Edexcel

A2

Chemistry

Questions and Answers

PHILIP ALLAN
UPDATES

Contents

Introduction 3

Unit 4 Rates, equilibria and further organic chemistry

Multiple-choice questions 7

Structured questions 13

Data question 18

Unit 5 Transition metals, arenes and organic nitrogen chemistry

Multiple-choice questions 20

Structured questions 25

Data question 31

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Introduction

The new Edexcel specification for A2 chemistry will be examined for the first time in 2010. This online resource contains samples of questions that might be asked in the examinations, together with the sort of answers that an A-grade candidate should give. There is also important advice about how examinations should be tackled and examples of common mistakes made by candidates who achieve low grades. These questions with their answers provide a useful resource in the important matter of examination technique, as well as helping to clarify chemical ideas.

The questions given here are not balanced in each unit in terms of type of question or level of demand — they are not intended to typify real papers, only the sort of questions that could be asked.

The answers are those that examiners would expect from a grade-A candidate. They are not 'model answers' to be regurgitated without understanding. In answers that require more extended writing, it is the ideas that count rather than the form of words used. The principle is that correct and relevant chemistry, clearly and logically explained by the candidate, scores.

Below you will find important advice on how to cope with answer papers that are marked online and some information on marking exams and how this differs from the marking of homework.

The new specification

There are some significant differences in question style between previous examinations and the new ones. You should bear these differences in mind if you have to work through past papers based on the previous specification.

Multiple-choice questions

The Unit 4 and 5 examinations each have 20 multiple-choice questions, and these should take you no more than 20 minutes. Examination papers are often written on the basis of approximately 1 mark a minute.

Contemporary contexts

Chemistry questions often involve contexts, i.e. a particular area of chemistry is linked to an industrial process or a feature of everyday life. A context question may ask you to read a passage and then examine the underlying chemistry. It is not a simple comprehension exercise. The chemistry behind the context must be known, including any equations. It is in your answers to such questions that your quality of written communication will be assessed.

Context questions appear in both A2 papers.

How science works (HSW)

Although billed as new in this specification, HSW is not really new. It involves using theories and models, posing questions that can be answered scientifically, carrying out practical investigations and being able to use scientific terminology properly. All these skills have featured in previous specifications, but in the new one the role of HSW in assessment and its proportion in an examination paper are specified. It is unlikely that you would notice any difference between HSW questions and questions on similar topics from past papers.

An example of HSW involves the use of theories, models and ideas to develop and modify scientific explanations. A question that starts with data on initial rates and uses the results to explain whether the reaction is S_N1 or S_N2 is an example of HSW. Any question on entropy could be classified as HSW because it is a general theory that enables predictions to be made.

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HSW includes:

- the assessment of risk in experiments, and understanding the difference between risk and hazard
- considering the way in which science is communicated and how the quality of the work is judged by other scientists (peer review)
- green chemistry; particularly the efforts to make chemical processes less hazardous and more efficient both in terms of the proportion of the atoms started with that finish up in the product (atom economy) and in terms of lower energy consumption

The examinations

The A2 written examination papers (Unit 4 and Unit 5) are marked out of 90 and last for 1 hour 40 minutes.

Unit 4 has three sections:

- Section A — multiple-choice questions, each with a choice of four answers.
- Section B — a mixture of short-answer and extended-answer questions. This section looks similar to the papers in the previous modular tests, where the more extended writing is about 4 or 5 marks-worth of material.
- Section C — one or more questions that require analysis of data. Some data might be given on the question paper, but candidates are also required to find necessary data inthe Edexcel data booklet.

Unit 5 has three sections:

- Section A — multiple-choice questions, as in Unit 4.
- Section B — a mixture of short-answer and extended-answer questions. These questions can include analysis and evaluation of practical work.
- Section C — one or more questions using a contemporary context. Such questions could contain stimulus material which should to be read carefully before answering the questions that follow. The stimulus material could take the form of a passage of up to a page in length that contains information essential to answering some of the questions.

Marking examinations: Edexcel online marking (ePEN)

It is important to understand how examinations are marked, because it affects how you must present your answers. As the examiner reads your answer, decisions have to be made — is this answer worth the mark? Those who think that these decisions are always easy 'because science is right or wrong' have misunderstood the nature of marking and the nature of science.

Your job is to give the *clearest possible answer* to the question asked, in such a way that your chemical understanding is made obvious to the examiner. In particular, you must not expect the examiner to guess what is in your head; you can be judged only by what you write.

Not all marking is the same

The marking of homework or other school work is not the same as the marking of examinations.

Teachers marking their students' work are engaging in formative assessment and their comments are geared towards helping students to improve their understanding of chemistry. It will include suggestions for improving understanding, which are far more important than the mark awarded, as is any discussion resulting from the work. An examination is a summative assessment; candidates have no opportunity to improve, so the mark is everything. This is why the answers to questions that are designed to improve your understanding of chemistry during the course are fuller than the answers usually demanded by the examiners. Many of the answers in this online resource are explained more fully than explanations given on A2 level mark schemes.

You should not regard examination questions and answers as chemical education; they are an attempt to test whether you have acquired that education through the influence of your teachers and your own reading. Chemical education is designed to make you into a competent chemist rather than one who can simply regurgitate 'model answers' with no underlying

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understanding. If you do the necessary work throughout the course, the examination content should look after itself. What you need is the right answering technique.

Because examination answers cannot be discussed, you must make your answers as clear as possible. Do not expect examiners to guess what is in your head. This is one reason why you are expected to show working in calculations, for example. It is especially important to *think before you write*. You are given a reasonable amount of space in which to write your answer. However, differing handwriting size, false starts and crossings-out, and a tendency to repeat the question mean that this space is never exactly right for all candidates. The best advice is that *before you begin your answer you must have a clear idea of how it will end*. There is neither time nor space for subsequent editing. It is a good plan to practise putting your answer into a list of the points you wish to make, and then join them up into coherent sentences. You can also leave them as a list and still earn marks for good quality of written communication.

Read the question through

Candidates are, unsurprisingly, eager to get on and write something, but you should be patient. In Sections B and C, it is a good idea to read through a whole question before you start to answer it.

Reading a question through gives an opportunity for the brain to do some subconscious processing while the conscious mind is busy directing the writing. You need to have an idea of what is around the corner and what dangers to avoid. This technique becomes more important the more chemistry you know, since the A2 papers increasingly expect you to make links between different areas of the specification and to acquire synoptic understanding. These links can be made by the brain in the background as you begin to answer the question.

Online marking: how to avoid common pitfalls

- **Do *not* write in any colour other than black. This is now an exam board regulation.**
- **Do *not* write outside the space provided without saying, *in that space*, where the remainder of the answer can be found.**

Edexcel scripts are marked online, so few examiners handle the original paper script. The process is as follows:

- The exam paper is divided into items, usually a single part of a question. These items are also called clips.
- The items are set up so that they display on screen, with check-boxes for the score and various buttons to allow the score to be submitted or for the item to be processed in some other way.
- Your written paper is scanned; from that point your paper is only handled electronically. Your answers are tagged with an identity number and each item becomes part of a pool.
- It is impossible for examiners to identify a centre or a candidate from any of the information supplied.
- Examiners mark items over about 3 weeks.
- They are instructed on how to apply the marking scheme and are tested to make sure that they know what is required and can mark the paper fairly.
- Examiners are monitored throughout the marking period. They are prevented from marking an item if they do not achieve the necessary standard of accuracy; defective marking is re-marked.
- Examiners mark items, not whole scripts. Depending on the length of an item, between 20 and 50 examples are marked and then the examiner moves on to another item. This style of marking means that your paper could be marked by as many as 20 different people.
- Items are allocated to examiners randomly, so generally they do not see more than one item from a given candidate.

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It is important to avoid the following potential pitfalls:

- Do not write in any colour other than black. The scans are black-and-white, so any colour used simply comes out black — unless you write in red, which does not come out at all. The scanner cannot see red (or pink or orange) writing. If, for example, you want to highlight different areas under a graph, or distinguish lines on a graph, you must use a different sort of shading rather than a different colour.
- Do not write too small. Because the answer appears on a screen, the definition is slightly degraded. In particular, very small numbers used for powers of 10 can be difficult to see. The original paper script can be checked but it takes a long time to get hold of it.
- Do not write in pencil. Faint writing does not scan well.
- Do not write outside the space provided without saying, *within that space*, where the remainder of the answer can be found. Examiners only have access to the items they are marking; they cannot see the rest of your script. So if you carry on your answer elsewhere but do not tell the examiner within the clip where the remainder of your answer can be found, it will not be marked. Although the examiner cannot mark the out-of-clip work, the paper will be referred to the Principal Examiner for marking.
- Do not use asterisks or arrows as a means of directing examiners to out-of-clip items.
- Explain in words. Examiners cannot be expected to guess what the asterisks mean.
- Do not write across the centre fold of the paper from the left-hand to the right-hand page. A strip about 8 mm wide is lost when the papers are guillotined for scanning.
- Do not repeat the question in your answer. For example, the answer to the question 'Define the enthalpy of hydration of a calcium ion' is: 'The enthalpy change when one mole of calcium ions in the gas phase is dissolved in excess water' or, using an equation, 'The energy change per mole for $Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq)$'. Do not start by writing 'The enthalpy of hydration of a calcium ion is defined as...' because this will take up most of the space available for the answer. Examiners know what the question is — you do not need to repeat it.

George Facer

George Facer was Head of Science at Sherborne School, Deputy Headmaster at Kamuzu Academy, Malawi and Instructor in Advanced Placement Chemistry at Phillip's Academy Massachusetts. He is currently Chair of Examiners for Edexcel A-Level Chemistry. The questions presented here are a sample of those that will appear in the new Unit Guides for the 2008 Edexcel specification.

For further questions and answers, with examiner comments, and specific content guidance on each unit, see our *Student Unit Guides* for Edexcel AS Chemistry (available now) and for Edexcel A2 Chemistry (available from early summer 2009). For more information and to order copies online, visit **www.philipallan.co.uk**, or contact Bookpoint on 01235 827720.

Edexcel AS Chemistry Student Unit Guides – written by Rod Beavon

978-0-340-95012-8 Edexcel AS Chemistry Unit 1: The Core Principles of Chemistry

978-0-340-94818-7 Edexcel AS Chemistry Unit 2: Applications of the Core Principles of Chemistry

Edexcel A2 Chemistry Student Unit Guides – written by George Facer

978-0-340-94949-8 Edexcel A2 Chemistry Unit 4: General Principles of Chemistry I — Rates, Equilibria and Further Organic Chemistry

978-0-340-94948-1 Edexcel A2 Chemistry Unit 5: General Principles of Chemistry II — Transition Metals and Organic Nitrogen Chemistry

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Unit 4: Multiple-choice questions

Each question or incomplete statement is followed by four suggested answers, A, B, C and D. Select the *best* answer in each case. The answers are given, with some commentary, after Question 15.

1 Consider the reaction:

$A + 2B \rightarrow C + D$

The reaction was studied and the following data on initial rates were obtained.

Experiment	[A]/mol dm^{-3}	[B]/mol dm^{-3}	Rate/mol dm^{-3} s^{-1}
1	0.10	0.10	4.6×10^{-4}
2	0.30	0.10	1.4×10^{-3}
3	0.15	0.20	1.4×10^{-3}

What is the correct rate equation?

- ☐ **A** rate = k[A]
- ☐ **B** rate = k[A]^3
- ☐ **C** rate = k[A][B]
- ☐ **D** rate = k[A][B]^2

2 For a specific reaction, the rate equation is:

rate = k[X]^2[Y]

The units of rate are mol dm^{-3} s^{-1}. The units of the rate constant, k, for this reaction are:

- ☐ **A** mol^{-1} dm^3 s^{-1}
- ☐ **B** mol dm^{-3} s
- ☐ **C** mol^{-2} dm^6 s^{-1}
- ☐ **D** mol^2 dm^{-6} s

3 An exothermic reaction is thermodynamically spontaneous at 20°C. Which of the following statements is correct?

- ☐ **A** It will be spontaneous at all temperatures whatever the sign of ΔS_{system}.
- ☐ **B** It will only proceed at 20°C if the activation energy is not too high.
- ☐ **C** It will only proceed if ΔS_{system} is positive.
- ☐ **D** The value of ΔS_{total} is larger at 40°C than at 20°C.

4 Which of the following does **not** have a positive value of ΔS_{system}?

- ☐ **A** $MgSO_4(s) + aq \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$
- ☐ **B** $Ba(OH)_2.8H_2O(s) + 2NH_4Cl(s) \rightarrow BaCl_2(s) + 10H_2O(l) + 2NH_3(g)$
- ☐ **C** $NaCl(s) \rightarrow NaCl(l)$
- ☐ **D** $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$

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5 Consider the equilibrium reaction:

$$A(g) + B(g) \rightleftharpoons C(g) \qquad \Delta H = +23\ kJ\ mol^{-1}$$

Which of the following statements is true?

- ☐ **A** An increase in pressure will drive the position of equilibrium to the right and hence will increase the value of the equilibrium constant, *K*.
- ☐ **B** An increase in pressure will increase the value of the equilibrium constant, *K*, and hence drive the position of equilibrium to the right.
- ☐ **C** An increase in temperature will drive the position of equilibrium to the right and hence will increase the value of the equilibrium constant, *K*.
- ☐ **D** An increase in temperature will increase the value of the equilibrium constant, *K*, and hence drive the position of equilibrium to the right.

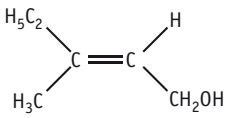
6 The Haber process for the manufacture of ammonia utilises the exothermic reaction between nitrogen and hydrogen. It is carried out at 400°C at a pressure of 200 atm in the presence of a heterogeneous catalyst of iron. Which of the following statements is **not** true about this process?

- ☐ **A** High pressure is used to increase the equilibrium yield.
- ☐ **B** High pressure is used to speed up the rate of reaction.
- ☐ **C** The value of the equilibrium constant is small at 400°C and is even smaller at 500°C.
- ☐ **D** A temperature of 400°C and an iron catalyst are chosen because these conditions result in a reasonable yield at a fast rate.

7 A buffer solution of a weak acid and its salt has a pH of 5.00. When it is diluted ten-fold, its pH:

- ☐ **A** stays the same
- ☐ **B** alters by a small amount only, because a buffer resists changes in pH.
- ☐ **C** falls to 4.00
- ☐ **D** increases to 6.00

8 The correct name for the following compound is:



- ☐ **A** *E*-1-hydroxy-3-methylpent-2-ene
- ☐ **B** *Z*-1-hydroxy-3-methylpent-2-ene
- ☐ **C** *cis*-1-hydroxy-3-methylpent-2-ene
- ☐ **D** *trans*-1-hydroxy-3-methylpent-2-ene

9 The compound $CH_3CH(OH)CH(CH_3)COOH$ has:

- ☐ **A** no optical isomers
- ☐ **B** two optical isomers
- ☐ **C** three optical isomers
- ☐ **D** four optical isomers

10 In the nucleophilic addition of HCN to propanone, the first step is attack by a lone pair of electrons:

- ☐ **A** on the oxygen atom of propanone onto the δ^+ hydrogen atom of HCN
- ☐ **B** on the carbon atom of HCN onto the δ^+ carbon atom in propanone
- ☐ **C** on the carbon atom of the CN^- ion onto the δ^+ carbon atom in propanone
- ☐ **D** on the nitrogen atom of the CN^- ion onto the δ^+ carbon atom in propanone

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11 In which of the following is there hydrogen bonding?

- ☐ **A** between different molecules of propanone
- ☐ **B** between different molecules of propanal
- ☐ **C** between propanal and propanone molecules
- ☐ **D** between propanal molecules and water

12 Consider the reaction scheme:

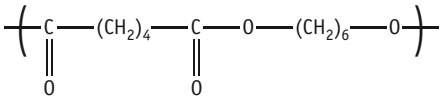
$$CH_3COOH \xrightarrow{\text{step 1}} CH_3COCl \xrightarrow{\text{step 2}} CH_3CONH_2$$

What are the correct reagents for steps 1 and 2?

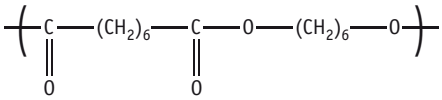
	Step 1	Step 2
☐ **A**	PCl_5	KCN
☐ **B**	PCl_5	NH_3
☐ **C**	HCl	KCN
☐ **D**	HCl	NH_3

13 The correct repeat unit for the polyester formed by reacting hexane-1,6-dioic acid with hexane-1,6-diol is:

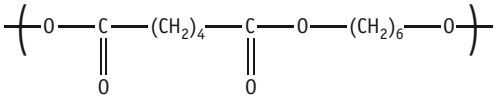
☐ **A**



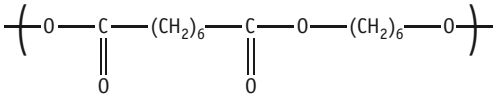
☐ **B**



☐ **C**



☐ **D**



14 The NMR spectra of CH_3CH_2Cl and CH_3CH_2Br:

- ☐ **A** both have two peaks in the ratio 3:2 at the same chemical shift
- ☐ **B** both have two peaks in the ratio 3:2 at different chemical shifts
- ☐ **C** both have two peaks split into 2 and 3
- ☐ **D** both have three peaks in the ratio 3:2:1 due to the C–H bond in CH_3, the C–H bond in CH_2 and the C–halogen bond

15 The mass spectrum of CH_3CH_2Br will have:

- ☐ **A** a peak at *m/e* = 109
- ☐ **B** peaks at *m/e* = 108 and 110
- ☐ **C** peaks at *m/e* = 93, 94 and 95
- ☐ **D** peaks at *m/e* = 79, 80 and 81

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Answers

1 C When experiments 1 and 2 are compared, [A] increases by a factor of 3 and the rate increases by a factor of $1.4 \times 10^{-3}/4.6 \times 10^{-4} = 3.0$, so it is first order with respect to A. Consider experiments 2 and 3: [A] halves and [B] doubles, but the rate stays the same. The halving of [A] would reduce the rate by a factor of 2, but as the rate did not alter, the doubling of [B] must have increased the rate by a factor of 2, cancelling out the decrease due to the lower concentration of A. This means that the reaction is first order with respect to B.

2 C The rate equation has to be rearranged into:

$$k = \frac{\text{rate}}{[X]^2[Y]}$$

which, on substituting, becomes:

$$k = \frac{\text{concentration} \times \text{time}^{-1}}{\text{concentration}^2 \times \text{concentration}} = \text{concentration}^{-2}\,\text{time}^{-1} = \text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$$

In options **B** and **D** the expression for k is upside down; options **A** and **B** do not show that it is second order in [X].

3 B For a thermodynamically feasible reaction to be observed, the activation energy must be reasonably low, so that the reactants are kinetically unstable as well as being thermodynamically unstable. Thus **B** is the correct response. It is worth checking the others. For a reaction to be spontaneous, ΔS_{total} must be positive. Since the reaction is exothermic, ΔS_{surr} is positive. If ΔS_{system} is negative, the reaction will cease to be spontaneous as the temperature is increased, because ΔS_{surr} will become less positive. This means that **A** is false. ΔS_{system} need not be positive. If it is negative and numerically less than the positive ΔS_{surr}, the reaction is feasible. Thus option **C** is false. ΔS_{total} is not larger at 40°C. It is an exothermic reaction and so the value of ΔS_{total} (and hence the equilibrium constant K) will decrease with an increase in temperature. Thus option **D** is also false.

4 A Even though there is a large increase in entropy of the solute going from solid to aqueous solution, the water is ordered by the high charge density of the group 2 cation. This more than outweighs the increase in entropy of the magnesium sulfate. Therefore ΔS_{system} is negative, making option **A** the correct answer to this negative question. It is worth putting '+' or '–' beside each response. Then the one marked '–' will be your answer. In **B**, a highly disordered gas is produced, so ΔS_{system} is positive. A molten liquid always has a higher entropy than its solid, so option **C** is positive. In **D**, two moles of gas are formed from one mole of gas, which causes an increase in entropy. Therefore, **D** is positive. The only answer with a negative ΔS_{system} is **A**.

5 D A change in pressure will not alter the value of the equilibrium constant, K, so options **A** and **B** cannot be correct. The logic in option **C** is wrong, but is correct in option **D**. For any endothermic reaction, an increase in temperature will cause an increase in the value of K, which becomes bigger than the equilibrium term $[\text{products}]^n/[\text{reactants}]^m$. This term has to get larger, so that it once again equals the value of K. To do this, the value of the upper line must increase and that of the bottom line decrease. This happens as the position of equilibrium shifts to the right, so the answer is **D**. The logic for an *endo*thermic reaction is:

T increases, therefore K increases, therefore the equilibrium position moves to the right

and is **not**:

T increases, therefore the equilibrium position moves to the right, so K increases.

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6 B This question is best answered by putting *true* or *false* beside each option:

- Option A: True — there are fewer gas moles on the right, so an increase in pressure will drive the equilibrium to the right and so increase the yield.
- Option B: False — the rate of a reaction involving a solid metallic catalyst at a given temperature is not altered by pressure. It depends solely on the number of active sites on the surface of the catalyst.
- Option C: True — the value of *K* is small at 400°C (which is why it is economic to use high pressure). Since the reaction is exothermic, the value of *K* will decrease as the temperature rises.
- Option D: True — a catalyst allows the reaction to proceed at a fast rate at a lower temperature. This results in a higher yield than if a higher temperature were used.

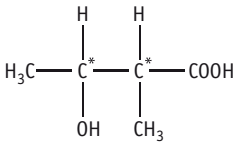
Options **A, C** and **D** are all true. Option **B** is false and is the correct answer to this negative question.

7 A $[H^+] = \dfrac{K_a\,[\text{acid}]}{[\text{salt}]}$, so the pH of a buffer depends on the ratio of [acid] to [salt].

This ratio is not altered by dilution, so the pH stays the same. Option **B** shows a misunderstanding of the term 'buffer'. A buffer resists change in pH when a small amount of *acid* or *alkali* is added. Options **C** and **D** would be true if the ratio of [acid] to [salt] were to increase or decrease by a factor of 10.

8 A As there are four different groups around the C=C, the *cis/trans* method of naming geometric isomers cannot be used, so options **C** and **D** are incorrect. The group on the right-hand carbon of the C=C that has the higher priority is the C_2H_5 group; that with the higher priority on the left-hand carbon is the CH_2OH group. These are on opposite sides of the double bond, so the compound is an *E*-isomer.

9 D The compound has two different chiral centres, as shown by the asterisks * on the carbon atoms in the formula:



The four isomers are ++, −−, +− and −+. The last two are different because the four groups around the first chiral carbon atom are different from the four groups around the second chiral carbon atom.

10 C This reaction requires a catalyst of cyanide ions. The formula of a cyanide ion is usually written as CN^-. However, the charge is on the carbon atom, which has a lone pair of electrons. In the first step, the lone pair attacks the δ^+ carbon atom in propanone, forming a new carbon–carbon bond.

11 D For hydrogen bonding to occur there must be a δ^+ hydrogen atom in one molecule and a δ^- oxygen atom in the other molecule. Propanal has a δ^- oxygen (caused by the considerable difference in electronegativities of the carbon and the oxygen in the C=O group) and there are δ^+ hydrogen atoms in the water. This means that hydrogen bonding will occur. Neither propanone nor propanal has a hydrogen atom that is sufficiently δ^+ for hydrogen bonding, so there are no hydrogen bonds between propanone molecules (option **A**), between propanal molecules (option **B**) or between propanal and propanone molecules (option **C**).

12 B A carboxylic acid can be converted to an acid chloride by reaction with phosphorus pentachloride, PCl_5, not by reaction with hydrogen chloride. Thus options **C** and **D** are incorrect. The conversion of an acid chloride to an amide is carried out by reaction with ammonia. Thus, option **A** is incorrect.

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13 A Hexane-1,6-dioic acid has six carbon atoms (including the carboxylic acid carbon atoms), so options **B** and **D** are incorrect as they both have eight carbon atoms in the dioic acid parts of their chains. The polyester forms by loss of an OH from one monomer and an H from the other, so the repeat unit has only four oxygen atoms. This means that options **C** and **D** are incorrect because they have five oxygen atoms in their repeat units.

14 B Peaks in an NMR spectrum are caused by protons in different chemical environments. The protons of the CH_3 group are in a different environment from those in the CH_2 group, so there are two peaks in the spectra of both molecules. This discounts option **D**. The peaks will be split by spin–spin coupling according to the $(n + 1)$ rule, where n is the number of neighbouring hydrogen atoms. This means that the peak due to the CH_3 group will be split into three and that of the CH_2 into four, so option **C** is incorrect. The different halogen atoms will cause a different δ value (chemical shift), so option **A** is incorrect and **B** is correct.

15 B Bromine has a relative atomic mass of 80. However, there are no atoms of mass 80 units, as bromine consists of two isotopes of masses 79 and 81 in equal proportions. Thus it will *not* have a molecular ion of mass $(2 \times 12) + 5 + 80 = 109$ (option **A**). The molecular masses of $CH_3CH_2{}^{79}Br$ and $CH_3CH_2{}^{81}Br$ are 108 and 110, so there will be peaks at *m/e* 108 and 110 (the correct response **B**). There will also be peaks due to loss of CH_3 at $108 - 15 = 93$ and $110 - 15 = 95$, but no peak at $109 - 15 = 94$, so option **C** is incorrect. There will be peaks at $m/e = 79$ and 81 due to ${}^{79}Br^+$ and ${}^{81}Br^+$, but no peak at $m/e = 80$ because there is no ${}^{80}Br$ isotope. Therefore, option **D** is incorrect.

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Unit 4: Structured questions

Responses to questions with longer answers may have an examiner's comment preceded by the icon e. Some of the comments highlight common errors made by candidates who produce work of C-grade standard or lower.

Question parts marked with an asterisk* test 'Quality of Written Communication' (QWC). It is worth reading through the whole question before attempting to answer it.

Question 16

a What is meant by:

(i) order of reaction (1 mark)

(ii) rate of reaction (1 mark)

b 1-bromopropane and sodium hydroxide react to form propan-1-ol and sodium bromide. The rate of this reaction was measured using different concentrations of hydroxide ions and 1-bromopropane. The results are shown in the table below.

Experiment	$[OH^-]$/mol dm^{-3}	[1-bromopropane]/ mol dm^{-3}	Initial rate of reaction/mol dm^{-3} s^{-1}
1	0.25	0.25	1.4×10^{-4}
2	0.125	0.25	7.0×10^{-5}
3	0.50	0.125	1.4×10^{-4}

***(i)** Deduce the order of reaction with respect to hydroxide ions and to 1-bromopropane. Justify your answer. (4 marks)

(ii) Write the rate equation for this reaction. (1 mark)

(iii) Calculate the value of the rate constant. (2 marks)

(iv) Write a mechanism for this reaction that is consistent with your answer to (ii). (3 marks)

***c** In terms of collision theory, explain how the rate of this exothermic reaction would alter with an increase in temperature. (4 marks)

Total: 16 marks

Answers to Question 16

a (i) The sum of the powers to which the *concentrations* of the reactants are raised in the experimentally determined rate equation ✓.

e Do not say that it is the sum of the individual orders, unless you also define individual order.

(ii) The rate of change of concentration of a reactant or of a product with respect to time ✓.

e The answer 'It is the amount by which the concentration has changed divided by the time for that change' is also acceptable.

b (i) Consider experiments 1 and 2. When $[OH^-]$ is halved and [1-bromopropane] is kept constant, the rate also halves. Therefore, the order with respect to hydroxide ions is 1 ✓.

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Consider experiments 1 and 3. When $[OH^-]$ is doubled and [1-bromopropane] is halved, the rate does not alter. Since the rate should double because of the doubling of $[OH^-]$ ✓, the halving of [1-bromopropane] must have caused the rate to halve ✓, cancelling out the increase due to the rise in $[OH^-]$. Therefore, the reaction is first order ✓ with respect to 1-bromopropane.

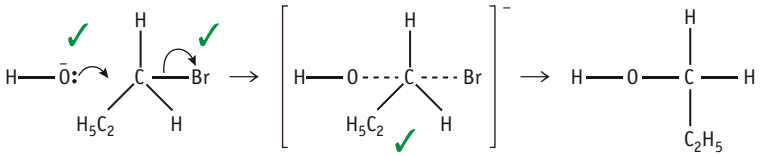
e You must make it clear which two experiments you are comparing.

(ii) rate $= k[OH^-][\text{1-bromopropane}]$ ✓

(iii) $k = \dfrac{\text{rate}}{[OH^-][\text{1-bromopropane}]} = \dfrac{1.4 \times 10^{-4}}{0.25 \times 0.25}$ ✓ $= 0.0022\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$ ✓

e The units of k can be calculated as $\dfrac{\text{concentration} \times (\text{time})^{-1}}{(\text{concentration})^2} = (\text{concentration})^{-1} \times (\text{time})^{-1}$

(iv) The rate equation is first order with repect to both reactants, so the mechanism is S_N2. It is attacked by the nucleophilic OH^- ion involving a transition state:



e The curly arrow should start from the lone pair of electrons on the oxygen atom of the OH^- ion and go towards the δ^+ carbon atom. A second curly arrow must be drawn from the σ C–Br bond to the δ^- bromine atom. The transition state must show a negative charge.

c An increase in temperature causes the molecules to gain kinetic energy ✓. As a result, more of the colliding molecules have energy ≥ the activation energy ✓, so a greater *proportion* of the collisions result in reaction ✓ (i.e. more of the collisions are successful). Hence the rate of reaction increases ✓.

e For the third mark, do not say that 'There will be more successful collisions'. The total number of successful collisions is independent of the temperature because the reaction will still go to completion, but over a longer time, at a lower temperature.

Question 17

Hydrogen can be made by reacting steam with coke at high temperature:

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ $\Delta H = +131\ \text{kJ mol}^{-1}$

a The reaction was allowed to reach equilibrium at a temperature T and at a pressure of 1.2 atm. It was found that 10% of the steam was converted into carbon monoxide and hydrogen.

(i) Write the expression for K_p. (1 mark)

(ii) Calculate the value of K_p at this temperature (to two significant figures). Include the units in your answer. (6 marks)

***b** State and explain the effect on the equilibrium constant, K_p, and *hence* on the equilibrium yield of hydrogen of:

(i) increasing the pressure to 2.4 atm (4 marks)

(ii) increasing the temperature (3 marks)

c Suggest why a temperature of 2000°C is not used. (1 mark)

Total: 15 marks

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Answers to Question 17

a (i) $K_p = \dfrac{p(CO)p(H_2)}{p(H_2O)}$ ✓

e A value for carbon (coke) is not included because it is a solid.

(ii)

	$H_2O(g)$	$CO(g)$	$H_2(g)$	
Initial moles	1	0	0	
Equilibrium moles	1 – 0.10 = 0.90	0.10	0.10	✓
Mole fraction	0.90/1.10 = 0.818	0.10/1.10 = 0.0909	0.10/1.1 = 0.0909	✓
Partial pressure/atm	0.818 × 1.2 = 0.982	0.0909 × 1.2 = 0.109	0.0909 × 1.2 = 0.109	✓

$$K_p = \frac{p(CO)p(H_2)}{p(H_2O)} = \frac{0.109\,\text{atm} \times 0.109\,\text{atm}}{0.982\,\text{atm}} = 0.012\,✓\,\text{atm}\,✓\,(2\text{ s.f.})\,✓$$

e The route is:
% → equilibrium moles → mole fraction → partial pressure → value for K_p → units of K_p.

b (i) Increasing the pressure has no effect on the value of K_p ✓; only temperature change affects this. However, the partial pressure term increases by a factor of two and so is no longer equal to the unaltered K_p ✓. The system is now not at equilibrium and reacts by moving to the left until the partial pressure term once again equals K_p ✓. Thus the equilibrium yield of hydrogen is decreased ✓.

(ii) Increasing the temperature will cause the value of K_p to increase, as the reaction is endothermic ✓. The partial pressure term is now smaller than K_p, so the system is not in equilibrium ✓ and reacts to make more hydrogen and carbon monoxide until the partial pressure term equals the new larger value of K_p ✓.

c This temperature would result in greater conversion to hydrogen, but would be uneconomic as water is cheap and such a high temperature is expensive to maintain ✓.

Question 18

a Propanoic acid, CH_3CH_2COOH, is a weak acid that reacts reversibly with water:

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH_2COO^-(aq)$$

When an aqueous solution of propanoic acid is mixed with solid sodium propanoate, a buffer solution is formed.

(i) Write the expression for the acid dissociation constant, K_a, of propanoic acid. (1 mark)

(ii) Define a buffer solution. (2 marks)

(iii) Calculate the mass of sodium propanoate that has to be added to 100 cm^3 of a 0.600 mol dm^{-3} solution of propanoic acid to make a buffer solution of pH 5.06 at 25°C. (The acid dissociation constant of propanoic acid = 1.31×10^{-5} mol dm^{-3} at 25°C; molar mass of sodium propanoate = 96.0 g mol^{-1}.) (4 marks)

***(iv)** Explain why a solution of propanoic acid alone is not a buffer solution. (3 marks)

b Under suitable conditions, both propanoic acid and propanoyl chloride react with methanol to form an ester.

(i) Name the ester produced. (1 mark)

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(ii) Write equations for the formation of this ester from:
- propanoic acid
- propanoyl chloride (2 marks)

(iii) Which method gives a better yield of ester. Explain your answer. (1 mark)

c Vegetable oils can be converted into biodiesel by a transesterification reaction. Give one example of this. (2 marks)

d Ethane-1,2-diol and benzene-1,4-dicarboxylic acid form a polyester. Write the structural formula of the repeat unit of this polymer showing all double bonds. (2 marks)

Total: 18 marks

Answers to Question 18

a (i) $K_a = \dfrac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$ ✓

(ii) A buffer solution is one that maintains a nearly constant pH ✓ when small amounts of acid or alkali are added ✓.

(iii) $[H_3O^+] = 10^{-pH} = 10^{-5.06} = 8.710 \times 10^{-6}\,\text{mol dm}^{-3}$ ✓

$[CH_3CH_2COO^-] = \dfrac{K_a[CH_3CH_2COOH]}{[H_3O^+]} = \dfrac{1.31 \times 10^{-5} \times 0.600}{8.710 \times 10^{-6}} = 0.9024\,\text{mol dm}^{-3}$ ✓

moles of salt = concentration × volume = $0.9024\,\text{mol dm}^{-3} \times 0.100\,\text{dm}^3 = 0.09024\,\text{mol}$

mass of salt needed = moles × molar mass = $0.09024 \times 96.0 = 8.66\,\text{g}$ ✓

(iv) The crucial point about a buffer is that the ratio [acid]:[salt] must not alter significantly when small amounts of acid or alkali are added. This can only happen if the acid and salt are present in similar amounts. Propanoic acid is a weak acid and so a solution has a significant $[CH_3CH_2COOH]$ but a tiny $[CH_3CH_2COO^-]$ ✓. When OH^- ions are added they react with propanoic acid molecules. This causes $[CH_3CH_2COO^-]$ to rise significantly, which alters the [acid]:[salt] ratio and affects the pH ✓. When H^+ ions are added, they react with some of the few $CH_3CH_2COO^-$ ions present, making $[CH_3CH_2COO^-]$ even smaller. This alters the [acid]:[salt] ratio and causes the pH to change ✓.

b (i) Methyl propanoate ✓

(ii) With propanoic acid:

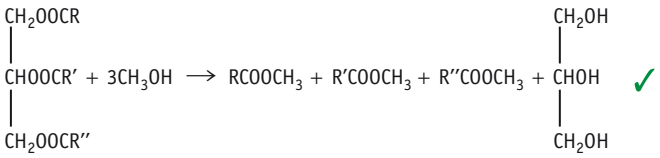
$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$ ✓

With propanoyl chloride:

$CH_3CH_2COCl + CH_3OH \rightarrow CH_3CH_2COOCH_3 + HCl$ ✓

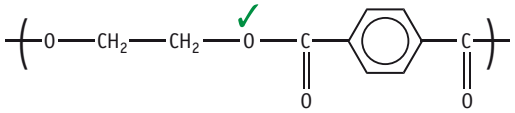
(iii) The reaction with propanoyl chloride because it is not a reversible reaction whereas the reaction with propanoic acid is reversible ✓.

c The transesterification reaction involved is when the ester of propane-1,2,3-triol and unsaturated long-chain fatty acids reacts with an alcohol such as methanol. This produces three methyl esters of the unsaturated acids, which are used as biodiesel ✓, and a by-product of propane-1,2,3-triol.



✓

d



✓ ✓

e Ester linkage ✓; rest of repeat unit with 'continuation' bonds ✓. The repeat unit of a polyester will have *four* oxygen atoms.

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Question 19

Propanone and propanal are isomers with molecular formula C_3H_6O.

a Write the equation for the reaction of propanone with 2,4-dinitrophenylhydrazine. (2 marks)

b Write the formula of the organic product of the reaction of propanal with:

(i) Fehling's solution (1 mark)

(ii) lithium aluminium hydride in dry ether followed by the addition of dilute hydrochloric acid (1 mark)

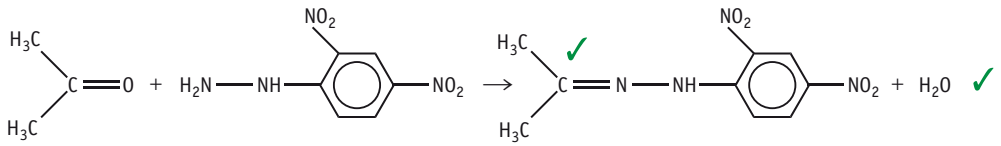
c (i) Both propanone and propanal react with hydrogen cyanide, HCN, in the presence of a catalyst of cyanide ions. Draw the mechanism of the reaction with propanal. (3 marks)

***(ii)** Explain why this reaction is very slow at both high and low pH. (2 marks)

Total: 9 marks

Answers to Question 19

a



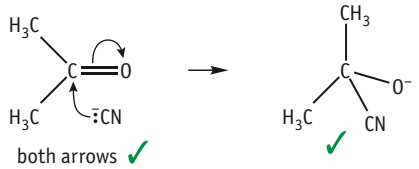
e C=N linkage ✓; rest of molecule ✓

b (i) $CH_3CH_2COO^-$ ✓

e Fehling's solution is alkaline and oxidises propanal to give the anion of propanoic acid, but not the acid itself.

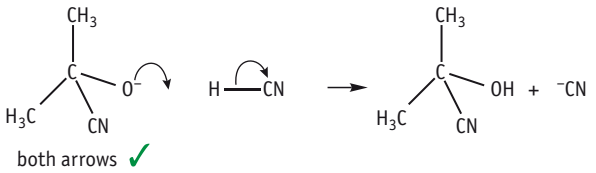
(ii) $CH_3CH_2CH_2OH$ ✓

c (i) **Step 1**



both arrows ✓

Step 2



both arrows ✓

(ii) At a high pH (very alkaline), the OH^- ions react with the HCN. As the [HCN] is now very small, the rate of step 2 is almost zero ✓. At a low pH (very acid), the H^+ ions protonate any CN^- ions. As the $[CN^-]$ is now very small, the rate of step 1 is almost zero ✓.

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Unit 4: Data question

Question 20

a Consider the reaction:

$$CaSO_4(s) \rightarrow CaO(s) + SO_3(g)$$

Use the data booklet to calculate:

(i) $\Delta S^{\ominus}_{system}$ (2 marks)

(ii) ΔH for the reaction and hence ΔS_{surr} at 500°C (3 marks)

(iii) Use your answers to (i) and (ii) to calculate ΔS_{total} at 500°C and hence the value of the equilibrium constant, K, at this temperature. ($R = 8.31\ J\,K^{-1}\,mol^{-1}$). (3 marks)

(iv) Calculate the value of the equilibrium constant at 1000°C. (1 mark)

b
- The lattice energy of calcium sulfate, $CaSO_4$, is $-2677\ kJ\,mol^{-1}$.
- The hydration enthalpy of the $Ca^{2+}(g)$ ion is $-1650\ kJ\,mol^{-1}$; the hydration enthalpy of the $SO_3(g)$ ion is $-1045\ kJ\,mol^{-1}$.

Draw a Hess's law diagram for the dissolving of calcium sulfate in water and calculate its enthalpy of solution. (4 marks)

***c** Which of strontium sulfate and barium sulfate is more soluble? Justify your answer using the data below to calculate the difference in ΔS_{total}.
- $\Delta H^{\ominus}_{solution} SrSO_4(s) = -9\ kJ\,mol^{-1}$
- $\Delta H^{\ominus}_{solution} BaSO_4(s) = +19\ kJ\,mol^{-1}$
- $S^{\ominus}\ Sr^{2+}(aq) = -33\ J\,K^{-1}\,mol^{-1}$
- $S^{\ominus}\ Ba^{2+}(aq) = +10\ J\,K^{-1}\,mol^{-1}$ (5 marks)

Total: 18 marks

Answers to Question 20

a (i) $\Delta S_{system} = S(CaO) + S(SO_3) - S(CaSO_4)$ ✓

$= +40 + 256 - (+107) = +189\ J\,K^{-1}\,mol^{-1}$ ✓

(ii) $\Delta H = \Delta H_f\ CaO + \Delta H_f\ SO_3 - \Delta H_f\ CaSO_4 = (-635) + (-396) - (-1434) = +403\ kJ\,mol^{-1}$ ✓

$$\Delta S_{surr} = \frac{-\Delta H}{T} \checkmark = -\frac{(+403\,000)\ J\,mol^{-1}}{773\ K} = -521\ J\,K^{-1}\,mol^{-1} \checkmark$$

e You need to look up the values of the standard entropies of these three substances in the data booklet for (i) and the standard enthalpies of formation for (ii). Remember to use values for $SO_3(g)$ not $SO_3(s)$.

(iii) $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$

$= +189 + (-521) = -332\ J\,K^{-1}\,mol^{-1}$ ✓

$\Delta S_{total} = RT \ln K$

$$\ln K = \frac{\Delta S_{total}}{RT} = \frac{-332}{8.31 \times 773} = -0.0517 \checkmark$$

$K = e^{-0.0517} = 0.950$ ✓

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(iv) $\Delta S_{surr} = \dfrac{-403\,000}{1273} = -317$

$\Delta S_{total} = +189 - 317 = -128$

$\ln K = \dfrac{-128}{8.31 \times 1273} = -0.0121$

$K = 0.988$ ✓

b

$$\begin{array}{ccccc} & & Ca^{2+}(g) & + & SO_4^{2-}(g) \\ & & \downarrow \Delta H_{hydr}\,Ca^{2+} & & \downarrow \Delta H_{hydr}\,SO_4^{2-} \\ CaSO_4(s) + aq & \longrightarrow & Ca^{2+}(aq) & + & SO_4^{2-}(aq) \end{array}$$

– lattice energy

e Cycle ✓; labels ✓

$\Delta H_{solution}$ = –lattice energy + sum of hydration energies of ions ✓

$= -(-2677) + (-1650) + (-1045) = -18\ kJ\ mol^{-1}$ ✓

c The value of $\Delta H_{solution}$ for barium sulfate is more endothermic by $28\ kJ\ mol^{-1}$ ✓. This means that ΔS_{surr} becomes $28\,000/298 = 94\ J\ K^{-1}\ mol^{-1}$ more negative ✓. The value of ΔS_{system} of barium sulfate is $43\ J\ K^{-1}\ mol^{-1}$ more positive ✓. As $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$ ✓, the value of ΔS_{total} for barium sulfate is $94 - 43 = 51\ J\ K^{-1}\ mol^{-1}$ less than that of strontium sulfate ✓. As ΔS_{total} is $51\ J\ K^{-1}\ mol^{-1}$ less positive, barium sulfate will be less soluble ✓ than strontium sulfate.

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Unit 5: Multiple choice questions

Each question or incomplete statement is followed by four suggested answers, A, B, C or D. Select the *best* answer in each case. The answers are given, with some commentary, after Question 15.

1 When the standard electrode potential of zinc is measured, a reference electrode is needed because:

- ☐ **A** the potential between a metal and its solution cannot be measured directly
- ☐ **B** a standard hydrogen electrode has a potential of zero
- ☐ **C** zinc is the cathode
- ☐ **D** a pressure of 1 atm must be used

2 If the standard electrode potential of a cell, $E^{\ominus}_{cell}$, is +0.10 V, the reaction:

- ☐ **A** is not thermodynamically feasible, as the value of $E^{\ominus}_{cell}$ is too small
- ☐ **B** will always take place
- ☐ **C** will take place under standard conditions, if the activation energy is not too high
- ☐ **D** will have a negative value of ΔS_{total}

3 Which of the following can act as a bidentate ligand?

- ☐ **A** NH_2NH_2
- ☐ **B** $NH_2(CH_2)_2NH_2$
- ☐ **C** $ClCH_2Cl$
- ☐ **D** $Cl(CH_2)_2Cl$

4 Which of the following is the electronic configuration of a stable coloured transition metal ion?

- ☐ **A** [Ar] $3d^{10}\ 4s^1$
- ☐ **B** [Ar] $3d^{10}\ 4s^0$
- ☐ **C** [Ar] $3d^6\ 4s^1$
- ☐ **D** [Ar] $3d^6\ 4s^0$

5 When solid hydrated copper sulfate, $CuSO_4.5H_2O$, is heated it produces steam and white anhydrous copper sulfate, $CuSO_4$. This compound is white because:

- ☐ **A** copper has an electron configuration of [Ar] $3d^{10}\ 4s^1$
- ☐ **B** the copper ion in $CuSO_4$ has a full *d*-shell
- ☐ **C** the copper ion no longer has any ligands and so the *d*-orbitals are not split
- ☐ **D** the copper ions are reduced to Cu^+ ions

6 An isomer of C_5H_8O gave a yellow precipitate with iodine and alkali, decolorised bromine water and gave a yellow precipitate with 2,4-dinitrophenylhydrazine. The isomer is

- ☐ **A** $CH_2{=}C{=}CHCH(OH)CH_3$
- ☐ **B** $CH_3CH{=}CHCH_2CHO$
- ☐ **C** $CH_2{=}CHCH_2COCH_3$
- ☐ **D** $CH_2{=}CHCOCH_2CH_3$

7 The electrophile in the Friedel–Crafts reaction between benzene and ethanoyl chloride is:

- ☐ **A** $CH_3\overset{+}{C}O$
- ☐ **B** $CH_3\overset{+}{C}O^-$
- ☐ **C** $\overset{+}{C}H_3COCl^-$
- ☐ **D** $CH_3\overset{\delta+}{C}\overset{\delta-}{O}$

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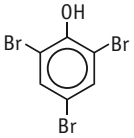
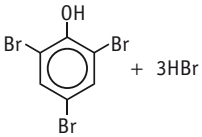
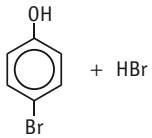
8 When phenol reacts with bromine water, the product(s) are:

☐ **A** 

☐ **B** 

☐ **C**

☐ **D** 

9 Which of the following is **not** an amide?

☐ **A** CH_3CONH_2

☐ **B** $CH_3CONHC_2H_5$

☐ **C** $C_6H_5CONH_2$

☐ **D** $CH_3COCH_2NH_2$

10 Which statement about amines, for example ethylamine, is **not** true?

☐ **A** They react with bases.

☐ **B** They are soluble in water.

☐ **C** They react with acid chlorides.

☐ **D** They form complex cations with hydrated copper(II) ions.

11 What are the reagents and conditions for the following two-step synthesis?

$$\text{nitrobenzene} \xrightarrow{\text{step 1}} \text{phenylamine} \xrightarrow{\text{step 2}} \text{benzenediazonium chloride}$$

	Step 1	Step 2
☐ **A**	Tin and concentrated hydrochloric acid	Sodium nitrite and hydrochloric acid below 0°C
☐ **B**	Iron and concentrated hydrochloric acid	Sodium nitrite and hydrochloric acid between 0°C and 10°C
☐ **C**	Concentrated hydrochloric acid	Sodium nitrite and hydrochloric acid above 10°C
☐ **D**	Hot acidified potassium dichromate(VI)	Sodium nitrite and hydrochloric acid heated under reflux

12 A polyamide such as Kevlar®:

☐ **A** is water soluble because of hydrogen bonds between the –NH groups and water

☐ **B** is made from an amine such as ethylamine and a dicarboxylic acid such as benzene-1,3-dicarboxylic acid

☐ **C** is a solid with hydrogen bonding between strands

☐ **D** is biodegradable

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13 Poly(ethenol) is:

- ☐ **A** made by polymerising ethenol at room temperature
- ☐ **B** made by polymerising ethenol using a Ziegler–Natta catalyst
- ☐ **C** made by a hydrolysis of polyvinyl acetate with dilute acid
- ☐ **D** insoluble in water because it cannot form enough hydrogen bonds with water molecules.

14 Which of the following compounds has an unsplit peak (a singlet) in its NMR spectrum?

- ☐ **A** CH_3CHO
- ☐ **B** $(CH_3)_3CH$
- ☐ **C** $(CH_3)_2CHCHO$
- ☐ **D** $CH_3COCH_2CH_3$

15 Heating under reflux is used if the reaction is slow at room temperature and:

- ☐ **A** the product has a low boiling temperature
- ☐ **B** one of the reactants has a low boiling temperature
- ☐ **C** the reactants and products have similar boiling temperatures
- ☐ **D** the reactants and product form separate layers

Answers

1 A Zinc ions go into solution and the electrons remain on the zinc rod, thus setting up a potential difference. However, this cannot be measured directly as any connection to a voltmeter using a metal wire dipping into the solution would alter the potential. A salt bridge has to be used which is then connected to a reference electrode. Options **B** and **D** are true statements but neither is the reason why a reference electrode has to be used. Option **C** is incorrect, as the zinc becomes oxidised and is, therefore, the anode.

2 C It is a common misunderstanding that the cell potential has to be above a value, such as > +0.03 V or > +0.3 V. As long as the cell potential is positive, the reaction is thermodynamically feasible. Therefore, option **A** is incorrect. Option **B** is incorrect because the reaction may not happen for kinetic reasons. Option **D** is incorrect because a positive value for the cell potential means that ΔS_{total} is also positive.

3 B Hydrazine, NH_2NH_2, has a lone pair of electrons on each nitrogen atom. If it formed a bidentate ligand, this would involve a triangle of the two nitrogen atoms and the metal ion. Such a triangular shape would cause too much strain in the bonds. Therefore, option **A** is incorrect. Option **B** is correct because 1,2-diaminoethane has two lone pairs of electrons, one on each nitrogen atom, and it forms a five-membered ring with the metal ion and this is stable. A covalently bound chlorine *atom* is not a ligand (although chlorine ions can be), so options **C** and **D** are incorrect.

4 D This is the electronic configuration of a Fe^{2+} ion. Option **A** is the configuration of a copper atom — note that the question asks about a transition metal *ion*. Option **B** is the configuration of Zn^{2+} or Cu^{+}. Zinc is not a transition metal, as its ion does not have an unpaired *d*-electron and copper(I) ions are not coloured. Option **C** is the configuration for a Fe^{+} ion, which does not exist.

5 C Hydrated copper sulfate has four water ligands. When it is heated, these are lost. As there are now no ligands, there is no splitting of the *d*-orbitals.

Option **A** is a true statement about a copper atom, but is irrelevant to this question. Option **B** is incorrect as the copper ion in $CuSO_4$ is 2+ and has the electron configuration [Ar] $3d^9$. Option **D** is incorrect because hydrated copper(II) sulfate is not reduced on heating.

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6 C The iodoform reaction tests for a $CH_3C{=}O$ or a $CH_3CH(OH)$ group. Bromine water tests for a C=C group and Brady's reagent for a C=O group. The question is best attempted by putting a ✓ or ✗ for each reaction.

	Iodoform reaction	Bromine water	Brady's reagent
A	✓	✓	✗
B	✗	✓	✓
C	✓	✓	✓
D	✗	✓	✓

7 A The Cl is removed along with the σ-bond electrons, leaving the positive charge on the carbonyl carbon atom. Options **B**, **C** and **D** are simply incorrect.

8 B Phenol and bromine react in a substitution reaction, so there must be two products. Thus options **A** and **C** are incorrect. The oxygen atom activates the benzene ring and three bromine atoms substitute into the ring in the 2, 4 and 6 positions. Thus **B** is correct.

9 D An amide has a nitrogen atom attached to the carbon of a C=O group. Option **A** has a $C{=}ONH_2$ group and is ethanamide. Option **B** is a substituted amide having a C=ONH group and is *N*-ethylethanamide. Option **C** is also an amide — benzamide. In option **D**, the C=O and NH_2 groups are separated by a CH_2 group. Therefore, this compound is a ketone and an amine; it is not an amide. Thus **D** is the correct answer to this negative question.

10 A Amines are bases and not acids. Therefore, they do not react with other bases, so option **A** is false and is the correct answer to this negative question. Amines are soluble in water, as they can form hydrogen bonds with H_2O molecules. They react with acid chlorides to form substituted amides. An amine molecule has a lone pair of electrons on the nitrogen atom which can act as a ligand with transition metal ions such as copper(II) ions. Therefore, options **B**, **C** and **D** are all true statements.

11 B The correct reagents for the reduction of nitrobenzene are either tin or iron plus concentrated hydrochloric acid. So, for step 1, options **A** and **B** are correct and options **C** (no reducing agent) and **D** (dichromate(VI) ions are an oxidising agent) are incorrect. For step 2, the temperature must not be above 10°C (another reason why option **C** is wrong) because this would cause the diazonium ions to decompose; it must be above 0°C or the reaction will be too slow. Therefore, option **A** is incorrect. Only option **B** has the correct reagents and conditions.

12 C Kevlar® is a polyamide and so forms strong hydrogen bonds between strands with the δ^+ hydrogen of the –NH forming a hydrogen bond with the lone pair of the δ^- oxygen atom in a C=O group in another strand. In addition, the benzene rings form van der Waals attractions between strands, making Kevlar® stronger than other polyamides. Option **A** is incorrect because the benzene rings are hydrophobic and the interstrand hydrogen bonding is so strong that Kevlar is not water-soluble. The monomers of a polyamide must have two functional groups. Ethylamine has only one functional group, so it cannot form polymers. Therefore, option **B** is incorrect. Kevlar is not a natural polymer and so is not biodegradable. Therefore, option **D** is also incorrect.

13 C Ethenol, $CH_2{=}CHOH$, does not exist. Attempts to make it produce ethanal, CH_3CHO, so options **A** and **B** are incorrect. Poly(ethenol) is water-soluble, so option **D** is wrong. It is manufactured either by transesterification with methanol or by the hydrolysis of polyvinyl acetate, $(H_2CCH(OOCCH_3))_n$ so **C** is the correct answer.

14 D A singlet can be due to the hydrogen of an OH group, or to the hydrogen atoms on a carbon atom that does not have an adjacent carbon atom with a hydrogen atom attached. Thus all alcohols and carboxylic acids have a singlet, as do methyl ketones,

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which have a CH_3CO group, thus the methyl hydrogen atoms have no neighbouring hydrogen atoms to cause splitting. The CH_3 hydrogen atoms in butanone (**D**) (on the left as written in the question) have a C=O group as their neighbour and so this peak will not be split. Ethanal (**A**) has two peaks, one split into four and the other into two. Methylpropane (**B**) has two peaks, one split into ten and the other into two. Methylpropanal (**C**) has three peaks, one split into seven and two split into two.

15 B Be careful here: it is the reactant not the product that must be prevented from boiling off, so option **A** is incorrect The responses in **C** and **D** have nothing whatsoever to do with heating under reflux.

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Unit 5: Structured questions

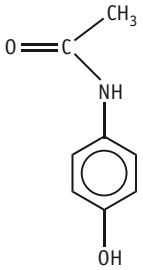
Responses to questions with longer answers may have an examiner's comment preceded by the icon e. Some of the comments highlight common errors made by candidates who produce work of C-grade standard or lower.

Question parts marked with an asterisk* test 'Quality of Written Communication' (QWC). It is worth reading through the whole question before attempting to answer it.

Question 16

a Ethanamide, CH_3CONH_2, can be prepared in the laboratory from ethanol. Outline how this could be carried out, stating the reagents and conditions needed and identifying all intermediate compounds formed. (6 marks)

b Tylenol is a secondary amide and a phenol.



It is used as a painkiller in the USA.

Predict the organic product of its reaction with:

(i) bromine water (1 mark)

(ii) aqueous sodium hydroxide at room temperature (1 mark)

c An organic compound **Z** contains only carbon, hydrogen, nitrogen and oxygen. When 1.00 g of **Z** was burnt, 1.48 g of carbon dioxide, 0.71 g of water and 0.52 g of nitrogen dioxide, NO_2, were produced.

(i) Calculate the percentage by mass of the elements in **Z.** (2 marks)

(ii) Use your answer to **(i)** to show that **Z** has the empirical formula $C_3H_7O_2N$. (2 marks)

d The molecular formula of compound **Z** is the same as its empirical formula. Compound **Z** melts at a high temperature, is soluble in water and reacts with both acids and alkalis. When heated with ninhydrin, a dark colour is produced. **Z** has a chiral centre.

(i) Draw the structural formula of **Z**. (2 marks)

***(ii)** Explain why compound **Z** has a high melting temperature and why it is soluble in water. (4 marks)

(iii) Write **ionic** equations to show the reactions of compound **Z** with H^+(aq) ions and with OH^-(aq) ions. (2 marks)

Total: 20 marks

Answers to question 16

a **Step 1:** $C_2H_5OH \rightarrow CH_3COOH$ ✓ (ethanoic acid)

Reagents: acidified potassium dichromate ✓ ($H^+/Cr_2O_7^{2-}$)

Conditions: heat under reflux ✓

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Step 2: $CH_3COOH \rightarrow CH_3COCl$ ✓ (ethanoyl chloride)

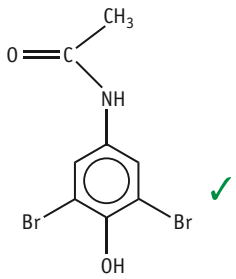
Reagent: phosphorus pentachloride ✓ (PCl_5)

Step 3: $CH_3COCl \rightarrow CH_3CONH_2$

Reagent: ammonia solution ✓ (NH_3)

e Alternative reagents for step 2 are PCl_3 or $SOCl_2$.

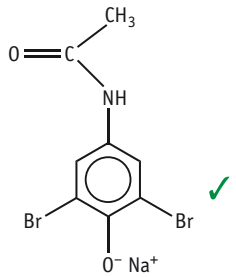
b (i)



✓

e Tylenol is a phenol. It reacts with bromine water to form a white precipitate.

(ii)



✓

e As Tylenol is a phenol, it reacts as an acid with aqueous sodium hydroxide. The amide group is not hydrolysed at room temperature.

c (i)

mass of carbon = 1.48 × 12.0 /44.0 = 0.404 g	% carbon = 40.4%
mass of hydrogen = 0.71 × 2.0/18.0 = 0.789 g ✓	% hydrogen = 7.89%
mass of nitrogen = 0.52 × 14.0/46.0 = 0.158 g	% nitrogen = 15.8% ✓
	% oxygen = 100 – 40.4 – 7.89 – 15.8 = 35.91%

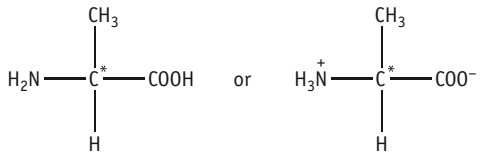
e Note that to obtain the mass of hydrogen, the mass of water has to be multiplied by 2, because there are two hydrogen atoms in each water molecule. In this example the percentage is 100 times the mass because the initial mass of Z was 1.00 g.

(ii)

Element	%	Divide by A_r	Divide by smallest
Carbon	40.4	40.4/12.0 = 3.37	3.37/1.13 = 3.0
Hydrogen	7.89	7.89/1.0 = 7.89	7.89/1.13 = 7.0
Nitrogen	15.8	15.8/14.0 = 1.13 ✓	1.13/1.13 = 1.0
Oxygen	35.91	35.91/16.0 = 2.24	2.24/1.13 = 2.0

This is consistent with an empirical formula of $C_3H_7O_2N$ ✓.

d (i) The formula is:



✓✓

e There is 1 mark for either an H_2N/H_3N^+ group or a $COOH/COO^-$ group and 1 mark for the remainder. The chiral centre is shown with an asterisk.

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e Ninhydrin reacts with amino acids to form a dark coloration. This is how the positions of different amino acids are identified in thin-layer chromatography.

(ii) Compound **Z** has a high melting temperature because it forms a zwitterion, $^{+}H_3NCH(CH_3)COO^{-}$ ✓. There are strong ionic forces of attraction between different zwitterions. This means that a lot of energy is required to separate zwitterions and therefore the melting temperature is high ✓.

It is soluble in water because hydrogen bonds form between the COO^{-} groups and the δ^{+} hydrogen atoms in water ✓ and between the $^{+}H_3N$ groups and the lone pairs of electrons on the δ^{-} oxygen atoms in water ✓.

(iii) Either $H_2NCH(CH_3)COOH + H^{+} \rightarrow {}^{+}H_3NCH(CH_3)COOH$ *or*

$^{+}H_3NCH(CH_3)COO^{-} + H^{+} \rightarrow {}^{+}H_3NCH(CH_3)COOH$ ✓

and

either $H_2NCH(CH_3)COOH + OH^{-} \rightarrow H_2NCH(CH_3)COO^{-} + H_2O$ *or*

$^{+}H_3NCH(CH_3)COO^{-} + OH^{-} \rightarrow H_2NCH(CH_3)COO^{-} + H_2O$ ✓

Question 17

a

$$Cr^{3+}(aq) + e^{-} \rightleftharpoons Cr^{2+}(aq) \qquad E^{\ominus} = -0.41\,V$$

$$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,V$$

$$S(s) + 2H^{+}(aq) + 2e^{-} \rightleftharpoons H_2S(aq) \qquad E^{\ominus} = +0.14\,V$$

(i) Hydrogen sulfide, H_2S, reduces dichromate(VI) ions in acid solution. Is the product Cr^{3+} ions or Cr^{2+} ions? Justify your answer, calculating the $E^{\ominus}_{cell}$ values for possible reductions. (4 marks)

(ii) Write the ionic equation for the reaction that takes place between hydrogen sulfide and dichromate(VI) ions in acid solution. (2 marks)

(iii) Define disproportionation. (1 mark)

***(iv)** Explain in terms of $E^{\ominus}$ values, whether $Cr^{3+}(aq)$ ions will disproportionate. (2 marks)

b The water from volcanic hot springs often contains significant amounts of the poisonous gas hydrogen sulfide. The amount present can be measured by titration against a standard solution of acidified potassium manganate(VII).

$$5H_2S + 2MnO_4^{-} + 6H^{+} \rightarrow 2Mn^{2+} + 5S + 8H_2O$$

A portion of hot spring water of volume 250 cm^3 was taken and 50.0 cm^3 portions were titrated against acidified 0.0100 mol dm^{-3} potassium manganate(VII) solution. The mean titre was 7.55 cm^3. Calculate the volume of hydrogen sulfide dissolved in the 250 cm^3 sample of hot spring water. (1 mol of gas, under the conditions of the experiment, has a volume of 24 000 cm^3) (4 marks)

Total: 13 marks

Answers to Question 17

a (i) Reduction to Cr^{3+}:

The third equation has to be reversed and multiplied by 3:

$$Cr_2O_7^{2-}(aq) + 14H^{+}(aq) + 6e^{-} \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,V$$

$$3H_2S(aq) \rightleftharpoons 6H^{+}(aq) + 3S(s) + 6e^{-} \qquad E^{\ominus} = -(+0.14\,V) = -0.14\,V$$

The value of $E^{\ominus}_{cell}$ is $(+1.33) + (-0.14) = +1.19\,V$ ✓

This is positive, so hydrogen sulfide will reduce chromium(VI) ions to chromium(III) ions ✓.

e Remember that when a redox half-equation is reversed, the sign of $E^{\ominus}$ must be altered; when it is multiplied by a number, the $E^{\ominus}$ value is unaltered.

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e The equations need not be written here, but it is safer to do so. The alternative is to realise that the $Cr_2O_7^{2-}/Cr^{3+}$ equation is the right way round but the S/H_2S equation has to be reversed. Therefore the value of:

$E^{\ominus}_{cell}$ = (the value of $Cr_2O_7^{2-}/Cr^{3+}$ half-equation) – (the value of S/H_2S half-equation)
= +1.33 –(+0.14) = +1.19 V

Reduction to Cr^{2+}:

The first equation has to be multiplied by 2 and the third equation reversed:

$2Cr^{3+}(aq) + 2e^- \rightarrow 2Cr^{2+}(aq)$ $E^{\ominus} = -0.41$ V

$H_2S(aq) \rightarrow 2H^+(aq) + S(s) + 2e^-$ $E^{\ominus} = -(+0.14\,V) = -0.14$ V

The value of $E^{\ominus}_{cell}$ is –0.41 + (–0.14) = –0.55 V ✓

This is negative so hydrogen sulfide will reduce chromium(VI) ions to chromium(III) ions but no further ✓.

(ii) The overall equation is obtained by adding:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

$3H_2S(aq) \rightarrow 6H^+(aq) + 3S(s) + 6e^-$ ✓

$Cr_2O_7^{2-}(aq) + 8H^+(aq) + 3H_2S \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3S(s)$ ✓

e You must remember to cancel the H^+ ions: $14H^+$ on the left-hand side and $6H^+$ on the right-hand side cancel to leave $8H^+$ on the left.

(iii) Disproportionation is when an element in a single species is simultaneously oxidised and reduced ✓.

(iv) The disproportionation reaction would involve Cr^{3+} ions being reduced to Cr^{2+} ions (first equation in the data) and Cr^{3+} ions being oxidised to $Cr_2O_7^{2-}$ ions (the second equation reversed) ✓.

The $E^{\ominus}_{cell}$ for this is ($E^{\ominus}$ for the first half-equation) – ($E^{\ominus}$ for the second half-equation):

$E^{\ominus}_{cell}$ = (–0.41) – (+1.33) = –1.74 V. This value is negative and so disproportionation of Cr^{3+} ions does not occur ✓.

b amount (moles) of MnO_4^- = concentration × volume

$= 0.0100\,mol\,dm^{-3} \times 0.00755\,dm^3 = 7.55 \times 10^{-5}$ mol ✓

amount (moles) of H_2S in 50 cm^3 = $5/2 \times 7.55 \times 10^{-5} = 1.8875 \times 10^{-4}$ mol ✓

amount (moles) in 250 cm^3 = $250/50 \times 1.8875 \times 10^{-4} = 9.4375 \times 10^{-4}$ mol ✓

volume of hydrogen sulfide dissolved = $9.4375 \times 10^{-4} \times 24\,000 = 22.7\,cm^3$ ✓

Question 18

a Explain, with the aid of an equation, why hydrated chromium(III) ions in solution are acidic. (2 marks)

b State what you would see when aqueous sodium hydroxide is added steadily until in excess to a solution of hydrated chromium(III) ions. Give the equations for the reactions. (4 marks)

***c** EDTA reacts with hydrated chromium(III) ions to form a polydentate complex ion in an exothermic reaction:

$EDTA^{4-}(aq) + [Cr(H_2O)_6]^{3+}(aq) \rightarrow [Cr(EDTA)]^-(aq) + 6H_2O(l)$

Explain why ΔS_{system} is positive for this reaction. (2 marks)

***d** The EDTA complex ion is coloured. Explain why it is coloured. (3 marks)

Total: 11 marks

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Answers to question 18

a The hydrated ions are reversibly deprotonated by water forming H_3O^+ ions which make the solution acidic ✓.

$$[Cr(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Cr(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq) \checkmark$$

b At first a dirty green precipitate ✓ is formed.

$$[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow [Cr(H_2O)_3(OH)_3](s) + 3H_2O(l) \checkmark$$

This then dissolves in excess sodium hydroxide to form a green solution ✓.

$$[Cr(H_2O)_3(OH)_3](s) + 3OH^-(aq) \rightarrow [Cr(OH)_6]^{3-} + 3H_2O(l) \checkmark$$

c The reaction with EDTA involves two particles reacting to form seven particles, all in the aqueous phase ✓. This is a significant increase in disorder and so ΔS_{system} is positive ✓.

d The six pairs of electrons forming the bonds between EDTA and the Cr^{3+} ion cause the *d*-orbitals in the chromium ion to split into two levels ✓. When white light is shone onto the complex, some of the frequencies are absorbed ✓ and an electron is promoted from the lower level of the split *d*-orbitals to a higher level ✓. This causes the ion to have the complementary colour to that of the wavelength absorbed.

Question 19

Arenes, such as benzene and its derivatives nitrobenzene and phenol, react with electrophiles.

a Nitrobenzene can be prepared from benzene. Give the reagents and conditions and write the equation for this reaction. Why must the temperature be controlled? (5 marks)

b Benzene also reacts with ethanoyl chloride in a Friedel–Crafts reaction. Give the mechanism for this reaction, including the production of the electrophile. (4 marks)

c Phenol reacts with bromine water.

(i) Write the equation for this reaction (1 mark)

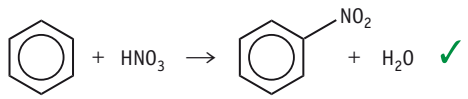
(ii) Explain why this reaction does not need a catalyst and is much faster than the reaction of bromine with benzene. (3 marks)

Total: 13 marks

Answers to Question 19

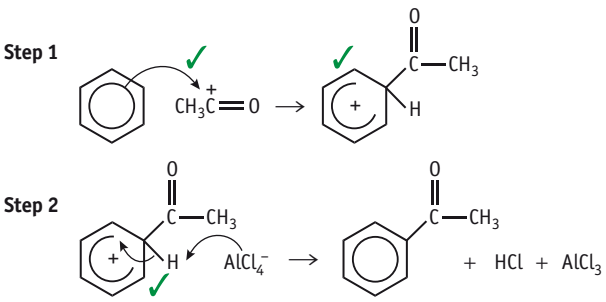
a The reagents are concentrated nitric acid ✓ and concentrated sulfuric acid ✓. The conditions are heat to 50°C ✓. At a higher temperature some dinitrobenzene will be produced and at a lower temperature the reaction will be too slow ✓.

The equation is:



b Formation of electrophile

$$CH_3COCl + AlCl_3 \rightarrow CH_3\overset{+}{C}{=}O + AlCl_4^- \checkmark$$



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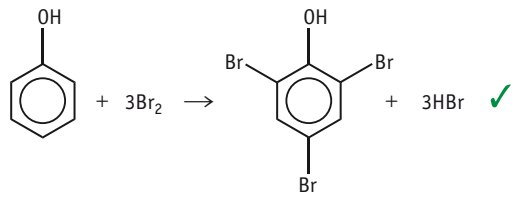
c (i)



✓

(ii) The lone pair of electrons (the $2p_z$ electrons) on the oxygen atom in phenol becomes partly delocalised into the benzene ring π-bond ✓. This increases the electron density in the ring and makes it more susceptible to electrophilic attack ✓, and so has a lower activation energy, making the reaction faster ✓.

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Unit 5: Contemporary context question

Question 20

Read the passage carefully and answer the questions that follow.

Electromagnetic radiation

Electromagnetic radiation is important in chemistry in a number of ways.

Radio waves of frequency around 100–400 MHz are used in NMR spectroscopy. The substance under investigation is placed in a very strong magnetic field. This causes the energy levels of spinning hydrogen nuclei to split into two. The peaks in the NMR spectrum measure the difference between these two levels, which varies according to the exact environment of the hydrogen nuclei. The peaks are also split by the hydrogen atoms on neighbouring carbon atoms; the splitting follows the $(n + 1)$ rule.

Microwaves have a higher frequency. This radiation is only absorbed by polar molecules. The molecules then rotate faster gaining rotational energy. On collision with another molecule, this energy is converted into kinetic energy, in the form of heat. Use of this is made in the pharmaceutical industry where microwaves are used to heat up reaction mixtures.

Infrared spectroscopy uses radiation of a higher frequency still. It detects the presence of functional groups and can be used to identify unknown compounds. When infrared radiation is absorbed by a molecule, one or more of its bonds bend or stretch. Absorption only takes place if the stretching or bending causes a change in dipole moment.

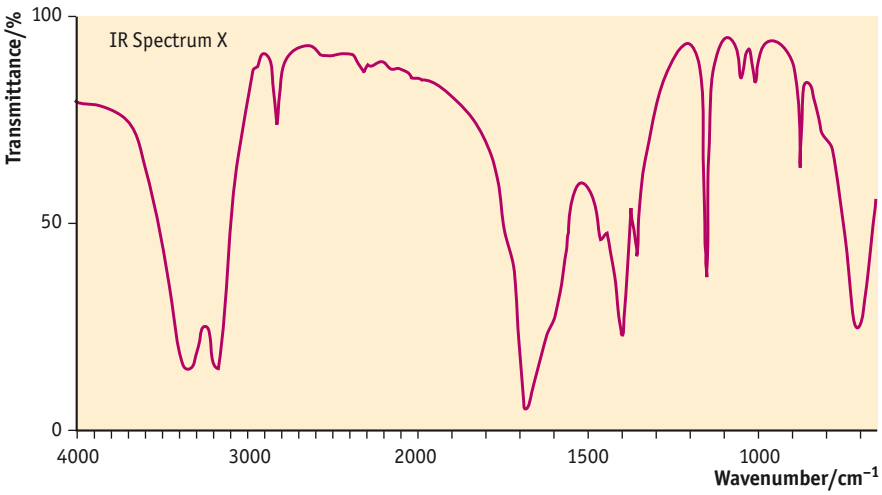
UV light is the highest frequency radiation normally used in chemistry. It causes bonds in a molecule to break homolytically, forming free radicals. When a mixture of chlorine and methane is exposed to a short pulse of UV radiation, chlorine radicals are produced. These then take part in a chain reaction, the first step being the removal of a hydrogen atom from methane to form hydrogen chloride and a methyl radical.

a Place the four types of electromagnetic radiation discussed in the passage in order of *decreasing* frequency. (1 mark)

***b** Explain why the air inside a microwave oven does not heat up when a cup of water is being heated in the oven. (1 mark)

***c** **(i)** State and explain the difference between the high-resolution NMR spectra of ethanol, CH_3CH_2OH, and ethanamide, CH_3CONH_2. (5 marks)

(ii) The infrared spectra of ethanol and ethanamide compounds are shown below as spectrum **X** and spectrum **Y**.



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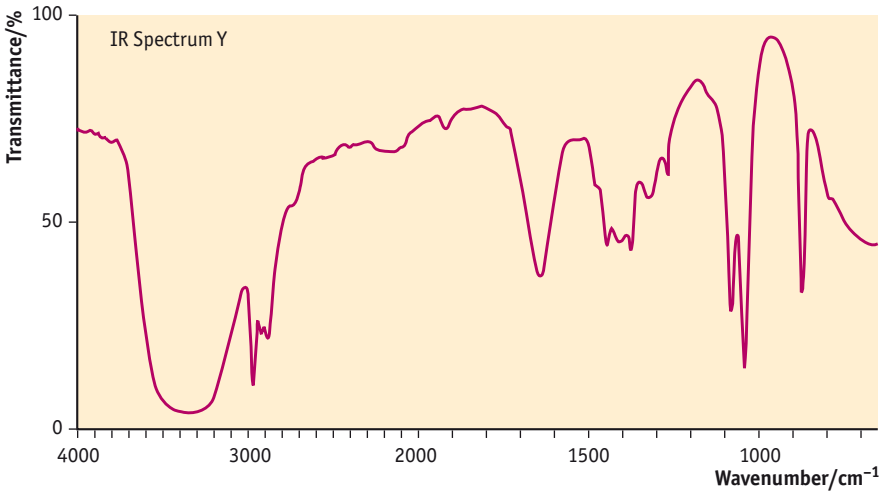

Identify the spectrum of ethanamide, giving reasons. (You should consult the Edexcel data booklet, the Edexcel A2 Chemistry textbook which this online resource accompanies or another source of data.) (3 marks)

d When chlorine gas is bubbled into liquid methylbenzene, $C_6H_5CH_3$, in the presence of UV radiation, a free radical substitution reaction takes place. One of the products is chloromethylbenzene, $C_6H_5CH_2Cl$. The mechanism of this reaction is similar to that between methane and chlorine.

(i) Write the mechanism of the reaction between chlorine gas and methylbenzene, showing the initiation step and two propagation steps. (3 marks)

(ii) Some 1,2-diphenylethane, $C_6H_5CH_2CH_2C_6H_5$ is formed in this reaction. Explain how this is evidence for the mechanism that you have written in **(i).** (2 marks)

***(iii)** Suggest how a pure dry sample of chloromethylbenzene could be extracted from the reaction mixture.

	Density/g cm^{-3}	Boiling temperature/°C	Solubility in water
Chloromethylbenzene	1.1	179	Insoluble
Methylbenzene	0.87	111	Insoluble

(5 marks)

Total: 20 marks

Answers to Question 20

a UV > IR > microwaves > radio waves ✓

b The air consists, mostly, of oxygen and nitrogen. These are non-polar molecules and so do not absorb microwaves ✓.

c (i) Ethanol has the formula CH_3CH_2OH and has hydrogen nuclei in three chemical environments. Its NMR spectrum has three different peaks in the ratio 3:2:1 ✓. The peak due to the hydrogen atoms in the CH_3 group is split into three and those due to the hydrogen atoms in the CH_2 group are split into four ✓. The peak due to the hydrogen in the OH group is not split ✓.

Ethanamide has the formula CH_3CONH_2 and has hydrogen nuclei in two chemical environments. Its spectrum has two peaks in the ratio 3:2 ✓ and neither of the peaks is split ✓.

e Do not forget to describe for both molecules the number of peaks, their relative heights and the extent of splitting due to spin coupling ($n + 1$) rule. The peaks in the ethanamide spectrum

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are not split, because there is no hydrogen atom on the carbon atoms adjacent to the CH_3 and NH_2 groups.

(ii) Both spectra have a broad peak at around 3350 cm^{-1}. These are caused by the O–H bond in ethanol and the N–H bond in ethanamide ✓. Spectrum **X** has a strong peak at 1680 cm^{-1}. This is typical of the C=O bond in amides (1700 to 1630 cm^{-1}) ✓, so spectrum **X** is that of ethanamide and spectrum **Y** is that of ethanol ✓.

d (i) Initiation step:

$Cl_2 \xrightarrow{UV} 2Cl\bullet$ ✓

Propagation steps:

$Cl\bullet + C_6H_5CH_3 \rightarrow C_6H_5CH_2\bullet + HCl$ ✓

$C_6H_5CH_2\bullet + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl\bullet$ ✓

(ii) The 1,2-diphenylethane is formed by two $C_6H_5CH_2\bullet$ radicals joining together in a chain termination step ✓

$C_6H_5CH_2\bullet + C_6H_5CH_2\bullet \rightarrow C_6H_5CH_2CH_2C_6H_5$ ✓

(iii) The reaction mixture will contain some hydrogen chloride, unreacted methylbenzene and some polysubstituted methylbenzene. The following procedure should be used to obtain pure chloromethylbenzene:

- Wash the reaction mixture with water and then with sodium carbonate (or sodium hydrogencarbonate) solution ✓ in a separating funnel, collecting the lower organic layer ✓ each time.

e This removes hydrogen chloride, which is a reaction product impurity.

- Dry the organic layer with anhydrous calcium chloride ✓.
- Filter off the calcium chloride and distil ✓ the clear dried organic layer. Discard any unreacted methylbenzene that distils over at around 111°C and collect the fraction that boils over between 177°C and 181°C ✓.

e The polysubstituted methylbenzenes have a higher boiling temperature and are left behind in the distillation flask.

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