Please check the examination details below before entering your candidate information

Candidate surname	Other names
StemUp Model Solution	

Pearson Edexcel Level 3 GCE

Centre Number	Candidate Number

Tuesday 11 June 2019

Afternoon (Time: 1 hour 45 minutes)	Paper Reference **9CH0/02**

Chemistry

Advanced

Paper 2: Advanced Organic and Physical Chemistry

Candidates must have: Scientific calculator
Data Booklet
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.
- Show all your working in calculations and include units where appropriate.
- Check your answers if you have time at the end.

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 some reactions of alcohols.

(a) (i) Which alcohol **cannot** be oxidised by acidified potassium dichromate(VI)?

(1)

☐ **A** hexan-2-ol

☒ **B** 2-methylpentan-2-ol

☐ **C** hexan-3-ol

☐ **D** 2-methylpentan-3-ol

(ii) Which alcohol reacts with iodine in the presence of alkali to form a yellow solid?

(1)

☒ **A** hexan-2-ol

☐ **B** 2-methylpentan-2-ol

☐ **C** hexan-3-ol

☐ **D** 2-methylpentan-3-ol

(b) Which reagent is used with iodine to prepare iodoalkanes from alcohols?

(1)

☒ **A** red phosphorus

☐ **B** concentrated phosphoric acid

☐ **C** sulfur

☐ **D** concentrated sulfuric acid

(Total for Question 1 = 3 marks)

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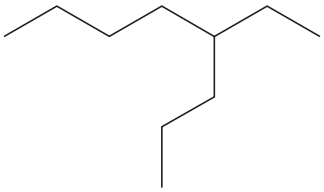
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2 This question is about alkanes and their reactions.

(a) What is the IUPAC name for this alkane?



(1)

☒ **A** 4-ethyloctane

☐ **B** 5-ethyloctane

☐ **C** 3-propylheptane

☐ **D** 5-propylheptane

(b) What is the name of the process that could be used to produce propane, C_3H_8, from decane, $C_{10}H_{22}$?

(1)

☐ **A** substitution

☐ **B** reforming

☐ **C** fractional distillation

☒ **D** cracking

(c) A student researched the reaction of propane with bromine and found that the reaction could be used to make 1-bromopropane.

$$C_3H_8(g) + Br_2(l) \rightarrow C_3H_7Br(l) + HBr(g)$$

(i) The first step of the reaction involves

(1)

☐ **A** heterolytic bond fission to form free radicals

☐ **B** heterolytic bond fission to form ions

☒ **C** homolytic bond fission to form free radicals

☐ **D** homolytic bond fission to form ions

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(ii) Calculate the atom economy by mass for the formation of 1-bromopropane in the reaction in (c).

(2)

atom economy = (M_r of desired product / total M_r of reactants) × 100

M_r C_3H_7Br = 122.9 M_r C_3H_8 + M_r Br_2 = 44.0 + 159.8 = 203.8

atom economy = (122.9 / 203.8) × 100

= 60.3 %

(iii) A source from the internet gave the percentage yield for this reaction as 31.0%. The best explanation for the low percentage yield of 1-bromopropane in this reaction is

(1)

- ☐ **A** bromine is very unreactive
- ☐ **B** a gaseous reactant always gives a low yield
- ☐ **C** the reaction is very slow
- ☒ **D** the reaction produces a mixture of organic products

(iv) Calculate the volume of propane, in dm^3, measured at room temperature and pressure, that is needed to produce 14.7 g of 1-bromopropane, assuming a percentage yield of 31.0%.
Give your answer to an appropriate number of significant figures.

[Molar gas volume at r.t.p. = 24.0 dm^3 mol^{-1}]

(3)

amount of 1-bromopropane = 14.7 / 122.9 = 0.11961 mol

amount of propane needed = 0.11961 × (100 / 31.0) = 0.38584 mol

volume of propane = 0.38584 × 24.0 = 9.2601 dm^3

volume of propane = 9.26 dm^3 (3 s.f.)

(Total for Question 2 = 9 marks)

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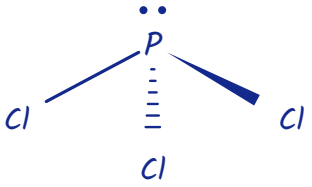
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3 This question is about compounds of Group 5 elements.

(a) Phosphorus forms two chlorides with the formulae PCl_3 and PCl_5.

(i) Explain the shape of the PCl_3 molecule. The bond angle is not required.

(3)



PCl_3 is (trigonal) pyramidal.

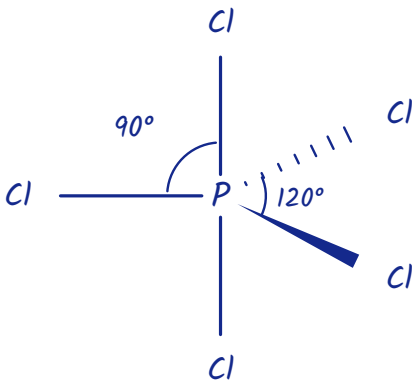
There are 3 bond pairs and 1 lone pair of electrons around the central P atom.

The electron pairs repel each other to positions of minimum repulsion (maximum separation), giving a pyramidal shape.

(ii) Draw a diagram to show the three-dimensional shape of the PCl_5 molecule in the gas phase.

Include bond angles and the name of the shape.

(3)



Shape: trigonal bipyramidal

Bond angles: 90° and 120°

(iii) Explain why phosphorus forms PCl_5 but nitrogen does not form NCl_5.

(2)

Phosphorus can expand its octet: it has available 3d orbitals, so electrons can be promoted and P can accommodate 10 electrons in its outer shell, forming five P–Cl bonds.

Nitrogen does not have 2d orbitals, so it can only accommodate eight electrons in its outer shell and cannot form NCl_5.

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(b) Nitrogen trichloride, NCl_3, has a boiling temperature of 344 K, and nitrogen trifluoride, NF_3, has a boiling temperature of 144 K.

Explain this difference in boiling temperatures, by referring to all the intermolecular forces present.

(5)

Both NCl_3 and NF_3 have London forces (instantaneous dipole to induced dipole forces) between their molecules.

The London forces are greater in NCl_3 because NCl_3 has more electrons (58) than NF_3 (34), as a Cl atom has more electrons than an F atom.

Both also have permanent dipole to permanent dipole forces, but these are stronger in NF_3 than in NCl_3.

This is because F is more electronegative than Cl, so the N–F bond is much more polar than the N–Cl bond (N and Cl have almost the same electronegativity).

Overall the London forces predominate (they are more significant than the dipole forces), so more energy is needed to overcome the intermolecular forces between NCl_3 molecules than between NF_3 molecules, so NCl_3 has the higher boiling temperature.

(c) Which of these compounds produces hydrogen chloride when it reacts with PCl_5?

(1)

☒ **A** propanal

☒ **B** propan-1-ol

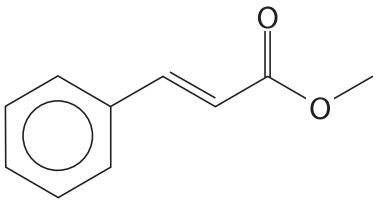
☒ **C** propanone

☒ **D** propyl propanoate

(Total for Question 3 = 14 marks)

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4 Methyl cinnamate, $C_{10}H_{10}O_2$, is a white crystalline solid used in the perfume industry.



methyl cinnamate

(a) Calculate the mass of carbon in 2.34 g of methyl cinnamate.

(2)

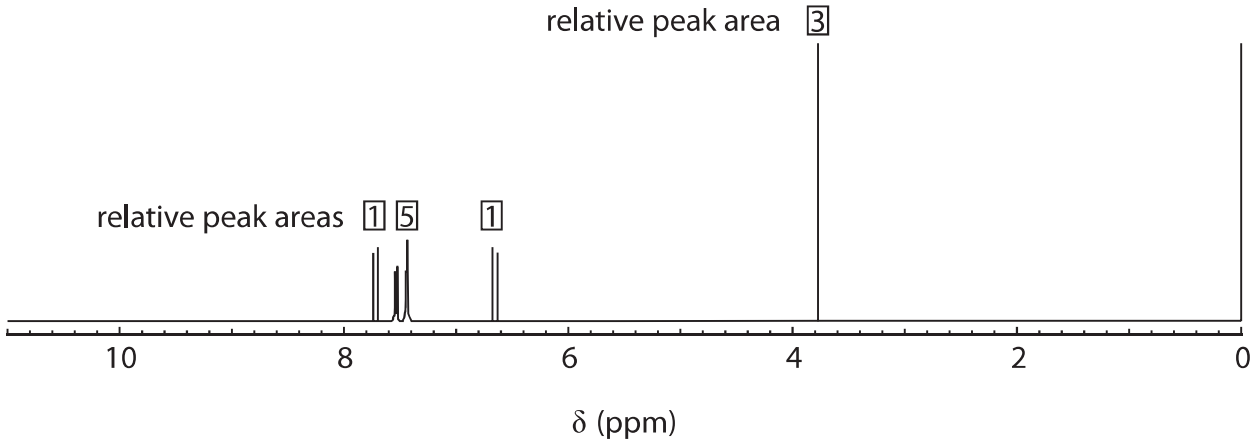
M_r of $C_{10}H_{10}O_2$ = (10 × 12.0) + (10 × 1.0) + (2 × 16.0) = 162.0

mass of carbon = 2.34 × (120.0 / 162.0)

= 1.73 g

(b) A sample of methyl cinnamate was analysed by high resolution proton NMR spectroscopy.

A simplified spectrum is shown.



(i) Name the compound responsible for the peak at a chemical shift of 0 ppm, stating its purpose.

(2)

Tetramethylsilane, TMS, $Si(CH_3)_4$.

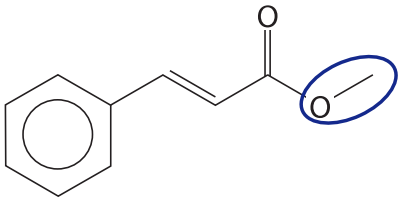
It is used as a reference (standard) at δ = 0 ppm, so that the chemical shifts of the other hydrogen atoms can be compared with it.

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(ii) Identify the proton environment that causes the peak at a chemical shift of 3.8 ppm by circling it on the diagram shown. Fully justify your answer.

(3)



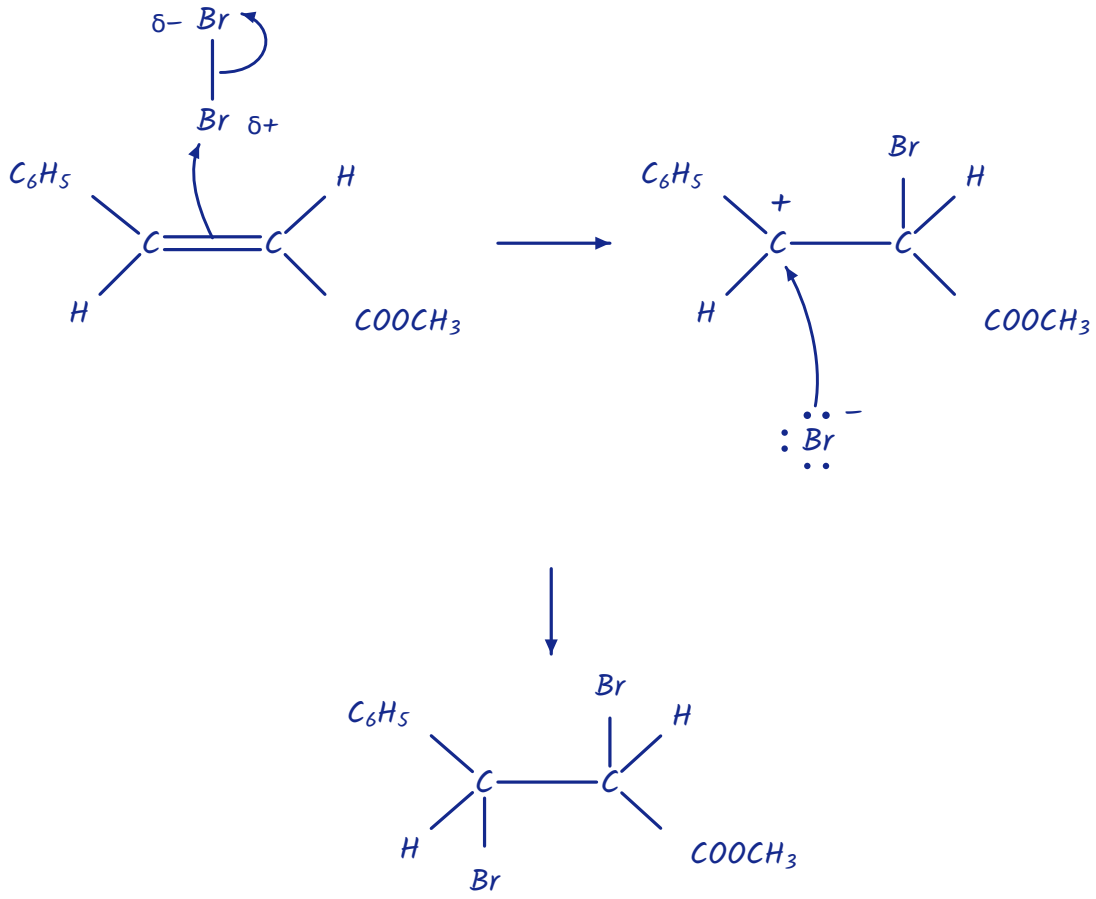
The circled CH_3 hydrogens give a singlet because there are no hydrogen atoms on the adjacent atom (the O has no H), so there is no splitting (n + 1 = 1).

The relative peak area of 3 shows there are 3 hydrogen atoms in this environment, i.e. the CH_3 group.

(c) Methyl cinnamate undergoes an addition reaction in the dark with bromine.

(i) Draw the mechanism for the reaction between methyl cinnamate and bromine, Br_2.
Include curly arrows, and relevant lone pairs and dipoles.

(4)



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(ii) Deduce the number of optical isomers of the addition product that can exist.

(1)

- ☒ **A** 2
- ☒ **B** 3
- ☒ **C** 4
- ☒ **D** 8

(iii) When plane-polarised light is passed through an optical isomer, the plane of polarisation is

(1)

- ☒ **A** diffracted
- ☒ **B** reflected
- ☒ **C** refracted
- ☒ **D** rotated

(Total for Question 4 = 13 marks)

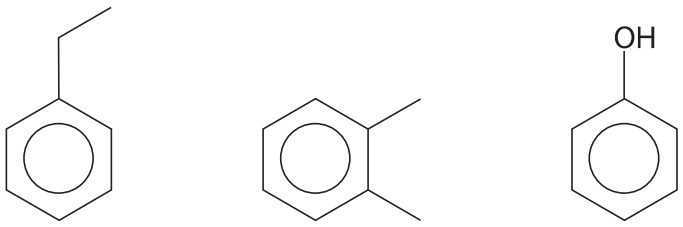
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5 This question is about the arenes, ethylbenzene, xylene, and phenol, which can be identified in wine samples using gas chromatography.

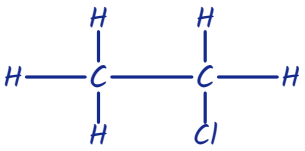


ethylbenzene xylene phenol

(a) Ethylbenzene can be formed by the reaction of a chloroalkane with benzene, catalysed by aluminium chloride, $AlCl_3$.

(i) Draw the **displayed** formula of the chloroalkane required for this reaction.

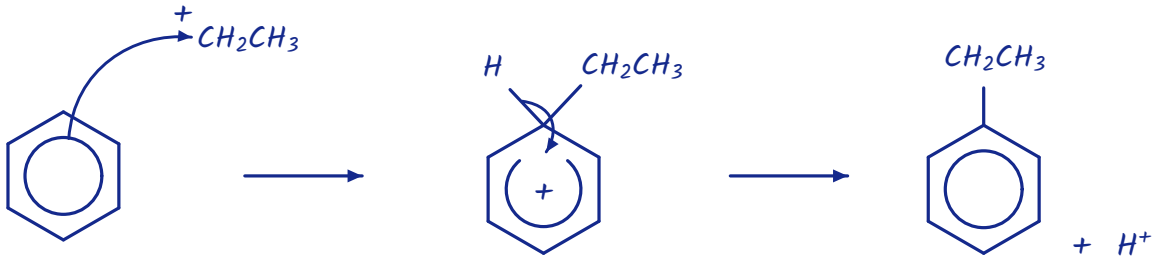
(1)



(ii) Draw the mechanism for this reaction.
Include equations showing the role of the catalyst and how it is regenerated.

(5)

$CH_3CH_2Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$



$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$

(the $AlCl_3$ catalyst is regenerated)

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(iii) Explain whether phenol is likely to be less or more reactive than benzene with the chloroalkane from (a)(i).

(3)

Phenol is likely to be more reactive than benzene.

A lone pair of electrons on the oxygen atom of the –OH group is delocalised into

(donated into) the π system of the benzene ring.

This increases the electron density of the ring,

so the ring is more susceptible to electrophilic attack by the $CH_3CH_2^+$ electrophile.

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(b) A student carried out an experiment to determine the molar mass of xylene.

The student's sample of xylene vapour had a mass of 0.271 g.

At a temperature of 165 °C and a pressure of 118 kPa, this sample had a volume of 70.5 cm^3.

Use the Ideal Gas Equation to calculate the molar mass, in g mol^{-1}, of this sample.

Give your answer to an appropriate number of significant figures.

You **must** show your working.

(4)

$p = 118\ kPa = 118\ 000\ Pa\ (N\ m^{-2})$ $\quad T = 165 + 273 = 438\ K$

$V = 70.5\ cm^3 = 70.5 \times 10^{-6}\ m^3$

$pV = nRT$ so $n = pV / RT$

$n = (118\ 000 \times 70.5 \times 10^{-6}) / (8.31 \times 438)$

$n = 2.2856 \times 10^{-3}\ mol$

$molar\ mass = m / n = 0.271 / 2.2856 \times 10^{-3} = 118.57$

$molar\ mass = 119\ g\ mol^{-1}$ (3 s.f.)

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(c) The time taken for a compound to pass through the column in gas chromatography is called the retention time.

Explain why different compounds will have different retention times in the same column, under the same conditions.

(2)

Different compounds have different polarities, so they have different attractions (affinities) for the stationary phase.

The greater the attraction of a compound for the stationary phase, the longer it takes to pass through the column, so the greater its retention time.

Also, compounds with higher boiling temperatures spend less time in the gas (mobile) phase, so they have longer retention times.

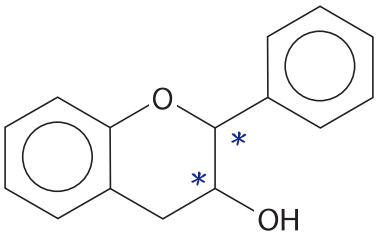
(Total for Question 5 = 15 marks)

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6 The compound flavan-3-ol is found in tea, fruit and wine.



(a) Clearly label all the chiral carbon atoms in flavan-3-ol.

(1)

(b) Give the molecular formula for flavan-3-ol.

(1)

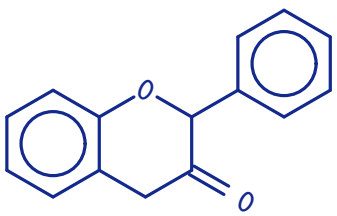
$C_{15}H_{14}O_2$

*(c) A sample of flavan-3-ol extracted from wine contained some ethanol. The sample was left in a flask, open to the air for several days. The contents were then analysed to identify any new compounds formed. Several new compounds were found to be present, including some with a distinctive fruity smell.

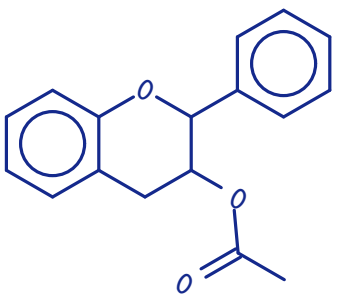
Identify **four** new organic compounds that could form under these conditions by considering the chemistry of alcohols. Justify your answers. Include the structure of two compounds formed from flavan-3-ol, one of which has a fruity smell.

(6)

Structures of the two compounds formed from flavan-3-ol:



flavan-3-one (ketone)



ester of flavan-3-ol and ethanoic acid (fruity smell)

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Ethanol and flavan-3-ol are both alcohols. Left open to the air for several days, they can be oxidised by oxygen in the air.

Ethanol is a primary alcohol, so it is oxidised first to ethanal, CH_3CHO, and then further to ethanoic acid, CH_3COOH.

The ethanoic acid formed then reacts with the remaining ethanol (esterification, catalysed by the acids in the wine) to form the ester ethyl ethanoate, $CH_3COOCH_2CH_3$, which has a fruity smell.

Flavan-3-ol is a secondary alcohol (the C bonded to the –OH is bonded to two other carbon atoms), so it is oxidised to a ketone, flavan-3-one (structure drawn on the previous page). It cannot be oxidised any further.

The –OH group of flavan-3-ol can also react with the ethanoic acid formed from the ethanol to form an ester, flavan-3-yl ethanoate (structure on the previous page), which also has a fruity smell.

So four new organic compounds are: ethanoic acid (and ethanal), ethyl ethanoate, flavan-3-one and the ethanoate ester of flavan-3-ol.

(Total for Question 6 = 8 marks)

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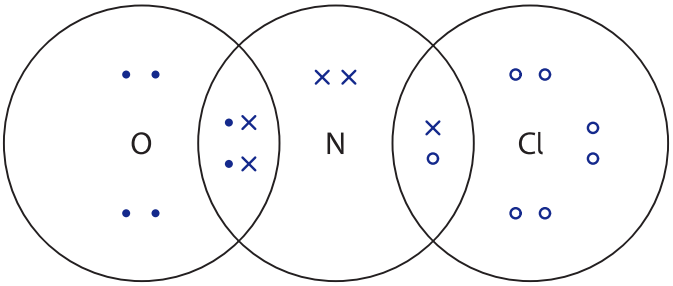
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7 Nitrogen monoxide and chlorine react together to form nitrosyl chloride.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

(a) Draw a dot-and-cross diagram for nitrosyl chloride, showing only the outer shell electrons.



(2)

(b) The rate equation for the formation of nitrosyl chloride is

Rate = $k[NO]^2[Cl_2]$

(i) Complete the table by adding the missing values.

Experiment	[NO] / mol dm^{-3}	[Cl_2] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.122	0.241	1.09×10^{-2}
2	0.244	0.482	8.72×10^{-2}
3	0.366	0.121	4.91×10^{-2}

(2)

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(ii) Calculate the rate constant, *k*, using data from Experiment 1.
Include units with your answer.

(3)

$k = \text{rate} / ([NO]^2[Cl_2])$

$k = 1.09 \times 10^{-2} / (0.122^2 \times 0.241)$

$k = 3.04\ dm^6\ mol^{-2}\ s^{-1}$

(iii) Explain how using a catalyst increases the rate constant, *k*.

(2)

The catalyst provides an alternative reaction pathway with a lower activation energy.

So a greater proportion of molecules have energy greater than or equal to the activation energy, so more collisions are successful and k increases.

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(iv) The heterogeneous catalyst palladium was suggested for use in this reaction. Explain how impurities in the gaseous reactants could make the catalyst less effective.

(3)

Impurities could adsorb onto the surface of the palladium catalyst, occupying the active sites.

This leaves fewer active sites available for the reactants (less surface area for reaction), so the reactant bonds are not weakened.

The impurities may form strong bonds to the surface, so they are less likely to desorb and remain on the surface, poisoning the catalyst.

(Total for Question 7 = 12 marks)

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8 Gentian violet is a purple crystalline solid used as an antifungal treatment.

It can be synthesised from dimethylphenylamine, $C_6H_5N(CH_3)_2$.

(a) The dimethylphenylamine used in the synthesis can be made by the stepwise reaction of phenylamine with chloromethane.

Step **1** $2C_6H_5NH_2 + CH_3Cl \rightarrow C_6H_5NH(CH_3) + C_6H_5NH_3^+Cl^-$

Step **2** $2C_6H_5NH(CH_3) + CH_3Cl \rightarrow C_6H_5N(CH_3)_2 + C_6H_5NH_2^+(CH_3)Cl^-$

The reaction mechanism for Step **1** between phenylamine and chloromethane is the same as that in the reaction between ammonia and chloromethane.

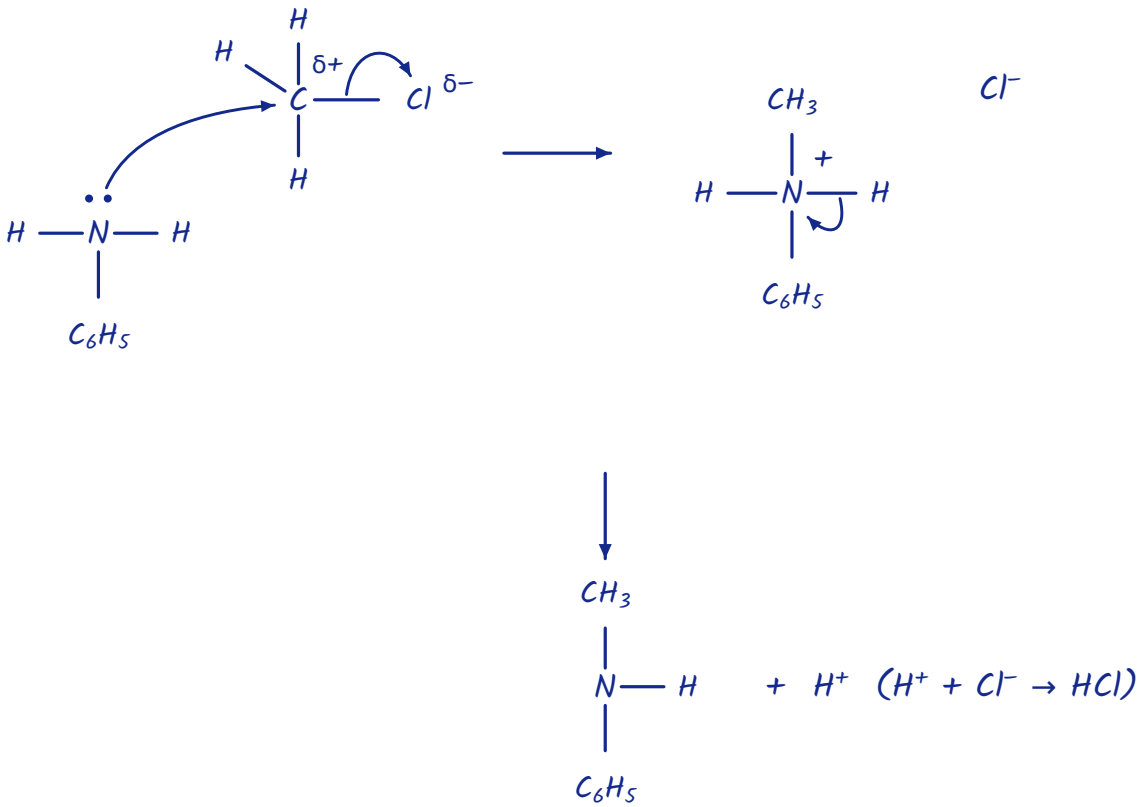
(i) What is the reaction type and mechanism in Step **1**?

(1)

- ☐ **A** electrophilic addition
- ☐ **B** electrophilic substitution
- ☐ **C** nucleophilic addition
- ☒ **D** nucleophilic substitution

(ii) Draw the mechanism for the reaction in Step **1**.
Include curly arrows, and relevant lone pairs and dipoles.

(4)



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(iii) Describe, in outline, how a sample of a solid, such as gentian violet, is purified by recrystallisation.
Specific details of the solvent used are not required.

(4)

Dissolve the impure solid in the minimum volume of hot solvent (and filter the hot solution to remove any insoluble impurities).

Leave the solution to cool, then cool it in ice, so the solid recrystallises while the soluble impurities stay in solution.

Filter off the crystals using vacuum (Buchner) filtration, under suction.

Dry the crystals between filter papers or in a desiccator.

(b) The rate constant for the reaction between a solution of gentian violet and aqueous sodium hydroxide was determined at different temperatures.

Temperature (T) / K	1 / Temperature ($1/T$) / K^{-1}	Rate constant, k / $dm^3\,mol^{-1}\,s^{-1}$	ln k
283.5	3.53×10^{-3}	2.71×10^{-3}	−5.91
287.5	3.48×10^{-3}	3.55×10^{-3}	*−5.64*
291.5	*3.43×10^{-3}*	4.75×10^{-3}	−5.35
295.0	3.39×10^{-3}	6.10×10^{-3}	−5.10
298.5	3.35×10^{-3}	7.60×10^{-3}	−4.88

(i) Complete the data in the table.

(1)

(ii) Plot a graph and use it to determine the activation energy for the reaction in kJ mol^{-1}.

You should include the value and units of the gradient of the line.

The Arrhenius equation can be shown as

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

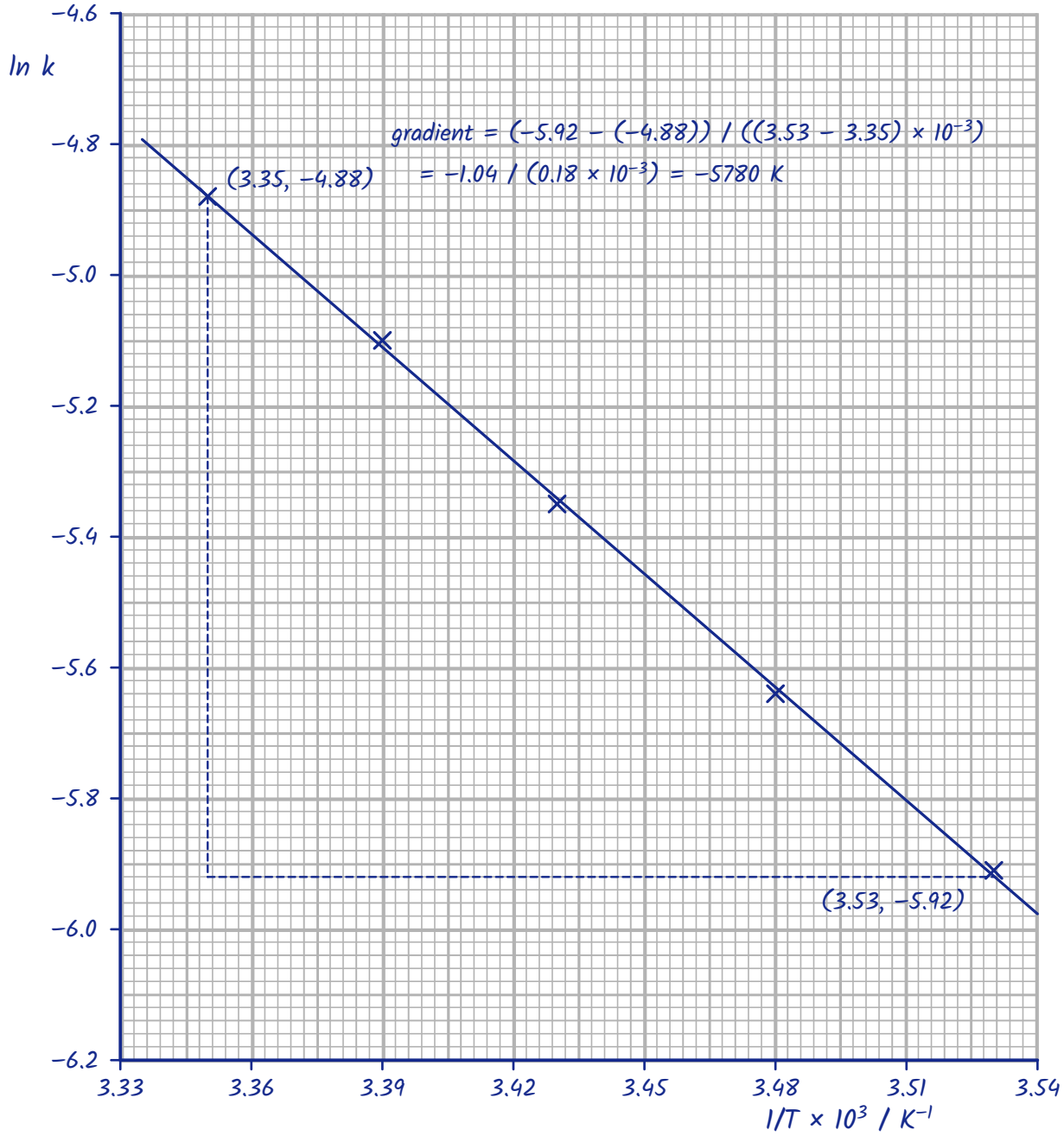
(6)

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Gradient

gradient = −5780 K (−5.78 × 10³ K)

Activation energy

E_a = −gradient × R = 5780 × 8.31 = 48 000 J mol⁻¹ = +48.0 kJ mol⁻¹

(Total for Question 8 = 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

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
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

* Lanthanide series

* Actinide series

P 5 8 3 0 7 A 0 2 4 2 4

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