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CHEMISTRY

9701/41

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.

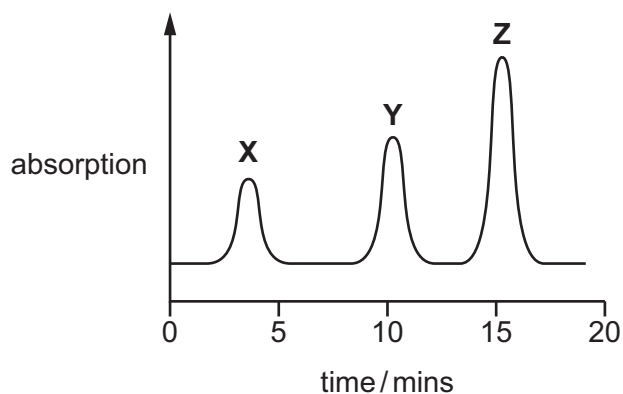
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.

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

- 1 (a) An aldehyde, an alkane and a carboxylic acid, all of similar volatility, are mixed together. The mixture is then analysed in a gas chromatograph.

The gas chromatogram produced is shown.



The separation of the compounds depends on their relative solubilities in the stationary phase. The stationary phase is a liquid alcohol.

- (i) Complete the table to suggest which compound in the mixture is responsible for each peak **X**, **Y** and **Z**. Explain your answer by reference to the intermolecular forces of the compounds.

peak	organic compound	explanation
X		
Y		
Z		

[2]

- (ii) A student calculates the areas underneath the three peaks in the chromatogram.

peak	X	Y	Z
area/mm ²	19	32	47

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 **Z**.

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

- (b) (i) The mass spectrum of a halogenoalkane containing one chlorine atom **or** bromine atom will show an additional peak at M+2.

State the isotopes of chlorine and bromine responsible for M+2 peaks.

chlorine bromine [1]

- (ii) The mass spectrum of bromochloromethane, CH₂BrCl, has a molecular ion peak, M, at an *m/e* value of 128. It also has M+2 and M+4 peaks.

Suggest the identity of the molecular ions that give rise to these peaks.

M peak

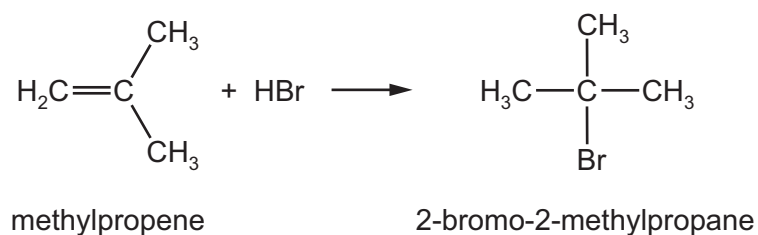
M+2 peak

M+4 peak

[2]

- (c) Halogenoalkanes can be formed from the reaction of an alkene with a hydrogen halide.

Methylpropene reacts with hydrogen bromide to form 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]

- (d) (i) Explain what is meant by the term *partition coefficient*, $K_{\text{partition}}$.

.....

.....

.....

..... [2]

- (ii) The partition coefficient of organic compound **H** between dichloromethane and water is 4.75.

- 2.50 g of compound **H** was dissolved in water and made up to 100 cm³ in a volumetric flask.
- 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane.

Calculate the mass of compound **H** that was extracted into the dichloromethane.

mass of compound **H** extracted = ... g [2]

[Total: 14]

- 2 (a) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

.....

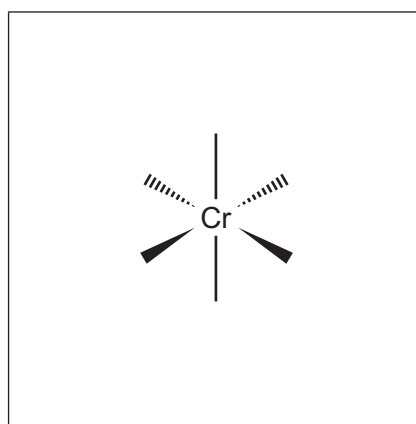
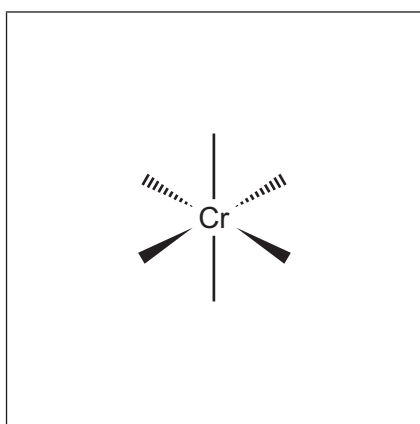
.....

..... [1]

- (b) $\text{Cr}^{3+}(\text{aq})$ and $\text{C}_2\text{O}_4^{2-}(\text{aq})$ ions form the complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$.

Draw **two** stereoisomers of this complex ion.

You may use  to represent $\text{C}_2\text{O}_4^{2-}$.



[2]

- (c) The solubility of calcium ethanedioate, CaC_2O_4 , is $6.65 \times 10^{-3} \text{ g dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of CaC_2O_4 . Include its units.

$K_{\text{sp}} =$

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.

$K_{\text{sp}} \text{ CaC}_2\text{O}_4 =$ [2]

[Total: 7]

- 3 (a) Complete the table to show the total number of **unpaired** electrons in the 3d and 4s orbitals of each isolated gaseous atom.

	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.

.....

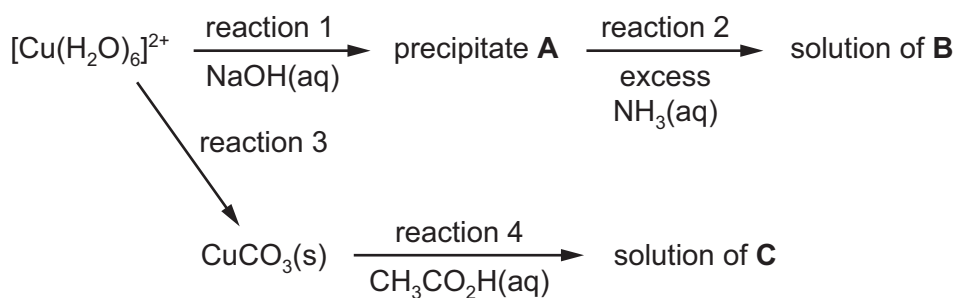
.....

.....

.....

..... [3]

(d) The reaction scheme shows some reactions of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.



(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, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, is a neutral complex of platinum(II).

Explain why $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has no charge.

.....
 [1]

- (f) (i) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, displays *cis-trans* isomerism.

Draw the structure of *trans*-platin. State its shape and the Cl-Pt-Cl bond angle.

shape Cl-Pt-Cl bond angle

[2]

- (ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

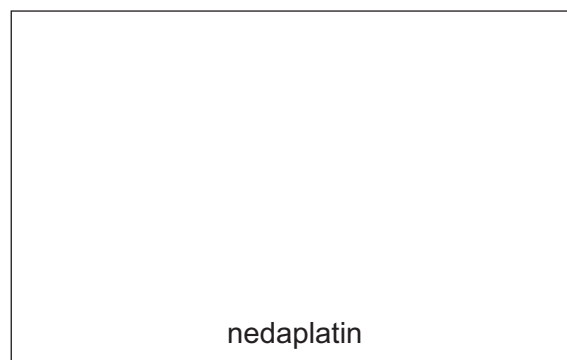
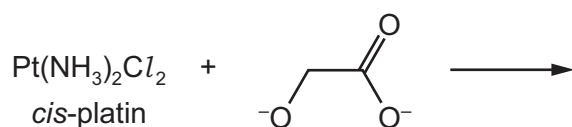
.....

 [2]

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

Nedaplatin can be synthesised from *cis*-platin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[1]

[Total: 19]

- 4 (a) The enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of the Group 2 sulfates becomes more endothermic down the group.

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 $[\text{H}^+]:[\text{OH}^-]$.

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

[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]

- (d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

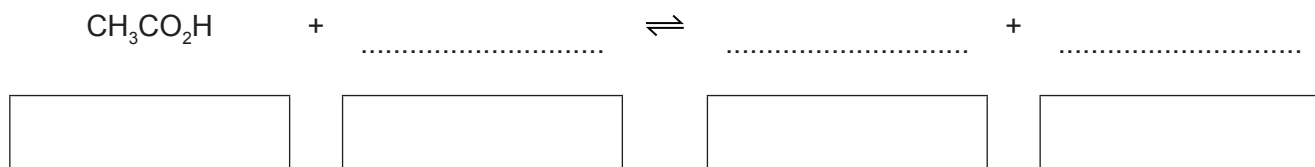
Write **two** equations to describe how hydrogencarbonate ions, HCO_3^- , and carbonic acid, H_2CO_3 , control the pH of blood.

.....
 [2]

- (e) The K_a for ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ 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.



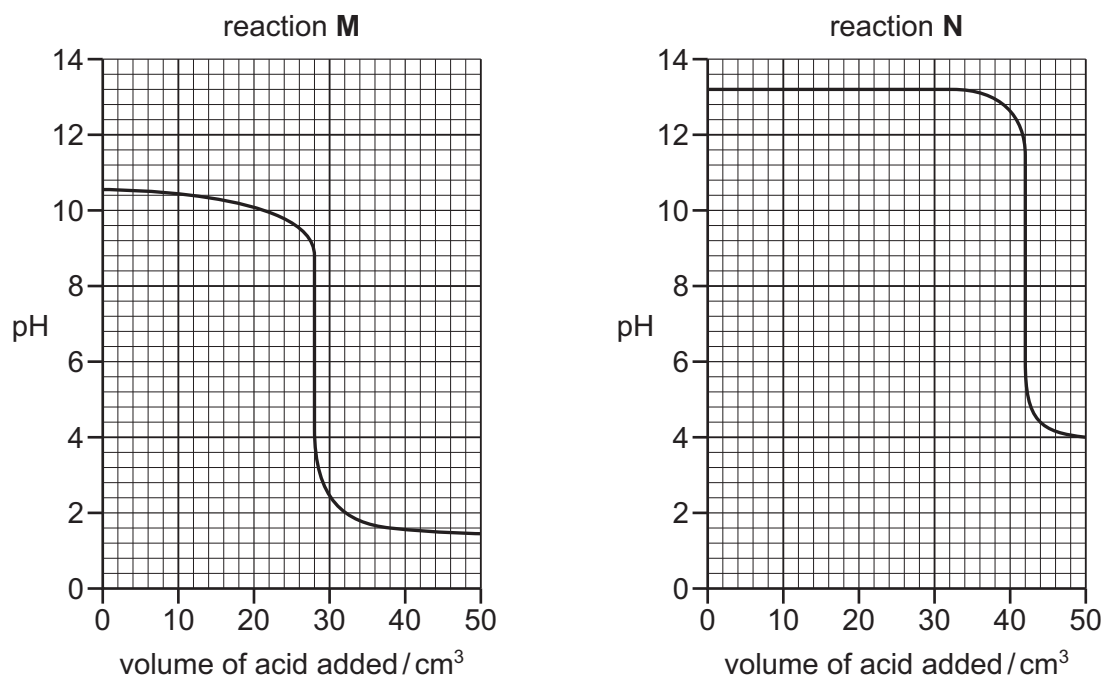
[2]

- (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.

pH = ... [4]

(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.



(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 = ... cm³ [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**

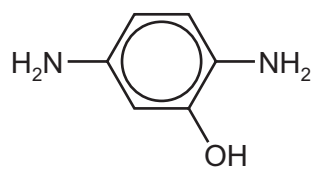
explanation

.....

[2]

[Total: 19]

- 5 (a) Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.

**F****G**

- (i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.

	number of peaks
F	
G	

[2]

- (ii) Draw the repeat unit of polyhydroxyamide. The amide bond should be shown displayed.

[2]

- (b) When poly(ethene) is formed from ethene, many bonds are broken and formed.

Place **one tick (✓)** in **each row** of the table to indicate the types of bonds broken and formed in this process.

	σ -bonds only	π -bonds only	both σ - and π -bonds
bonds broken			
bonds formed			

[2]

(c) Addition polymers can be classified into two types.

- 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, $\text{CH}_3\text{CH}=\text{CH}_2$, with phenylethene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, 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]

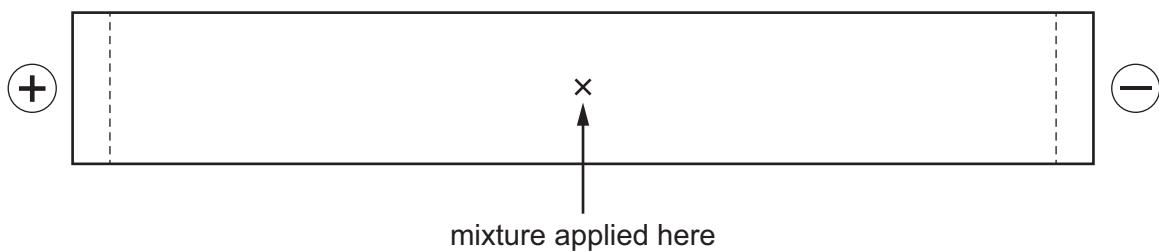
- 6 (a) Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[2]

- (b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



explanation

.....

.....

[5]

[Total: 7]

- 7 (a) Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = Cl or OH).

Explain why.

.....

.....

.....

.....

..... [3]

- (b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, $\text{C}_6\text{H}_4\text{BrOH}$, are formed.

Suggest structures for these products. Name each compound.

.....

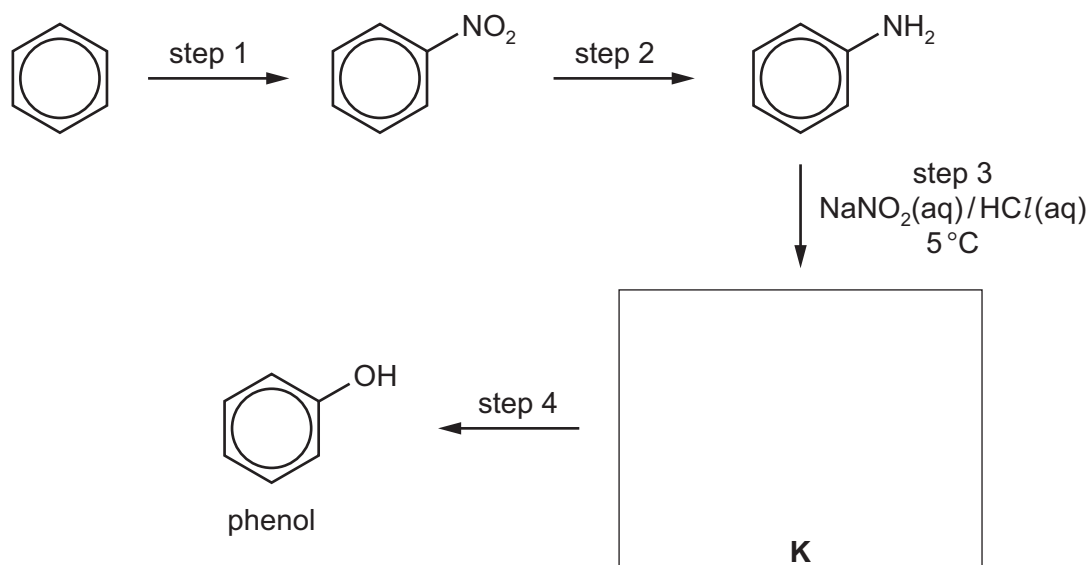
name:

.....

name:

[2]

(c) A student suggested that phenol can be prepared from benzene by the method shown.



(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.

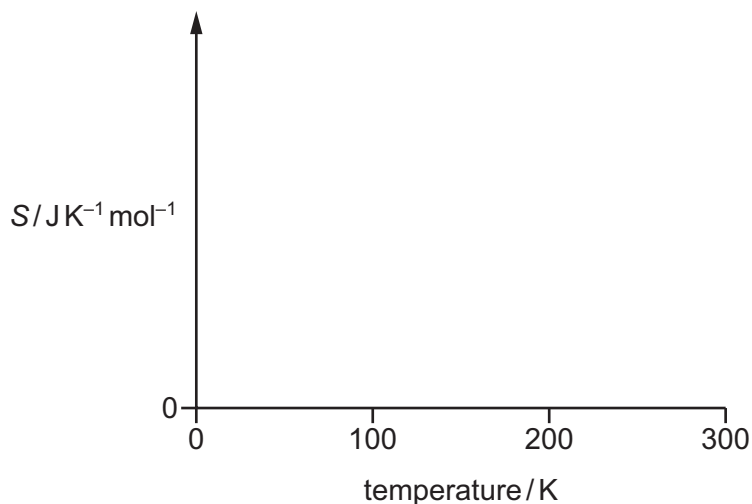
[1]

[Total: 11]

8 Entropy is a measure of the disorder of a system.

(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.



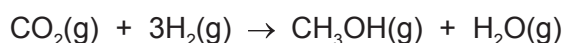
[2]

(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]

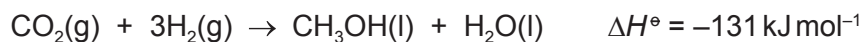
(c) The equation for a reaction that produces methanol is shown.



Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH , for this gas phase reaction.

$\Delta H = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(d) At 298 K, both products of this reaction are liquid.



Standard entropies are shown in the table.

substance	$\text{CO}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{CH}_3\text{OH}(\text{l})$	$\text{H}_2\text{O}(\text{l})$
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	+214	+131	+127	+70

(i) Calculate the standard entropy change, ΔS° , for this reaction.

$$\Delta S^\circ = \dots\dots\dots \text{J K}^{-1} \text{ mol}^{-1} \quad [2]$$

(ii) Calculate the standard Gibbs free energy change, ΔG° , for this reaction at 298 K.

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

.....
 [1]

- (e) In a methanol-oxygen fuel cell, $\text{CH}_3\text{OH}(\text{l})$ and $\text{O}_2(\text{g})$ are in contact with two inert electrodes immersed in an acidic solution.

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



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

.....

 [1]

- (ii) Use E° values to calculate the E°_{cell} for this reaction.

$$E^\circ_{\text{cell}} = \dots\dots\dots \text{V} \quad [1]$$

[Total: 12]

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CHEMISTRY

9701/42

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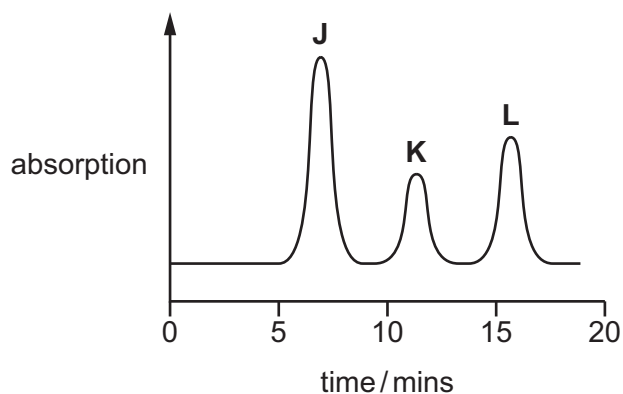
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This document consists of **23** printed pages and **1** blank page.

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.

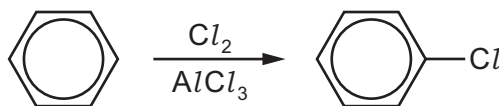
peak	J	K	L
area/mm ²	46	18	28

- (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]

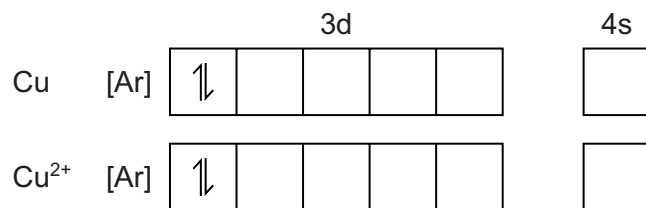
- (ii) Complete the table by placing **one** tick (✓) in **each row** to indicate the mode of action of the catalyst in each reaction.

	heterogeneous	homogeneous
Rh in the removal of NO ₂ from exhaust gases of cars		
Fe ³⁺ in the I ⁻ /S ₂ O ₈ ²⁻ reaction		

[1]

[Total: 11]

- 2 (a) Complete the electronic configuration for Cu and Cu²⁺.



[2]

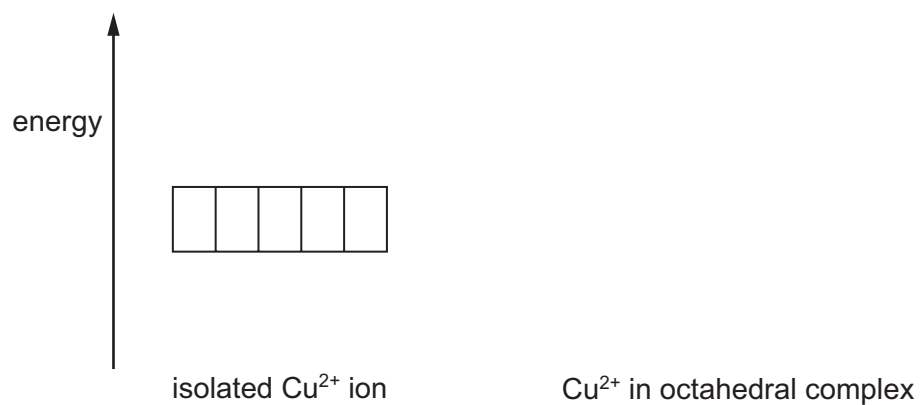
- (b) (i) The 3d orbitals in an isolated Cu²⁺ ion are degenerate.

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, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, *en*, is a bidentate ligand.

Explain what is meant by the term *bidentate*.

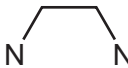
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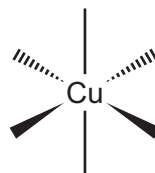
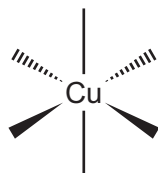
.....

..... [1]

- (ii) Cu^{2+} ions and *en* form the complex ion $[\text{Cu}(\text{en})_3]^{2+}$.

Draw the two optical isomers of this complex ion.

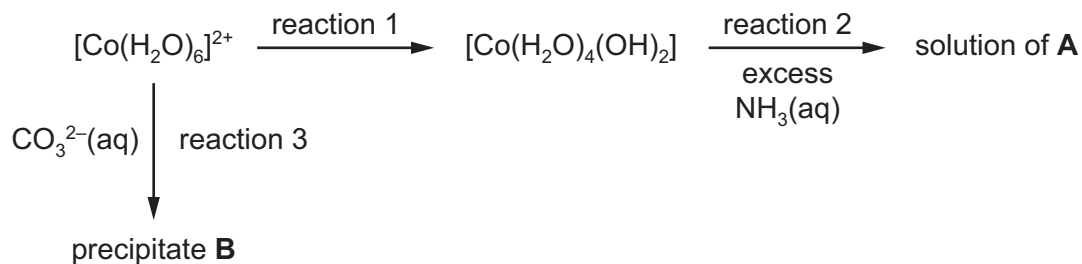
You may use  to represent *en*.



[2]

[Total: 7]

- 3 (a) The reaction scheme shows some reactions of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$.



- (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, $\text{C}_4\text{H}_4\text{O}_6^{2-}$, 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.

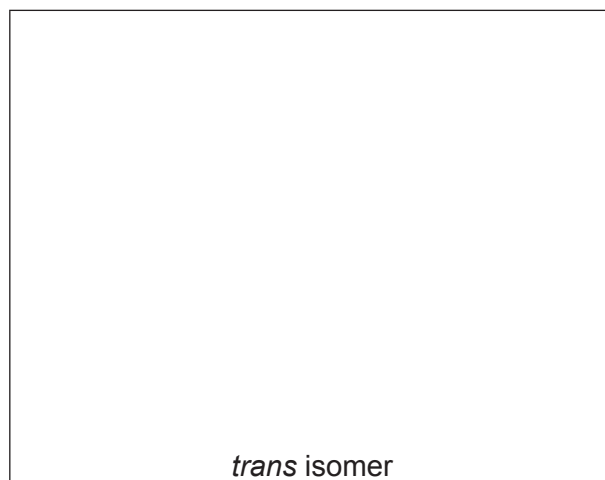
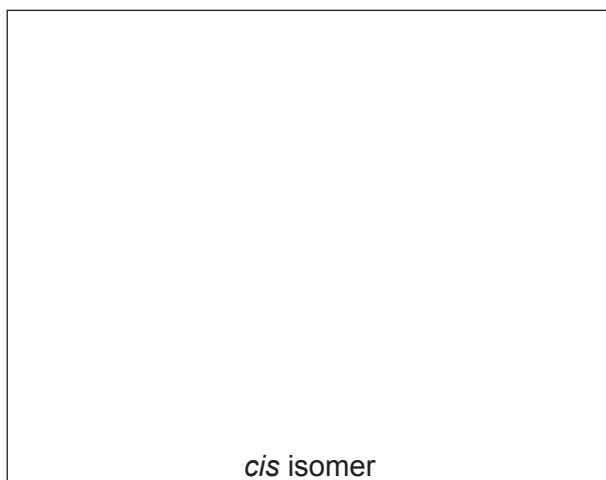
[1]

- (iii) Complete the equation for the oxidation of 2,3-dihydroxybutanedioate. Use [O] for the oxidising agent in this reaction.

$\text{C}_4\text{H}_4\text{O}_6^{2-} + \dots \rightarrow \dots$ [1]

(c) Platin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, displays *cis-trans* isomerism.

(i) Draw the structures of these isomers.



[2]

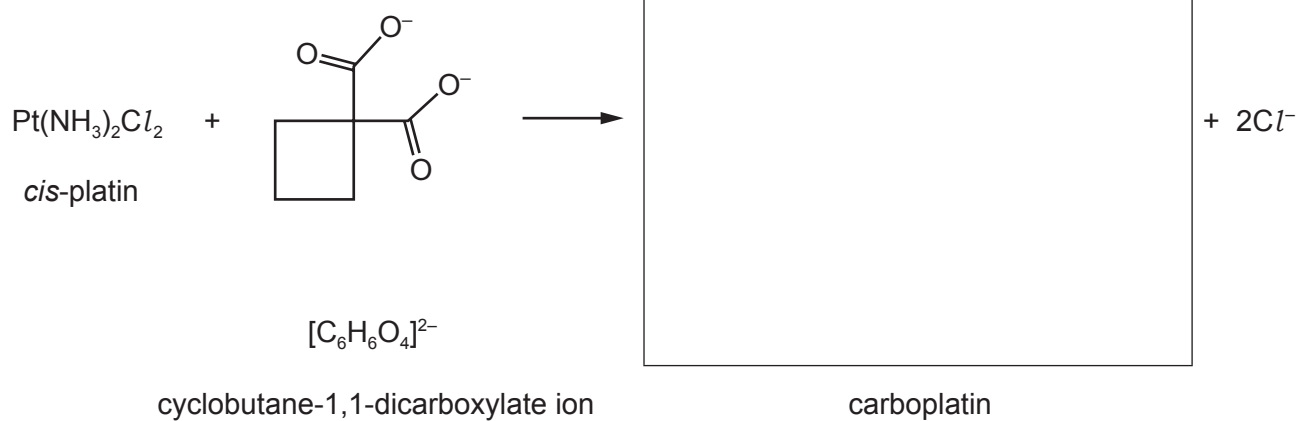
(ii) *Cis*-platin is an effective anti-cancer drug.

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, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, by replacing the two chloride ion ligands with a **single** cyclobutane-1,1-dicarboxylate ion ligand as shown.



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, $\Delta H_{\text{sol}}^\ominus$, 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.

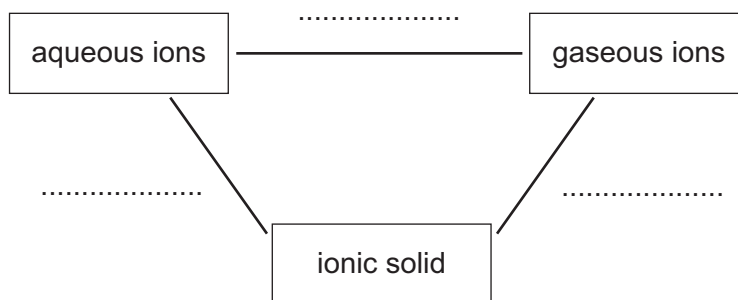
.....

 [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, $\Delta H_{\text{latt}}^\ominus$, enthalpy change of hydration, $\Delta H_{\text{hyd}}^\ominus$, or enthalpy change of solution, $\Delta H_{\text{sol}}^\ominus$.

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]

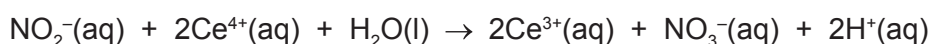
- 5 (a) Explain why the thermal stability of the Group 2 nitrates increases down the group.

.....

 [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, $\text{Ce}^{4+}(\text{aq})$. The equation for the titration reaction is shown.



- 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 $0.0400\text{ mol dm}^{-3}$ $\text{Ce}^{4+}(\text{aq})$ to reach the end-point.

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

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 $E^\ominus_{\text{cell}}$ for this reaction.

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

(d) Nitrous acid, HNO_2 , is a weak acid with a K_a of $6.9 \times 10^{-4} \text{ mol dm}^{-3}$ 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 $0.15 \text{ mol dm}^{-3} \text{ HNO}_2$.

pH = ... [2]

(iv) Calculate the percentage of HNO_2 molecules that are ionised in $0.15 \text{ mol dm}^{-3} \text{ HNO}_2$.

% 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*.

.....

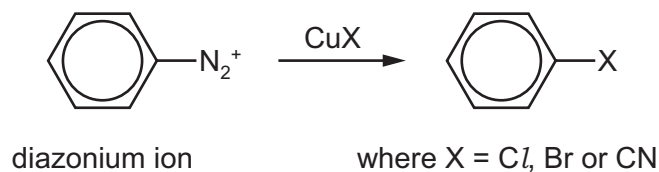
 [2]

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

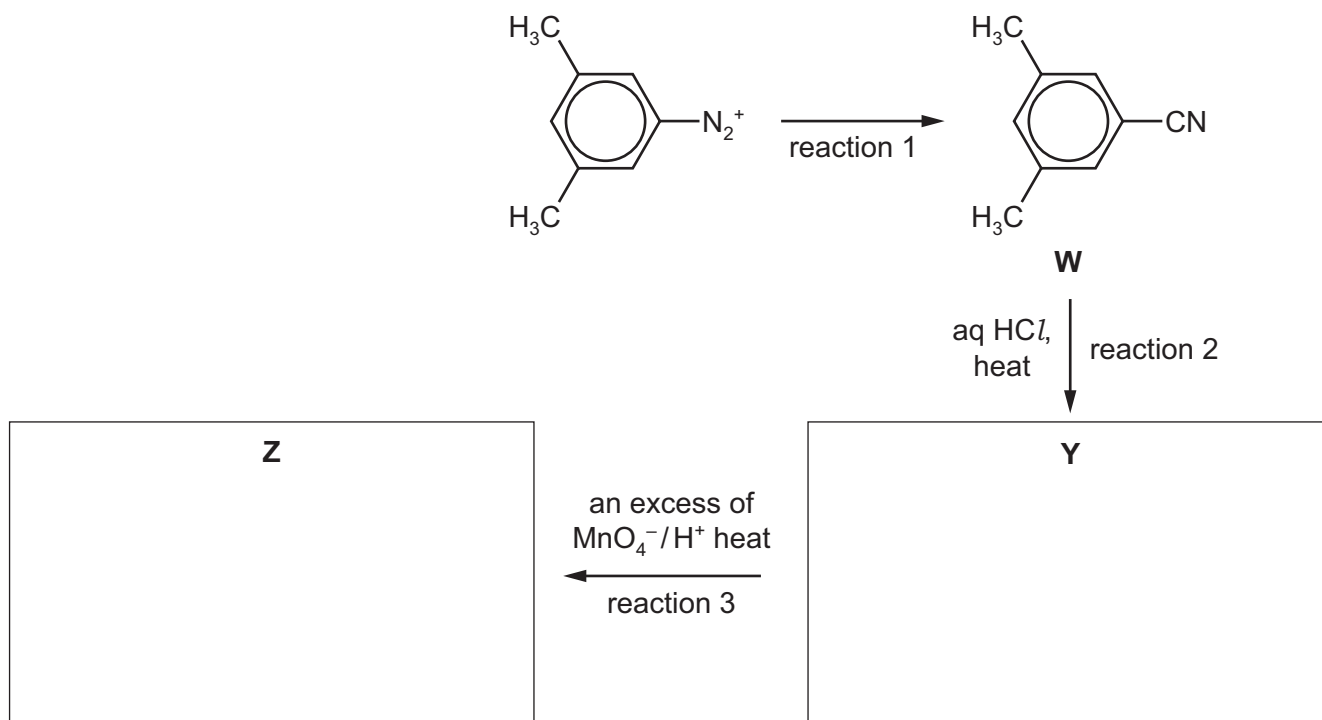
.....
 [2]

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

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



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**.

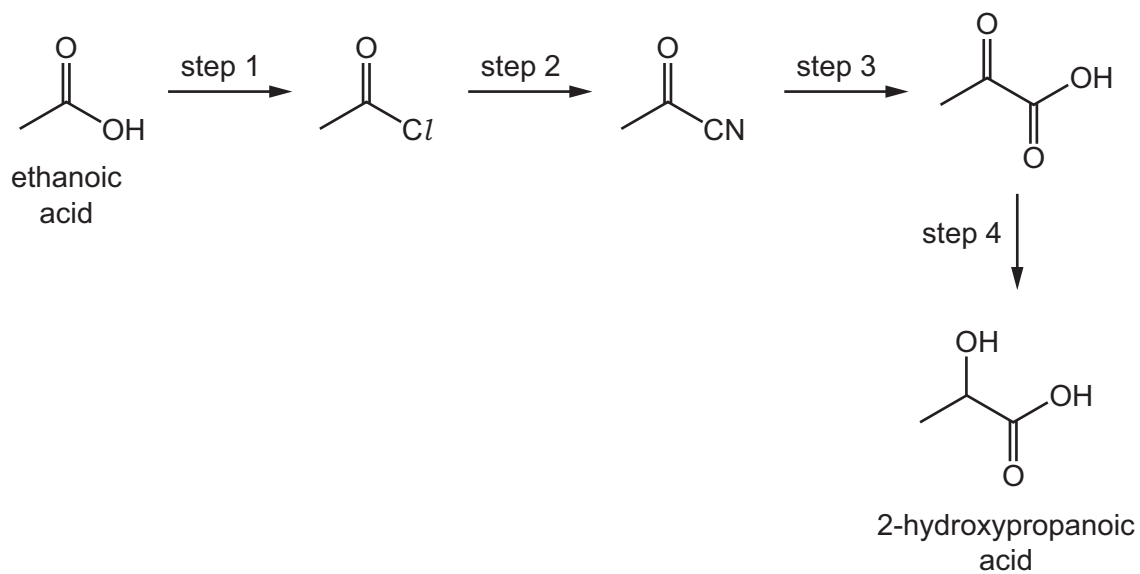
	number of peaks
W	
Z	

[2]

[Total: 22]

Question 6 starts on the next page.

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



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

..... [1]

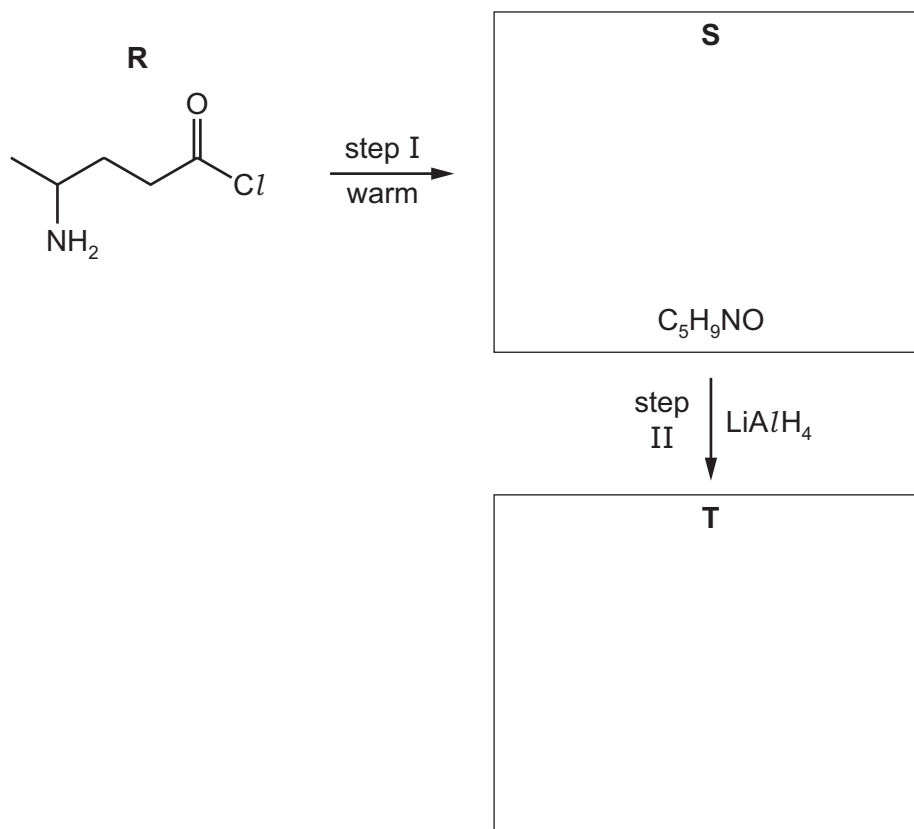
- (ii) Suggest reagents and conditions for steps 1 and 4.

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]

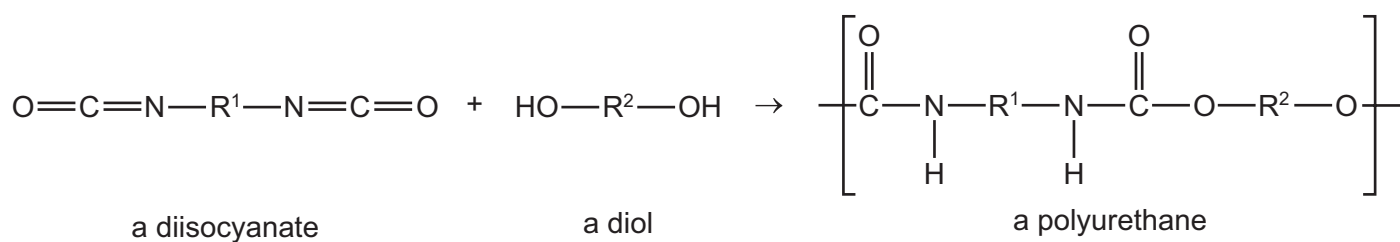
(c) Compound **R** can be polymerised.

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

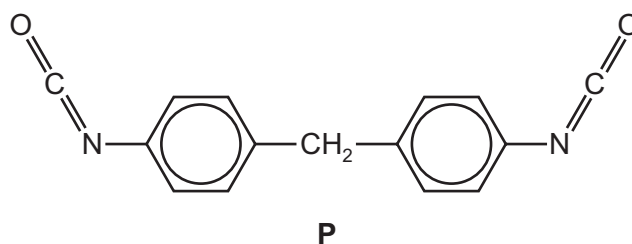
[2]

[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 $\text{HOCH}_2\text{CH}_2\text{OH}$.



- (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.

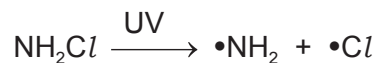
type of polymer	example
synthetic polyamide	
synthetic polyester	
conducting polymer	
non-solvent based adhesive	

[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.

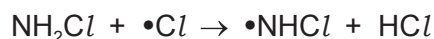
The initiation step in this process is shown.



- (i) What is meant by the term *free radical*?

.....
 [1]

The equation for a possible propagation step in the process is shown.



- (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 $\text{H}-\text{N}-\text{Cl}$ bond angle in the NH_2Cl molecule.

hybridisation of N

$\text{H}-\text{N}-\text{Cl}$ bond angle

[1]

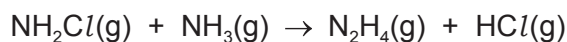
- (c) Some values for standard enthalpy changes of formation, ΔH_f° , and standard entropies, S° , are given in the table.

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{JK}^{-1} \text{mol}^{-1}$
$\text{NH}_2\text{Cl}(\text{g})$	+80.1	+241
$\text{NH}_3(\text{g})$	−45.9	+198
$\text{N}_2\text{H}_4(\text{g})$	+95.4	+237
$\text{HCl}(\text{g})$	−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.



- (ii) Calculate the standard entropy change, ΔS° , for this reaction.

$$\Delta S^\circ = \dots\dots\dots \text{JK}^{-1} \text{mol}^{-1} \quad [1]$$

- (iii) Calculate the standard enthalpy change, ΔH° , for this reaction.

$$\Delta H^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [1]$$

- (iv) Calculate the standard Gibbs free energy change, ΔG° , for this reaction at 298 K.

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

- (v) Explain, with reference to ΔG° , why this reaction becomes **less** feasible at higher temperatures.

.....

 [1]

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

.....

.....

.....

.....

.....

.....

.....

..... [4]

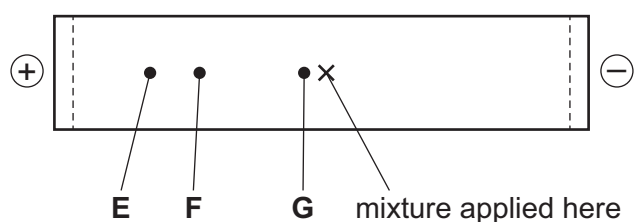
[Total: 14]

- 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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CHEMISTRY

9701/43

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.

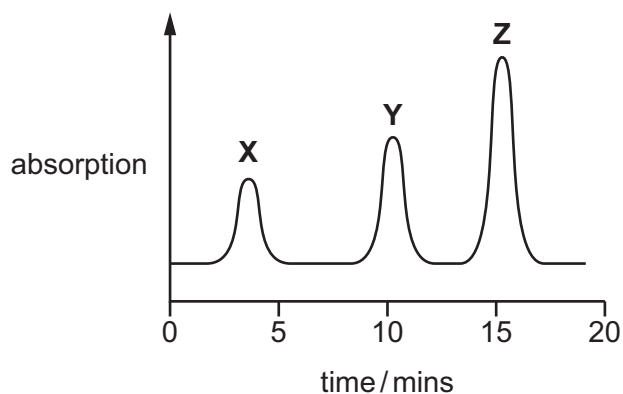
The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **20** printed pages.

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

- 1 (a) An aldehyde, an alkane and a carboxylic acid, all of similar volatility, are mixed together. The mixture is then analysed in a gas chromatograph.

The gas chromatogram produced is shown.



The separation of the compounds depends on their relative solubilities in the stationary phase. The stationary phase is a liquid alcohol.

- (i) Complete the table to suggest which compound in the mixture is responsible for each peak **X**, **Y** and **Z**. Explain your answer by reference to the intermolecular forces of the compounds.

peak	organic compound	explanation
X		
Y		
Z		

[2]

- (ii) A student calculates the areas underneath the three peaks in the chromatogram.

peak	X	Y	Z
area/mm ²	19	32	47

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 **Z**.

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

- (b) (i) The mass spectrum of a halogenoalkane containing one chlorine atom **or** bromine atom will show an additional peak at M+2.

State the isotopes of chlorine and bromine responsible for M+2 peaks.

chlorine bromine [1]

- (ii) The mass spectrum of bromochloromethane, CH₂BrCl, has a molecular ion peak, M, at an *m/e* value of 128. It also has M+2 and M+4 peaks.

Suggest the identity of the molecular ions that give rise to these peaks.

M peak

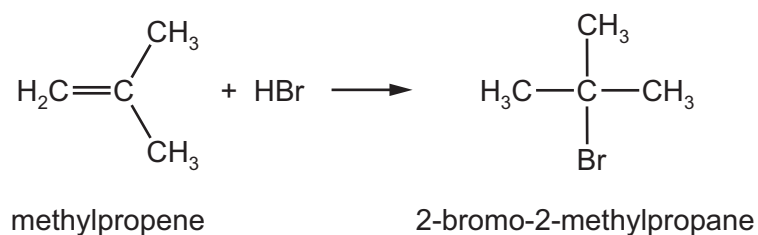
M+2 peak

M+4 peak

[2]

- (c) Halogenoalkanes can be formed from the reaction of an alkene with a hydrogen halide.

Methylpropene reacts with hydrogen bromide to form 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]

- (d) (i) Explain what is meant by the term *partition coefficient*, $K_{\text{partition}}$.

.....

.....

.....

..... [2]

- (ii) The partition coefficient of organic compound **H** between dichloromethane and water is 4.75.

- 2.50 g of compound **H** was dissolved in water and made up to 100 cm³ in a volumetric flask.
- 50 cm³ of this aqueous solution were shaken with 10 cm³ of dichloromethane.

Calculate the mass of compound **H** that was extracted into the dichloromethane.

mass of compound **H** extracted = ... g [2]

[Total: 14]

- 2 (a) Ethanedioate ions, $\text{C}_2\text{O}_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

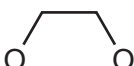
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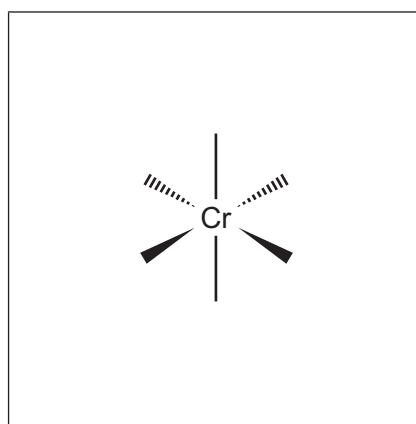
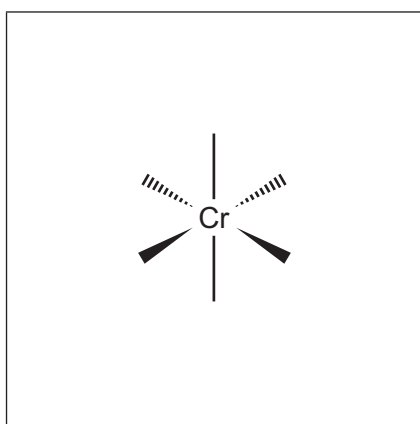
.....

..... [1]

- (b) $\text{Cr}^{3+}(\text{aq})$ and $\text{C}_2\text{O}_4^{2-}(\text{aq})$ ions form the complex ion $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$.

Draw **two** stereoisomers of this complex ion.

You may use  to represent $\text{C}_2\text{O}_4^{2-}$.



[2]

- (c) The solubility of calcium ethanedioate, CaC_2O_4 , is $6.65 \times 10^{-3} \text{ g dm}^{-3}$ at 298 K.

- (i) Write an expression for the solubility product, K_{sp} , of CaC_2O_4 . Include its units.

$K_{\text{sp}} =$

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.

$K_{\text{sp}} \text{ CaC}_2\text{O}_4 =$ [2]

[Total: 7]

- 3 (a) Complete the table to show the total number of **unpaired** electrons in the 3d and 4s orbitals of each isolated gaseous atom.

	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.

.....

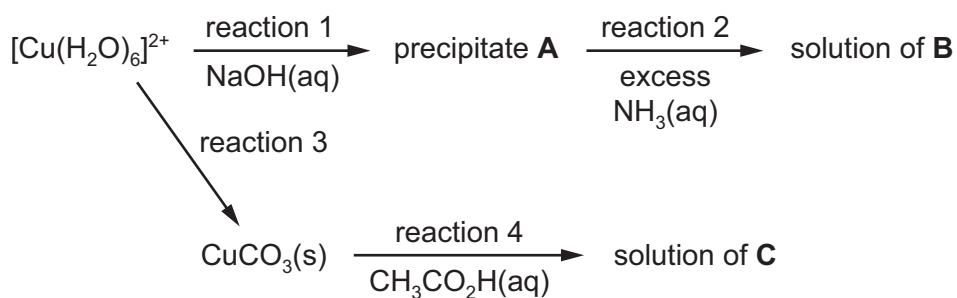
.....

.....

.....

..... [3]

(d) The reaction scheme shows some reactions of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.



(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, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, is a neutral complex of platinum(II).

Explain why $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has no charge.

.....
 [1]

- (f) (i) $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, displays *cis-trans* isomerism.

Draw the structure of *trans*-platin. State its shape and the Cl-Pt-Cl bond angle.

shape Cl-Pt-Cl bond angle

[2]

- (ii) *Cis*-platin is an effective anti-cancer drug.

Describe the action of *cis*-platin in this role.

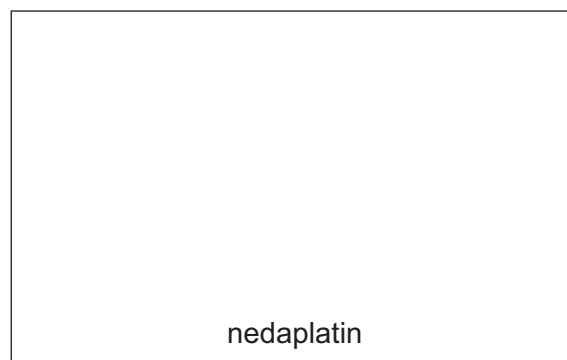
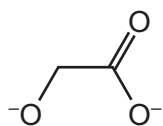
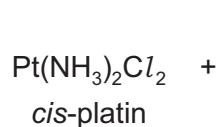
.....

 [2]

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

Nedaplatin can be synthesised from *cis*-platin, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[1]

[Total: 19]

- 4 (a) The enthalpy change of solution, $\Delta H_{\text{sol}}^{\ominus}$, of the Group 2 sulfates becomes more endothermic down the group.

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 $[\text{H}^+]:[\text{OH}^-]$.

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

[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]

- (d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

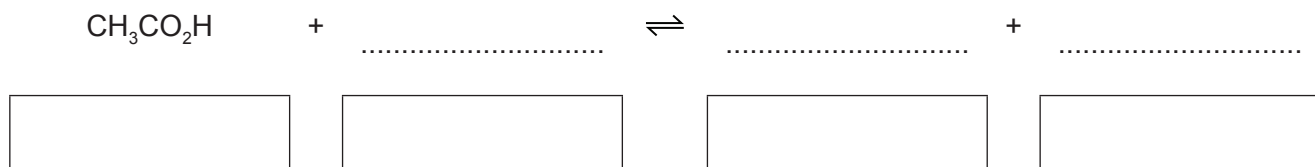
Write **two** equations to describe how hydrogencarbonate ions, HCO_3^- , and carbonic acid, H_2CO_3 , control the pH of blood.

.....
 [2]

- (e) The K_a for ethanoic acid is $1.75 \times 10^{-5} \text{ mol dm}^{-3}$ 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.



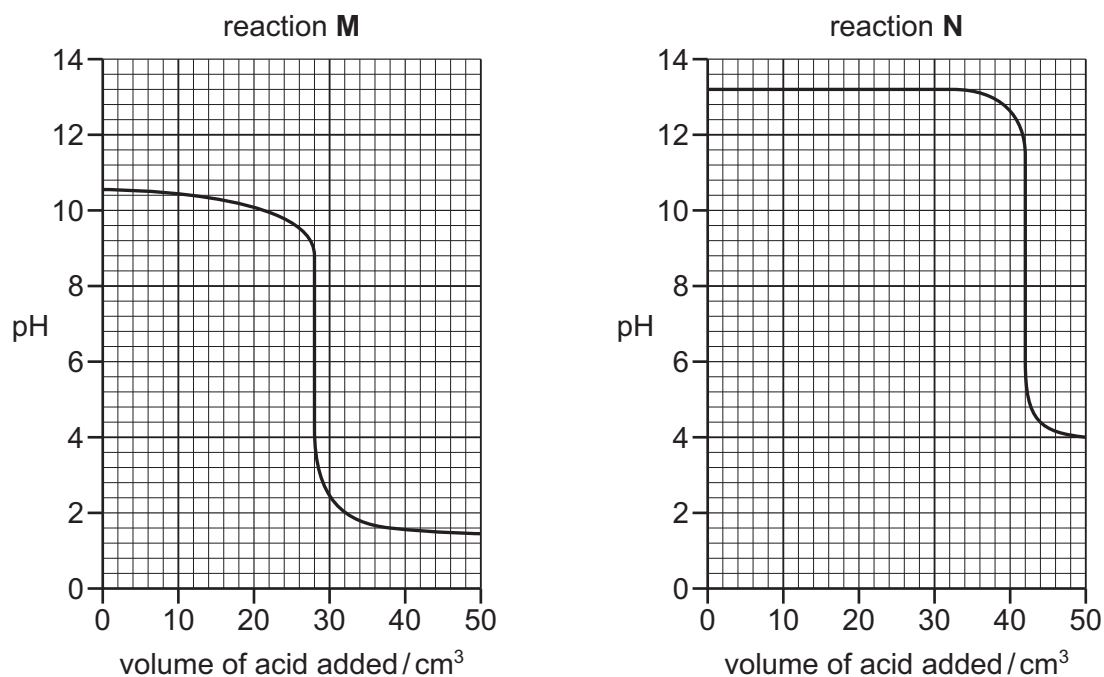
[2]

- (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.

pH = ... [4]

(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.



(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 = ... cm³ [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.

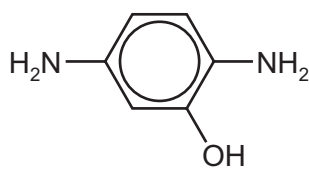
reaction **M** reaction **N**

explanation

..... [2]

[Total: 19]

- 5 (a) Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.

**F****G**

- (i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.

	number of peaks
F	
G	

[2]

- (ii) Draw the repeat unit of polyhydroxyamide. The amide bond should be shown displayed.

[2]

- (b) When poly(ethene) is formed from ethene, many bonds are broken and formed.

Place **one tick (✓)** in **each row** of the table to indicate the types of bonds broken and formed in this process.

	σ -bonds only	π -bonds only	both σ - and π -bonds
bonds broken			
bonds formed			

[2]

(c) Addition polymers can be classified into two types.

- 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, $\text{CH}_3\text{CH}=\text{CH}_2$, with phenylethene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, 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]

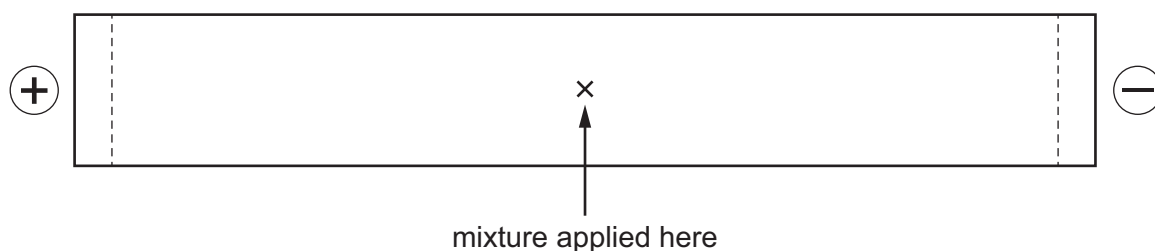
- 6 (a) Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[2]

- (b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



explanation

.....

.....

[5]

[Total: 7]

- 7 (a) Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = Cl or OH).

Explain why.

.....

.....

.....

.....

..... [3]

- (b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, $\text{C}_6\text{H}_4\text{BrOH}$, are formed.

Suggest structures for these products. Name each compound.

.....

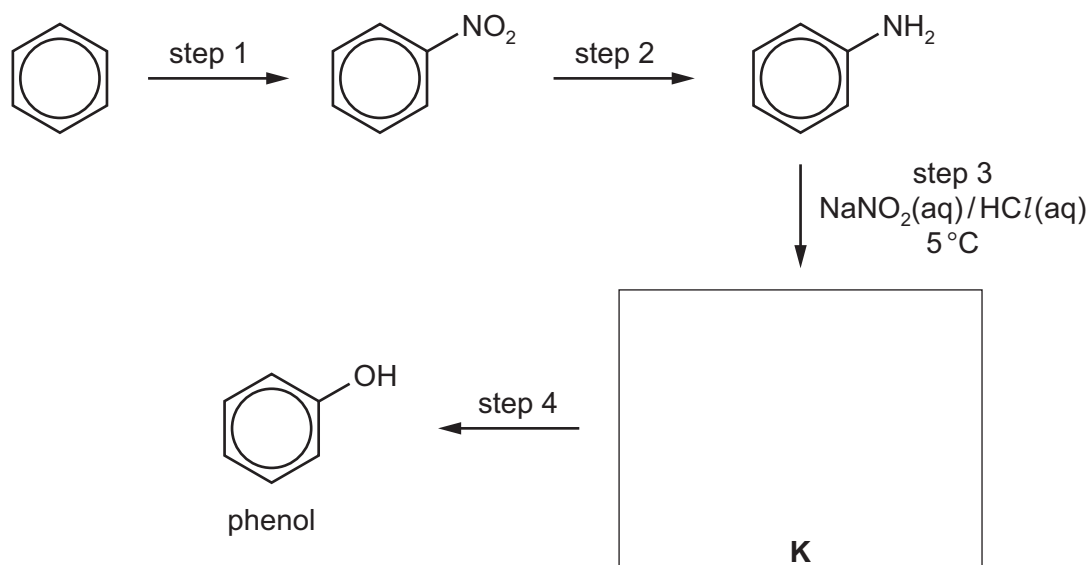
name:

.....

name:

[2]

(c) A student suggested that phenol can be prepared from benzene by the method shown.



(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.

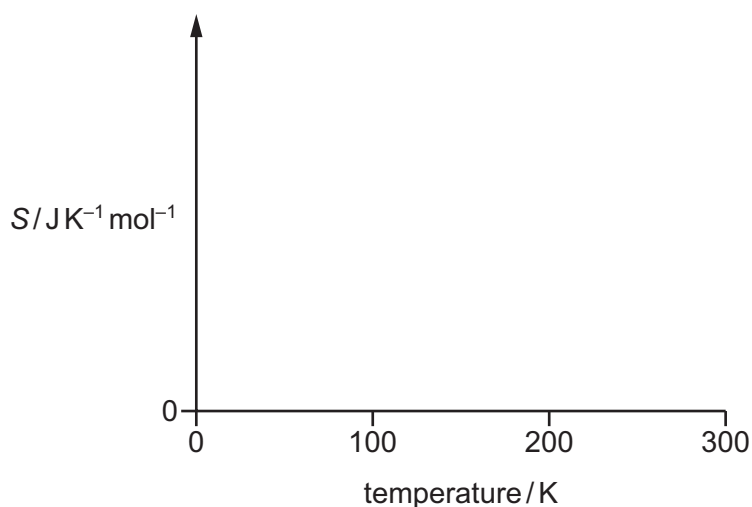
[1]

[Total: 11]

8 Entropy is a measure of the disorder of a system.

(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.



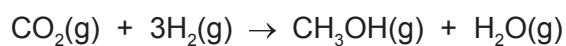
[2]

(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]

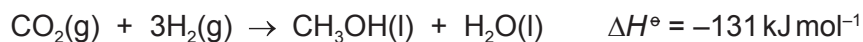
(c) The equation for a reaction that produces methanol is shown.



Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH , for this gas phase reaction.

$\Delta H = \dots\dots\dots \text{kJ mol}^{-1}$ [2]

(d) At 298 K, both products of this reaction are liquid.



Standard entropies are shown in the table.

substance	$\text{CO}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{CH}_3\text{OH}(\text{l})$	$\text{H}_2\text{O}(\text{l})$
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	+214	+131	+127	+70

(i) Calculate the standard entropy change, ΔS° , for this reaction.

$$\Delta S^\circ = \dots\dots\dots \text{J K}^{-1} \text{ mol}^{-1} \quad [2]$$

(ii) Calculate the standard Gibbs free energy change, ΔG° , for this reaction at 298 K.

$$\Delta G^\circ = \dots\dots\dots \text{kJ mol}^{-1} \quad [2]$$

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

.....
 [1]

- (e) In a methanol-oxygen fuel cell, $\text{CH}_3\text{OH}(\text{l})$ and $\text{O}_2(\text{g})$ are in contact with two inert electrodes immersed in an acidic solution.

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



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

.....

 [1]

- (ii) Use E° values to calculate the E°_{cell} for this reaction.

$$E^\circ_{\text{cell}} = \dots\dots\dots \text{V} \quad [1]$$

[Total: 12]

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