

SECTION A

Answer ALL parts of this question in the spaces provided.

1. Ascorbic acid, vitamin C, is an essential nutrient for many animals. It is a reducing agent which acts as an antioxidant in biological systems. It is very soluble in water and its concentration (e.g. in fruit juice) can be found as follows.

Procedure

- A known volume of the solution containing ascorbic acid is acidified with dilute sulphuric acid and about 1 g of solid potassium iodide is dissolved in the mixture.
- 2–3 cm³ of starch solution is added.

The mixture is titrated with a standard solution of potassium iodate(V), KIO₃, until the appearance of a permanent blue colour.

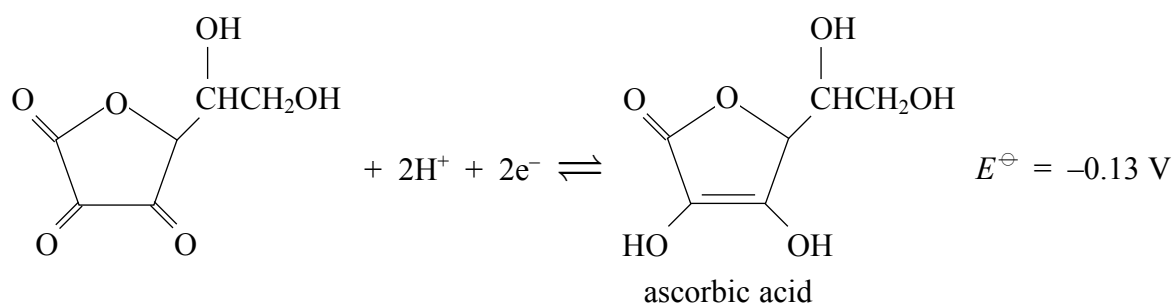
The following reactions occur.

- Iodate(V) ions react with iodide ions to form iodine.
- As soon as iodine is produced, it is reduced to iodide ions by the ascorbic acid.
- When the ascorbic acid has been used up, the next iodine to be produced by the iodate(V) ions reacts with the starch to give a blue colour.



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- (a) (i) Use the data below to show that iodine can be reduced by ascorbic acid. State the molar ratio in which they react.



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(2)

- (ii) The reaction that produces the iodine is



In an experiment as described on page 2, 25.00 cm³ of a solution containing ascorbic acid required a mean titre of 20.83 cm³ of a potassium iodate(V) solution of concentration 0.0100 mol dm⁻³.

Calculate the mass of ascorbic acid (molar mass 176 g mol⁻¹) present in 25.00 cm³ of the solution.

(4)



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- (b) (i) Explain how the intermolecular forces between ascorbic acid and water molecules form. Hence explain why it is very soluble in water.

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(3)

- (ii) Draw the structure of the molecule produced by heating ascorbic acid under reflux with potassium dichromate(VI) and sulphuric acid. Assume that the ring structure remains intact.

(1)

Q1

(Total 10 marks)

TOTAL FOR SECTION A: 10 MARKS



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NOW TURN OVER FOR SECTION B



SECTION B

Answer any TWO questions from this section in the spaces provided.

If you answer Question 2 put a cross in this box .

2. Double bonds are very important in synthetic chemistry, usually being much more reactive than single bonds.

(a) The C=C and C=O bonds have the same electronic structure.

(i) Draw 'dot and cross' diagrams of ethene, $\text{H}_2\text{C}=\text{CH}_2$, and of methanal, $\text{H}_2\text{C}=\text{O}$, to show that this is so. Show outer electrons only.

(1)

(ii) C=C and C=O bonds undergo different types of addition reaction. State the type of reaction in each case and explain the difference.

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(3)



(b) Propenenitrile, $\text{H}_2\text{C}=\text{CHCN}$, is polymerised to make *Orlon*. Assuming the presence of a radical initiator, $\text{R}\cdot$, show the polymerisation mechanism as far as a radical containing two propenenitrile units. Mechanistic arrows must **not** be used.

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(2)



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Turn over

(c) Propenenitrile, $\text{H}_2\text{C}=\text{CHCN}$, is also used to make Nylon.

Propenenitrile is first reduced to hexanedinitrile, $\text{NC}(\text{CH}_2)_4\text{CN}$, which is then reduced further to give 1,6-diaminohexane, $\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$.

(i) Suggest a suitable reagent and conditions for the reduction of hexanedinitrile to 1,6-diaminohexane.

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(2)

(ii) Explain whether, or not, your suggested method would be suitable for use on an industrial scale.

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(1)

(iii) Nylon-6,6 is made from 1,6-diaminohexane and hexanedioyl dichloride, $\text{ClOC}(\text{CH}_2)_4\text{COCl}$.

Draw the repeating unit of the polymer and identify the other molecule produced when the polymer is formed.

Repeating unit:

Identity of other molecule produced

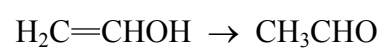
(2)



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(d) Polyvinyl alcohol $(\text{CH}_2\text{—CH(OH)})_n$ is a water-soluble polymer. All attempts to make its monomer vinyl alcohol, $\text{H}_2\text{C=CHOH}$, have failed, the product invariably being CH_3CHO .

Use the bond enthalpies below to calculate the enthalpy change for the conversion of $\text{H}_2\text{C=CHOH}$ to CH_3CHO and suggest why vinyl alcohol does **not** exist.



bond	C=C	C—O	O—H	C—H	C—C	C=O
bond enthalpy / kJ mol^{-1}	612	360	463	412	348	743

(2)

QUESTION 2 CONTINUES ON THE NEXT PAGE



N 3 3 9 1 3 A 0 9 2 0

(e) Give the mechanism for the reaction between ethanal and hydrogen cyanide, HCN, in the presence of cyanide ions.

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(3)



(f) The C=N bond also has the same electronic structure as C=C and C=O.

(i) By analogy with the reaction of the C=O bond with Grignard reagents, suggest the structural formula of the compound that is formed when methylmagnesium

bromide reacts with the compound $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{N} \\ / \\ \text{H} \end{array}$ and the product is then hydrolysed.

(1)

(ii) By analogy with compounds containing the C=C group, suggest in terms of the electronic structure and the bond angle around the nitrogen atom, why the

nitrogen compound $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{N} \\ / \\ \text{H} \end{array}$ has a stereoisomer.

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(2)

(iii) Draw the structure of the other stereoisomer.

(1)

Q2

(Total 20 marks)



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If you answer Question 3 put a cross in this box .

3. Water is one of the most important chemicals we use; this question is about various aspects of the chemistry of water.

(a) (i) Draw the shape of a water molecule, marking the bond angle on your diagram. Explain why the molecule has this shape and is polar overall.

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(3)

(ii) Explain why the polarity of the water is important in dissolving ionic compounds.

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(2)



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(iii) Draw a fully labelled Hess's Law cycle to show the enthalpy changes involved in dissolving potassium bromide, KBr, in water. Use it, and the data below, to determine the enthalpy of solution.

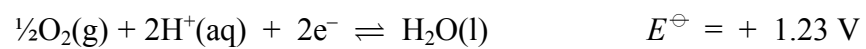
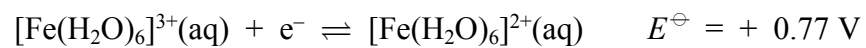
$\Delta H_{\text{latt}}(\text{KBr})$	-670 kJ mol^{-1}
$\Delta H_{\text{hydration}}(\text{K}^+)$	-322 kJ mol^{-1}
$\Delta H_{\text{hydration}}(\text{Br}^-)$	-335 kJ mol^{-1}

(3)

QUESTION 3 CONTINUES ON THE NEXT PAGE



(b) The following standard electrode potentials are required to answer this question.



(i) Write the overall equation for the oxidation of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ions by molecular oxygen in acidic solution. State, with a reason, whether the reaction is feasible under standard conditions.

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(2)

(ii) State, with a reason, whether the oxidation by molecular oxygen of hexacyanoferrate(II) ions, $[\text{Fe}(\text{CN})_6]^{4-}$, to hexacyanoferrate(III) ions, $[\text{Fe}(\text{CN})_6]^{3-}$, is more or less likely than the similar oxidation involving the hexaaqua ions.

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(1)

(c) Water reacts vigorously with silicon tetrachloride, SiCl_4 , at room temperature. However, carbon tetrachloride, CCl_4 , does **not** react with water.

(i) Give the equation for the reaction between water and silicon tetrachloride. State symbols are **not** required.

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(1)



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(ii) Explain why **carbon tetrachloride** does **not** react with water.

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(3)

(d) Solid magnesium chloride dihydrate, $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, gives off hydrogen chloride when heated in a dry tube. Explain why this occurs and identify the residue.

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(2)

(e) Primary halogenoalkanes are hydrolysed by water much more slowly than tertiary halogenoalkanes.

State briefly how you could demonstrate the difference in rate, using test tube reactions and the compounds 1-bromobutane and 2-bromo-2-methylpropane.

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(Total 20 marks)

Q3

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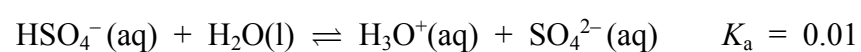
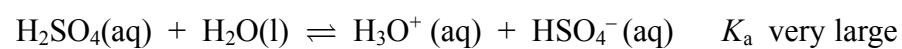
If you answer Question 4 put a cross in this box .

4. Sulphuric acid is one of the most important of all inorganic chemicals.

- (a) (i) Commercial concentrated sulphuric acid contains 98% H_2SO_4 and 2% water, and has a density of 1800 g dm^{-3} . Calculate its concentration in mol dm^{-3} .

(2)

- (ii) In an aqueous solution of sulphuric acid the following equilibria exist.



(K_a values at 25°C)

The pH of a 0.10 mol dm^{-3} solution of sulphuric acid at 25°C is 0.98. The strong monobasic acid, hydrochloric acid, of the same concentration has a pH of 1.

Explain, in terms of the equilibria above, why the pH values are very similar.

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(2)



(b) Concentrated sulphuric acid is a strong acid and an oxidising agent and reacts in different ways with different halide ions.

(i) Write the equation for the reaction of concentrated sulphuric acid with solid sodium chloride. State symbols are **not** required.

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(1)

(ii) The reaction of concentrated sulphuric acid with solid sodium bromide gives hydrogen bromide, bromine, and sulphur dioxide. With sodium iodide the products include iodine, sulphur dioxide, sulphur and hydrogen sulphide.

Use this information, and your answer to (i), to state and explain the trend in reducing ability of the halide ions.

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(3)

(c) Chloroalkanes and bromoalkanes can be made by reacting an alcohol with the sodium halide in 50% aqueous sulphuric acid. This method cannot be used to make iodoalkanes.

(i) State the reagents which are used to make 1-iodobutane from butan-1-ol.

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(2)

(ii) Give the formula of the compound formed from the reagents in (i) that then reacts with the alcohol.

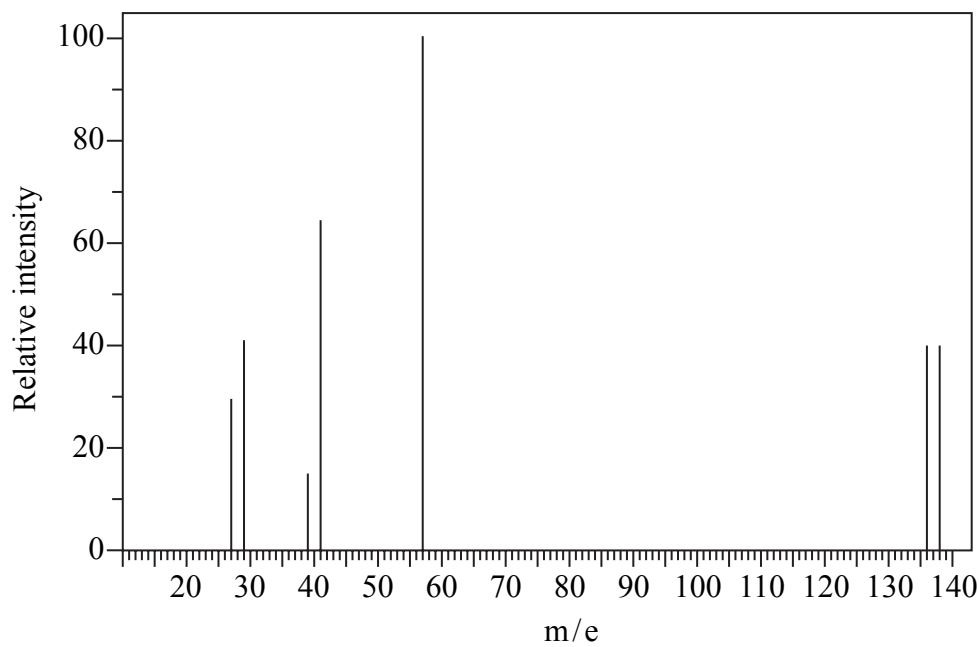
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(1)

QUESTION 4 CONTINUES ON THE NEXT PAGE



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(d) The mass spectrum of a primary halogenobutane is given below.



(i) Explain why the peak at m/e 29 is consistent with the compound being an unbranched halogenobutane.

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(1)

(ii) The natural isotopic composition of the halogens is given below, with the percentage abundance of each isotope shown in brackets.

chlorine-35 (75%)	chlorine-37 (25%)
bromine-79 (50%)	bromine-81 (50%)
iodine-127 (100%)	

Which halogenobutane generated the mass spectrum? Give TWO reasons for your choice.

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(2)



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(e) 1-bromobutane can be converted into but-1-ene.

(i) Give the reagent and the solvent needed for this conversion.

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(1)

(ii) If HBr is added to 1-butene, the major product is 2-bromobutane. Give the mechanism for this reaction.

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(iii) Explain why the major product is 2-bromobutane rather than 1-bromobutane.

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(2)

Q4

(Total 20 marks)

TOTAL FOR SECTION B: 40 MARKS

TOTAL FOR PAPER: 50 MARKS

END

19



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THE PERIODIC TABLE

Period **1** **2** **3** **4** **5** **6** **7** **0** Group

Period

		Key																																																			
		Molar mass g mol ⁻¹		Symbol		Name		Atomic number																																													
1	1	1	H	Hydrogen	1							4	He	Helium	2																																						
2	2	7	Li	Lithium	3	9	Be	Beryllium	4							20	Ne	Neon	10																																		
3	3	23	Na	Sodium	11	24	Mg	Magnesium	12	31	P	Phosphorus	15	32	S	Sulphur	16	35.5	Cl	Chlorine	17	40	Ar	Argon	18																												
4	4	39	K	Potassium	19	40	Ca	Calcium	20	59	Ni	Nickel	28	63.5	Cu	Copper	29	70	Ga	Gallium	31	75	As	Arsenic	33	79	Se	Selenium	34	80	Br	Bromine	35	84	Kr	Krypton	36																
5	5	85	Rb	Rubidium	37	88	Sr	Strontium	38	99	Mn	Manganese	25	101	Ru	Ruthenium	44	106	Pd	Palladium	46	108	Ag	Silver	47	112	Cd	Cadmium	48	119	Sn	Tin	50	122	Sb	Antimony	51	127	I	Iodine	53	131	Xe	Xenon	54								
6	6	133	Cs	Caesium	55	137	Ba	Barium	56	186	Re	Rhenium	75	190	Os	Osmium	76	195	Pt	Platinum	78	197	Au	Gold	79	201	Hg	Mercury	80	204	Tl	Thallium	81	209	Bi	Bismuth	83	210	Po	Polonium	84	210	At	Astatine	85	222	Rn	Radon	86				
7	7	223	Fr	Francium	87	226	Ra	Radium	88	227	Ac	Actinium	89																																								
		140	Ce	Cerium	58	141	Pr	Praseodymium	59	144	Nd	Neodymium	60	150	Sm	Samarium	62	152	Eu	Europium	63	157	Gd	Gadolinium	64	159	Tb	Terbium	65	163	Dy	Dysprosium	66	165	Ho	Holmium	67	167	Er	Erbium	68	169	Tm	Thulium	69	173	Yb	Ytterbium	70	175	Lu	Lutetium	71
		232	Th	Thorium	90	231	Pa	Protactinium	91	237	Np	Neptunium	93	242	Pu	Plutonium	94	243	Am	Americium	95	247	Cm	Curium	96	245	Bk	Berkelium	97	251	Cf	Californium	98	254	Es	Einsteinium	99	253	Fm	Fermium	100	256	Md	Mendelevium	101	254	No	Nobelium	102	257	Lr	Lawrencium	103

