Write your name here

Surname: StemUp Model Solution

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Pearson Edexcel Level 3 GCE

Centre Number | Candidate Number

Chemistry

Advanced

Paper 2: Advanced Organic and Physical Chemistry

Monday 19 June 2017 – Morning
Time: 1 hour 45 minutes

Paper Reference
9CH0/02

You 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.
- Try to answer every question.
- 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 is a question about alkanes.

(a) What is the reaction mechanism when ethane and chlorine react in UV light?

(1)

☐ **A** electrophilic addition

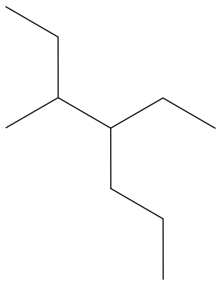
☐ **B** electrophilic substitution

☐ **C** free radical addition

☒ **D** free radical substitution

(b) What is the name of this alkane?

(1)



☐ **A** 2-ethyl-3-propylpentane

☒ **B** 4-ethyl-3-methylheptane

☐ **C** 3-methyl-4-propylhexane

☐ **D** 4-methyl-3-propylhexane

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(c) Alkanes are obtained by processing crude oil.

(i) Explain why different alkanes in crude oil can be separated by fractional distillation.

(2)

Different alkanes have different boiling temperatures, so they condense at different temperatures (heights) in the fractionating column.

This is because they have different chain lengths: longer alkanes have more electrons, so stronger London forces between molecules and higher boiling temperatures.

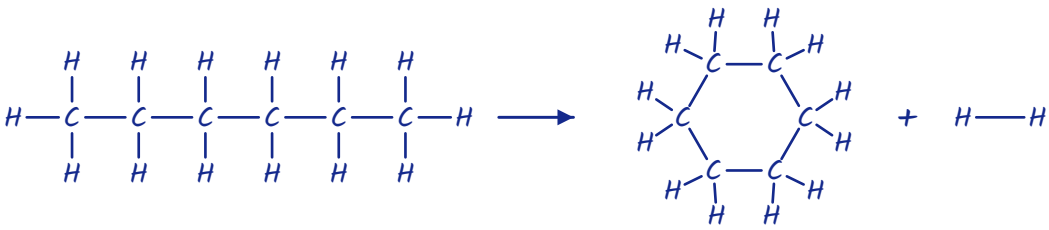
(ii) Complete the equation for the cracking of octane to produce ethene and only one other organic compound. State symbols are not required.

(1)

$C_8H_{18} \rightarrow$ *C_2H_4* + *C_6H_{14}*

(iii) Write the equation for the reforming of hexane into cyclohexane, using **displayed** formulae for the organic compounds. State symbols are not required.

(1)



(Total for Question 1 = 6 marks)

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2 Diamond, graphene and graphite are different forms of carbon.

(a) The structural feature that graphene and graphite have in common is that the carbon atoms are arranged in

(1)

☒ **A** layers with each atom bonded to four others

☒ **B** hexagonal and pentagonal rings within a layer

☒ **C** hexagonal rings within a layer

☒ **D** a three-dimensional structure

(b) The bond angles within a layer of graphene and a layer of graphite are

(1)

☒ **A** 90° and 109.5°

☒ **B** all 109.5°

☒ **C** 109.5° and 120°

☒ **D** all 120°

(c) One way in which diamond differs from graphene and graphite is that only diamond has

(1)

☒ **A** a high melting temperature

☒ **B** a precise molecular formula

☒ **C** poor electrical conductivity

☒ **D** a giant structure

(Total for Question 2 = 3 marks)

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3 This is a question about halogenoalkanes and related compounds.

(a) Explain the trend in reactivity of the **primary** chloro-, bromo- and iodoalkanes with aqueous hydroxide ions.

(2)

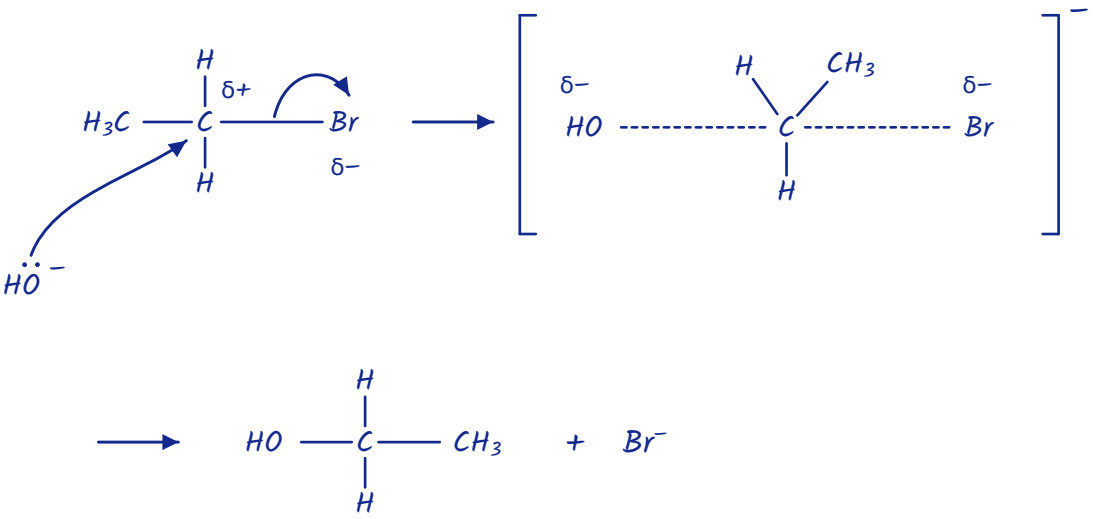
Reactivity increases from the chloroalkane to the bromoalkane to the iodoalkane (down Group 7).

This is because the C–X bond enthalpy decreases down the group (C–I is the weakest bond), so the C–X bond breaks more easily.

(b) In aqueous sodium hydroxide, 1-bromoethane reacts to produce ethanol.

(i) Write the mechanism for this reaction, including all relevant curly arrows, lone pairs and dipoles. Include the transition state.

(4)



(ii) Give the reagents that are used to test that bromide ions are formed in this reaction mixture. Include the result of the test.

(2)

Add excess dilute nitric acid, HNO_3, (to neutralise the hydroxide ions) and then add silver nitrate solution, $AgNO_3(aq)$.

Result: a cream (off-white) precipitate forms, showing bromide ions are present.

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(c) The halogenoalkane 2-bromobutane reacts with ethanolic potassium hydroxide to produce a mixture of alkenes.

Draw the **skeletal** formulae of all the alkenes that could be produced.

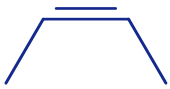
(3)



but-1-ene



trans-but-2-ene



cis-but-2-ene

(d) Explain why ethene has a boiling temperature of −104 °C, whereas ethanol has a boiling temperature of 78 °C.

(3)

Ethanol has an O–H group, so hydrogen bonds form between ethanol molecules (as well as London forces and permanent dipole-dipole forces).

Ethene is non-polar, so there are only weaker London forces (instantaneous dipole-induced dipole) between molecules.

Hydrogen bonds are much stronger than London forces, so more energy is needed to overcome the intermolecular forces in ethanol.

(Total for Question 3 = 14 marks)

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4 Traditionally, high-flying aircraft and Formula 1 racing cars have had their tyres inflated with nitrogen gas instead of air. Recently, this practice has been extended to some other cars.

(a) A car tyre is filled with nitrogen gas to a volume of 8.98 dm^3 and a pressure of 207 kPa at 20 °C.

(i) Using the Ideal Gas Equation, calculate the mass of nitrogen gas, in grams, present in the car tyre under these conditions. Give your answer to an appropriate number of significant figures.

(3)

$p = 207\,000$ Pa $V = 8.98 \times 10^{-3}$ m^3 $T = 20 + 273 = 293$ K

$pV = nRT$ so $n = pV \div RT$

$n = (207\,000 \times 8.98 \times 10^{-3}) \div (8.31 \times 293) = 0.7634$ mol

mass $= n \times M(N_2) = 0.7634 \times 28.0 = 21.38$ g

mass of nitrogen = 21.4 g (3 s.f.)

(ii) During a car journey, the tyres become warm. Use the Ideal Gas Equation to deduce the effect that this has on the pressure in the tyres.

(1)

From $pV = nRT$, at constant volume and amount of gas, p is directly proportional to T, so the pressure in the tyres increases.

(b) One reason for the use of nitrogen gas in car tyres is that less gas is lost from the tyres during use because nitrogen molecules are larger than oxygen molecules. A suggested explanation for this is that nitrogen atoms are larger than oxygen atoms.

Explain why a nitrogen atom is larger than an oxygen atom.

(2)

A nitrogen atom has fewer protons (7) than an oxygen atom (8), so it has a smaller nuclear charge.

The outer electrons are in the same shell (2p) with the same shielding, so in nitrogen they are less strongly attracted to the nucleus, giving a larger atomic radius.

(Total for Question 4 = 6 marks)

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5 This is a question about catalytic converters in car exhaust systems.

(a) When petrol is burnt in a car engine, pollutant gases including carbon monoxide and nitrogen monoxide are formed.

(i) Write the equation for the reaction between these two polluting gases that takes place on the surface of a catalytic converter. State symbols are not required.

(1)

$2NO + 2CO \rightarrow N_2 + 2CO_2$

(ii) Describe the stages by which the reaction in (a)(i) occurs in a catalytic converter.

(3)

The CO and NO molecules are adsorbed onto the surface of the catalyst (platinum/rhodium) at active sites.

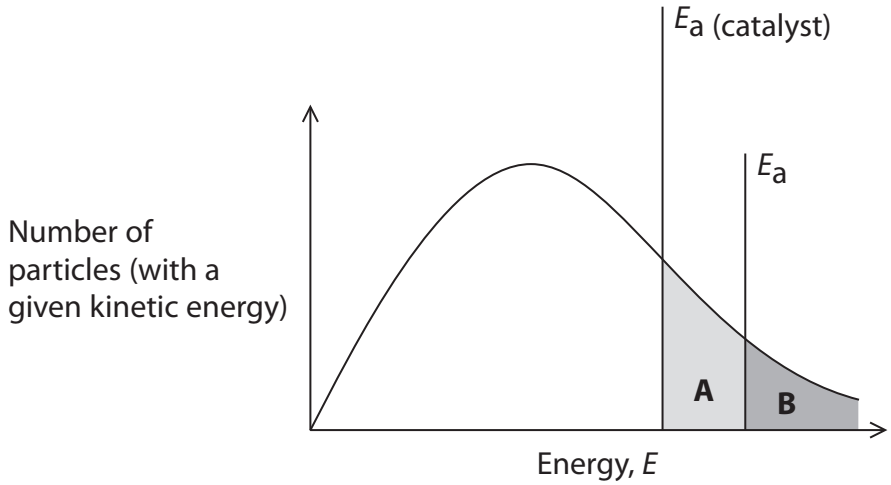
The bonds in the reactant molecules are weakened (and broken), so the reaction takes place on the catalytic surface, forming N_2 and CO_2.

The products, N_2 and CO_2, are then desorbed (released) from the catalytic surface, freeing the active sites for more gas molecules.

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(b) Which area in the Maxwell-Boltzmann distribution diagram represents the **increase** in the number of particles with sufficient energy to react in the presence of a catalyst?



(1)

☒ **A** area A

☐ **B** area B

☐ **C** area A – area B

☐ **D** area A + area B

(c) In the UK, the exhaust emissions of a petrol-fuelled vehicle must be less than 1.00 g of carbon monoxide per kilometre.

What is the maximum number of carbon monoxide molecules that can be emitted per kilometre for a vehicle to meet this regulation?

(1)

☐ **A** 1.37×10^{22}

☒ **B** 2.15×10^{22}

☐ **C** 6.02×10^{23}

☐ **D** 1.69×10^{25}

(Total for Question 5 = 6 marks)

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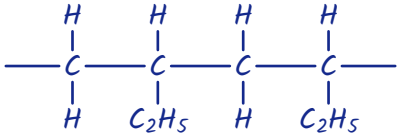
6 This is a question about polymerisation.

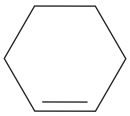
(a) But-1-ene and cyclohexene both form addition polymers.

Draw a section of each polymer, showing **two** repeat units.

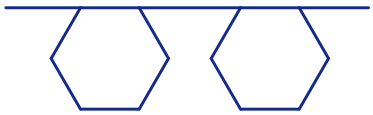
(2)

$CH_2{=}CHCH_2CH_3$ →



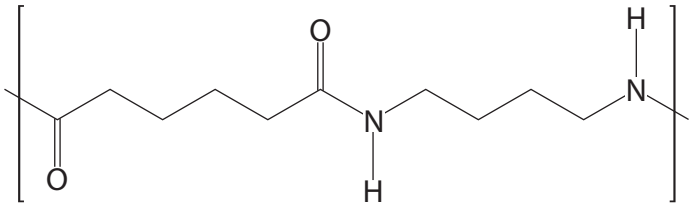


→



(b) Deduce the two monomers needed to produce the polyamide shown.

(2)



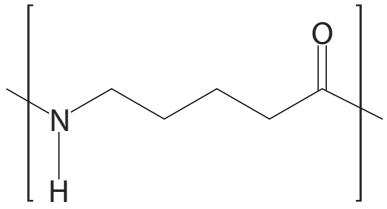
$HOOC(CH_2)_4COOH$	and	$H_2N(CH_2)_4NH_2$

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(c) Deduce the single monomer that could be used to produce the polyamide shown.

(1)

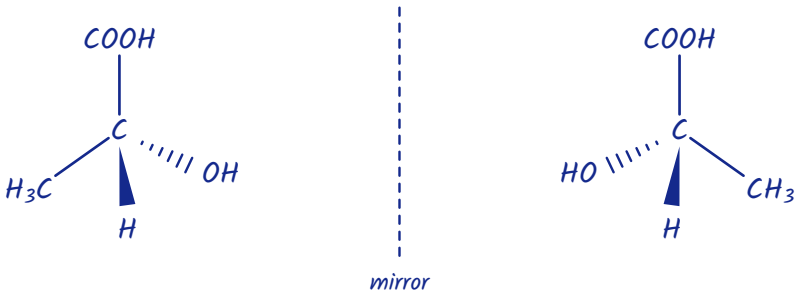


$H_2N(CH_2)_4COOH$

(d) PLA is a biodegradable polyester which is made from 2-hydroxypropanoic acid, $CH_3CH(OH)COOH$.

(i) Draw the two enantiomers of 2-hydroxypropanoic acid.

(2)



(ii) State how separate samples of these two enantiomers could be distinguished in a laboratory.

(1)

They rotate the plane of plane-polarised light (by the same amount) but in opposite directions; use a polarimeter.

(iii) Biodegradable polyesters break down naturally.

State why this is an advantage.

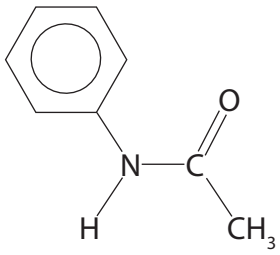
(1)

They do not accumulate in the environment or take up landfill space, and do not need to be incinerated.

(Total for Question 6 = 9 marks)

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7 Antifebrin was the trade name for N-phenylethanamide which was used as a painkiller until paracetamol was discovered.



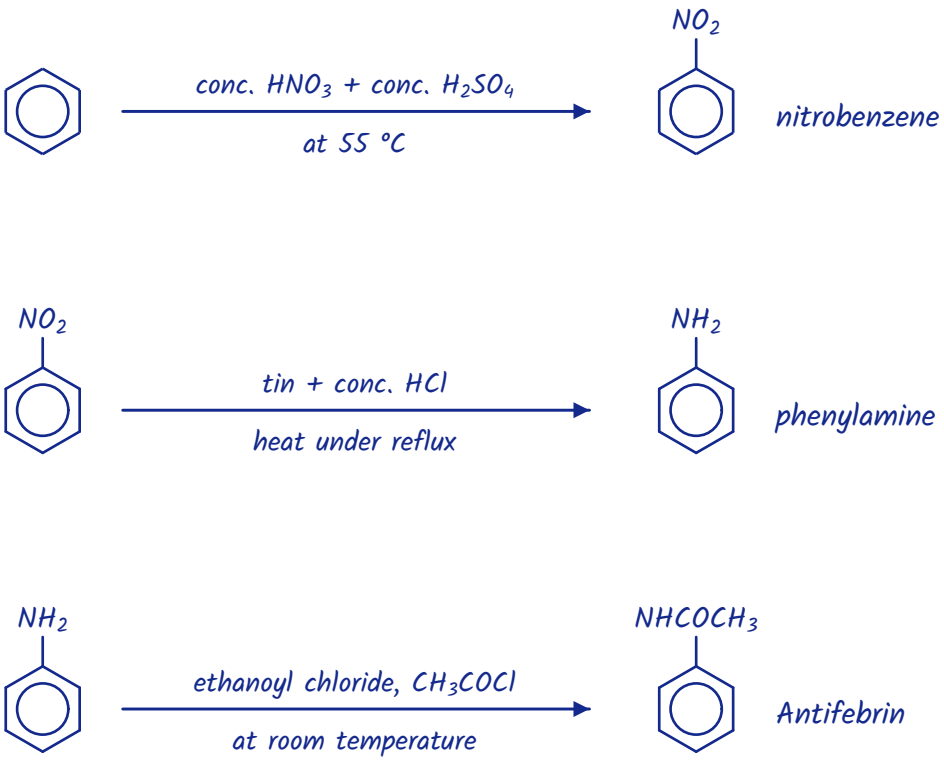
Antifebrin

(a) Some of the following reagents can be used to produce Antifebrin from benzene.

- Aluminium chloride
- Ammonia, concentrated
- Benzene
- Ethanal
- Ethanoic acid
- Ethanol
- Ethanoyl chloride
- Hydrochloric acid, concentrated
- Hydrochloric acid, dilute
- Iron
- Nitric acid, concentrated
- Nitric acid, dilute
- Propanone
- Sodium chloride
- Sulfuric acid, concentrated
- Tin

Selecting from only these reagents, devise a **three-step** synthetic pathway to convert benzene into Antifebrin. You should include the structures of the two intermediate compounds and the reaction conditions.

(5)



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(b) What is the number of peaks in a C-13 NMR spectrum of Antifebrin?

(1)

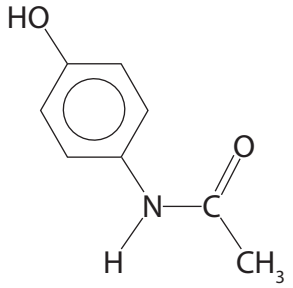
☒ **A** 5

☒ **B** 6

☒ **C** 7

☒ **D** 8

(c) Paracetamol is structurally similar to Antifebrin, but has a hydroxy group attached directly to the benzene ring.



The bromination of the benzene ring in paracetamol occurs much more readily compared to the bromination of benzene.

Explain this increased reactivity.

(2)

A lone pair of electrons on the oxygen of the OH group (and on the nitrogen) is delocalised into the ring, increasing the π electron density of the benzene ring. So the ring is more readily attacked by electrophiles, and the bromine molecule is more easily polarised ($Br^{\delta+}$).

(d) A tablet with a total mass of 500 mg contained 3.10×10^{-3} mol of paracetamol.

Calculate the percentage by mass of paracetamol in the tablet, quoting your answer to an appropriate number of significant figures.

(2)

M_r of paracetamol, $C_8H_9NO_2$ = 151

mass = $3.10 \times 10^{-3} \times 151 = 0.4681$ g

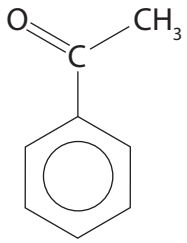
% = $(0.4681 \div 0.500) \times 100 = 93.62$ %

percentage by mass = 93.6 %

(Total for Question 7 = 10 marks)

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8 Phenylethanone is an ingredient in many types of chewing gum.



One method for the production of phenylethanone involves the reaction of benzene with ethanoyl chloride, CH_3COCl.

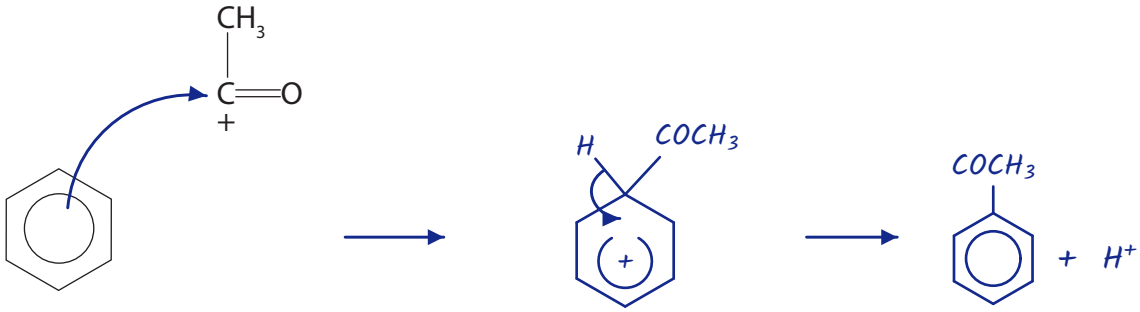
(a) (i) Write the equation for the formation of the electrophile, CH_3CO^+, from ethanoyl chloride using the catalyst aluminium chloride.

(1)

$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$

(ii) Complete the diagram, including curly arrows, to show the mechanism for the reaction between this electrophile and benzene to produce phenylethanone. Include the regeneration of the catalyst.

(4)

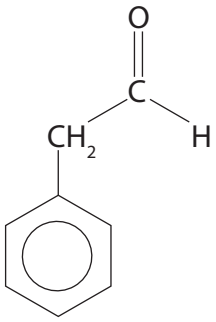


$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$

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(b) Phenylethanone can be distinguished from its structural isomer, phenylethanal, in a number of different ways.



(i) Which would react with phenylethanone but **not** with phenylethanal?

(1)

- ☐ **A** acidified sodium dichromate(VI)
- ☒ **B** alkaline iodine solution
- ☐ **C** Fehling's solution
- ☐ **D** Tollens' reagent

(ii) Give the steps to show how 2,4-dinitrophenylhydrazine could be used to distinguish between phenylethanone and phenylethanal.

(4)

Add a few drops of 2,4-dinitrophenylhydrazine (Brady's reagent) to a separate sample of each compound: each gives a yellow/orange crystalline precipitate (the 2,4-dinitrophenylhydrazone).

Filter off each precipitate and purify it by recrystallisation (from the minimum volume of hot ethanol), then dry it.

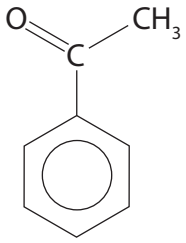
Measure the melting temperature of each purified, dry derivative.

Compare the melting temperatures with known (data book) values for the 2,4-dinitrophenylhydrazones of phenylethanone and phenylethanal. The derivatives have different melting temperatures, so each compound can be identified.

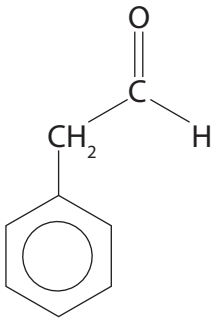
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*(iii) Compare and contrast the high resolution proton NMR spectra of phenylethanone and phenylethanal.

You should use the Data Booklet.



Phenylethanone



Phenylethanal

(6)

Similarities: both compounds contain a monosubstituted benzene ring, so both spectra show peaks for the aromatic hydrogens in the same region (6.5 to 8.4 ppm), which look very similar.

Both also have hydrogens on a carbon next to the C=O group (H–C–C=O), the CH_3 in phenylethanone and the CH_2 in phenylethanal, so both show a peak in the range 1.7 to 3.0 ppm.

Differences: phenylethanone has 4 hydrogen environments (three aromatic and CH_3) but phenylethanal has 5 (three aromatic, CH_2 and CHO), so phenylethanone shows one fewer peak.

Splitting: the CH_3 peak of phenylethanone is a singlet, as there are no hydrogens on the adjacent carbon. In phenylethanal the CH_2 peak is a doublet (split by the one CHO hydrogen) and the CHO peak is a triplet (split by the two CH_2 hydrogens).

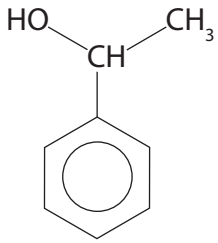
Peak areas: the CH_3 peak in phenylethanone has a relative area of 3, whereas in phenylethanal the CH_2 and CHO peaks are in the ratio 2 : 1.

Chemical shift: only phenylethanal has an aldehyde hydrogen, so only its spectrum has a peak at 9.0 to 10.1 ppm; phenylethanone has no peak in this region.

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(c) The compound 1-phenylethanol can be formed from phenylethanone.



Give the reagent and conditions that would be used to form 1-phenylethanol.

(2)

Reagent: lithium tetrahydridoaluminate(III), $LiAlH_4$.

Conditions: in dry ether (ethoxyethane).

(Total for Question 8 = 18 marks)

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9 This question is about reaction kinetics.

(a) Compound **A** decomposes in a first order reaction.

Calculate the time it takes for the mass of **A** to decrease from 600 g to 37.5 g if the decomposition has a constant half-life of 14 minutes.

(1)

600 → 300 → 150 → 75 → 37.5 g so 4 half-lives

time = 4 × 14 = 56 minutes

(b) The 'initial rates' method was used to investigate the orders of reaction with respect to reactants **X**, **Y** and **Z**. The table shows the results obtained.

Run	Initial concentration / mol dm^{-3}			Initial rate / mol dm^{-3} s^{-1}
	X	**Y**	**Z**	
1	0.00100	0.00300	0.00600	2.17×10^{-6}
2	0.00100	0.00600	0.00600	8.68×10^{-6}
3	0.00050	0.00600	0.00600	4.34×10^{-6}
4	0.00300	0.00300	0.00300	6.51×10^{-6}

(i) Calculate the orders with respect to **X**, **Y** and **Z**.

(3)

X *1 (first order)*

Y *2 (second order)*

Z *0 (zero order)*

(ii) Give the rate equation for the reaction and hence calculate the rate constant, *k*, to an appropriate number of significant figures. Include units in your answer.

(4)

rate = $k[X][Y]^2$

k = rate ÷ $[X][Y]^2$

$k = 2.17 \times 10^{-6} \div (0.00100 \times 0.00300^2) = 241.1$

$k = 241\ dm^6\ mol^{-2}\ s^{-1}$

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(c) The kinetics of the 'bromine clock' were investigated and the rate equation was found to be

$$\text{Rate} = k[BrO_3^-][Br^-][H^+]^2$$

(i) What is the overall reaction order?

(1)

- ☐ **A** First
- ☐ **B** Second
- ☐ **C** Third
- ☒ **D** Fourth

(ii) Calculate the concentration of bromide ions required to produce a reaction rate of 4.08×10^{-3} mol dm^{-3} s^{-1} at 298 K given that

$k = 8.00$ dm^9 mol^{-3} s^{-1}

$[BrO_3^-] = 0.200$ mol dm^{-3}

$[H^+] = 0.100$ mol dm^{-3}

(2)

$[Br^-] = \text{rate} \div (k[BrO_3^-][H^+]^2)$

$[Br^-] = 4.08 \times 10^{-3} \div (8.00 \times 0.200 \times 0.100^2)$

$[Br^-] = 4.08 \times 10^{-3} \div 0.0160$

$[Br^-] = 0.255 \text{ mol dm}^{-3}$

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(d) The rate constant for the reaction between bromoethane and aqueous hydroxide ions was determined at five different temperatures.

The results are given in the table.

Temperature (T) / K	1 / Temperature (1 / T) / K^{-1}	Rate constant, k / $dm^3\ mol^{-1}\ s^{-1}$	ln k
293	3.41×10^{-3}	5.83×10^{-5}	−9.75
303	3.30×10^{-3}	1.67×10^{-4}	−8.70
313	3.19×10^{-3}	5.26×10^{-4}	−7.55
323	3.10×10^{-3}	1.36×10^{-3}	−6.60
333	3.00×10^{-3}	3.77×10^{-3}	−5.58

Complete the data in the table and use them to plot a graph of ln k against 1 / T and hence determine the activation energy, E_a, in kJ mol^{-1}.

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

The Arrhenius equation can be expressed as

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

(7)

Two points on the line: $(2.95 \times 10^{-3}, -5.08)$ and $(3.50 \times 10^{-3}, -10.71)$

gradient = $(-10.71 - (-5.08)) \div (3.50 \times 10^{-3} - 2.95 \times 10^{-3})$

gradient = $-5.63 \div 0.55 \times 10^{-3} = -1.02 \times 10^{4}$ K

gradient = $-E_a \div R$ so $E_a = 1.02 \times 10^{4} \times 8.31$

$E_a = 85\ 100$ J mol^{-1}

$E_a = +85.1$ kJ mol^{-1}

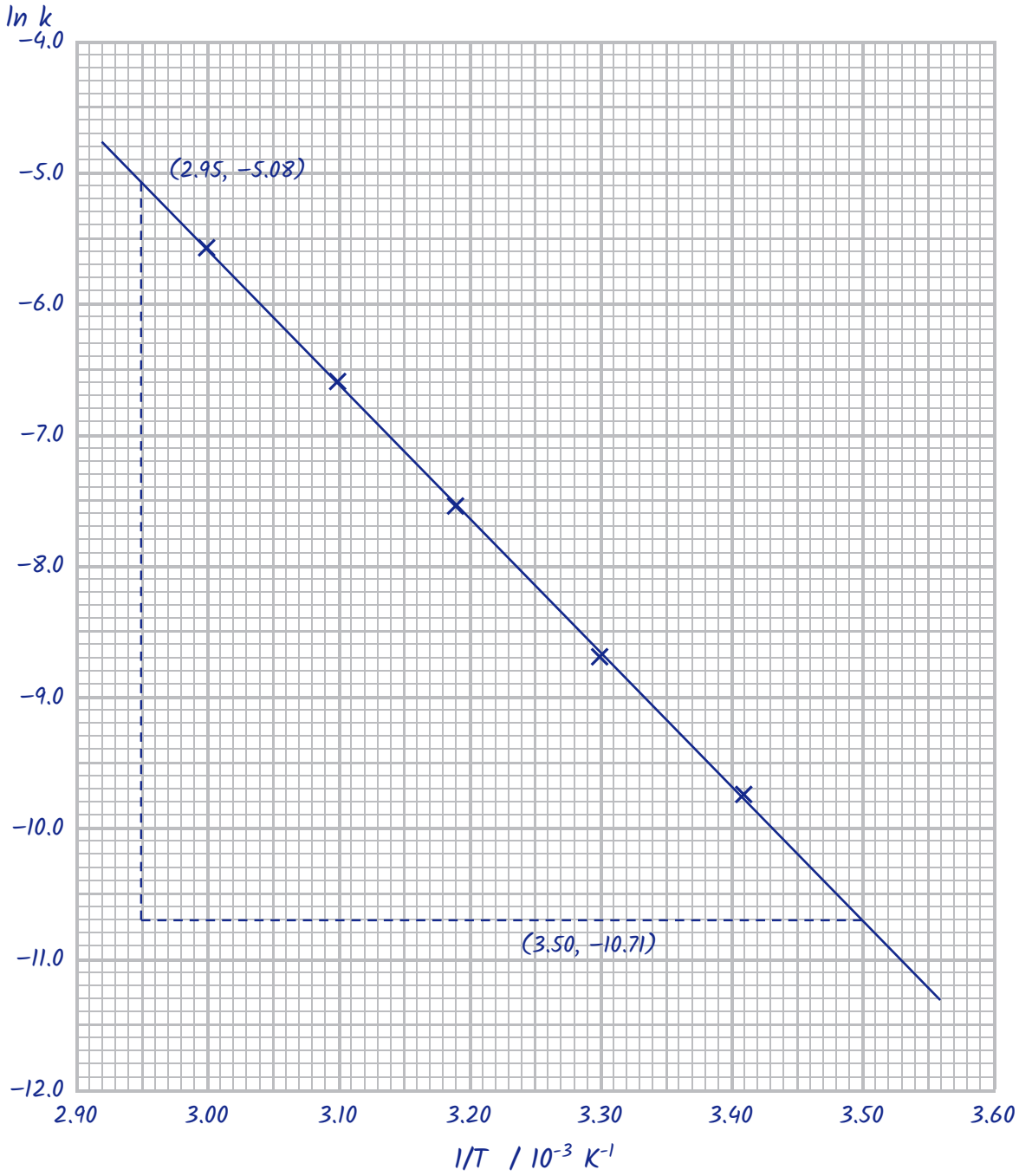
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gradient = -1.02×10^4 K

(Total for Question 9 = 18 marks)

TOTAL FOR PAPER = 90 MARKS

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The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8) (18)
							1.0 H hydrogen 1										4.0 He helium 2
(1)	(2)		Key: relative atomic mass / atomic symbol / name / atomic (proton) number									(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4											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 damstadtium 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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