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Surname: StemUp Model Solution | Other names:

Pearson Edexcel Level 3 GCE

Centre Number | Candidate Number

Chemistry

Advanced

Paper 2: Advanced Organic and Physical Chemistry

Tuesday 12 June 2018 – Afternoon
Time: 1 hour 45 minutes

Paper Reference
9CH0/02

Candidates must have: Data Booklet
Scientific calculator
Ruler

Total Marks

Instructions

- Use **black** ink or **black** ball-point pen.
- **Fill in the boxes** at the top of this page with your name, centre number and candidate number.
- Answer **all** questions.
- Answer the questions in the spaces provided
  – *there may be more space than you need.*

Information

- The total mark for this paper is 90.
- The marks for **each** question are shown in brackets
  – *use this as a guide as to how much time to spend on each question.*
- For the question marked with an asterisk (*), marks will be awarded for your ability to structure your answer logically showing the points that you make are related or follow on from each other where appropriate.
- A Periodic Table is printed on the back cover of this paper.

Advice

- Read each question carefully before you start to answer it.
- Check your answers if you have time at the end.
- Show all your working in calculations and include units where appropriate.

Turn over ▶

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Answer ALL questions.

Some questions must be answered with a cross in a box ☒.
If you change your mind about an answer, put a line through the box ☒ and then mark your new answer with a cross ☒.

1 This question is about alkanes.

(a) The reaction of ethane and chlorine in UV radiation produces chloroethane.

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

This reaction is classified as

(1)

☒ **A** addition

☒ **B** elimination

☒ **C** initiation

☒ **D** substitution

(b) The black smoke produced from the incomplete combustion of alkane fuels is

(1)

☒ **A** carbon particulates

☒ **B** oxides of nitrogen

☒ **C** oxides of sulfur

☒ **D** unburnt hydrocarbons

(c) A reaction of hexane is shown below.



This is **best** described as

(1)

☒ **A** elimination

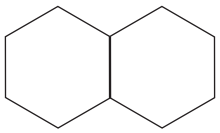
☒ **B** hydrogenation

☒ **C** isomerisation

☒ **D** reforming

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(d) The skeletal formula of decalin is



The molecular formula of decalin is

(1)

☒ **A** $C_{10}H_{22}$

☒ **B** $C_{10}H_{20}$

☒ **C** $C_{10}H_{18}$

☒ **D** $C_{10}H_{16}$

(Total for Question 1 = 4 marks)

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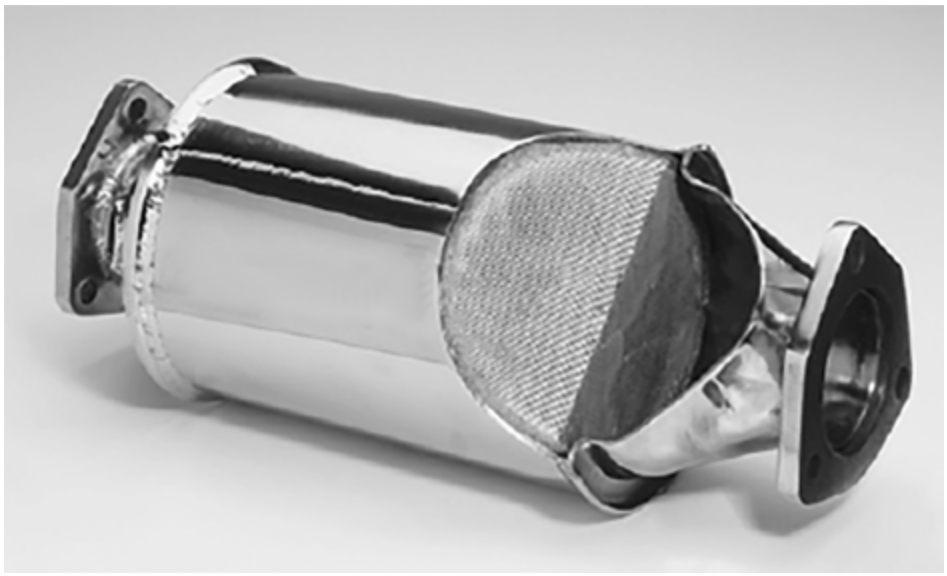
2 This question is about how catalysts work.

(a) Gaseous reactants attach to the catalytic surface by the process of

(1)

- ☒ **A** absorption
- ☒ **B** activation
- ☒ **C** adsorption
- ☒ **D** desorption

(b) Catalytic converters of car exhaust systems have internal honeycomb structures as shown.



Explain why the honeycomb structure is used in a car exhaust system.

(2)

The honeycomb gives the catalyst a very large surface area, so there are more active sites for the exhaust gases to adsorb onto.

The open channels also allow the exhaust gases to flow through the exhaust easily without blocking it.

(Total for Question 2 = 3 marks)

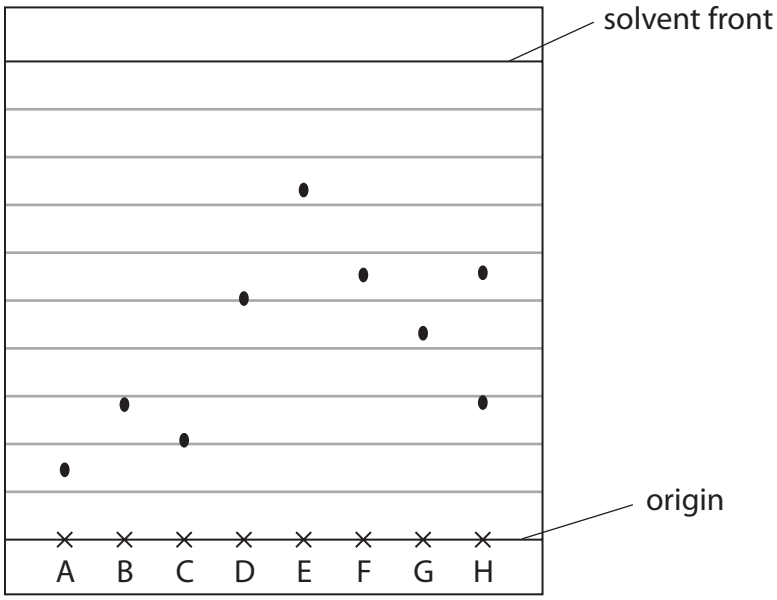
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3 Chromatography is a technique used to separate the components of a mixture.

(a) A sample of a tripeptide was hydrolysed and then placed on a thin layer chromatography (TLC) plate. Samples of possible amino acids present were also placed on the TLC plate for reference.
A simplified diagram of the developed TLC plate is shown.



A – Lysine	B – Serine	C – Histidine	D – Tyrosine
E – Isoleucine	F – Methionine	G – Proline	H – Hydrolysed tripeptide

(i) Calculate the R_f value for the amino acid lysine.
Give your answer to an appropriate number of significant figures.

(1)

R_f = distance moved by lysine ÷ distance moved by solvent

R_f = 1.5 ÷ 10 = 0.15

(ii) Identify by **name** the two amino acids present in the tripeptide, giving a reason for the lack of a third spot.

(3)

Serine and methionine (the spots for H match B and F).

There is no third spot because one of these amino acids is present twice in the tripeptide (e.g. two serine units), so only two different amino acids are released on hydrolysis.

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(iii) Give **two** reasons why different amino acids have different R_f values.

(2)

The amino acids have different solubilities in the mobile phase (the solvent).

They have different adsorption to (affinity for) the stationary phase, due to different intermolecular forces.

(iv) In chromatography, a 'locating' reagent is often used when the components in a mixture are colourless.

Which reagent is used to locate the amino acid spots?

(1)

- ☒ **A** iodine
- ☒ **B** methyl orange
- ☒ **C** ninhydrin
- ☒ **D** phenolphthalein

(b) Gas chromatography can be used both to separate the components in a mixture and to determine the amount of each present.

(i) State why argon and nitrogen are suitable carrier gases for gas chromatography.

(1)

They are inert, so they do not react with the components of the mixture.

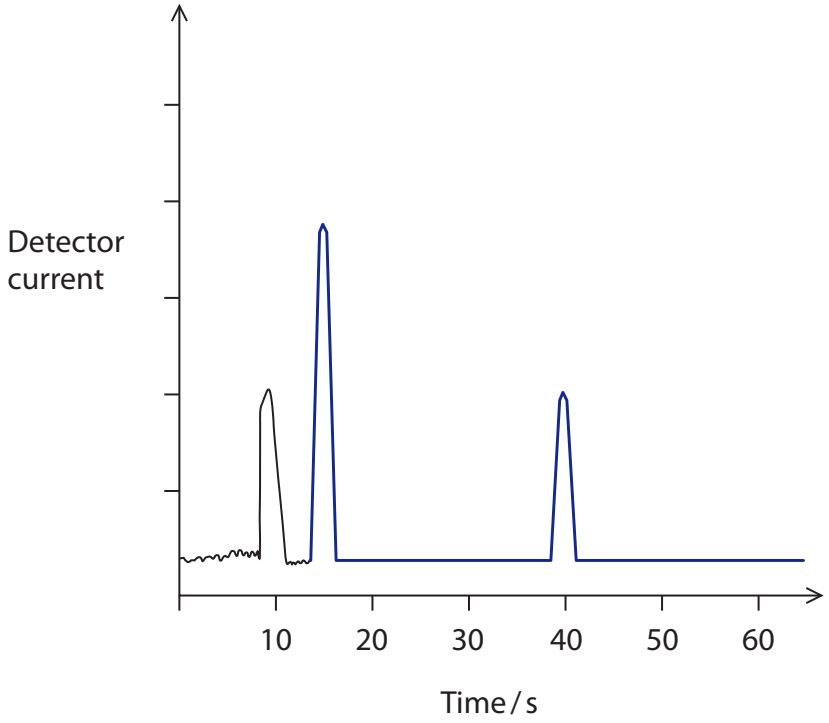
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(ii) A mixture containing one part substance **X**, two parts substance **Y** and one part substance **Z** was separated by gas chromatography.

Substance **X** has a retention time of 10 seconds, substance **Y** of 15 seconds and substance **Z** of 40 seconds.

Complete the sketch of this chromatogram.

(3)



(Total for Question 3 = 11 marks)

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4 Many vehicles are fitted with airbags which provide a gas-filled safety cushion to protect the occupant of the vehicle if there is a crash.

(a) The first reaction in airbags is the thermal decomposition of sodium azide, NaN_3, to form sodium and nitrogen gas.

(i) Write the equation for this decomposition of sodium azide.
State symbols are not required.

(1)

$2NaN_3 \rightarrow 2Na + 3N_2$

(ii) In the reaction in (a)(i), a typical airbag is inflated by about 67 dm^3 of gas. Calculate the **minimum mass** of sodium azide, in grams, needed to produce this volume of gas. Use the Ideal Gas Equation and give your answer to an appropriate number of significant figures.

For the purpose of this calculation, assume that the temperature is 300 °C and the pressure is 140 000 Pa.

(4)

$T = 300 + 273 = 573$ K and $V = 67\ dm^3 = 0.067\ m^3$

$pV = nRT$, so $n(N_2) = pV \div RT$

$n(N_2) = (140\ 000 \times 0.067) \div (8.31 \times 573) = 1.970$ mol

$n(NaN_3) = 2/3 \times 1.970 = 1.313$ mol

$M(NaN_3) = 23.0 + (3 \times 14.0) = 65.0\ g\ mol^{-1}$

mass $= 1.313 \times 65.0 = 85.4$ g

minimum mass of $NaN_3 = 85.4$ g

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(b) The second reaction in the airbag is between the sodium produced in the reaction (a)(i) and potassium nitrate.

$$10\ Na + 2\ KNO_3 \rightarrow 1\ K_2O + 5\ Na_2O + 1\ N_2$$

Balance the above equation, justifying your answer in terms of the changes in oxidation numbers.

(3)

Na: 0 → +1 (oxidised, loses $1e^-$); N in KNO_3: +5 → 0 in N_2 (reduced, gains $5e^-$).

2N gain $10e^-$, so 10Na lose $10e^-$: $10Na + 2KNO_3 \rightarrow K_2O + 5Na_2O + N_2$

(c) The third reaction in the airbag is between the metal oxides and silicon dioxide.

State the type of reaction taking place and justify why this reaction is necessary.

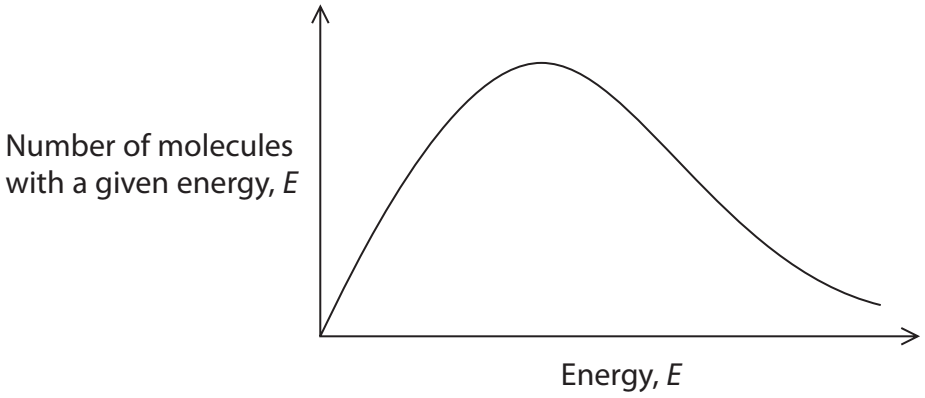
(3)

It is a neutralisation (acid-base) reaction: the basic metal oxides react with acidic SiO_2 to form salts (silicates).

It is necessary because sodium oxide and potassium oxide are caustic (corrosive) and would harm the occupant.

The silicates formed are inert (unreactive), so they are not harmful.

(d) The Maxwell-Boltzmann distribution diagram shows the molecular energies for the gaseous system immediately after the airbag has been deployed.



What is the change in shape of the curve when the airbag **cools**?

(1)

☒ **A** the peak would shift to the left and be higher

☒ **B** the peak would shift to the left and be lower

☒ **C** the peak would shift to the right and be higher

☒ **D** the peak would shift to the right and be lower

(Total for Question 4 = 12 marks)

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5 Some alcohols can be oxidised by acidified sodium dichromate(VI), $Na_2Cr_2O_7$.

(a) Balance the ionic half-equation for the reduction of the dichromate(VI) ion. Give the colours of all of the species involved, or state colourless if appropriate.

(2)

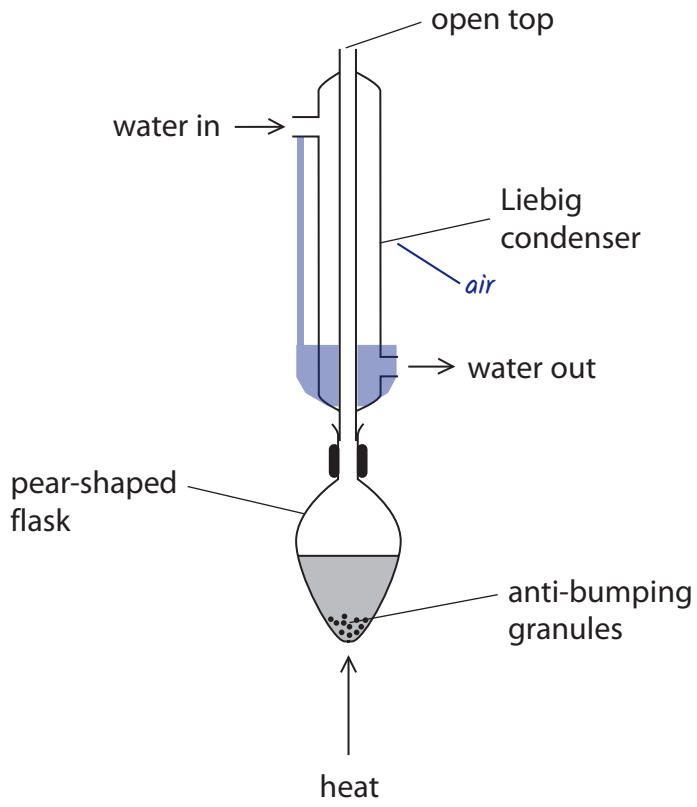
$$Cr_2O_7^{2-} + \underline{14}H^+ + \underline{6}e^- \rightarrow \underline{2}Cr^{3+} + \underline{7}H_2O$$

Colour *orange* *colourless* *green* *colourless*

(b) Reflux apparatus can be used to carry out the oxidation of alcohols.

(i) This Liebig condenser has been set up incorrectly. Add shading to the diagram to show the water in the condenser, illustrating the effect of the incorrect water flow.

(1)



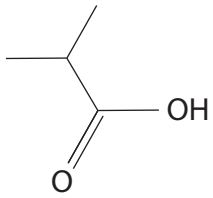
(ii) State how the granules prevent bumping.

(1)

The granules provide a rough surface (nucleation sites) on which many small bubbles form, so the liquid boils smoothly instead of forming large bubbles suddenly.

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(c) The carboxylic acid shown can be produced by oxidation of an alcohol under reflux.



Which alcohol would be oxidised under reflux to produce this carboxylic acid?

(1)

☒ **A** 1,1-dimethylethanol

☒ **B** 2-methylpropan-1-ol

☒ **C** 2-methylbutan-1-ol

☒ **D** propan-2-ol

(d) Using the apparatus for distillation instead of reflux is not an efficient way to produce ethanoic acid from ethanol. Explain why.

(2)

Ethanol is only partially oxidised to ethanal (an aldehyde) in distillation.

Ethanal has a low boiling temperature (it is more volatile), so it distils off as soon as it forms, before it can be oxidised further to ethanoic acid.

(Total for Question 5 = 7 marks)

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6 This is a question about the hydrolysis of halogenoalkanes.

(a) Devise an experiment, giving outline details only, that would enable the relative rates of hydrolysis of halogenoalkanes to be compared.

(5)

Put equal volumes (e.g. 1 cm^3) of ethanol, as a solvent, into three test tubes.

Add equal amounts (e.g. 5 drops) of 1-chlorobutane, 1-bromobutane and 1-iodobutane, one to each tube.

Stand the tubes, and a tube of aqueous silver nitrate solution, in a water bath at the same temperature (e.g. 50 °C).

Add equal volumes (e.g. 1 cm^3) of silver nitrate solution to each tube at the same time and start a stop clock.

Water hydrolyses the halogenoalkane, and the halide ions released form a silver halide precipitate.

Measure the time taken for a precipitate to appear in each tube: the shorter the time, the faster the rate of hydrolysis.

(b) Explain the trend in the rates of hydrolysis of 1-chlorobutane, 1-bromobutane and 1-iodobutane.

(2)

The rate of hydrolysis increases in the order 1-chlorobutane < 1-bromobutane < 1-iodobutane.

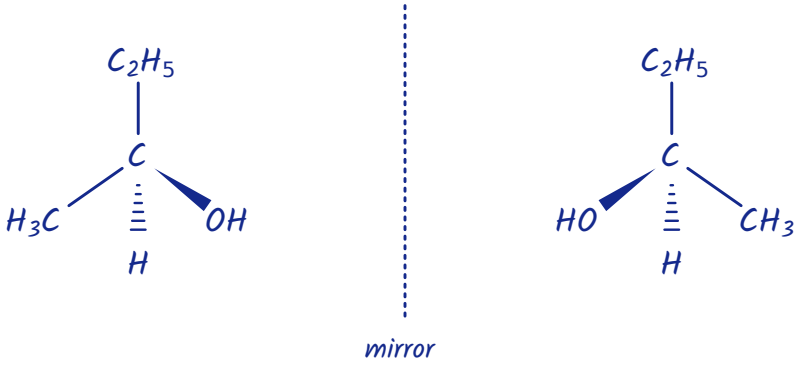
This is because the C-Cl bond is stronger than the C-Br bond, which is stronger than the C-I bond, so the C-I bond breaks most easily.

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(c) The product of the hydrolysis of 2-bromobutane is butan-2-ol. Both molecules are chiral.

State what is meant by the term chiral, using three-dimensional diagrams of the enantiomers of butan-2-ol to illustrate your answer.

(3)



A chiral molecule has a carbon atom with four different groups attached (here H, OH, CH_3 and C_2H_5).

So it exists as two optical isomers (enantiomers), which are non-superimposable mirror images of each other.

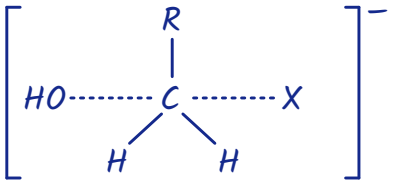
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*(d) Compare and contrast the mechanism of hydrolysis, using aqueous potassium hydroxide, of the primary halogenoalkane, RCH_2X, with that of the tertiary halogenoalkane, R_3CX. Include diagrams of any intermediate or transition state.

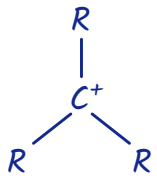
Curly arrows are not required.

(6)

S_N2 transition state (RCH_2X):



S_N1 carbocation intermediate (R_3CX):



Similarity: both are nucleophilic substitution reactions, in which the OH^- ion (the nucleophile) replaces the halogen X to form an alcohol and X^-.

Difference: the primary halogenoalkane, RCH_2X, is hydrolysed by an S_N2 mechanism, which goes through a transition state (drawn above), whereas the tertiary halogenoalkane, R_3CX, is hydrolysed by an S_N1 mechanism, which goes through a carbocation intermediate (drawn above).

In S_N2 the OH^- attacks the δ+ carbon from the side opposite to X while the C-X bond breaks, in a single step. So both RCH_2X and OH^- are in the rate-determining step and rate = $k[RCH_2X][OH^-]$.

In S_N1 the C-X bond first breaks heterolytically in the slow, rate-determining step, forming the carbocation R_3C^+ and X^-. Only R_3CX is in the rate-determining step, so rate = $k[R_3CX]$.

The carbocation then reacts with OH^- in a second, fast step to give R_3COH.

The tertiary halogenoalkane reacts by S_N1 because the three alkyl groups release electrons and stabilise the carbocation, and they also block attack by OH^- (steric hindrance). A primary carbocation is too unstable, so RCH_2X reacts by S_N2 instead.

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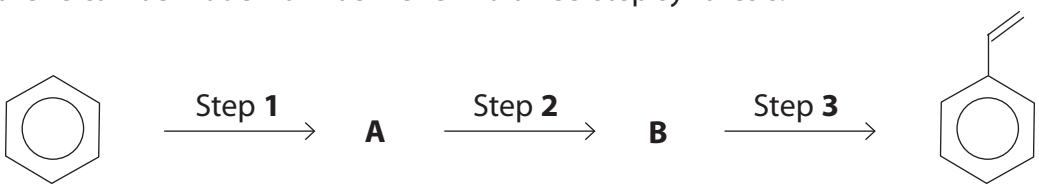
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(Total for Question 6 = 16 marks)

7 Phenylethene, commonly known as styrene, is an important substance in the production of polystyrene which is used for some types of plastic packaging. Phenylethene can be made from benzene in a three-step synthesis.



(a) Some of the following compounds can be used to make phenylethene from benzene.

Aluminium chloride	Chloroethane	Ethanal	Ethanol
Ethanoic acid	Ethanoyl chloride	Ethene	Ether
Hydrochloric acid, concentrated	Lithium tetrahydridoaluminate(III)	Phosphoric acid, concentrated	Sulfuric acid, concentrated

Selecting **only** from these compounds, devise a synthetic pathway for converting benzene into phenylethene, clearly identifying compounds **A** and **B** and stating the appropriate conditions for each step.

(5)

Step 1: react benzene with ethanoyl chloride, CH_3COCl, using aluminium chloride, $AlCl_3$, as catalyst, warm under reflux (Friedel-Crafts acylation).

A = phenylethanone, $C_6H_5COCH_3$

Step 2: reduce A with lithium tetrahydridoaluminate(III), $LiAlH_4$, in dry ether.

B = 1-phenylethanol, $C_6H_5CH(OH)CH_3$

Step 3: dehydrate B by heating with concentrated phosphoric acid, H_3PO_4, to give phenylethene, $C_6H_5CH=CH_2$.

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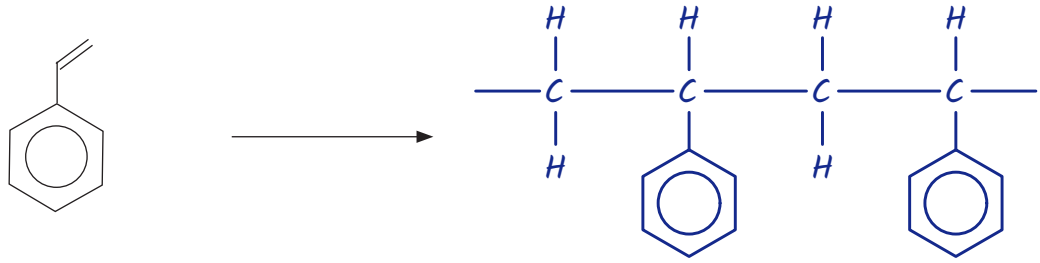
(b) Which reagent could produce a diol from phenylethene?

(1)

- ☒ **A** acidified potassium dichromate(VI)
- ☒ **B** acidified potassium manganate(VII)
- ☒ **C** aqueous sodium hydroxide
- ☒ **D** steam

(c) Draw a section of the polymer, polystyrene, showing **two** repeat units.

(1)



(d) Give one advantage and one disadvantage of the disposal of polystyrene by incineration.

(2)

Advantage: the energy released can be used to generate electricity, and it avoids landfill.

Disadvantage: toxic fumes such as carbon monoxide are released, and carbon dioxide (a greenhouse gas) is produced.

(e) Calculate the percentage by mass of carbon in phenylethene, giving your answer to an appropriate number of significant figures.

(2)

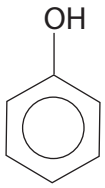
$M_r(C_8H_8) = (8 \times 12.0) + (8 \times 1.0) = 104.0$

% C = $(96.0 \div 104.0) \times 100 = 92.3$ %

(Total for Question 7 = 11 marks)

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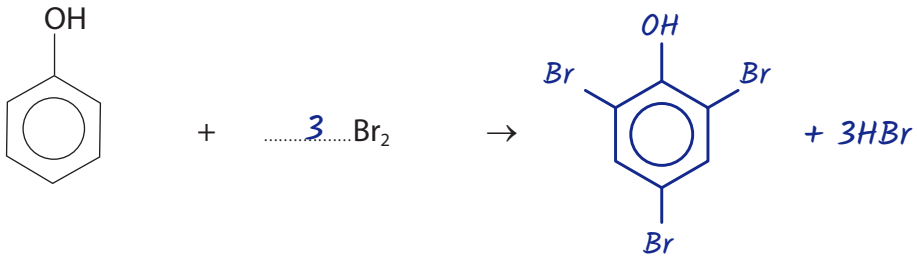
8 Phenol is a feedstock in the production of many organic molecules.



(a) Phenol reacts with bromine water.

(i) Complete the equation for the reaction of phenol with excess bromine water, using the **skeletal** formula of the organic product.

(2)



(ii) Compare and contrast the bromination of phenol with the bromination of benzene.

(3)

Similarity: both are electrophilic substitution reactions.

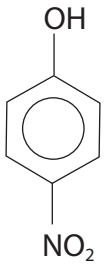
Phenol reacts with bromine water at room temperature with no halogen carrier, whereas benzene needs liquid bromine, heating under reflux and a halogen carrier such as $FeBr_3$.

This is because a lone pair of electrons on the oxygen of the OH group is delocalised into the benzene ring, increasing its electron density, so electrophilic attack by bromine is more likely.

Phenol is trisubstituted (2,4,6-tribromophenol), whereas benzene is only monosubstituted (bromobenzene).

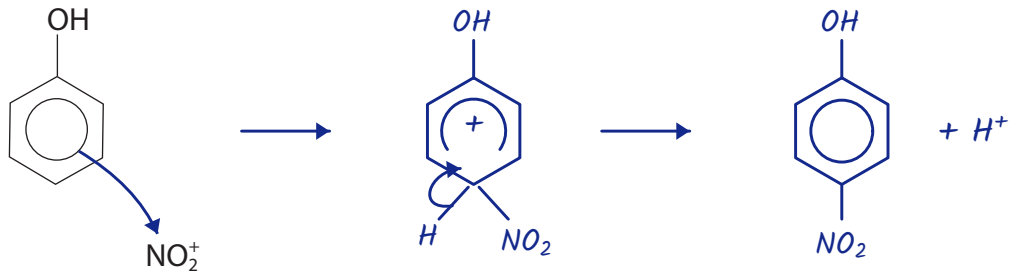
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(b) Phenol can be nitrated to produce 4-nitrophenol.



(i) The mechanisms of the nitration of phenol and of benzene are similar. Complete the diagram, using curly arrows, to show a possible mechanism for the reaction between the electrophile, NO_2^+, and phenol to produce 4-nitrophenol.

(3)



(ii) What is the mass, in grams, of 4-nitrophenol produced from 0.94 g of phenol if the yield of this isomer is 15%?

(1)

☒ **A** 0.14

☒ **B** 0.21

☒ **C** 0.68

☒ **D** 1.39

(iii) Draw **two** structural isomers of 4-nitrophenol which have a benzene ring.

(1)



(Total for Question 8 = 10 marks)

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9 This question is about the reaction kinetics of an 'iodine clock' reaction.

One example of an 'iodine clock' reaction that involves the iodate(V) ions and iodide ions in acidic solution is

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightarrow 3I_2(aq) + 3H_2O(l)$$

(a) State why the order of reaction with respect to iodide ions cannot be five, even though 5 mol of iodide ions are shown in the equation.

(1)

The rate-determining step involves only the particles that collide in it, and the chance of five iodide ions colliding at the same time is negligible.

(b) A series of experiments was carried out by a student to determine the order of reaction with respect to iodate(V) ions. The concentrations of the iodide ions and the acid were in large excess and the volume of the iodate(V) solution was varied.
The total volume of the reaction mixture was kept constant by the addition of suitable volumes of deionised water.
The following results were obtained:

Experiment Number	1	2	3	4	5	6
Volume of iodate(V) solution / cm^3	10.0	7.0	5.0	3.0	2.0	1.0
Time (t) / s	180	260	357	606	900	800
(1000/t) / s^{-1}	5.56	3.85	2.80	1.65	1.11	1.25

(i) In experiment 6, the student forgot to add deionised water to keep the total volume the same for each experiment.
State why the total volume should be kept the same.

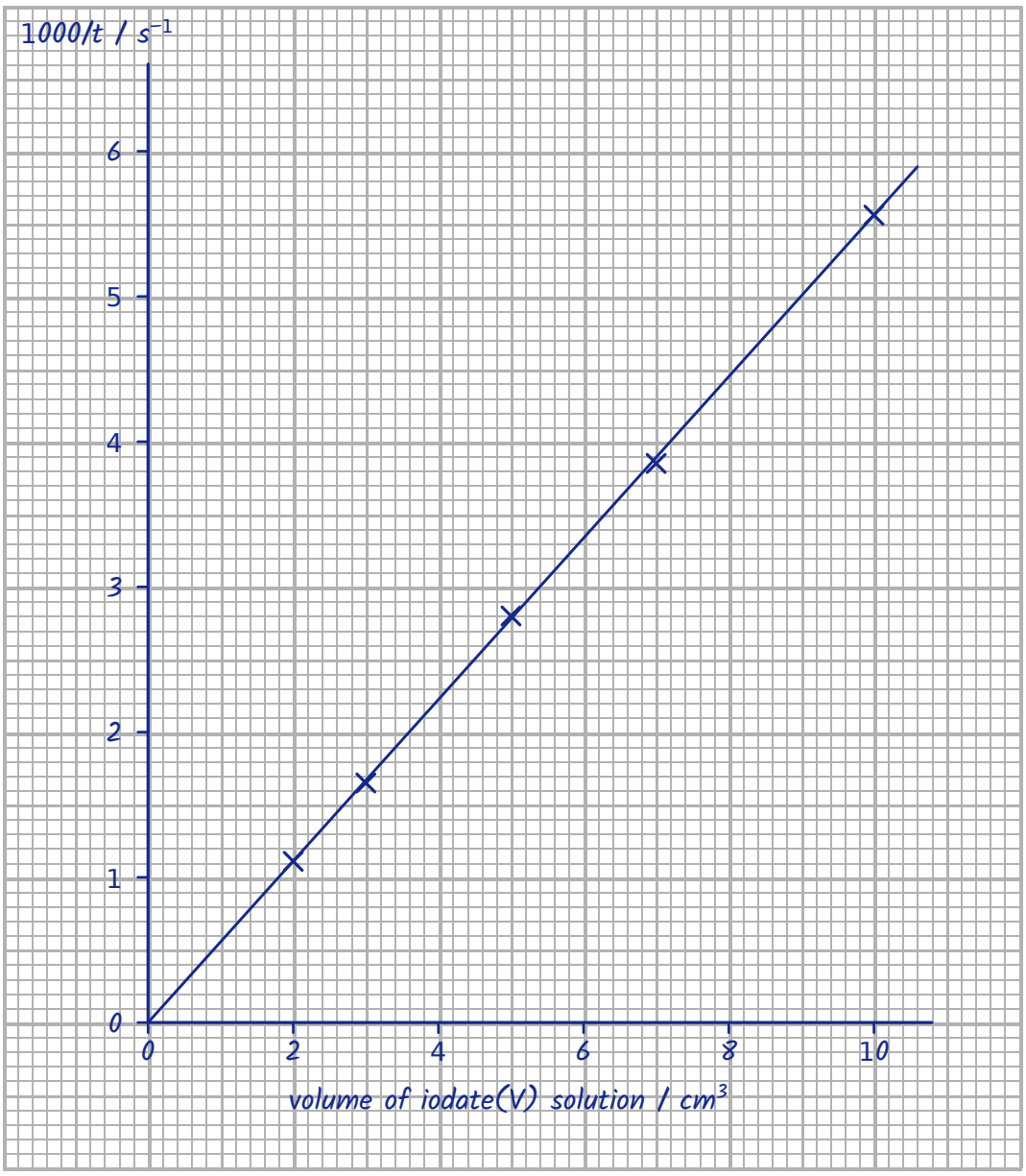
(1)

So that the volume of iodate(V) solution is proportional to its concentration, so volume can be used instead of concentration.

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(ii) Complete the table and use the results from experiments 1, 2, 3, 4 and 5 to plot a graph of 1000/t against volume of iodate(V) ions.

(4)



(iii) Deduce the order of reaction with respect to the iodate(V) ions. Justify your answer.

(2)

First order with respect to iodate(V) ions, because the graph is a straight line through the origin, so rate is directly proportional to $[IO_3^-]$.

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(c) A different version of the 'iodine clock' reaction involves mixing hydrogen peroxide with aqueous solutions of potassium iodide, sodium thiosulfate and starch.

The main reaction is

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

The reaction is first order with respect to hydrogen peroxide and iodide ions but zero order with respect to hydrogen ions.

(i) In one experiment, the following data were obtained:

Reactants	Initial concentration / mol dm^{-3}
$H_2O_2(aq)$	1.50×10^{-3}
$I^-(aq)$	2.10×10^{-3}
$H^+(aq)$	2.10×10^{-3}

Initial rate = 1.24×10^{-3} mol dm^{-3} s^{-1}

Write the rate equation and hence deduce the value of the rate constant, *k*, from these data. Include units and give your answer to an appropriate number of significant figures.

(2)

rate = $k[H_2O_2][I^-]$

k = rate ÷ $([H_2O_2][I^-])$

$k = 1.24 \times 10^{-3} \div (1.50 \times 10^{-3} \times 2.10 \times 10^{-3})$

$k = 394\ dm^3\ mol^{-1}\ s^{-1}$

(ii) Explain the purpose of the starch present in the reaction mixture when starch is neither in the rate equation, nor in the reaction equation.

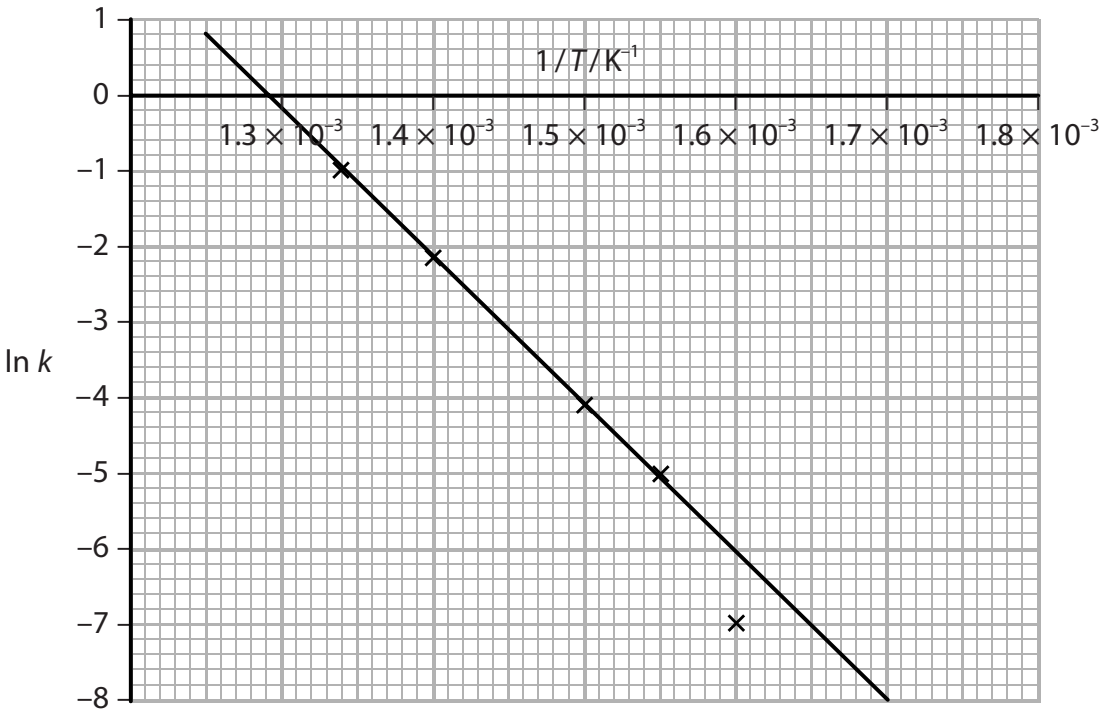
(2)

Starch is an indicator: once all the thiosulfate has been used up, the iodine formed reacts with starch to give a blue-black colour.

The time taken for the blue-black colour to appear is measured and used to calculate the rate.

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(d) Another 'iodine clock' reaction produced data that enabled the following graph of $\ln k$ against $1/T$ to be drawn.



(i) The Arrhenius equation can be expressed as

$$\ln k = -\frac{E_a}{R} \times \left[\frac{1}{T}\right] + \text{constant}$$

From the gradient of the graph, determine the activation energy, E_a, for this reaction.

Include a sign and units in your answer.

(3)

gradient = (−8.0 − 0) ÷ (1.70 × 10^{-3} − 1.29 × 10^{-3}) = −19 500 K

$-E_a/R$ = −19 500, so E_a = 19 500 × 8.31 = 162 045 J mol^{-1}

E_a = +162 kJ mol^{-1}

(ii) Give a reason for the point at $\ln k = -7$ **not** being included in the line drawn on the graph.

(1)

It is an anomalous result (an outlier), as it lies well away from the line of best fit.

(Total for Question 9 = 16 marks)

TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 4.0 He helium 2
(1)	(2)		Key									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4		relative atomic mass atomic symbol name atomic (proton) number									10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Elements with atomic numbers 112-116 have been reported but not fully authenticated

* Lanthanide series	140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	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
* Actinide series	232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[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

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