	**1**
12(b)(i)	carbon-13 NMR = 5 peaks [1] proton NMR = 3 peaks [1]	**2**
12(b)(ii)	**OH** proton had disappeared due to proton exchange with D / D_2O [1] **ALLOW** $OH + D_2O \rightarrow OD + HOD$	**1**

P41/O/N/19/Q4(iv>v)

Question	Answer	Marks
13(d)(iv)	6	**1**
13(d)(v)	• 25–50 • 110–160 • 190–220 Award 1 mark for two points, award 2 marks for three points	**2**

P41/O/N/19/Q9cd

14(c)(i)	2 [1]	**1**
14(c)(ii)	CH_2 next to ester **and** terminal CH_3 are circled [1]	**1**
14(c)(iii)	• one less peak • the lost peak is NH_2 / aryl amine • protons exchange with D **OR** protons are labile **OR** valid equation •✓✓ for two marks [2]	**2**
14(d)	$C_6H_4NH_2^+$ **and** $CH_3CH_2CH_2CH_2^+$ [1]	**1**

15(g)(i)	**M1:** δ12.7 is COOH **M2:** δ3.3 is CH **and** δ1.1 is CH_3	**2**
15(g)(ii)	quadruplet / quartet 53 H / protons on neighbouring / adjacent carbon / carbons / C	**1**
15(g)(iii)	2 (butanedioic acid) and 3 (methylpropanedioic acid)	**1**

16(d)

chemical shift (δ)	environment of the carbon atom	hybridisation of the carbon atom
27	**C**H_3 circled	sp^3
163	**C**OOH circled	sp^2
192	**C**=O(COOH) circled	sp^2

Award one mark for each correct column

2

16(e)

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3	alk / CH / CH_3	triplet	3
2.2	CH_3CO **or** alkyl / CH next to C=O	singlet	3
4.0	CH_2O **or** alkyl / CH next to electronegative atom / C=O	quartet / quadruplet	2

Award one mark for every three correct responses.

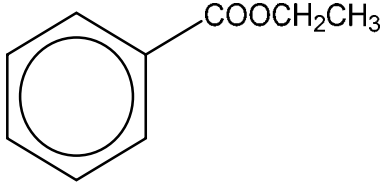
3

16(f)

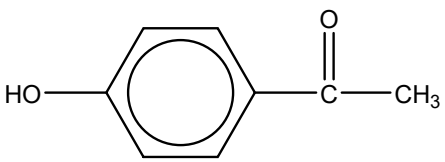
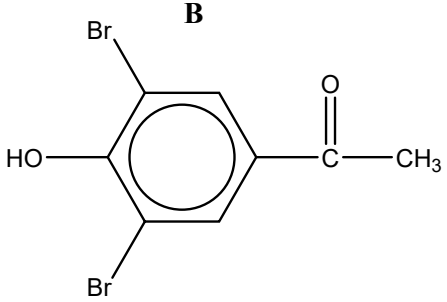
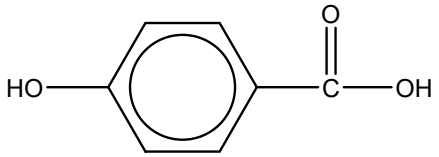
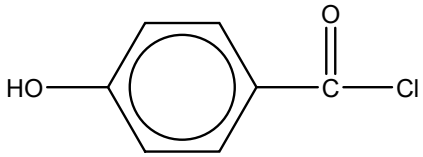
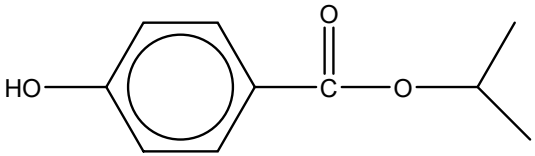
AND CH_3 **circled**

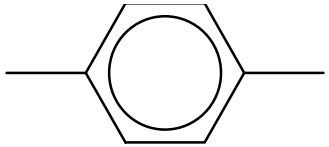
these protons do not exchange with D_2O
OR OH and NH protons exchange with D_2O

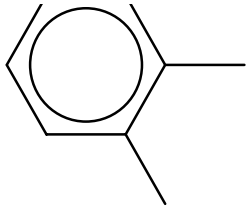
2

17(a)	(because $CDCl_3$ / it) does not give a peak [1] **OR** because $CHCl_3$ does give a peak	**1**
17(b)	as a **standard / reference** for (chemical shift measurements) [1]	**1**
17(c)	ester [1]	**1**
17(d)(i)	• (δ = 1.4) triplet • (δ = 1.4) two H on neighbouring C atom • (δ = 4.3) quartet / quadruplet • (δ = 4.3) three H on neighbouring C atom mark as • ✓ • ✓ [2]	**2**
17(d)(ii)	aryl group / arene / phenyl [1]	**1**
17(d)(iii)	 **OR** $C_6H_5CO_2C_2H_5$ [1]	**1**
17(e)	$_3CH_2^+$ / $C_2H_5^+$ [1] $C_6H_5^+$ [1]	**2**

18(c)(i)	CH_3COCl [1] ethanoyl chloride [1]	**2**
18(c)(ii)	Step 1: PCl_5 / PCl_3 / $SOCl_2$ or names [1] Step 2: NH_3 / ammonia [1]	**2**
18(d)(i)	(because $CDCl_3$) doesn't give a signal / peak / absorption **OR** because $CHCl_3$ does give a signal / peak / absorption [1]	**1**
18(d)(ii)	Clockwise from left: absorption at σ = 1.9 to 2.1 absorption at σ = 6.5 to 7 [1] absorption at σ = 3 to 3.5 absorption at σ = 1 to 1.5 [1]	**2**
18(d)(iii)	the peak at 6.6 to 6.8 / due to NH would disappear [1] H exchanges with D [1]	**2**
18(e)	fragment with *m*/*e* = 58 is CH_3CONH^+ [1]	**1**
18(f)(i)	$LiAlH_4$ [1]	**1**
18(f)(ii)	2 [1]	**1**

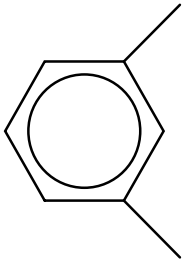
19(a)	**A**  **B**  **C** CHI_3 **D**  **E**  **F**  one mark for each structure	**6**

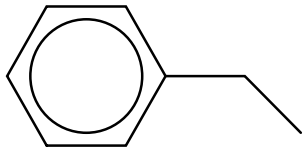




five peaks

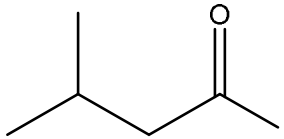
six peaks





P42/M/J/21/Q8c

21(c)(i)



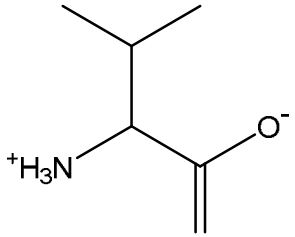
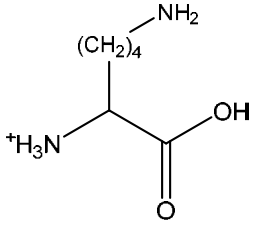
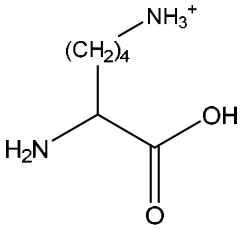
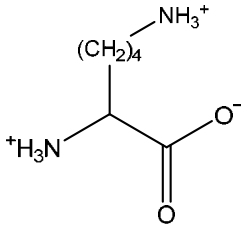
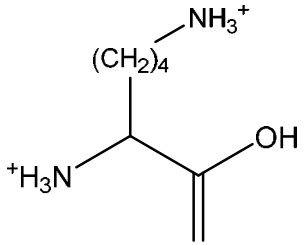
1

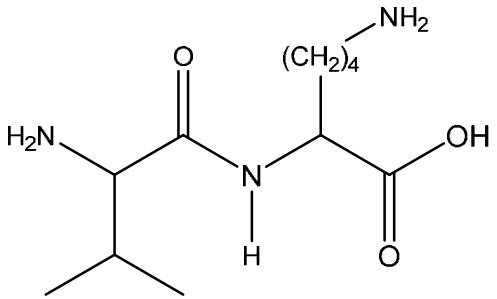
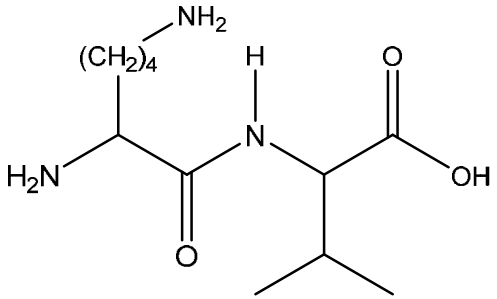
21(c)(ii)

chemical shift (δ)	environment of proton	splitting pattern (words required)	number of ^1H atoms responsible for the peak
0.95	al / CH_3	doublet	6
1.90	al / CH **ALLOW** alkyne	multiplet	1
2.20	/ alkyl / CH_3 next to	doublet	2

3

Question	Answer	Marks
22(d)(i)	relative abundance = 2 carbons × 1.1 × 0.62 = **1.36** / **1.4** [1] min 2sf	**1**
22(d)(ii)	$CH_3CH_2^+$ / $C_2H_5^+$ [1]	**2**
	$C_6H_5CH_2^+$ [1]	
22(e)(i)	a [1]	**1**
22(e)(iii)	d [1]	**1**
22(e)(iii)	b, fc, [1]	**1**
22(e)(iv)	f [1]	**1**

Question	Answer	Marks
23(a)	 [1]	**1**
23(b)	**A** and **B** any two from: [all net single positive charge]    [1] × 2 **C** at pH 1.0 [2+ positive charge]  [1]	**3**

23(c)	M1: peptide link correct and displayed unit including C=O M2: everything else correct  **OR**  [2]	**2**

24(a)	M1 one diagram correct [1] M2 both diagrams correct 3D and different [1]	**2**
24(b)	alanine because glutamic acid would have more than two / three peaks / absorb^{ns} / proton environments [1] reason why alanine has a **doublet** given as one neighbouring proton [1] glutamic acid would have (two) **triplet**(s) **OR** a **multiplet** [1] reason why alanine has a **quartet / quadruplet** given as three neighbouring protons [1]	**3**
24(c)(i)	147 [1]	**1**
24(c)(ii)	88 = $[H_2NCH(CH_2)CO_2H]+$ [1] 131 = $[CH(CH_2CH_2CO_2H)CO_2H]+$ [1]	**2**
24(d)(i)	use of buffer [1]	**1**
24(d)(ii)	• correct circuit including **DC** power supply • paper or gel labelled [1] • sample towards the middle of the paper / gel **OR** on cathode side [1]	**2**
24(d)(iii)	anode / positive / + **AND** anode / positive / + [1]	**1**
24(d)(iv)	M1 ala is –1 and glu is –2 [1]	**2**

Paper 4
Topic 12
Organic Synthesis

(i) State which product causes the fumes in this reaction.

..... [1]

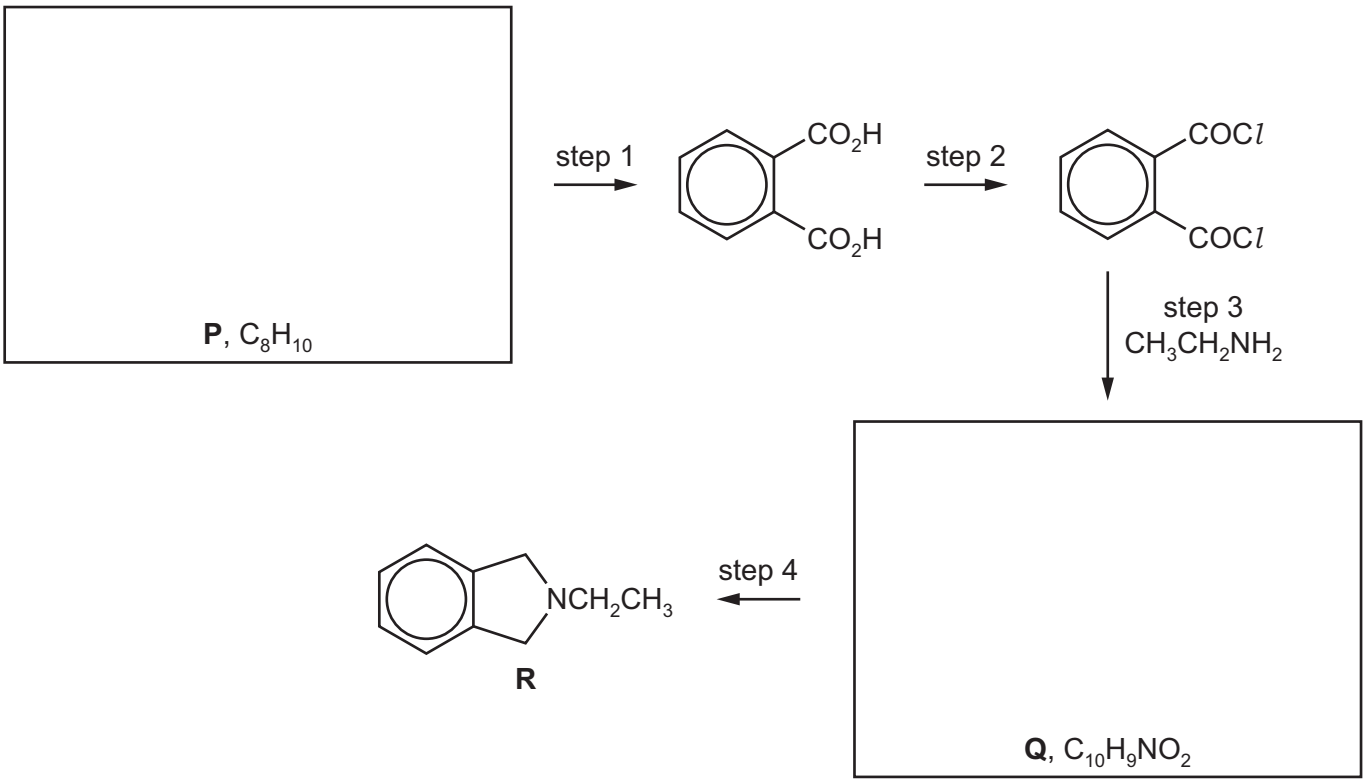
(ii) Explain why the reactivities of chloroalkanes and acyl chlorides differ.

.....

.....

..... [1]

(b) Compound **R** is a useful intermediate in the synthesis of pharmaceutical compounds. It can be made from compound **P** by the following route.



(i) Suggest structures for the starting material **P** and the intermediate **Q**. [2]

(ii) Suggest reagents and conditions for the following steps in the above scheme.

step 1 .....

step 2 .....

step 4 .....

[3]

[Total: 7]

(i) After extraction and purification, what is the first step in **analysing** a sample of DNA?

.....

..... [1]

(ii) What can be done to increase the amount of DNA for analysis?

.....

..... [1]

(iii) During electrophoresis, it is observed that amino acids can move in **different** directions or not at all, whilst DNA fragments always move in the **same** direction.

Explain these two observations.

.....

.....

.....

..... [2]

(iv) DNA fingerprinting can also be useful in archaeology.

Which of the following would be suitable for analysis by DNA fingerprinting?
Put a cross (x) in the appropriate box(es).

a piece of leather from an Egyptian tomb	☐
a sample of skin from a mummified body	☐
a fragment of ancient pottery	☐
a piece of wood from a Roman chariot	☐

[1]

(b) (i) X-ray crystallography can be used to help analyse the structure of macromolecules.

What does this technique tell us about a particular macromolecule?

.....

..... [1]

Explain your answer.

.....

..... [1]

(c) (i) Explain what is meant by a *partition coefficient*.

.....

..... [1]

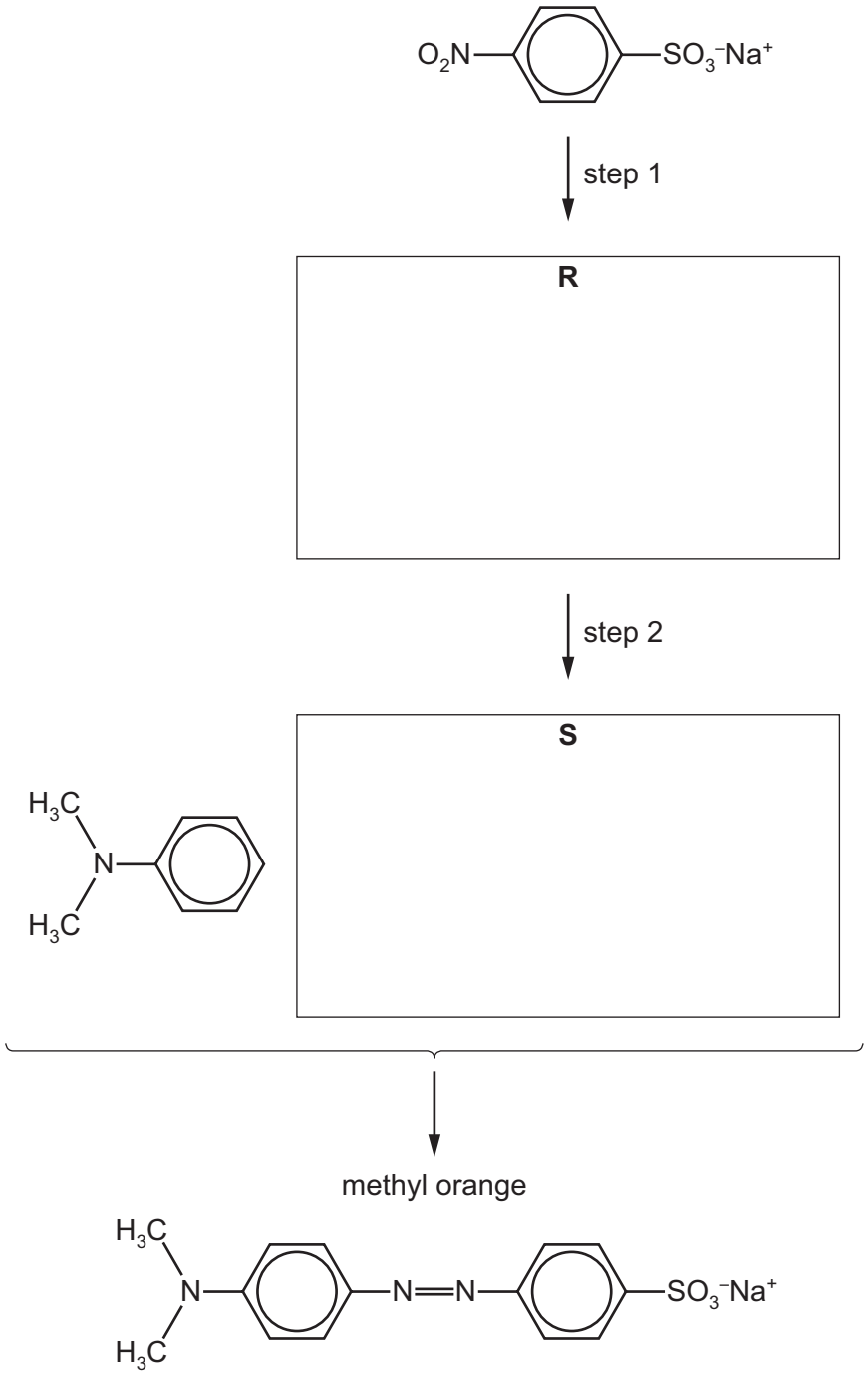
(ii) The partition coefficient of a particular pesticide between hexane and water is 6.0.

A solution contains 0.0042 g of the pesticide dissolved in 25 cm^3 of water. The solution is shaken with 25 cm^3 of hexane.

Calculate the mass of pesticide that will be dissolved in the hexane layer at equilibrium

[2]

[Total: 10]



(i) Deduce the identities of compounds **R** and **S** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1 and step 2.

step 1 .....

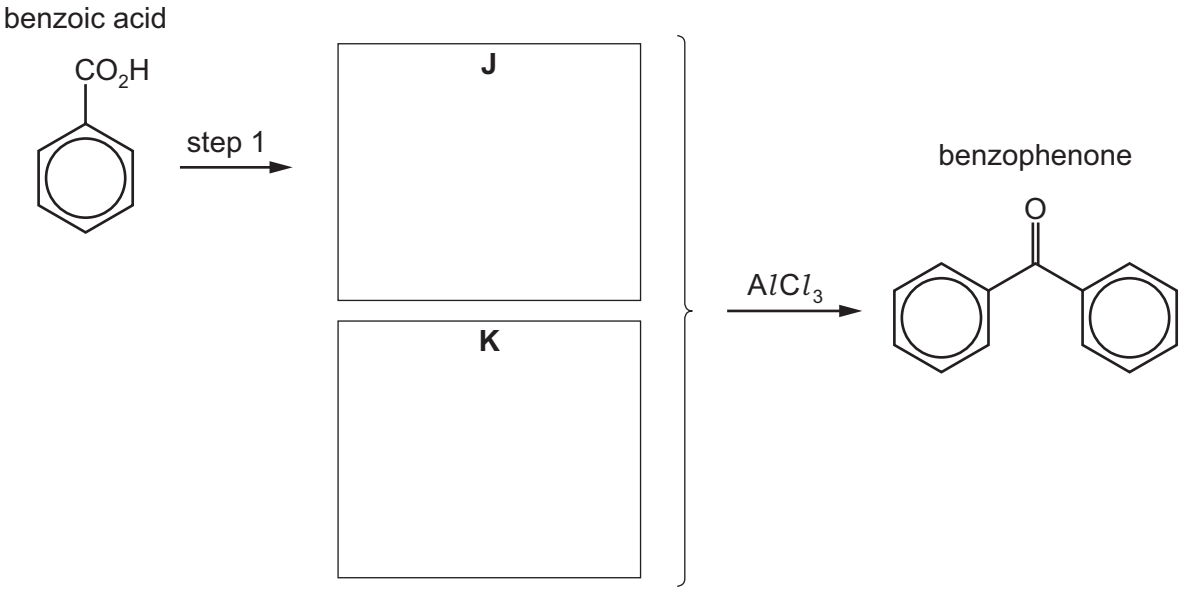
step 2 .....

[3]

[Total: 19]

In step 1 compound **J**, a reactive reaction intermediate, is formed.

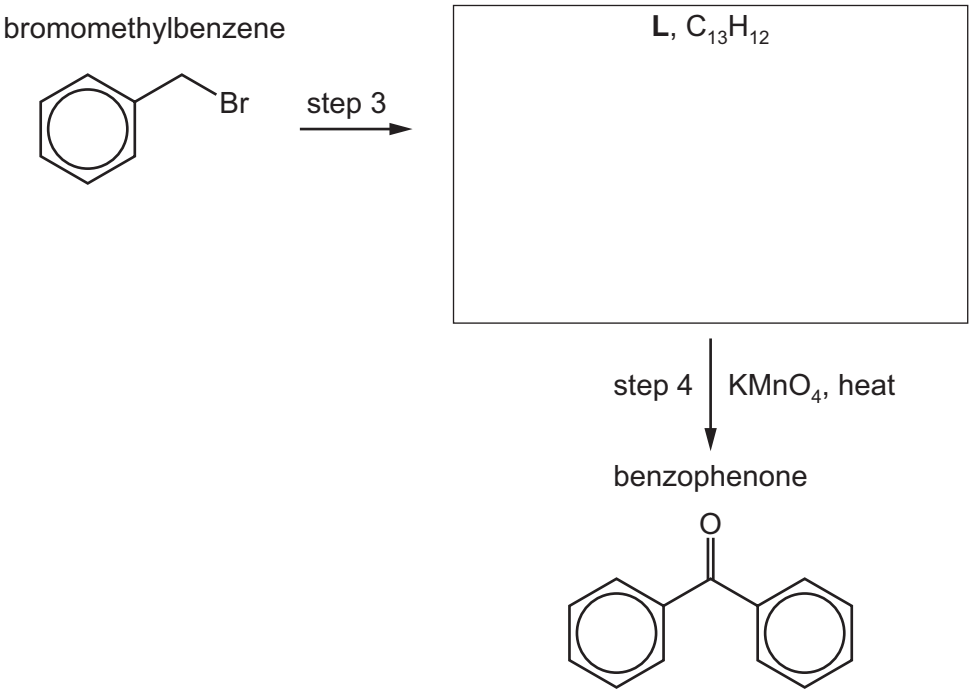
Compound **J** then reacts with an organic compound, **K**, to form benzophenone.



(i) Deduce the identities of organic compounds **J** and **K** and draw their structures in the boxes. [2]

(ii) Suggest reagents and conditions for step 1.

..... [1]



(i) Deduce the identity of compound **L** and draw its structure in the box. [1]

(ii) Name the mechanism of step 3 and suggest reagents and conditions for step 3.

mechanism of step 3 .....

reagents and conditions .....

[2]

(iii) Deduce the *type of reaction* in step 4.

..... [1]

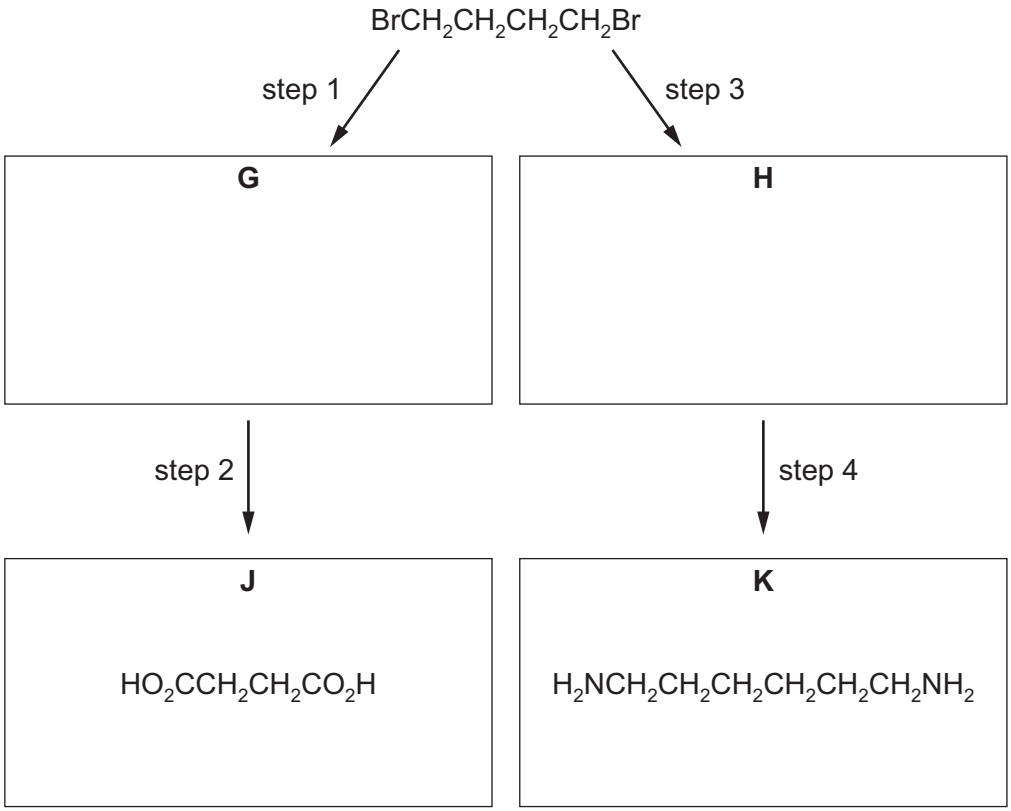
(e) (i) Deduce the number of peaks that would be present in the carbon-13 NMR spectrum of benzophenone.

number of peaks ..... [1]

(ii) Identify **two** different environments of carbon atom that would result in different chemical shift ranges in this carbon-13 NMR spectrum of benzophenone.

environment of carbon atom	chemical shift range (δ)

[2]



(i) Draw the structures of **G** and **H** in the boxes. [2]

(ii) Suggest reagents and conditions for each of steps 1 to 4.

step 1 .....

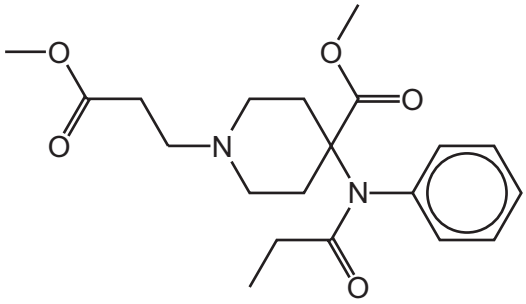
step 2 .....

step 3 .....

step 4 .....

[4]

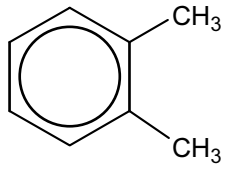
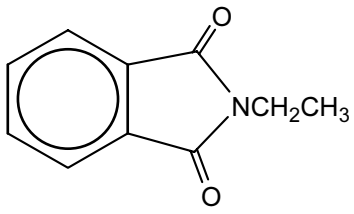
remifentanil



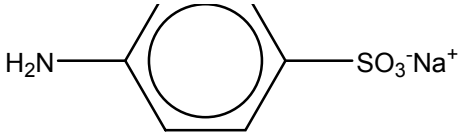
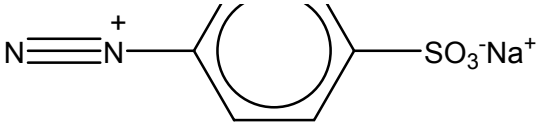
Remifentanil is **completely** hydrolysed under acidic conditions. Three different organic compounds are formed.

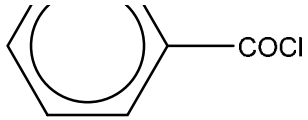
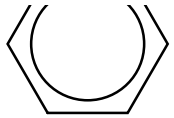
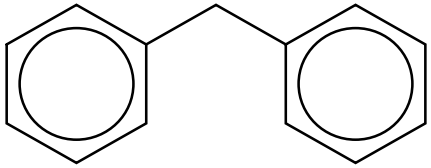
Draw the structures for these organic compounds in the boxes.

[3]

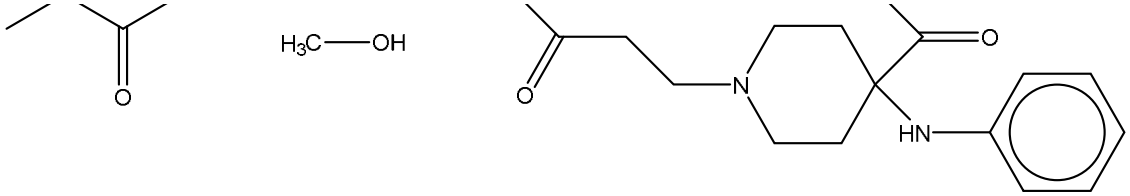
1	**(a) (i)**	hydrogen chloride ***or*** HC*l*	**1**
	(ii)	***either*** (RCOC*l*) has two electron-withdrawing groups/atoms, making the **more** δ+/electron deficient ***or*** (RCOC*l*) has an oxygen, making the **carbon more** δ+/electron deficient ***or*** (RCOC*l*) has two electron-withdrawing groups, **weakening** the **C–C*l*** bond	**1**
	(b) (i)	 **P**  **Q**	**1** **1**
	(ii)	step 1: heat with MnO_4^-/$KMnO_4$ (+ acid or alkali) step 2: PCl_3 + heat ***or*** $SOCl_2$ ***or*** PCl_5 step 4: $LiAlH_4$ (in dry ether)	**1** **1** **1**
			[Total: 7]

2 (a) (i)	use restriction enzymes ***or*** using an enzyme to break (the DNA) down into smaller fragments	**1**
(ii)	use the polymerase chain reaction ***or*** use DNA polymerase to replicate / copy (the sample of DNA)	**1**
(iii)	• amino acids have different charges due to their side-chain / R group / pH / CO_2^- **and** NH_3^+ groups • DNA fragments have negatively-charge phosphates(or PO_4) ***or*** DNA has PO_4^{3-} groups	**1** **1**
(iv)	<table><tr><td>A piece of leather from an Egyptian tomb</td><td></td></tr><tr><td>A sample of skin from a mummified body</td><td></td></tr><tr><td>A fragment of ancient pottery</td><td>**X**</td></tr><tr><td>A piece of wood from a Roman chariot</td><td></td></tr></table>	**1**
(b) (i)	the electron density in the molecule ***or*** positions of atoms ***or*** interatomic distance / spacing between the atoms	**1**
(ii)	phosphorus has the most electrons ***or*** phosphorus has the highest electron density	**1**
(c) (i)	equilibrium constant (for the solution) of a solute between two (immiscible) solvents ***or*** ratio of the concentration of the solute in (each of the) two solvents ***or*** ratio of the solubility of the solute in (each of the) two solvents	**1**
(ii)	$\underline{x / (25 / 1000)}$ $(0.0042 - x)/(25 / 1000)$ $x = 0.0252 - 6x$ $x =$ **0.0036g**	**1** **1**
		[Total: 10]

	  **R** **S** Award one mark for each correct structure	
3(g)(ii)	**M1** step 1 Sn and HC*l* conc. and heat **M2** step 2 $NaNO_2$ and HC*l* and 0-10 °C	**3**

	J =  K =  Award one mark for each correct structure	
4(c)(ii)	step 1 PCl_5 **OR** $SOCl_2$ **OR** PCl_3 + heat	**1**
4(d)(i)		**1**
4(d)(ii)	**M1** step 3 electrophilic substitution **M2** step 3 benzene and $AlCl_3$ (and heat)	**2**
4(d)(iii)	step 4 oxidation	**1**
4(e)(i)	5 peaks	**1**
4(e)(ii)	<table><tr><th>environment of carbon atom</th><th>chemical shift range (δ)</th></tr><tr><td>carbonyl / RCOR</td><td>190–220</td></tr><tr><td>arene / benzene</td><td>110–160</td></tr></table>Award one mark for each correct for each row	**2**

5(c)(i)	**G** = $HOCH_2CH_2CH_2CH_2OH$ **H** = $NCCH_2CH_2CH_2CH_2CN$	**2**
5(c)(ii)	**M1:** step 1 NaOH(aq) + heat **M2:** step 2 acidified $KMnO_4$ + heat / acidified $K_2Cr_2O_7$ + heat **M3:** step 3 CN^- / KCN / NaCN + heat **M4:** step 4 $LiAlH_4$ **ALLOW** Na in ethanol or H_2 + Ni / Pd / Pt	**4**



ALLOW amine salt for the third structure – mono or di ion

Paper 4
Topic 13
A.S Inorganic And Physical Chemistry

1 **(a)** Complete the electronic configurations of the following atoms.

oxygen: $1s^2$.....

fluorine: $1s^2$.....

[1]

(b) A compound of fluorine and oxygen contains three atoms in each molecule.

(i) Predict its formula.

..... [1]

(ii) Draw a 'dot-and-cross' diagram to show its bonding.

[1]

(iii) Suggest the shape of this molecule.

..... [1]

(c) **(i)** Use $E^\ominus$ values from the *Data Booklet* to predict the relative oxidising abilities of fluorine and chlorine.

.....

.....

..... [2]

(ii) Predict the *type of reaction* that would occur between the interhalogen compound chlorine fluoride, C*l*F, and potassium bromide solution.

..... [1]

(iii) Construct an equation for this reaction.

..... [1]

[Total: 8]

	Na	Mg	Al	Si	P	S	Cl	Ar
number of unpaired electrons								

[3]

(b) (i) Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
$SiCl_4$		
PCl_5		

[3]

(ii) Write an equation for the reaction between $SiCl_4$ and H_2O.

..... [1]

[Total: 7]

	solubility product in water at 298 K, K_{sp} / mol^2 dm^{-6}
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	5.0×10^{-9}
$SrCO_3$	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

.....

..... [1]

(b) (i) Write an equation to show the equilibrium for the solubility product for $MgCO_3$. Include state symbols.

$\rightleftharpoons$

..... [1]

(ii) With reference to your equation in **(i)**, suggest what is observed when a few cm^3 of concentrated Na_2CO_3(aq) are added to a saturated solution of $MgCO_3$. Explain your answer.

.....

.....

..... [2]

(c) Use the data in the table to calculate the solubility of $MgCO_3$ in water at 298 K, in g dm^{-3}.

solubility of $MgCO_3$ = ... g dm^{-3} [2]

Explain why.

.....

.....

..... [2]

(ii) A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

..... [1]

(iii) When water was added to the white solid produced in **(d)(ii)**, an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

.....

..... [2]

[Total: 11]

(i) Write an equation for this reaction.

..... [1]

(ii) A 2.52 g sample of Mg_3N_2 is added to an excess of water.

Calculate the mass of $Mg(OH)_2$ formed.

mass of $Mg(OH)_2$ = ... g [2]

(d) The temperature at which the Group 2 hydroxides and carbonates start to decompose increases down the group.

Suggest an explanation for this trend in the decomposition temperature of the Group 2 hydroxides.

.....

.....

..... [2]

The geometry of a cation in an ionic compound can be predicted from the ratio of the ionic radii of the cation and anion involved.

$\frac{\text{cation radius}}{\text{anion radius}}$	geometry of cation
0.155–0.225	trigonal planar
0.225–0.414	tetrahedral
0.414–0.732	octahedral

Use data from the *Data Booklet* to predict the geometry of, and hence the co-ordination number of, the cation for

- sodium chloride, NaCl,

geometry of Na^+ = ... co-ordination number of Na^+ = ...

- magnesium chloride, MgCl_2.

geometry of Mg^{2+} = ... co-ordination number of Mg^{2+} = ...
[2]

P42/O/N/17/Q7a

6 **(a)** Calcium carbide, CaC_2, reacts readily with water, forming ethyne, C_2H_2, and a sparingly soluble white ionic compound.

(i) Write an equation for the reaction of CaC_2 with water.

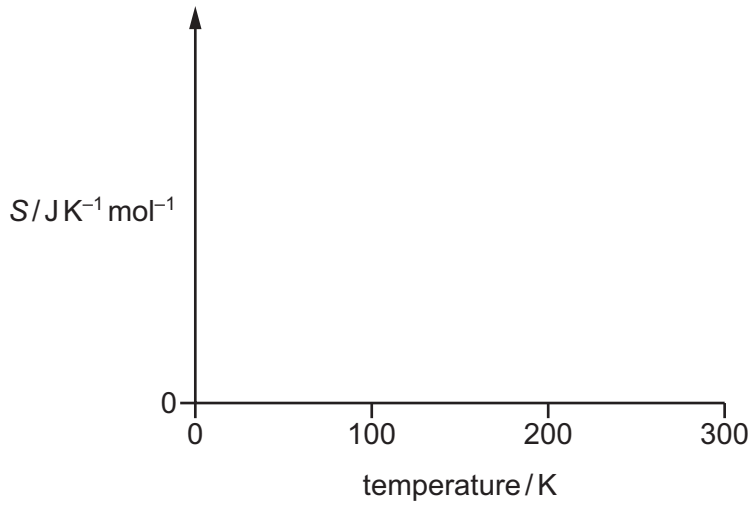
..... [1]

(ii) Draw a 'dot-and-cross' diagram for the carbide ion, C_2^{2-}. Show outer electrons only.

[1]

(a) Assume the entropy, *S*, for H_2O is zero at 0 K.

Sketch a graph on the axes to show how the entropy changes for H_2O between 0 K and 300 K.



[2]

(b) Place **one tick** (✓) in **each row** of the table to show the sign of the entropy changes, ΔS.

	ΔS is negative	ΔS is positive
solid dissolving in water		
water boiling to steam		

[1]

(c) The equation for a reaction that produces methanol is shown.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$$

Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH, for this gas phase reaction.

ΔH = ... kJ mol^{-1} [2]

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \qquad \Delta H^{\ominus} = -131\,kJ\,mol^{-1}$$

Standard entropies are shown in the table.

substance	$CO_2(g)$	$H_2(g)$	$CH_3OH(l)$	$H_2O(l)$
$S^{\ominus}$ / $J\,K^{-1}\,mol^{-1}$	+214	+131	+127	+70

(i) Calculate the standard entropy change, $\Delta S^{\ominus}$, for this reaction.

$\Delta S^{\ominus}$ = ... $J\,K^{-1}\,mol^{-1}$ [2]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for this reaction at 298 K.

$\Delta G^{\ominus}$ = ... $kJ\,mol^{-1}$ [2]

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

.....

..... [1]

The half-equation for the reaction at the methanol electrode is shown.

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- \qquad E^\ominus = -0.02\,V$$

(i) Use the *Data Booklet* to write an equation for the overall cell reaction.

.....

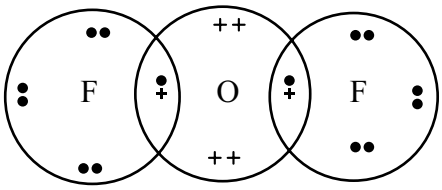
.....

..... [1]

(ii) Use $E^\ominus$ values to calculate the $E^\ominus_{cell}$ for this reaction.

$E^\ominus_{cell}$ = ... V [1]

[Total: 12]

Question	point	Marks
1 (a)	oxygen: $(1s^2)\ 2s^2 2p^4$ fluorine: $(1s^2)\ 2s^2 2p^5$	1
(b) (i)	F_2O / OF_2	1
(ii)		1
(iii)	bent ***or*** non-linear	1
(c) (i)	$E^{\ominus}$ values: F_2 / F^- = 2.87 V **and** Cl_2 / Cl^- = 1.36 V	1
	fluorine (has the more positive $E^{\ominus}$ so) is more oxidising	1
(ii)	redox	1
(iii)	$ClF + 2KBr \longrightarrow KCl + KF + Br_2$	1
		[Total: 8]

<table>
<tr><th>Question</th><th>Marking point</th><th>Marks</th></tr>
<tr><td>2 (a)</td><td>
<table>
<tr><td>Na</td><td>M</td><td>Al</td><td>Si</td><td></td><td>S</td><td>Cl</td><td>Ar</td></tr>
<tr><td>1</td><td></td><td>1</td><td>2</td><td>3</td><td>2</td><td>1</td><td>0</td></tr>
</table>
</td><td>3</td></tr>
<tr><td>(b) (i)</td><td>$SiCl_4$ white solid / ppt or misty / white / steamy fumes pH 0–3
PCl_5 misty / white / steamy fumes pH 0–3</td><td>3</td></tr>
<tr><td>(ii)</td><td>$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$</td><td>1</td></tr>
<tr><td></td><td></td><td>7</td></tr>
</table>

P41/O/N/17/Q2

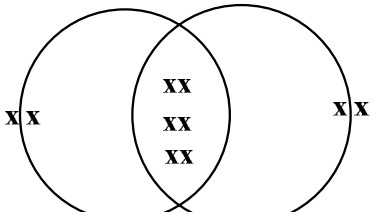
Question	Answer	Marks
3(a)	it / solubility **decreases** down the group **and** K_{sp} decreases	**1**
3(b)(i)	$MgCO_3$**(s)** ⇌ Mg^{2+}**(aq)** + CO_3^{2-}**(aq)**	**1**
3(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	**1**
	as [CO_3^{2-}] increases shifting equilibrium to the LHS (precipitating out $MgCO_3$)	**1**
3(c)	solubility = $\sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3}$ mol dm^{-3}	**1**
	solubility= $3.2 \times 10^{-3} \times 84.3$ = **0.27** g dm^{-3}	**1**
3(d)(i)	Mg^{2+} ion is smaller than Ba^{2+} ion **or** ionic radii increase down group ora	**1**
	(Mg^{2+}) distorts / polarises / the anion / nitrate group / nitrate **ion** / $NO_3^{(1)-}$ / NO_3 ion more easily (than Ba^{2+}) ora	**1**
3(d)(ii)	$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½O_2$	**1**
3(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	**1**
	$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$	**1**

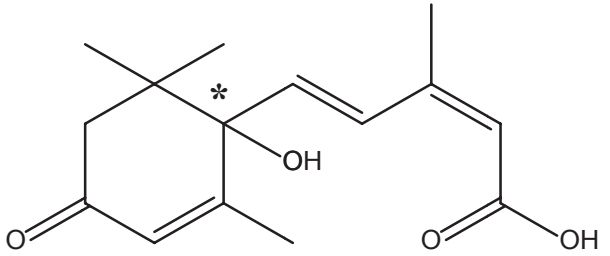
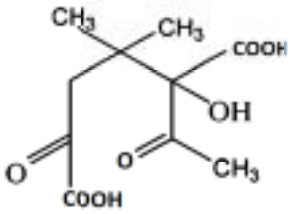
4(a)(i)	$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$	**1**
4(a)(ii)	moles of Mg_3N_2 = 2.52 / 100.9 = 0.025 (0.0249)	**1**
	(moles of $Mg(OH)_2$ = 0.075 (0.0749)) mass of $Mg(OH)_2$ = (0.075 × 58.3) = 4.37 g or 4.4 g	**1** **1**
4(d)	cations become bigger / ionic radius increases	**1**
	polarisation/distortion of anion / hydroxide ion decreases	**1**

P42/O/N/17/Q5a

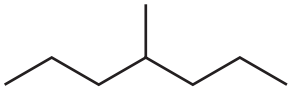
Question	Answer	Marks
5(a)	(Na^+) 0.095 / 0.181 = 0.525 **and** octahedral **and** co-ordination no. = 6	**1**
	(Mg^{2+}) 0.065 / 0.181 = 0.359 **and** tetrahedral **and** co-ordination no. = 4	**1**

P42/O/N/17/Q7a

Question	Answer	Marks
6(a)(i)	$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$	**1**
6(a)(ii)		**1**

7(a)	correct chiral centre labelled **only**  $C_{15}H_{22}O_4$	**1**
7(b)	$_{15}H_{22}O_4$	**1**
7(c)(i)	 	**1**
7((c)(ii)	CO_2	**1**
	oxidat<sub>ion / oxidative cleavage	**1**
7(c)(iii)	CH_3COCO_2H	**1**

Paper 4
Topic 14
A.S
Organic



4-methylheptane

→ **B** C_3H_8 + a mixture of **C**, **D** and **E** (isomers of C_5H_{10})

(i) State the conditions necessary for this reaction to take place.

..... [1]

(ii) Suggest the structure of **B**.

B

[1]

(iii) Compounds **C**, **D** and **E** are isomers with the molecular formula C_5H_{10}.

On heating with concentrated acidified $KMnO_4$,

- compound **C** gives CO_2 and compound **F** ($C_4H_8O_2$),
- **D** and **E** each give a 1 : 1 mixture of compounds **G** ($C_2H_4O_2$) and **H** ($C_3H_6O_2$).

Suggest structures for compounds **C** to **H**.

C **D** **E**

F **G** **H**

[3]

(iv) Name the type of isomerism shown between **D** and **E**.

..... [1]

(i) How is this reaction usually carried out?

..... [1]

(ii) State the *type of reaction* that is occurring here.

..... [1]

(iii) Draw the mechanism of this reaction, including the structures of any intermediates, and any dipoles, lone pairs and curly arrows to show the movements of electrons.

[2]

[Total: 10]

(a) One of the problems associated with using shale gas is its variable composition.
Table 1 shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

source	CH_4	C_2H_x	C_3H_y	CO_2	N_2
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formulae above, ***x*** and ***y*** are variables.

Table 1

(i) Draw the structures of **three** possible compounds with the formula C_3H_y.

[2]

(ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

.....

..... [1]

(iii) Suggest **two** methods by which carbon dioxide can be removed from shale gas.

1 .....

.....

2 .....

.....
[2]

air pollutant	shale gas	fuel oil	coal
CO_2	117	164	208
CO	0.040	0.033	0.208
NO_2	0.092	0.548	0.457
SO_2	0.001	1.12	2.59
particulates	0.007	0.84	2.74

Table 2

(i) Suggest why shale gas produces the smallest amount of CO_2.

.....

..... [1]

(ii) Explain which of the three fuels, shale gas, fuel oil or coal, is the **largest** contributor to 'acid rain'.

fuel .....

.....

..... [1]

(iii) Suggest a reason why fuel oil and coal produce more NO_2 than shale gas.

.....

..... [1]

(iv) State **one** environmental consequence of raised levels of

- CO, ...
- CO_2. .....

[2]

[Total: 10]

(a) The compound diborane, B_2H_6, can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3, with sodium borohydride, $NaBH_4$.

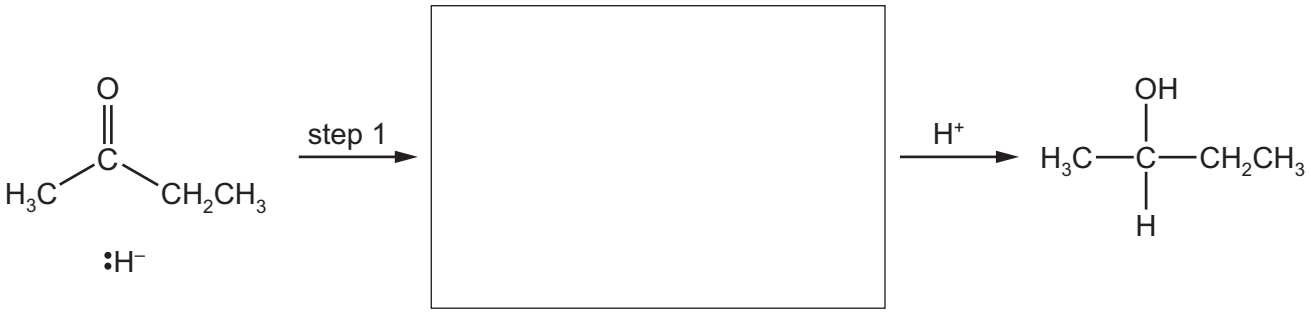
Balance this equation.

$$.....BF_3 + ...NaBH_4 \rightarrow .....B_2H_6 + ...NaBF_4$$

[1]

(b) Primary and secondary alcohols can be formed by the reaction of carbonyl compounds with $NaBH_4$, which is a source of hydride ions, H^-.

Complete the mechanism for the reaction of butanone with hydride ions, H^-, and draw the intermediate in the box. Include all necessary curly arrows and relevant dipoles.

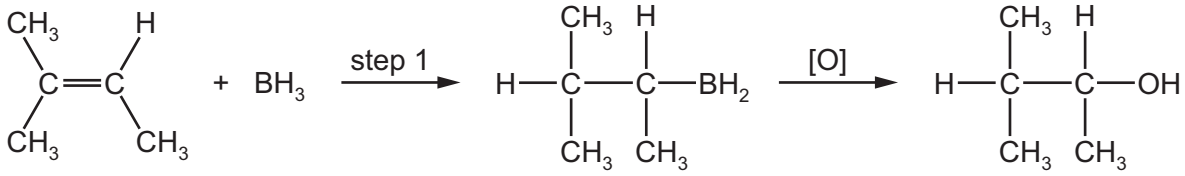


intermediate

[3]

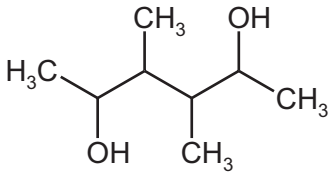
(c) Borane, BH_3, is used to synthesise alcohols from alkenes.
The reaction occurs in two steps.

The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



(i) Suggest the *type of reaction* in step 1.

..... [1]



Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

(d) Benzene, C_6H_6, and borazine, $B_3N_3H_6$, have planar, cyclic structures.

(i) Describe the structure of and bonding in benzene, C_6H_6.

.....

.....

.....

.....

.....

.....

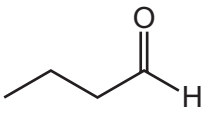
..... [3]

(ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

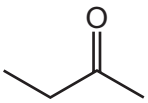
Suggest and draw the structure of borazine.

[1]

[Total: 10]



butanal



butanone

The following results are obtained with reagents **L**, **M** and **N**.
(✓ means a reaction takes place.)

reagent	butanal	butanone
L	✓	✓
M	✓	no reaction
N	no reaction	✓

(i) Suggest a possible identity for each reagent **L**, **M** and **N**.

L .....

M .....

N .....

[3]

(ii) Give the structure of the organic product formed when **M** reacts with butanal.

[1]

(iii) What is observed when **N** reacts with butanone?

..... [1]

(iv) What *type of reaction* is occurring when **N** reacts with butanone?

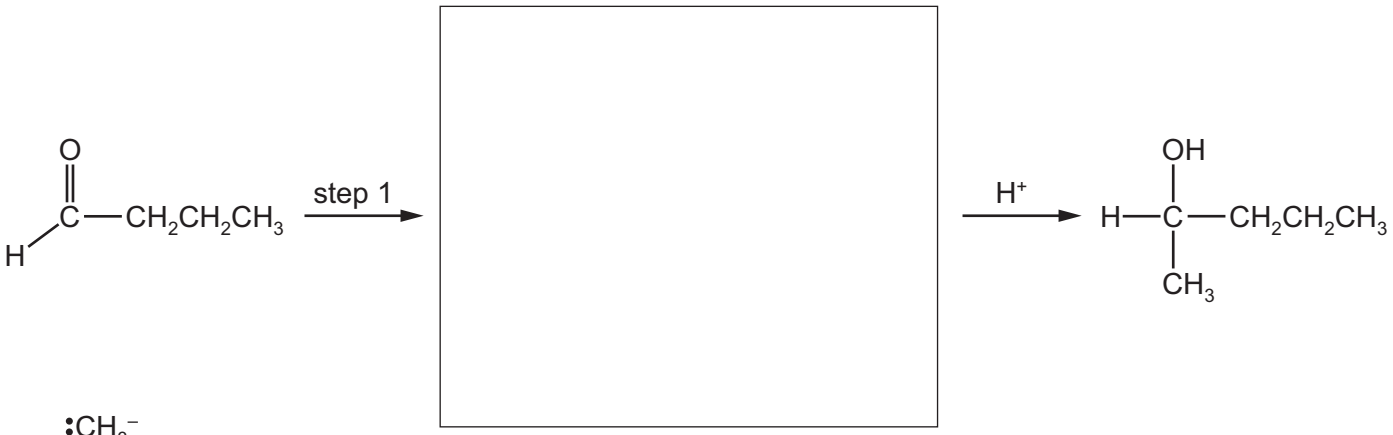
..... [1]

$$CH_3Li \rightleftharpoons CH_3^- + Li^+$$

The CH_3^- ion can act as a nucleophile.

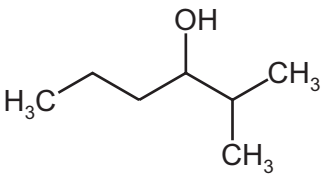
The reaction between methyl lithium and carbonyl compounds can be used to make alcohols.

(i) Suggest a mechanism for the reaction of butanal with CH_3^- ions. Include all necessary curly arrows, lone pairs and relevant dipoles.



[3]

(ii) A chemist decides to prepare the following organic compound **G** from butanal.



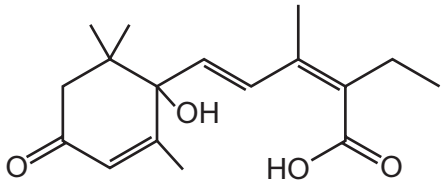
G

Draw the structure of the **organolithium** reagent which could be used to prepare **G** from butanal.

[1]

[Total: 10]

A



(i) Compound **A** shows optical and geometrical isomerism.

On the structure of **A** above,
- draw a **line** through the bond(s) that give rise to geometrical isomerism,
- **circle** all chiral carbon atoms.

[2]

(ii) Give the **names** of four functional groups present in **A**.

.....

..... [2]

(iii) A molecule of **A** has 17 carbon atoms.

State the number of carbon atoms that are sp, sp^2 and sp^3 hybridised in **A**.

sp carbons = ... sp^2 carbons = ... sp^3 carbons = ...

[1]

(iv) When **A** is reacted with an excess of hot, concentrated manganate(VII) ions, a mixture of three organic compounds is formed.

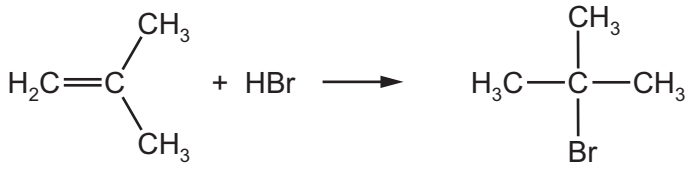
$$\mathbf{A} \rightarrow \underset{(C_{10}H_{14}O_7)}{\mathbf{X}} \text{ and } \underset{(C_3H_4O_3)}{\mathbf{Y}} \text{ and } \underset{(C_4H_6O_3)}{\mathbf{Z}}$$

Suggest the structures of **Y** and **Z**.

Y ($C_3H_4O_3$)	**Z** ($C_4H_6O_3$)

[2]

Methylpropene reacts with hydrogen bromide to form 2-bromo-2-methylpropane.



methylpropene 2-bromo-2-methylpropane

(i) Draw the mechanism of this reaction. Include all relevant curly arrows, dipoles and charges.

[3]

(ii) 1-bromo-2-methylpropane is also formed in this reaction.

Explain why 2-bromo-2-methylpropane will be the **major** product in this reaction.

.....

.....

..... [1]

The initiation step in this process is shown.

$$NH_2Cl \xrightarrow{UV} \bullet NH_2 + \bullet Cl$$

(i) What is meant by the term *free radical*?

.....

..... [1]

The equation for a possible propagation step in the process is shown.

$$NH_2Cl + \bullet Cl \rightarrow \bullet NHCl + HCl$$

(ii) Suggest an equation for a possible termination step in this process.

..... [1]

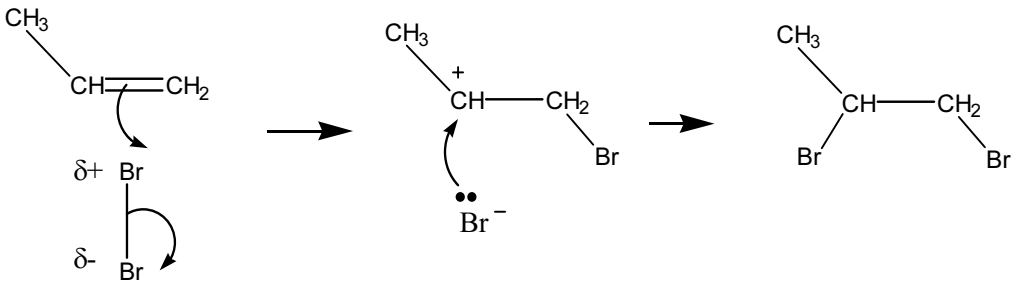
(b) (i) Draw the 'dot-and-cross' diagram of NH_2Cl. Show outer electrons only.

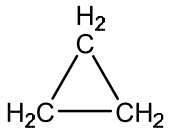
[1]

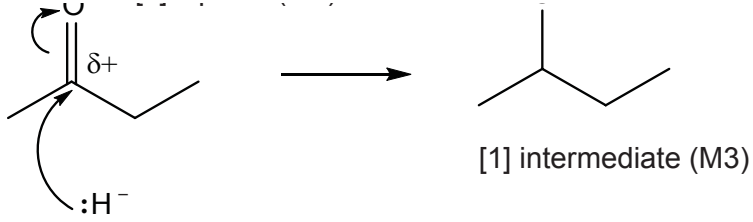
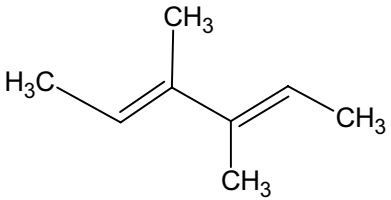
(ii) State the hybridisation of the nitrogen atom and suggest the H–N–Cl bond angle in the NH_2Cl molecule.

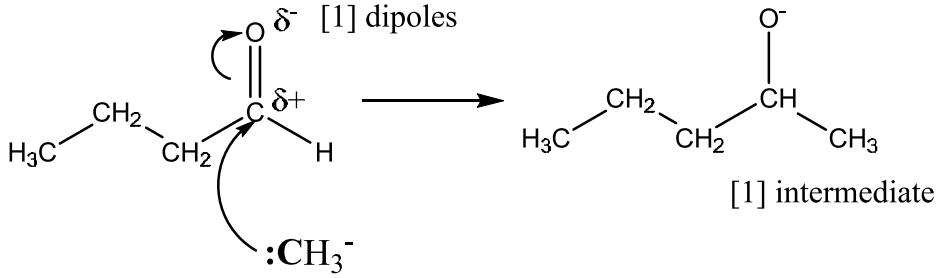
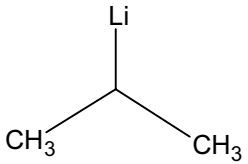
hybridisation of N .....

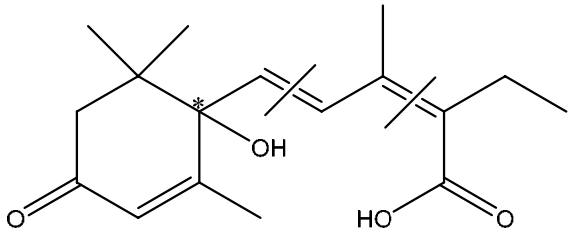
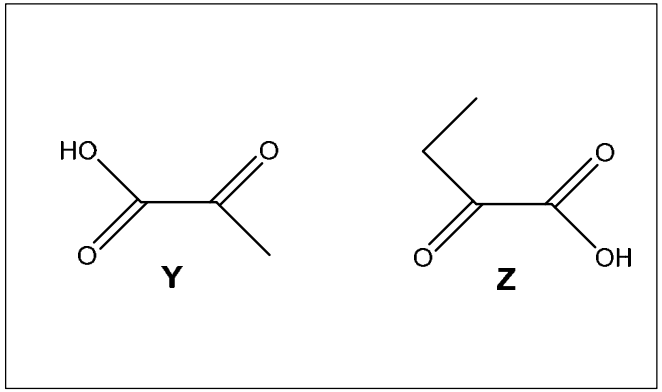
H–N–Cl bond angle .....
[1]

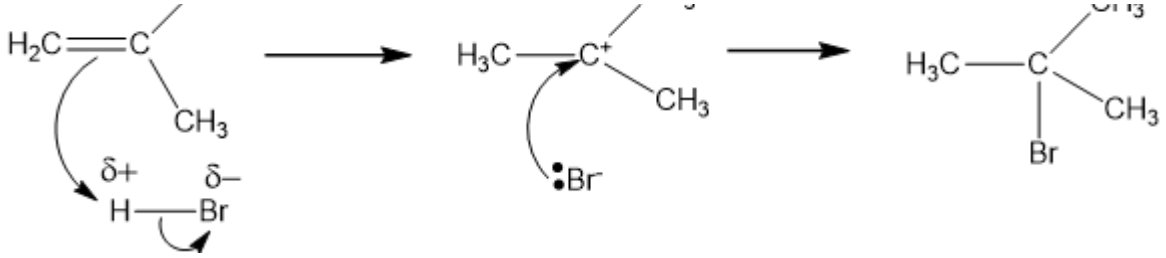
(ii)	**B** is $CH_3CH_2CH_3$	**1**
(iii)	**C** is $CH_2=CHCH_2CH_2CH_3$	**1**
	D and **E** are $CH_3CH=CHCH_2CH_3$ (one shown as cis, the other as trans)	**1**
	F is $CH_3CH_2CH_2CO_2H$	**1**
	G is CH_3CO_2H	
	H is $CH_3CH_2CO_2H$	
(iv)	geometrical *or* cis-trans *or E–Z*	**1**
(b) (i)	No particular conditions ***or*** in the dark	**1**
(ii)	electrophilic addition	**1**
(iii)		**1** **1**
		[Total: 10]

2 (a) (i)	any **three** of the following structures $CH_3CH_2CH_3$ $CH_3CH=CH_2$ $CH_3C\equiv CH$ $CH_2=C=CH_2$  	**2**
(ii)	**K** since it has the greatest % of hydrocarbons / carbon-containing compounds ***or*** 99.6 % of it is burnt for energy	**1**
(iii)	any **two** from • reacted with lime / CaO / soda lime / $Ca(OH)_2$ / KOH / NaOH / • liquefied under pressure / ≥5 atm • dissolved in water under pressure / ≥5 atm	**2**
(b) (i)	have a shorter carbon / hydrocarbon chain ***or*** shorter hydrocarbon ***or*** fewer carbon atoms in its chain ***or*** have high H / C ratio	**1**
(ii)	Coal	**1**
	produces the largest amount of SO_2 ***or*** largest combined amount of SO_2 and NO_2	
(iii)	they burn at higher temperatures ***or*** release more heat on burning	**1**
(iv)	CO – the gas is toxic/poisonous ***or*** references to Hb **and** ability to carry oxygen CO_2 – the gas contributes to global warming	**1** **1**
		[Total: 10]

	 [1] both curly arrows (M2) arrow must come from lone pair [1] intermediate (M3)	
(c) (i)	(electrophilic) addition	**1**
(ii)		**1**
(d) (i)	*any four of* M1: σ-bonds between C–C **or** C–H M2: π-bonds formed from overlap of p-orbitals M3: (π-bonds/electrons) above and below the ring M4:bonds/electrons are delocalised M5: bond angle 120° M6: intermediate C–C bond length / all C–C same length / strength M7: carbons are sp^2 hybridised	**3**
(ii)	correct delocalised structure of borazine 	**1**

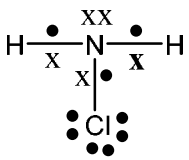
4 (a) (i)	**L** 2,4-DNPH or Brady's reagent or LiAlH$_4$ or NaBH$_4$ **M** Fehling's solution or Tollens' reagent or acidified $K_2Cr_2O_7$ or MnO_4^- **N** alkaline I_2	**3**	
(ii)	$CH_3CH_2CH_2CO_2Na$ or $CH_3CH_2CH_2CO_2^-Na^+$ or $CH_3CH_2CH_2CO_2H$	**1**	
(iii)	yellow precipitate	**1**	
(iv)	redox or oxidation	**1**	
(b) (i)	 two curly arrows [1] dipole [1] intermediate [1]	**3**	
(ii)		**1**	

5(a)(i)	 circle or asterisk on correct C atom only [1] lines through the two correct bonds only [1]	**2**
5(a)(ii)	ketone, (tertiary) alcohol, alkene, carboxylic acid two for each mark	**2**
5(a)(iii)	sp carbons = 0 sp^2 carbons = 8 sp^3 carbons = 9	**1**
5(a)(iv)		**2**



M1 correct dipole on HBr **AND** any correct curly arrow [1]
M2 two **other** correct curly arrows **AND** lone pair required on Br^- [1]
M3 intermediate [1]

6(c)(ii)	(major product is) formed via the most **stable tertiary carbocation / intermediate** **OR tertiary** halogenoalkane formed via more **stable carbocation / intermediate**	**1**

7(a)(i)	species with an unpaired electron	**1**
7(a)(ii)	$NH_2 + Cl \rightarrow NH_2Cl$	**1**
7(b)(i)		**1**
7(b)(ii)	sp^3 **AND** 100–107°	**1**