Cambridge Assessment International Education

Cambridge International AS & A Level

CANDIDATE NAME	

CENTRE NUMBER						CANDIDATE NUMBER					

6410435209

CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **October/November 2022**

2 hours

You must answer on the question paper.

No additional materials are needed.

INSTRUCTIONS

- Answer **all** questions.
- Use a black or dark blue pen. You may use an HB pencil for any diagrams or graphs.
- Write your name, centre number and candidate number in the boxes at the top of the page.
- Write your answer to each question in the space provided.
- Do **not** use an erasable pen or correction fluid.
- Do **not** write on any bar codes.
- You may use a calculator.
- You should show all your working and use appropriate units.

INFORMATION

- The total mark for this paper is 100.
- The number of marks for each question or part question is shown in brackets [ ].
- The Periodic Table is printed in the question paper.
- Important values, constants and standards are printed in the question paper.

This document has **24** pages.

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

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

Table 1.1

energy change	value / kJ mol^{-1}
lattice energy, $\Delta H^{\ominus}_{latt}$, $CaCl_2(s)$	–2237
standard enthalpy change of atomisation of calcium	+193
first ionisation energy of calcium	+590
second ionisation energy of calcium	+1150
standard enthalpy change of atomisation of chlorine	+121
first electron affinity of chlorine	–364

(a) Define lattice energy.

.....

..... [1]

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

$\Delta H^{\ominus}_{f}(CaCl_2(s))$ = ... kJ mol^{-1} [2]

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

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

Table 1.2

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

explanation .....

..... [1]

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

Table 1.3

energy change	value / kJ mol^{-1}
standard enthalpy change of solution of $CaCl_2(s)$	–83
standard enthalpy change of hydration of $Ca^{2+}(g)$	–1650

(i) Define the following terms.

enthalpy change of solution .....

.....

enthalpy change of hydration .....

.....
[2]

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

$\Delta H^{\ominus}_{hyd}(Cl^-(g))$ = ... kJ mol^{-1} [2]

(e) Calcium fluoride, $CaF_2(s)$, can be synthesised directly from its elements.

The value of $\Delta H_f^{\ominus}(CaF_2(s))$ is $-1214\,kJ\,mol^{-1}$.

(i) Predict the sign of the entropy change, $\Delta S^{\ominus}$, for this synthesis. Explain your answer.

The sign of the entropy change is ..... .

explanation .....

.....
[1]

(ii) Use the value of $\Delta H_f^{\ominus}(CaF_2(s))$ given in **(e)** and your answer to **(e)(i)** to predict how the feasibility for this synthesis will change with increasing temperature.

.....

.....

.....

..... [2]

[Total: 11]

2 **(a)** Nitrogen monoxide, NO, reacts with ozone, O_3.

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

This reaction is first order with respect to both NO and O_3.
At 298 K, the rate constant k = 11 500 $mol^{-1} dm^3 s^{-1}$.

(i) Complete the rate equation for this reaction.

rate = ...
[1]

(ii) A reaction is carried out in which the initial concentrations of NO and O_3 are both 1.20×10^{-6} $mol\,dm^{-3}$.

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

rate of reaction = ... units = ... [2]

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

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

prediction .....

explanation .....

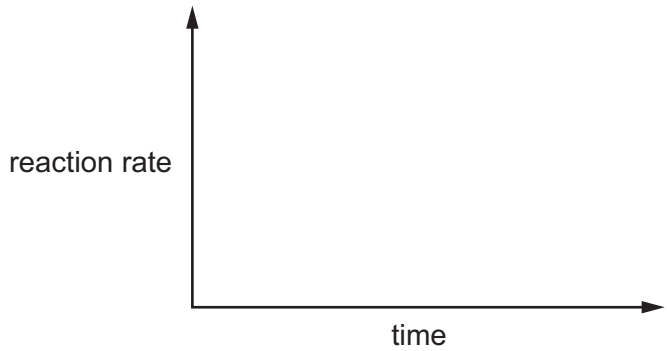
..... [1]

(b) Nitrous oxide, N_2O, decomposes into its elements.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

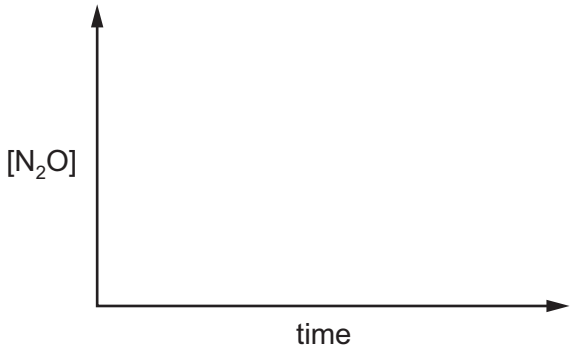
At a high temperature, a small amount of platinum wire is added to a large amount of nitrous oxide. The reaction follows zero order kinetics. The platinum wire behaves as a catalyst.

(i) Sketch a graph, on the axes below, of reaction rate against time for the catalysed decomposition of N_2O under these conditions.



[1]

(ii) Sketch a graph, on the axes below, of $[N_2O]$ against time for this reaction.



[1]

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

Describe the mode of action of a heterogeneous catalyst.

.....

.....

.....

..... [3]

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

.....

..... [1]

[Total: 10]

Question 3 starts on the next page.

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

Table 3.1

electrode reaction	$E^{\ominus}$/V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	–1.18
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1.49
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52

(a) An electrochemical cell can be constructed from a Mg^{2+}/Mg half-cell and a MnO_4^-/Mn^{2+} half-cell. The standard cell potential of this cell can be calculated using the standard electrode potentials of the two half-cells.

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

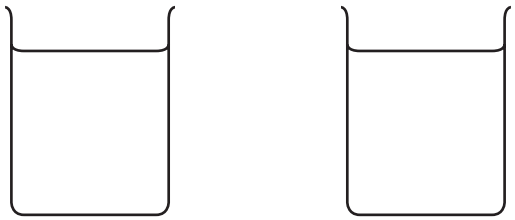
.....

.....

.....

..... [2]

(ii) Complete the diagram below to show an electrochemical cell constructed from a Mg^{2+}/Mg half-cell and a MnO_4^-/Mn^{2+} half-cell.
Label your diagram.



[3]

(iii) Use a positive (+) sign and a negative (–) sign to identify the polarity of each of the two electrodes in your diagram.
Use an arrow and the symbol ‘e’ to show the direction of electron flow in the external circuit. [1]

(iv) Calculate the standard cell potential, $E^{\ominus}_{cell}$, of this cell.

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

(v) Construct an equation for the cell reaction.

..... [1]

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

.....

.....

..... [1]

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

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

Calculate the value of the current used.

current = ... A [2]

[Total: 11]

4 **(a)** The value of the solubility product, K_{sp}, of iron(III) hydroxide, $Fe(OH)_3$, is given by the following expression.

$$K_{sp} = [Fe^{3+}][OH^-]^3 = 2.0 \times 10^{-39}\,mol^4\,dm^{-12}$$

(i) Calculate the solubility of $Fe(OH)_3$ in water.

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

(ii) Calculate the solubility of $Fe(OH)_3$ in $0.010\,mol\,dm^{-3}$ barium hydroxide, $Ba(OH)_2(aq)$.

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

(iii) $Fe(OH)_3$ is less soluble in $Ba(OH)_2(aq)$ than it is in pure water.

Name this effect.

..... [1]

(b) The numerical value of the K_a of HBrO is 2.00×10^{-9}.

X is a solution of HBrO which contains 4.00×10^{-3} mol of HBrO in $100\,cm^3$ of solution. In this solution the following equilibrium is established in which there are two conjugate acid-base pairs.

$$HBrO + H_2O \rightleftharpoons BrO^- + H_3O^+$$

(i) Define conjugate acid-base pair.

.....

..... [1]

(ii) Identify the two conjugate acid-base pairs shown in the equation above.

pair one ....
acid base

pair two ....
acid base

[1]

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

pH = ... [2]

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

Calculate the pH of this buffer solution.

pH = ... [1]

[Total: 9]

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

(a) Define transition element.

.....

..... [1]

(b) An aqueous solution of copper(II) sulfate, $CuSO_4$, contains $[Cu(H_2O)_6]^{2+}$ complex ions. If an excess of concentrated hydrochloric acid is added to this solution a ligand exchange reaction occurs and $[CuCl_4]^{2-}$ complex ions are formed.

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

Table 5.1

complex ion	geometry	coordination number	bond angle
$[Cu(H_2O)_6]^{2+}$			
$[CuCl_4]^{2-}$			

[3]

(ii) In an isolated Cu^{2+} ion the d-orbitals are all degenerate. In a complex ion such as $[Cu(H_2O)_6]^{2+}$ the d-orbitals are non-degenerate.

Define degenerate and non-degenerate in this context.

degenerate .....

non-degenerate .....
[1]

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

.....

..... [1]

(c) Cu^{2+} forms a complex ion containing water molecules and ethanedioate ions, $C_2O_4^{2-}$, as ligands. The formula of the complex is $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$. The ethanedioate ion is a bidentate ligand.

(i) Explain what is meant by bidentate.

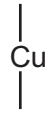
.....

..... [1]

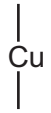
(ii) There are three stereoisomers with the formula $[Cu(C_2O_4)_2(H_2O)_2]^{2-}$.

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

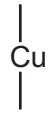
stereoisomer 1



stereoisomer 2



stereoisomer 3



[2]

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

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

Name these two types of isomerism.

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

type of isomerism	pair of stereoisomers
	and
	and

[2]

(d) A solution contains 3.70 g of $Na_2[Cu(C_2O_4)_2(H_2O)_2]$ dissolved in 100 cm^3 of solution. A 25.0 cm^3 sample of this solution is warmed and then oxidised by 0.0100 mol dm^{-3} acidified potassium manganate(VII).

The equation for the redox reaction is shown.

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Calculate the minimum volume of 0.0100 mol dm^{-3} acidified potassium manganate(VII) needed to oxidise all of the ethanedioate ions, $C_2O_4^{2-}$, in the 25.0 cm^3 sample. Show all your working.

[M_r: $Na_2[Cu(C_2O_4)_2(H_2O)_2]$, 321.5]

minimum volume = ... cm^3 [3]

(e) Copper(II) nitrate, $Cu(NO_3)_2$, and barium nitrate, $Ba(NO_3)_2$, both decompose when heated.

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

Suggest a reason for this difference. Explain your answer.

.....

.....

.....

..... [2]

[Total: 16]

6 An aqueous solution of cobalt(II) chloride is a pink colour due to the presence of $[Co(H_2O)_6]^{2+}$ complex ions.

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

Table 6.1

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

[2]

(ii) Write an equation for the reaction between $[Co(H_2O)_6]^{2+}$ ions and NaOH(aq).

..... [1]

(iii) Write an equation for the reaction between $[Co(H_2O)_6]^{2+}$ ions and an excess of conc. HC*l*.

..... [1]

(b) (i) Define stability constant.

.....

..... [1]

(ii) Write an expression for the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion.

K_{stab} =

[1]

(iii) Give the units of the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion.

units = ... [1]

(iv) The numerical value of the stability constant, K_{stab}, of the $[Co(NH_3)_6]^{2+}$ complex ion is 7.7×10^4.

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

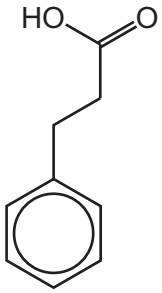
Calculate the concentration of $[Co(H_2O)_6]^{2+}$ in this solution.

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

[Total: 8]

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

$C_6H_5CH_2CH_2COOH$

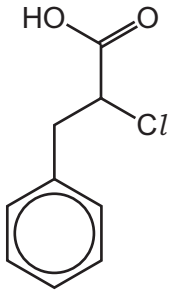


A

$CH_3C_6H_4OH$

B

$C_6H_5CH_2CHClCO_2H$



C

Fig. 7.1

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

..... > ..... > .....
most acidic least acidic

Explain your answer.

.....

.....

.....

..... [3]

(b) Methylbenzene, $C_6H_5CH_3$, can be made from benzene by an electrophilic substitution reaction.

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

compound .....

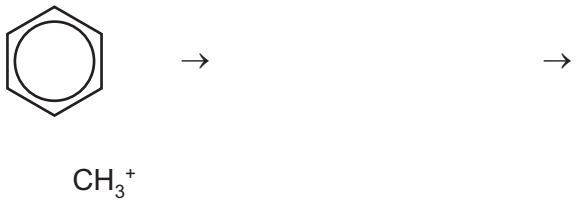
catalyst .....
[1]

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

Write an equation for the reaction that generates this electrophile.

..... [1]

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



[3]

(iv) Identify a suitable reagent to oxidise methylbenzene to benzoic acid, C_6H_5COOH.

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

reagent .....

equation .....

[2]

(v) Methylbenzene and benzoic acid are both nitrated with a mixture of concentrated nitric acid and sulfuric acid to give mononitrated products. The structural formulae of these products are $CH_3C_6H_4NO_2$ and $HOOCC_6H_4NO_2$ respectively.

Draw the structures of these two products.

[1]

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

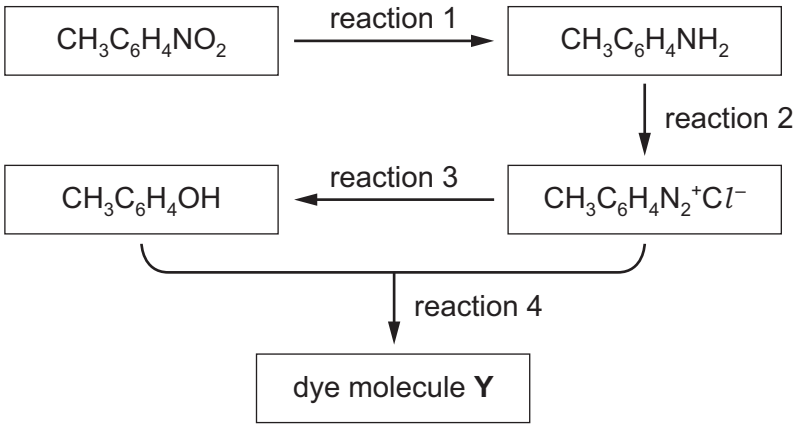


Fig. 7.2

(i) Describe the reagents and conditions to produce $CH_3C_6H_4N_2^+Cl^-$ from $CH_3C_6H_4NH_2$ in reaction 2.

reagents .....

conditions .....
[1]

(ii) Describe how $CH_3C_6H_4OH$ can be produced from $CH_3C_6H_4N_2^+Cl^-$ in reaction 3.

..... [1]

(iii) Draw the structure of the dye molecule **Y** formed when $CH_3C_6H_4N_2^+Cl^-$ and $CH_3C_6H_4OH$ react together in reaction 4. Describe the conditions for this reaction.

structure

conditions .....
[2]

[Total: 15]

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

P $C_6H_5COCH(CH_3)_2$

Q $C_6H_5COCH_2CH_2CH_3$

R $C_6H_5CH_2COCH_2CH_3$

S $C_6H_5CH_2CH_2COCH_3$

T $C_6H_5CH(CH_3)COCH_3$

(a) Identify all the chiral carbon atoms on the structures above. Label each chiral carbon atom with an asterisk (*). [1]

(b) The proton (^1H) NMR spectrum of one of the five isomers, **P**, **Q**, **R**, **S** or **T**, is shown in Fig. 8.1.

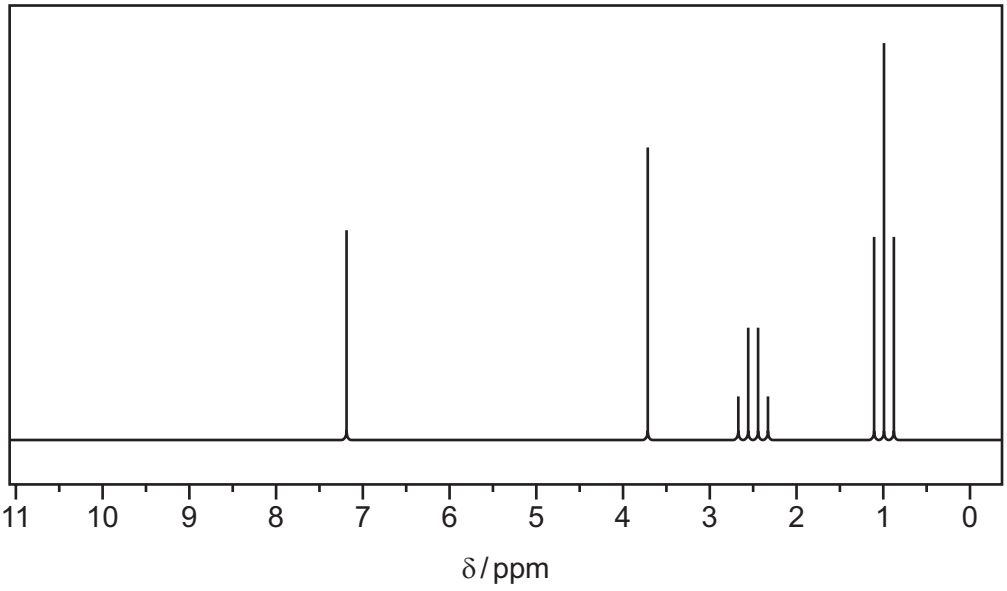


Fig. 8.1

(i) Identify which of the compounds **P**, **Q**, **R**, **S** or **T** gives this spectrum.
Draw the displayed formula of the compound you have identified. Identify the protons responsible for the peaks at δ = 3.7, δ = 2.5 and δ = 1.0 on the structure you have drawn.

[2]

(ii) Name the splitting pattern of the peak at δ = 3.7. Explain why it has this splitting pattern.

.....

..... [1]

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

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

..... [1]

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

..... [1]

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

..... [1]

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

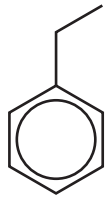
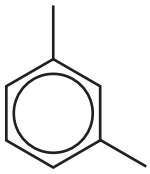
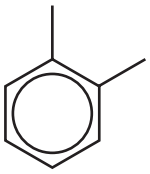
Describe any difference between the two spectra. Explain your answer.

.....

..... [1]

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

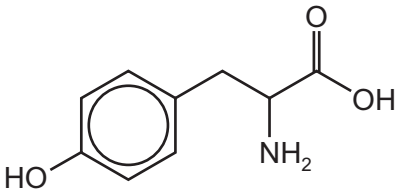
Table 8.1

compound	number of peaks	compound	number of peaks
			
			

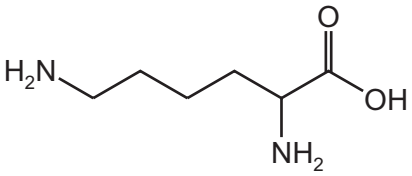
[2]

[Total: 10]

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



tyrosine



lysine

Fig. 9.1

(a) The isoelectric point of lysine is 9.47.

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

lysine at pH 7.00	lysine at pH 9.47	lysine at pH 12.00

[2]

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

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

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

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

D	**E**	**F**

[3]

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

Ignore the directing effect of the $–CH_2CHNH_2COOH$ substituent.

Table 9.1

reagent	structure
an excess of Br_2(aq)	
an excess of NaOH(aq)	
an excess of HNO_3(aq)	

[3]

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

(i) Explain what is meant by R_f value.

.....

..... [1]

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

.....

..... [1]

[Total: 10]

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Important values, constants and standards

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

The Periodic Table of Elements

Key

atomic number
atomic symbol
name
relative atomic mass

Group

1	2											13	14	15	16	17	18
							1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

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