Cambridge Assessment International Education
Cambridge International Advanced Subsidiary and Advanced Level

CANDIDATE NAME			
CENTRE NUMBER		CANDIDATE NUMBER	

2283347273

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2019**

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.

Cambridge Assessment International Education

[Turn over

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

1 **(a)** **(i)** Complete the electronic configuration of the copper(II) ion.

$1s^2 2s^2 2p^6$ .... [1]

(ii) State the colour of the solutions containing the following ions.

- $[Cu(H_2O)_6]^{2+}(aq)$ ....
- $[CuCl_4]^{2-}(aq)$ ....

[1]

(iii) Octahedral complexes of Cu^{2+} with different ligands can have different colours.

Explain why.

....

....

....

....

.... [2]

(b) 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} =

[1]

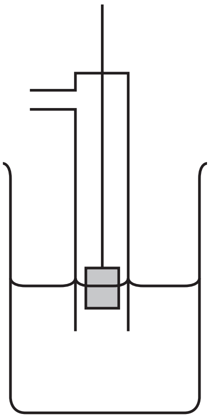
(d) Define the term *standard electrode potential, $E^{\ominus}$*.

....

....

.... [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]

2 **(a)** Group 2 carbonates decompose when heated.

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]

3 **(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-

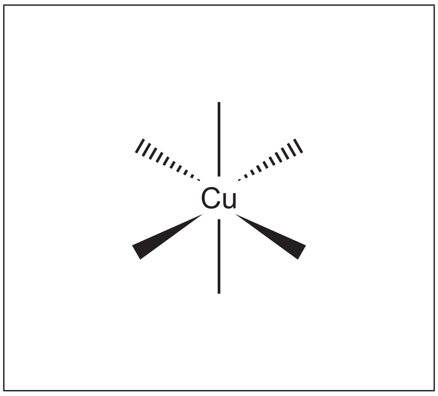
[2]

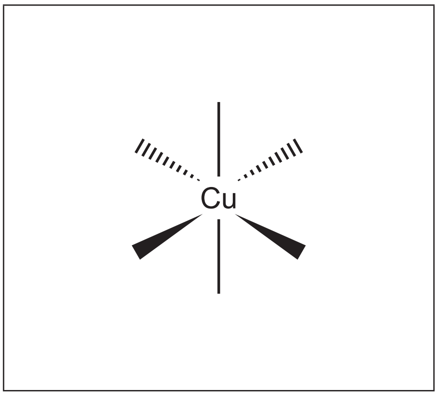
(e) Transition element complexes can exhibit stereoisomerism. $[Cu(H_2O)_4(NH_3)_2]^{2+}$ and $Pt(NH_3)_2Cl_2$ show the **same** type of isomerism.

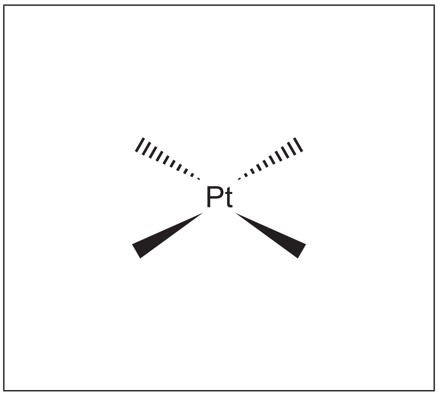
(i) Name this type of isomerism.

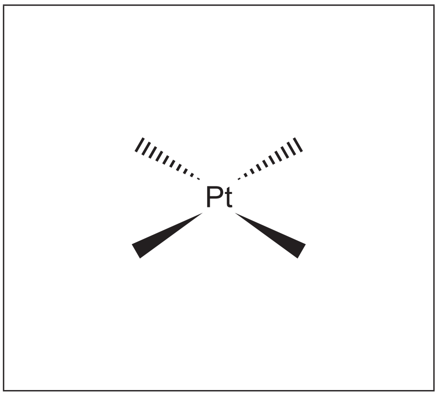
.... [1]

(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]

(f) Copper can form complexes with the ligands ammonia and *en*, $H_2NCH_2CH_2NH_2$, as shown.

$[Cu(H_2O)_6]^{2+}(aq) + en(aq) \rightleftharpoons [Cu(H_2O)_4(en)]^{2+}(aq) + 2H_2O(l)$ $K_{stab} = 3.98 \times 10^{10}$ 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]

Question 4 starts on the next page.

4 The initial rate of reaction for propanone and iodine in acid solution is measured in a series of experiments at a constant temperature.

$$CH_3COCH_3 + I_2 \xrightarrow{H^+ \text{ catalyst}} CH_3COCH_2I + HI$$

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 $5.40 \times 10^{-3}\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$ when

- the concentration of CH_3COCH_3 is $1.50 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$
- the concentration of I_2 is $1.25 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$
- the concentration of H^+ is $7.75 \times 10^{-1}\,\text{mol}\,\text{dm}^{-3}$.

(i) Calculate the rate constant, *k*, for this reaction. State the units of *k*.

k = ...

units = ...

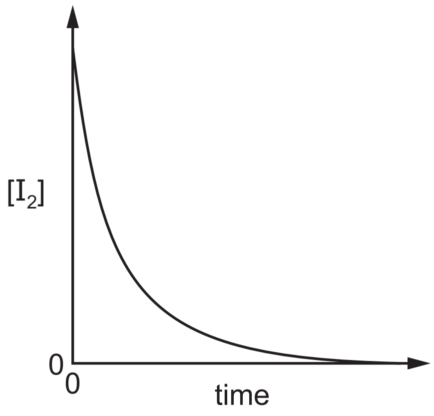
[2]

(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]

(c) From the results, a graph is produced which shows how the concentration of I_2 changes during the reaction.



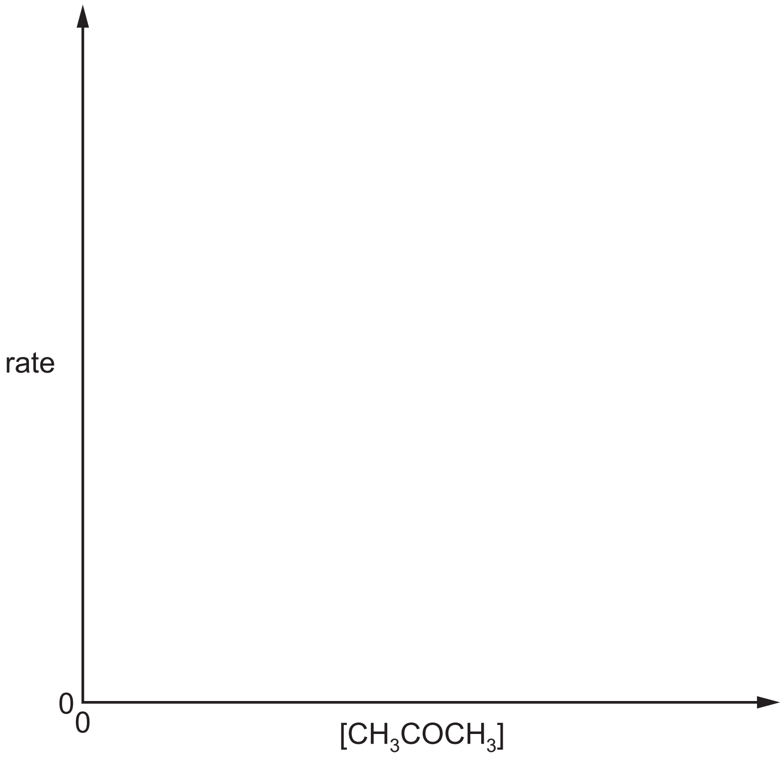
Describe how this graph could be used to determine the initial rate of the reaction.

....

....

.... [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]

(e) The rate of a reaction between metal ions was studied. The following three-step mechanism has been suggested for this reaction. Step 1 is the rate-determining step.

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]

5 **(a)** Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

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]

(d) Some lattice energy values are shown in the table.

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.

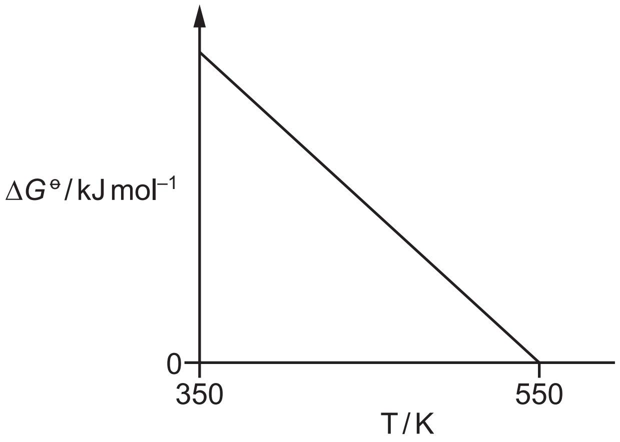
....

....

.... [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]

Question 6 starts on the next page.

6 **(a)** By reference to the formation of σ and π bonds, describe and explain the shape of a benzene molecule, C_6H_6.

....

....

....

....

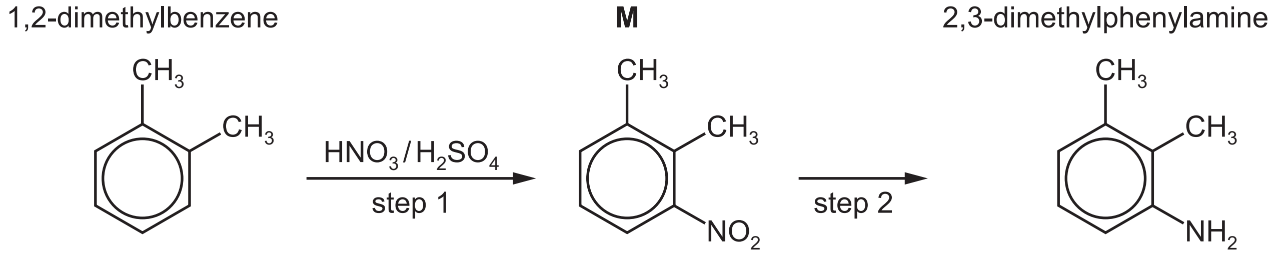
....

....

....

.... [3]

(b) 2,3-dimethylphenylamine can be prepared from 1,2-dimethylbenzene in two steps as shown.

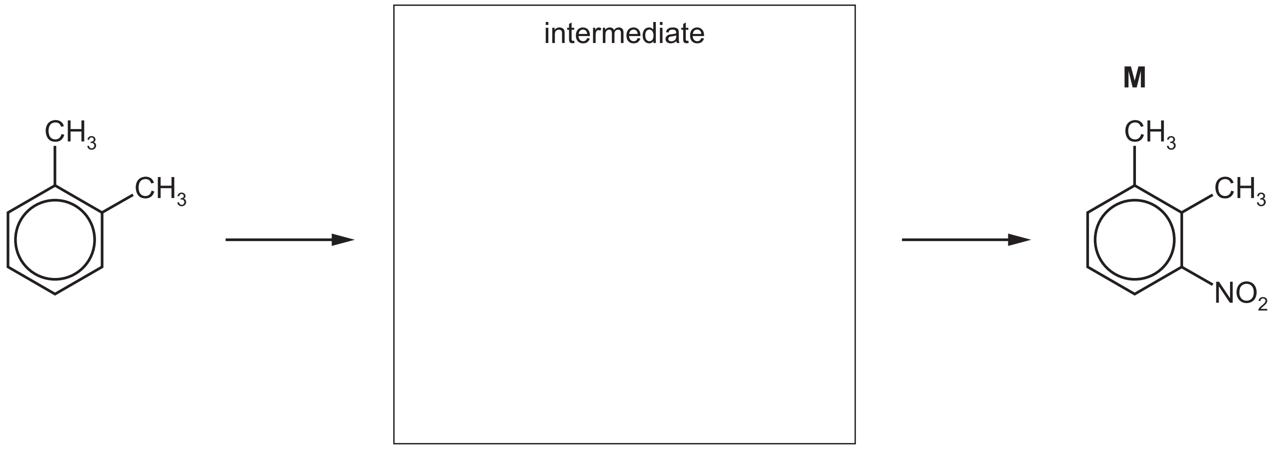


Step 1 is catalysed by H_2SO_4.

(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]

(iii) Write an equation to show how the H_2SO_4 catalyst is reformed.

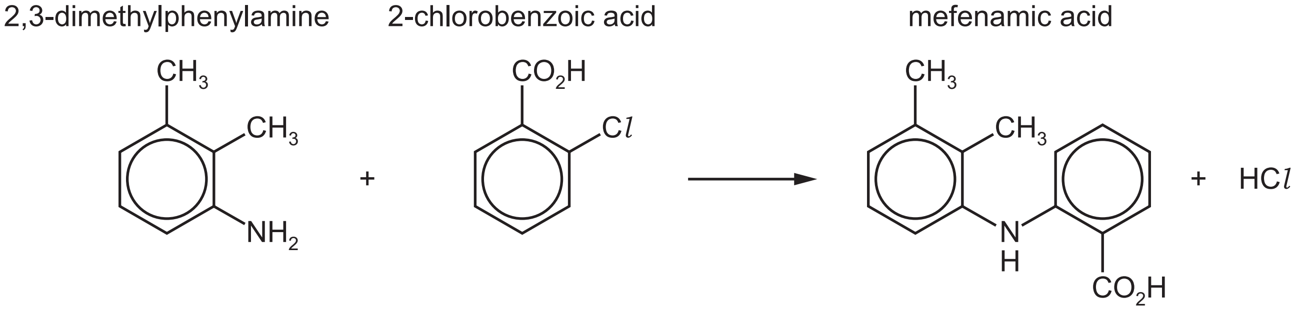
.... [1]

(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.



(i) Deduce the molecular formula of mefenamic acid.

.... [1]

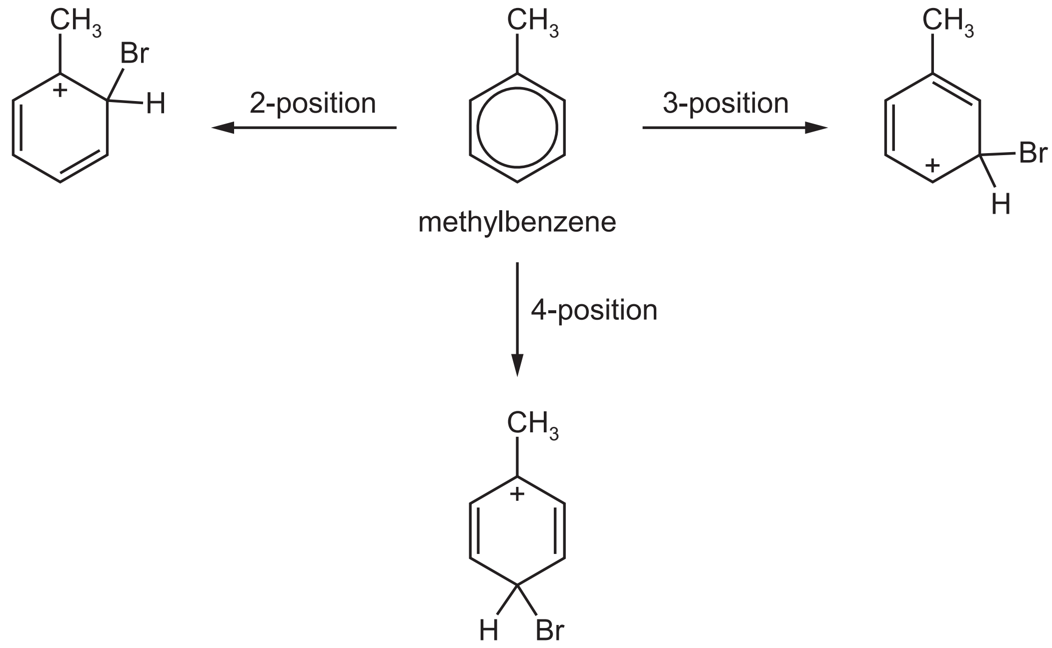
(ii) Name the functional groups, apart from the benzene ring, in mefenamic acid.

.... [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]

(d) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate cations formed in the first step. The example given involves 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.

....

....

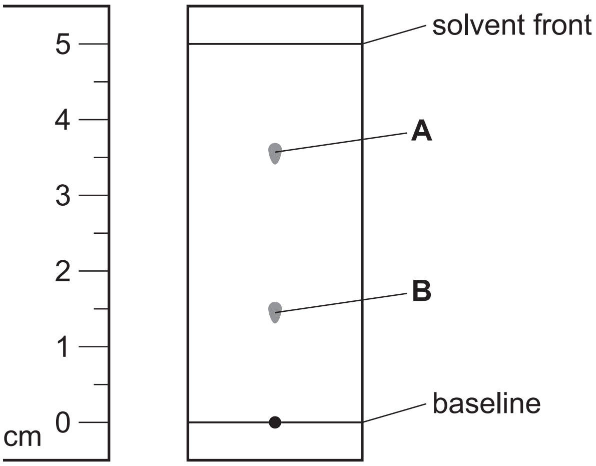
....

.... [2]

[Total: 16]

7 **(a)** Amino acids can be separated by thin-layer chromatography. A mixture of amino acids is analysed using this technique.

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]

(b) 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]

(d) The amino acid alanine can be synthesised from 2-chloropropanoic acid, $CH_3CHClCO_2H$.

(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.

....

....

....

....

.... [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 ($C_6H_{12}N_2O_4$)

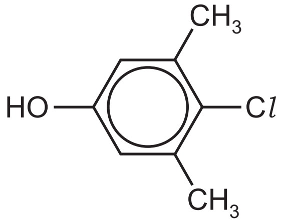
isomer 3 ($C_6H_{12}N_2O_4$)

[3]

[Total: 15]

8 Compound **R** is shown.

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.

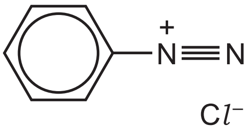
Explain why.

....

.... [1]

(c) Compound **R** reacts separately with the four reagents shown in the table.

Complete the table by
- drawing the structures of the organic products formed,
- stating the type of reaction.

reagent	organic product structure	type of reaction
Na		
CH_3COCl		
$Br_2(aq)$		
		

[6]

[Total: 10]

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