Cambridge International Examinations
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME	
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2968382613

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2018**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, candidate number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.
DO **NOT** WRITE IN ANY BARCODES.

Answer **all** questions.

Electronic calculators may be used.
You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

This document consists of **23** printed pages and **1** blank page.

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CAMBRIDGE
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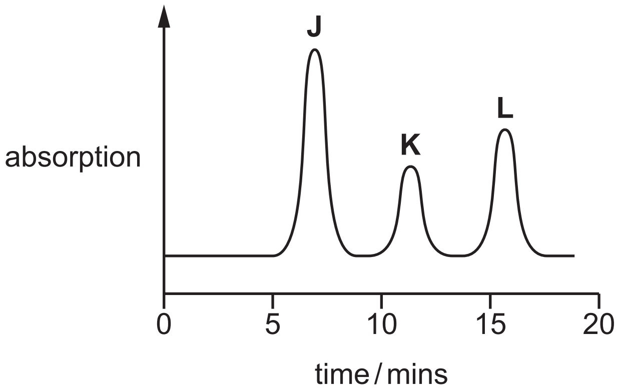
[Turn over

Answer **all** the questions in the spaces provided.

1 **(a)** An alkene, a carboxylic acid and a ketone, all of similar volatility, are mixed together. The mixture is then analysed by gas chromatography.

The gas chromatogram produced is shown.



The separation of the three compounds depends on their relative solubilities in the liquid stationary phase. The liquid stationary phase is an alkane.

(i) Complete the table to suggest which compound in the mixture is responsible for each peak **J**, **K** and **L**. Explain your answer by reference to the intermolecular forces of each compound.

peak	organic compound	explanation
J		
K		
L		

[2]

A student calculates the areas underneath the three peaks in the chromatogram.

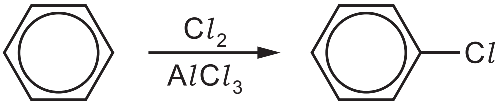
peak	**J**	**K**	**L**
area / mm^2	46	18	28

(ii) The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **K**.

% of mixture responsible for peak **K** = ... [1]

(b) Chlorobenzene can be prepared from benzene as shown.



Aluminium chloride, $AlCl_3$, catalyses this reaction.

(i) Write an equation to show how $AlCl_3$ generates the electrophile needed in this reaction.

.... [1]

(ii) Draw the mechanism of the reaction between this electrophile and benzene to form chlorobenzene. Include all relevant curly arrows and charges.

[4]

(iii) Write an equation to show how the catalyst is regenerated.

.... [1]

(c) **(i)** Catalysts can be heterogeneous or homogeneous.

Explain what is meant by a *homogeneous catalyst*.

....

.... [1]

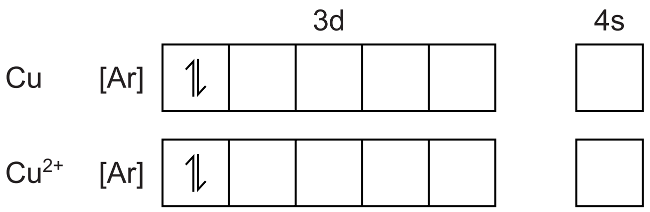
(ii) Complete the table by placing **one** tick (✓) in **each row** to indicate the mode of action of the catalyst in each reaction.

	heterogeneous	homogeneous
Rh in the removal of NO_2 from exhaust gases of cars		
Fe^{3+} in the $I^-/S_2O_8^{2-}$ reaction		

[1]

[Total: 11]

2 **(a)** Complete the electronic configuration for Cu and Cu^{2+}.



[2]

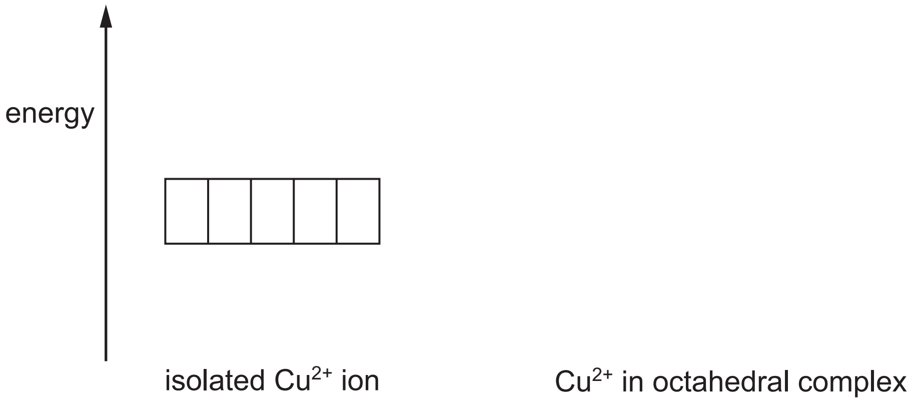
(b) **(i)** The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

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]

(c) **(i)** 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$, *en*, is a bidentate ligand.

Explain what is meant by the term *bidentate*.

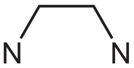
....

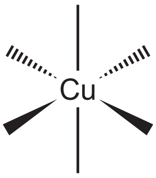
....

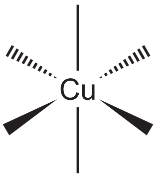
.... [1]

(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*.

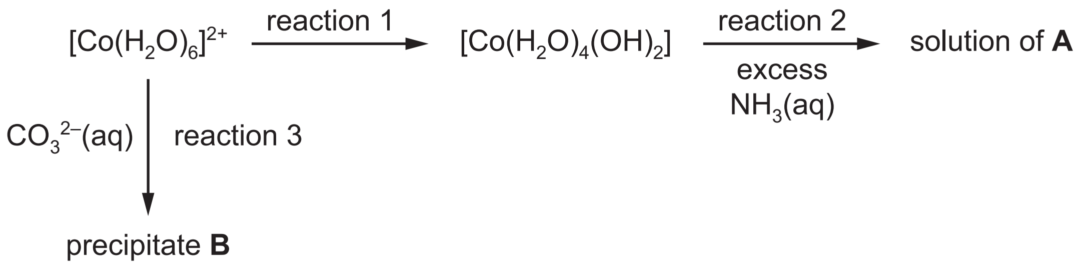




[2]

[Total: 7]

3 **(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]

(c) Platin, $Pt(NH_3)_2Cl_2$, displays *cis-trans* isomerism.

(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.

....

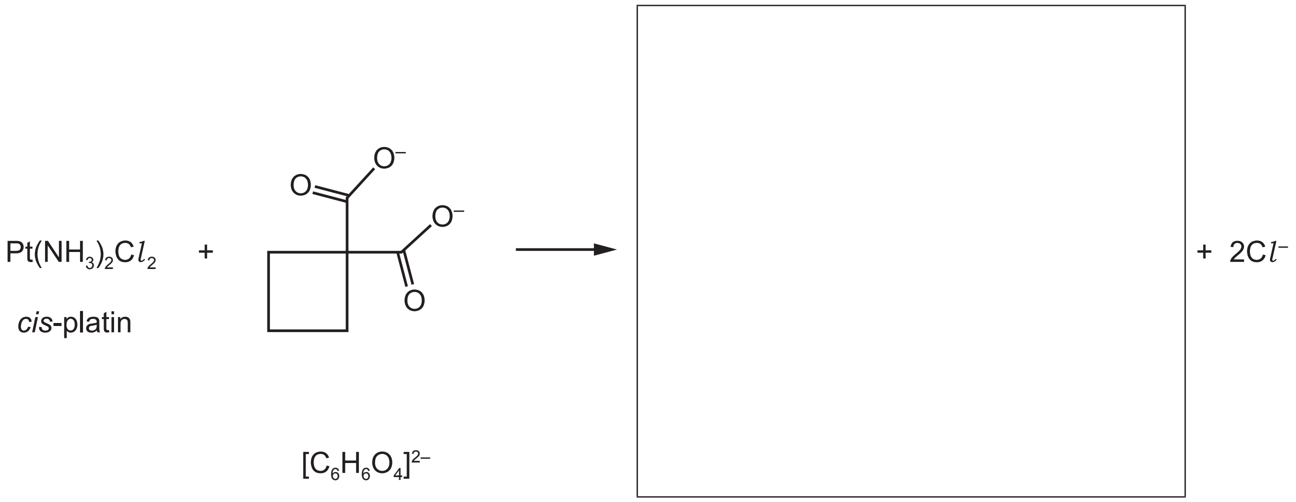
....

....

.... [2]

(d) The use of *cis*-platin can cause side effects so carboplatin has been developed.

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.



cyclobutane-1,1-dicarboxylate ion

carboplatin

Suggest the structure for carboplatin and draw it in the box. [1]

[Total: 13]

4 **(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.

....

....

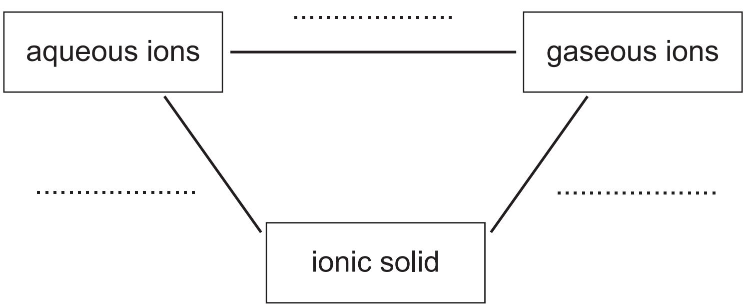
....

.... [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]

(d) The numerical value of the solubility product, K_{sp}, of CaF_2 is 3.45×10^{-11} at 298 K.

(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]

5 **(a)** Explain why the thermal stability of the Group 2 nitrates increases down the group.

....

....

.... [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]

(c) Acidified manganate(VII) ions, MnO_4^-, can also be used to analyse solutions containing nitrite ions, NO_2^-, by titration. In acidic solution, NO_2^- ions exist as HNO_2.

(i) Use the *Data Booklet* to construct an ionic equation for this reaction.

....

....

.... [2]

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

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

(d) Nitrous acid, HNO_2, is a weak acid with a K_a of 6.9×10^{-4} mol dm^{-3} at 298 K.

(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]

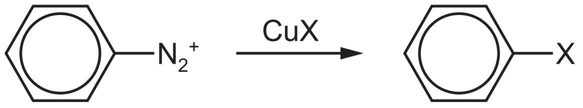
(ii) Write **two** equations to show how a solution containing a mixture of HNO_2 and $NaNO_2$ acts as a buffer.

....

.... [2]

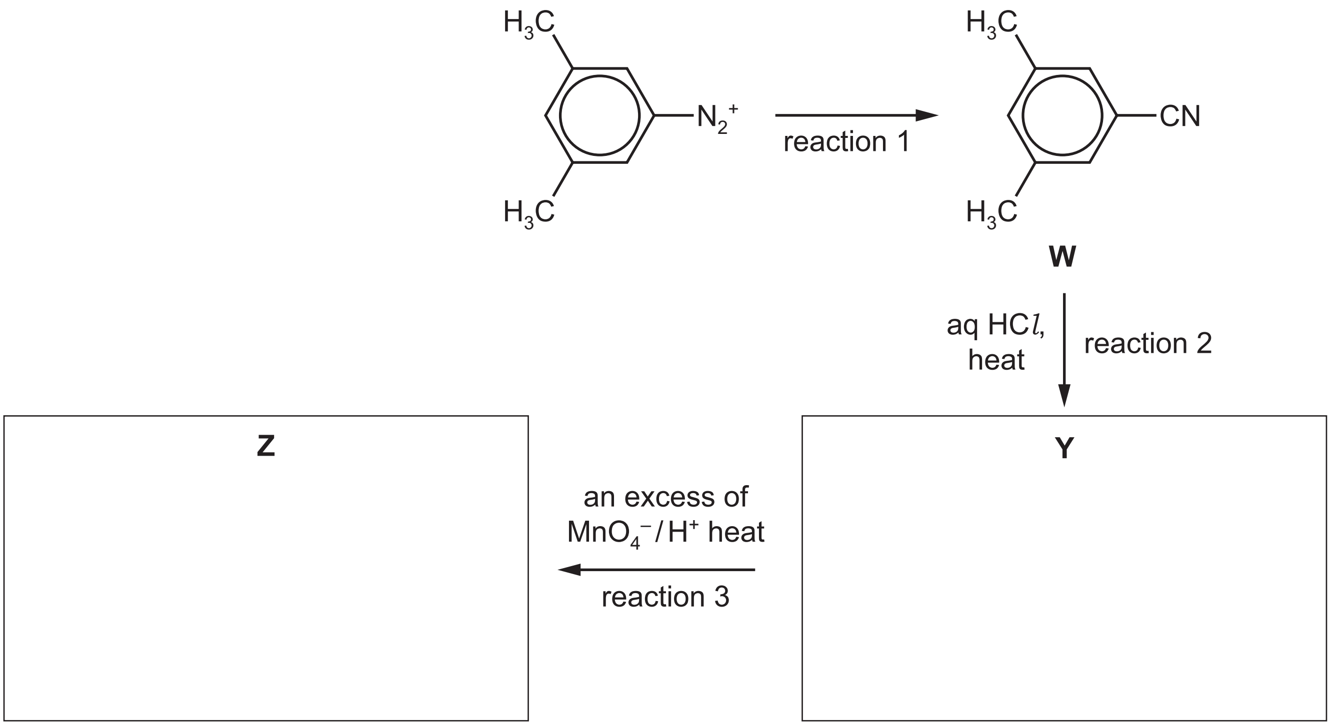
(f) Nitrous acid is used in the preparation of diazonium salts. The $-N_2^+$ group in the diazonium ion can be replaced with C*l*, Br or CN as shown.

The reagent used is a copper(I) salt, CuX.



diazonium ion   where X = C*l*, Br or CN

This reaction can be used in the synthesis of compound **Z** as shown.



(i) Suggest the reagent used in reaction 1.

.... [1]

(ii) Suggest structures of compounds **Y** and **Z** and draw them in the boxes above. [2]

Compounds **W** and **Z** were analysed using carbon-13 NMR spectroscopy.

(g) Predict the number of peaks in the carbon-13 NMR spectra of **W** and **Z**.

	number of peaks
W	
Z	

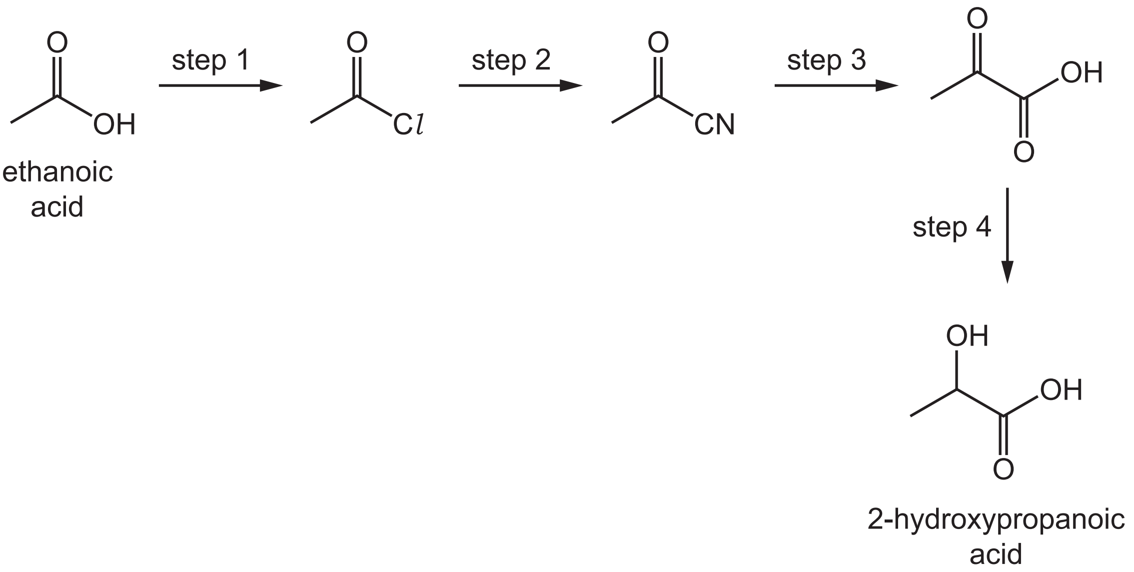
[2]

[Total: 22]

Question 6 starts on the next page.

[Turn over

6 2-hydroxypropanoic acid can be synthesised in four steps from ethanoic acid.



(a) **(i)** Suggest a reagent for step 2.

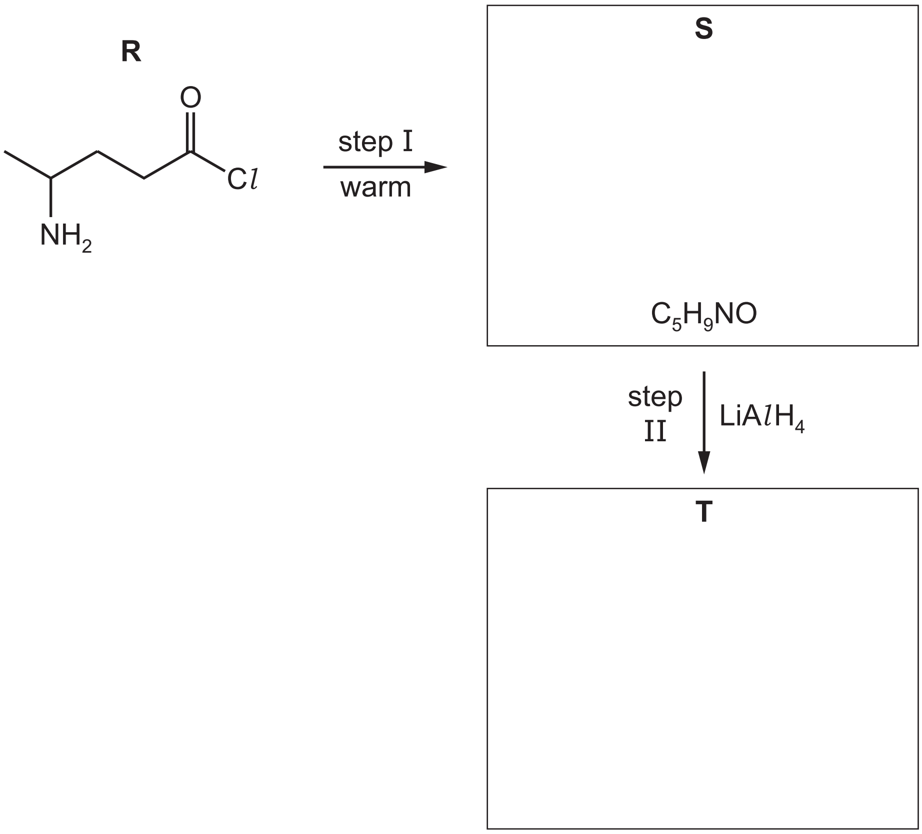
.... [1]

(ii) Suggest reagents and conditions for steps 1 and 4.

step 1 ....

step 4 ....
[2]

(b) Compound **R** can be used in the synthesis of compound **T** as shown.



(i) Suggest the structures of **S** and **T** and draw them in the boxes. [2]

(ii) Name the *type of reaction* for step I and step II.

step I ....

step II ....

[2]

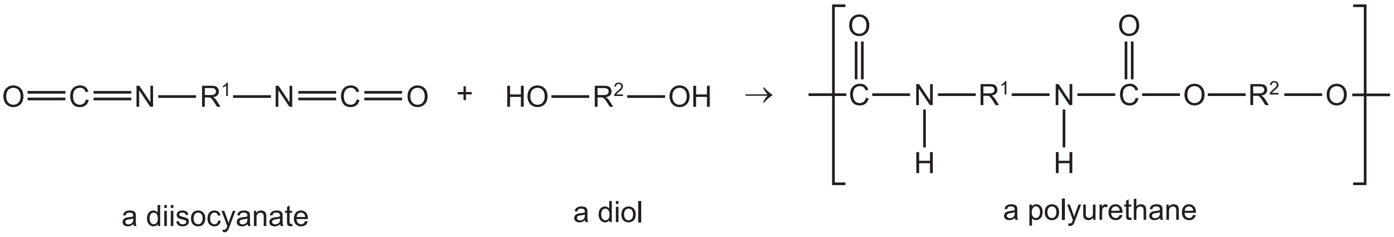
(c) Compound **R** can be polymerised.

Draw a section of this polymer showing **two** repeat units.

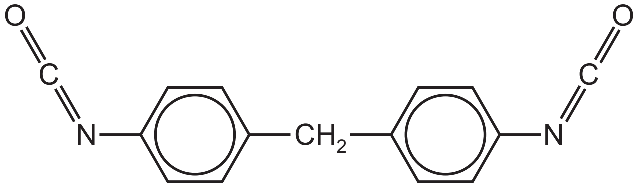
[2]

[Total: 9]

7 **(a)** Polyurethanes are polymers made by the reaction of a diisocyanate with a diol as shown. R^1 and R^2 are hydrocarbon groups.



Lycra® is a polyurethane formed from the diisocyanate **P** and $HOCH_2CH_2OH$.



P

(i) Give the molecular formula for **P**.

.... [1]

(ii) Draw the repeat unit of Lycra®.

[2]

(iii) Fibres of Lycra® are strong due to the intermolecular forces between the polymer chains.

Complete the table to identify two intermolecular forces responsible for this property and the group(s) involved.

intermolecular force	group(s) involved

[2]

(b) Name **one** example of each of the following types of polymer.

type of polymer	example
synthetic polyamide	
synthetic polyester	
conducting polymer	
non-solvent based adhesive	

[3]

[Total: 8]

8 **(a)** Chloramine, NH_2Cl, can be used in the treatment of drinking water to kill bacteria. Excess chloramine in water is destroyed using UV light. The mechanism for this involves free radicals.

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]

(c) Some values for standard enthalpy changes of formation, $\Delta H_f^{\ominus}$, and standard entropies, $S^{\ominus}$, are given in the table.

	$\Delta H_f^{\ominus}$ / 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]

(d) Compare and explain the basicities of ammonia, ethylamine and phenylamine.

....

....

....

....

....

....

....

.... [4]

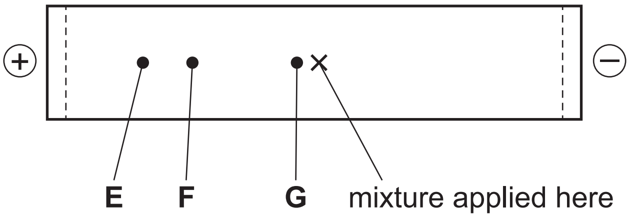
[Total: 14]

9 **(a)** Use information from the *Data Booklet* to draw the structure of the dipeptide glu-cys.

[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]

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