CAIE A Level Chemistry

Paper 4

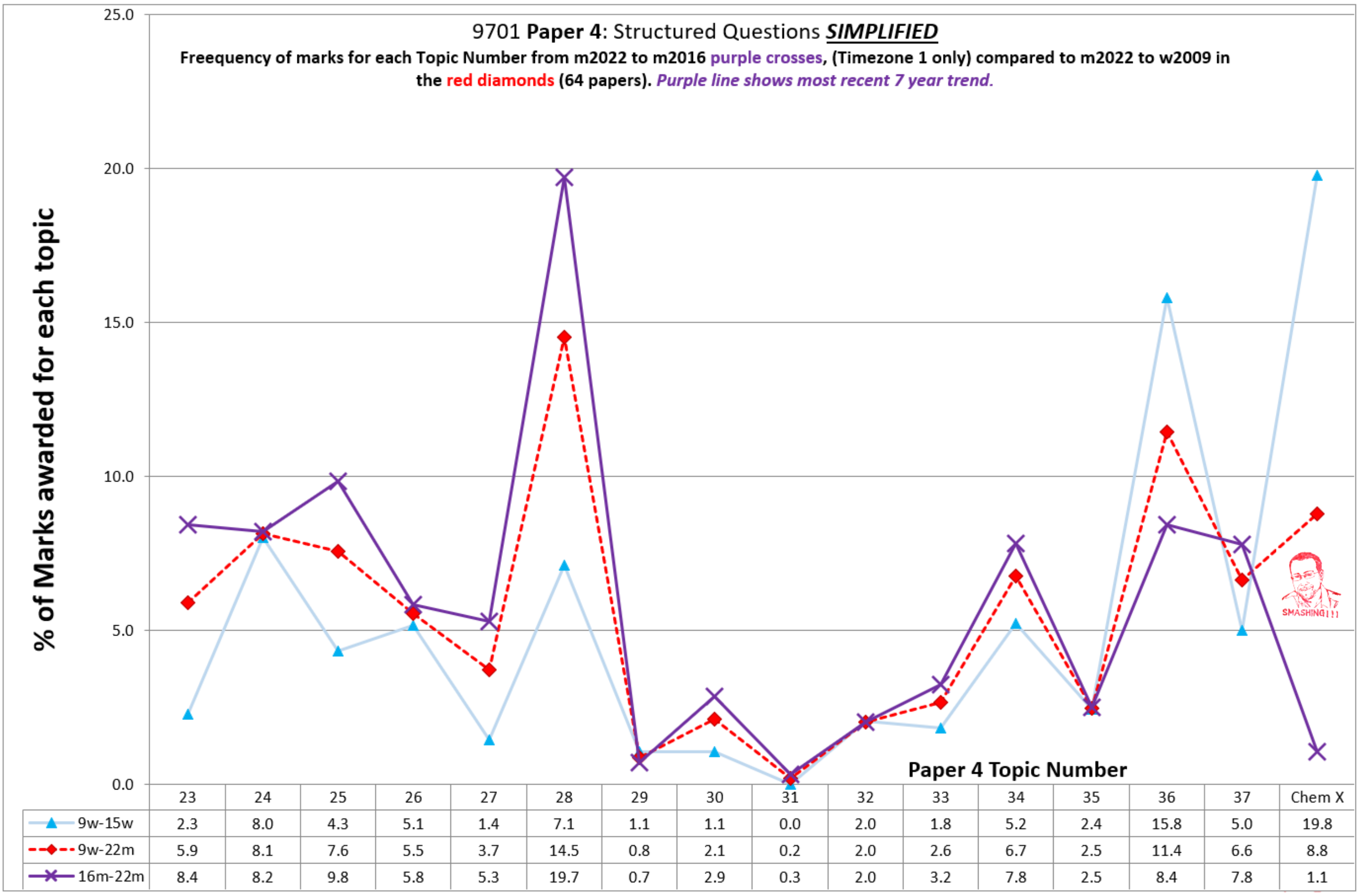
Past Exam Questions

Organised by Topic Number

Winter 2009 to March 2022 (32 Papers)

Name: ____________________________

Class: ____________



9701 **Paper 4**: Structured Questions ***SIMPLIFIED***

Freequency of marks for each Topic Number from m2022 to m2016 purple crosses, (Timezone 1 only) compared to m2022 to w2009 in the red diamonds (64 papers). *Purple line shows most recent 7 year trend.*

	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
9w-15w	2.3	8.0	4.3	5.1	1.4	7.1	1.1	1.1	0.0	2.0	1.8	5.2	2.4	15.8	5.0	19.8
9w-22m	5.9	8.1	7.6	5.5	3.7	14.5	0.8	2.1	0.2	2.0	2.6	6.7	2.5	11.4	6.6	8.8
16m-22m	8.4	8.2	9.8	5.8	5.3	19.7	0.7	2.9	0.3	2.0	3.2	7.8	2.5	8.4	7.8	1.1

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Patrick Brannac

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Contents

Calendars and time management

Organising your months in 2024

January						
S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

February						
S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29		

March						
S	M	T	W	T	F	S
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30
31						

April						
S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30				

May						
S	M	T	W	T	F	S
			1	2	3	4
5	6	7	8	9	10	11
12	13	14	15	16	17	18
19	20	21	22	23	24	25
26	27	28	29	30	31	

June						
S	M	T	W	T	F	S
						1
2	3	4	5	6	7	8
9	10	11	12	13	14	15
16	17	18	19	20	21	22
23	24	25	26	27	28	29
30						

CAMBRIDGE
International Education

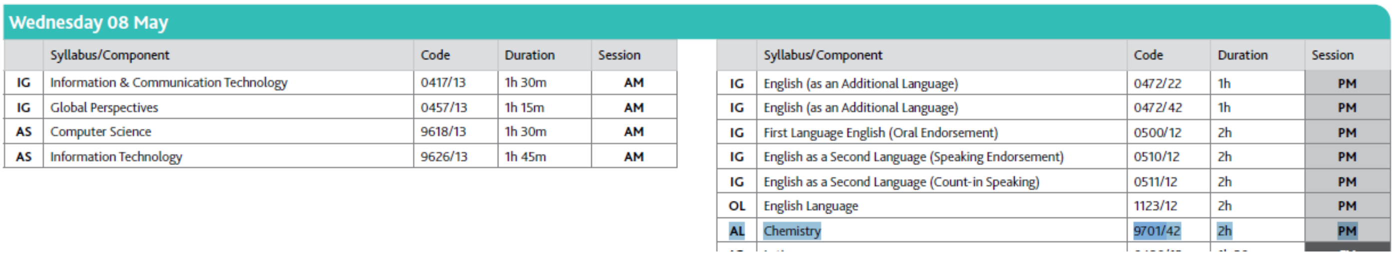
Cambridge IGCSE™
Cambridge O Level
Cambridge International AS & A Level

Cambridge Final Exam Timetable June 2024

Administrative zone 5

CAIE Chemistry 9701 A Level Chemistry Exam Timetable for *<u>Administrative Zone 5 (Time Zone 2)</u>*:

Paper 4

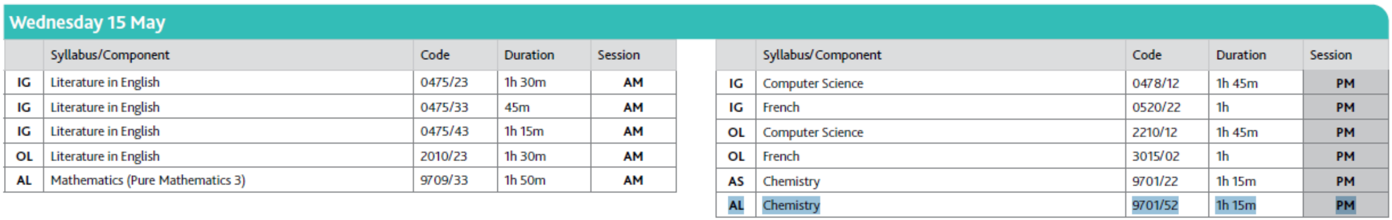


Wednesday 08 May

	Syllabus/Component	Code	Duration	Session
IG	Information & Communication Technology	0417/13	1h 30m	AM
IG	Global Perspectives	0457/13	1h 15m	AM
AS	Computer Science	9618/13	1h 30m	AM
AS	Information Technology	9626/13	1h 45m	AM

	Syllabus/Component	Code	Duration	Session
IG	English (as an Additional Language)	0472/22	1h	PM
IG	English (as an Additional Language)	0472/42	1h	PM
IG	First Language English (Oral Endorsement)	0500/12	2h	PM
IG	English as a Second Language (Speaking Endorsement)	0510/12	2h	PM
IG	English as a Second Language (Count-in Speaking)	0511/12	2h	PM
OL	English Language	1123/12	2h	PM
AL	Chemistry	9701/42	2h	PM

Paper 5



Wednesday 15 May

	Syllabus/Component	Code	Duration	Session
IG	Literature in English	0475/23	1h 30m	AM
IG	Literature in English	0475/33	45m	AM
IG	Literature in English	0475/43	1h 15m	AM
OL	Literature in English	2010/23	1h 30m	AM
AL	Mathematics (Pure Mathematics 3)	9709/33	1h 50m	AM

	Syllabus/Component	Code	Duration	Session
IG	Computer Science	0478/12	1h 45m	PM
IG	French	0520/22	1h	PM
OL	Computer Science	2210/12	1h 45m	PM
OL	French	3015/02	1h	PM
AS	Chemistry	9701/22	1h 15m	PM
AL	Chemistry	9701/52	1h 15m	PM

Organising your weeks

Week Starting	Wk #	Events	Topic Focus
11-Mar	9		
18-Mar	10		
25-Mar	11		
1-Apr	12		
8-Apr	13		
15-Apr	14		
22-Apr	15		
29-Apr	16	**Thur 2nd PM Paper 33 (TZ2)**	
6-May	17	**Wed 8th PM Paper 4 (TZ2)**	
13-May	18	**Wed 15th PM Paper 2 (TZ2)** **Wed 15th PM Paper 5 (TZ2)**	
20-May	11		
27-May	12	**Thur 30th PM Paper 34 (TZ2)**	
3-Jun	13	**Tues 4th PM Paper 1 (TZ2)**	
10-Jun	14		
17-Jun	15		
24-Jun	16		

Planning your days

V1.0 – Continue to refine these to find and RECORD times you study best (and when you never study)

Period	Time	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
	5:00 am							
	5:30 am							
	6:00 am							
	6:30 am							
	7:00 am							
Regstn	7:25 am							
1	7:50 am							
2	8:40 am							
3	9:30 am							
4	10:20 am							
5	11:00 am							
Lunch	11:50 pm							
6	1:10 pm							
7	2:00pm							
8	2:50 pm							
9	3:40 pm							
	4:20 pm							
	5:00 pm							
	5:30 pm							
	6:00 pm							
	6:30 pm							
	7:00 pm							
	7:30 pm							
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	8:30 pm							
	9:00 pm							
	9:30 pm							
	10:00 pm							
	10:30 pm							

Planning your days – v2.0

Period	Time	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
	5:00 am							
	5:30 am							
	6:00 am							
	6:30 am							
	7:00 am							
Regstn	7:25 am							
1	7:50 am							
2	8:40 am							
3	9:30 am							
4	10:20 am							
5	11:00 am							
Lunch	11:50 pm							
6	1:10 pm							
7	2:00pm							
8	2:50 pm							
9	3:40 pm							
	4:20 pm							
	5:00 pm							
	5:30 pm							
	6:00 pm							
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	8:30 pm							
	9:00 pm							
	9:30 pm							
	10:00 pm							
	10:30 pm							

Planning your days – v3.0

Period	Time	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
	5:00 am							
	5:30 am							
	6:00 am							
	6:30 am							
	7:00 am							
Regstn	7:25 am							
1	7:50 am							
2	8:40 am							
3	9:30 am							
4	10:20 am							
5	11:00 am							
Lunch	11:50 pm							
6	1:10 pm							
7	2:00pm							
8	2:50 pm							
9	3:40 pm							
	4:20 pm							
	5:00 pm							
	5:30 pm							
	6:00 pm							
	6:30 pm							
	7:00 pm							
	7:30 pm							
	8:00 pm							
	8:30 pm							
	9:00 pm							
	9:30 pm							
	10:00 pm							
	10:30 pm							

Planning your days – v4.0

Period	Time	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
	5:00 am							
	5:30 am							
	6:00 am							
	6:30 am							
	7:00 am							
Regstn	7:25 am							
1	7:50 am							
2	8:40 am							
3	9:30 am							
4	10:20 am							
5	11:00 am							
Lunch	11:50 pm							
6	1:10 pm							
7	2:00pm							
8	2:50 pm							
9	3:40 pm							
	4:20 pm							
	5:00 pm							
	5:30 pm							
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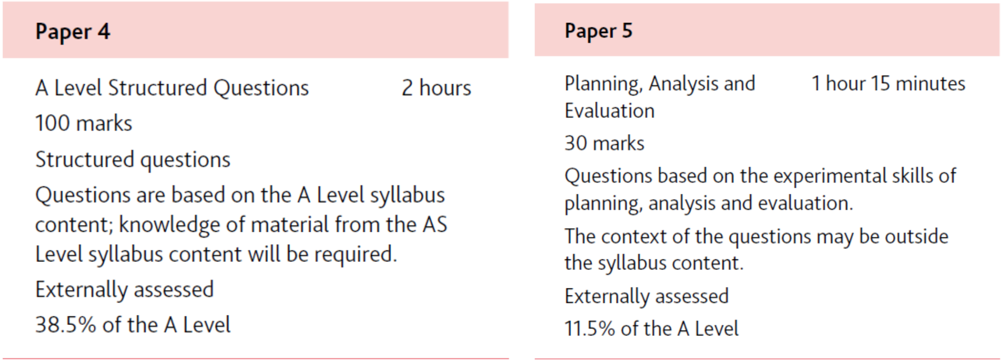
	10:00 pm							
	10:30 pm							

Paper 4: Analysis, notes and points of interest



Paper 4	Paper 5
A Level Structured Questions 2 hours	Planning, Analysis and Evaluation 1 hour 15 minutes
100 marks	30 marks
Structured questions	Questions based on the experimental skills of planning, analysis and evaluation.
Questions are based on the A Level syllabus content; knowledge of material from the AS Level syllabus content will be required.	The context of the questions may be outside the syllabus content.
Externally assessed	Externally assessed
38.5% of the A Level	11.5% of the A Level

Overview of main syllabi changes:

Changes in exam format, presentation, and explanation of syllabus across time:

- 2006 and before P5 (30marks, 90mins) is more like paper 3, so requires experimental work under exam conditions. Paper 6 also existed which were questions on the options.
- 2007 first year which had two versions of paper 3. 2007 Paper 5 went from 90minutes to 75minutes 30marks, but removed the practical experiment part, a format which continues to 2027.
- 2009 winter is the first session to have more than one Time Zone, with 2 time zones.
- 2010 introduced all the current Time Zones: 1, 2 and 3. These continue for winter and summer sessions to 2027.
- 2012w and before each question section in the Paper 5 mark scheme are given their “Experimental skills and investigations” label.
- 2013s and onwards no longer gives details about the Skill Sections being assessed by each question.
- 2015 winter was the last Paper 4 with a Section B (30marks) assessing only *Topic 11 Applications of Chemistry*.
- 2016 introduced the March series, which is always assigned only one Time Zone: 2.
- 2022 syllabus updates changed content and wording (almost no substantive changes)
- 2022 Data Booklet was no longer provided in Paper 1, 2 or 4 not given in any exams
- 2022 Paper 1 Section B (where answers A to D correspond to a range of combinations of options 1 to 3) was replaced with standard A to D multiple choice questions, and 15minitues was added to the total exam time (same number of marks however).
- 2025-2027 Exactly the same as 2022-2024 syllabi

Main syllabi changes discussion

Paper 4 The largest change has been a shift away from assessing AS content in Paper 4, which in exams 2015 and before represented almost 1 in 5 marks, since 2016 it is about 1 mark in 20. This shift could be explained by looking at the combined frequencies for Papers 4 and 5, where we see that the number of marks assigned to AS level remained stable. From 2009w to 2015w AS material in both papers was 26.6% of all marks and from 2016m to 2022m it was 27.9%. AS material then is still examinable, but it has been moved from Paper 4 to Paper 5.

The other major change at the topic level has been in Topic 28: Chemistry of transition elements which now is the single most important topic. In exams from 2015 and before, it was part of what was then described as *Topic 11 Applications of Chemistry* (e.g. in 2015 syllabus), which itself was a version of the Optional Topics from 2006 and before. Much of the material from the 2015 *T11 Applications of Chemistry* topic was removed, but transition metals was incorporated into the main syllabus from 2016. So it was larger syllabus restructuring and major deletion events that have indirectly lead to its increase in frequency.

It was also the 2015 *Topic 11 Applications of Chemistry* material that explains the large amount of material that has been deleted from the syllabus in 2016 syllabi and later.

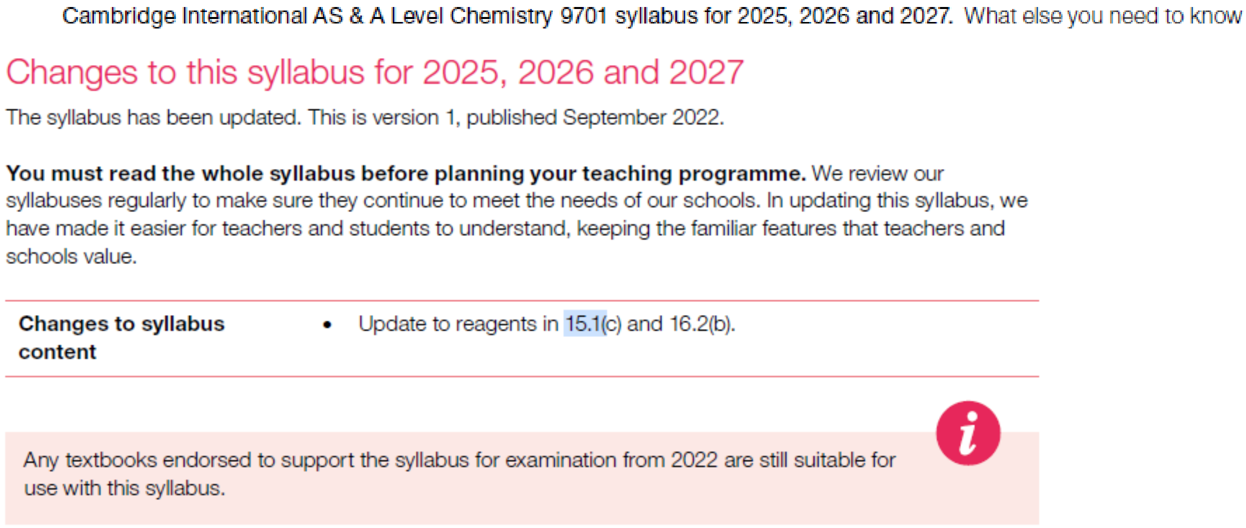
In addition, marks assigned to *Topic 23 Chemical Energetics* and *Topic 25 Equilibria* have more than doubled since 2016, and *Topic 27 Group 2* is now a larger part to more paper 4 exams.

Topic 36 Organic Synthesis has become less important in exams from 2016 and later largely because marks covering organic synthesis are easier to allocate to individual organic topics. In 2015 and before more marks required working and question parts assessing other organic topics, which became less common in 2016 and onwards.

If we combine all marks from both Papers 4 and 5, we can see that of the 4 main chemistry branches in this syllabus, Physical Chemistry (54.9% of all Paper 4 and 5 marks from 2016m onwards) not only is by far the dominant category, it has also grown substantially, by about 50%, largely by taking in all of the marks that were part of material no longer assessed from 2016 onwards (which had been given 12.8% of marks), but also by taking about a third of the 2015 and before marks of Organic Chemistry. Physical Chemistry is not only the dominant Paper 4 branch of chemistry (34.4% of Paper 4 marks) compared to Organic Chemistry (30.0% of Paper 4 marks), but it is also easily a major part of Paper 5. This substantial decrease in Organic Chemistry relevance has resulted in this topic now being less important in terms of mark frequency (being awarded 18.4% of 2026 and later marks) than even Inorganic Chemistry, which grew in importance in the same period (to 20.8%).

By looking at the various graphs gives an indication of the variability of this syllabus across time, but nearly all of this is actually just the result of 2 large changes to the syllabus structure, in 2007 and 2016, which both were part of a process to remove the Optional aspects to the course, which originated in a splendid, exciting new idea from the 1990s which didn't quite pan out. This itself gives a broader sense that historically across the decades, A level Chemistry has been a stable syllabus: it appears to resist change and English language Key Stage 5 (high school) syllabi like it are therefore trending towards a canonical content. Looking ahead, until 2027, there are no real changes, either to the structure, description, or content of the syllabus. The only single change to content, shown in the following section, is a single detail (using KCl instead of KBr) in an organic reaction.

Changes to this syllabus for 2025, 2026 and 2027



Cambridge International AS & A Level Chemistry 9701 syllabus for 2025, 2026 and 2027. What else you need to know

Changes to this syllabus for 2025, 2026 and 2027

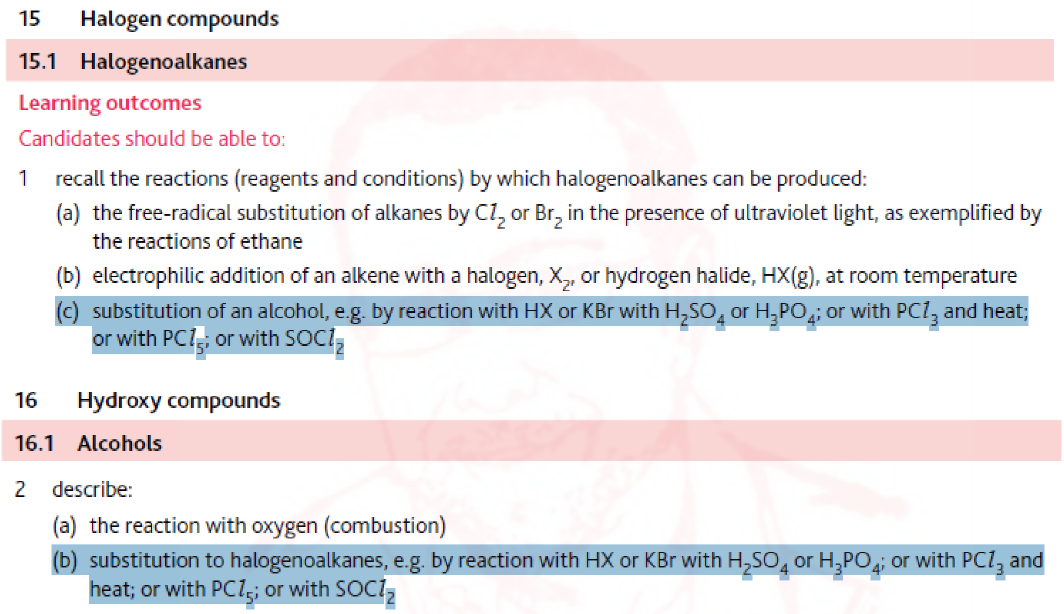
The syllabus has been updated. This is version 1, published September 2022.

You must read the whole syllabus before planning your teaching programme. We review our syllabuses regularly to make sure they continue to meet the needs of our schools. In updating this syllabus, we have made it easier for teachers and students to understand, keeping the familiar features that teachers and schools value.

Changes to syllabus content	• Update to reagents in 15.1(c) and 16.2(b).

Any textbooks endorsed to support the syllabus for examination from 2022 are still suitable for use with this syllabus.

2024 version:



15 Halogen compounds

15.1 Halogenoalkanes

Learning outcomes

Candidates should be able to:

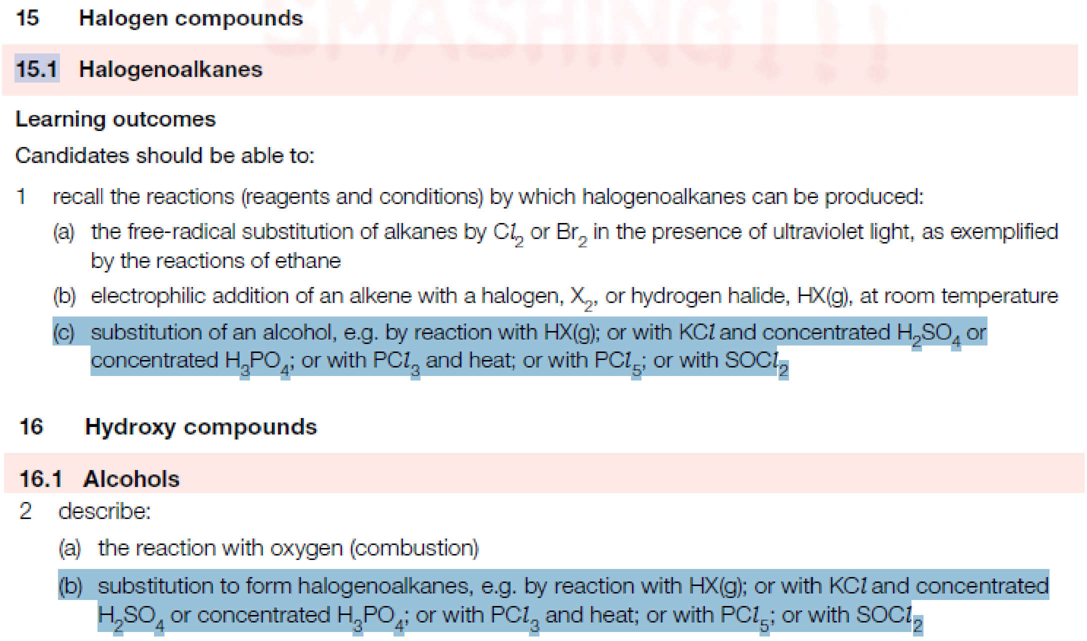
1 recall the reactions (reagents and conditions) by which halogenoalkanes can be produced:
  (a) the free-radical substitution of alkanes by Cl_2 or Br_2 in the presence of ultraviolet light, as exemplified by the reactions of ethane
  (b) electrophilic addition of an alkene with a halogen, X_2, or hydrogen halide, HX(g), at room temperature
  (c) substitution of an alcohol, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$

16 Hydroxy compounds

16.1 Alcohols

2 describe:
  (a) the reaction with oxygen (combustion)
  (b) substitution to halogenoalkanes, e.g. by reaction with HX or KBr with H_2SO_4 or H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$

2025-2027 version



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  (b) electrophilic addition of an alkene with a halogen, X_2, or hydrogen halide, HX(g), at room temperature
  (c) substitution of an alcohol, e.g. by reaction with HX(g); or with KC*l* and concentrated H_2SO_4 or concentrated H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$

16 Hydroxy compounds

16.1 Alcohols

2 describe:
  (a) the reaction with oxygen (combustion)
  (b) substitution to form halogenoalkanes, e.g. by reaction with HX(g); or with KC*l* and concentrated H_2SO_4 or concentrated H_3PO_4; or with PCl_3 and heat; or with PCl_5; or with $SOCl_2$

Notes on taking apart these exam papers and how they were separated

- AS level topics are separated from A2 topics so that you can see how often they are examined at A2 (increasingly less and less). So Topic 6 electrochemistry would be separated from Topic 24 Electrochemistry.
- The 2015 Syllabus *Topic 11: Applications of Chemistry* was removed in the march 2016 paper, so it was last examined in w2015. It represented 30% of Paper 4 and was examined in Section B part of the exam. Roughly a third was kept but placed into various other topics. However, essentially all *T11.1 The Chemistry of Life* was removed (except amino acids, moved into T35 in 2024 syllabus. *T11.3 Design and Materials* was also largely deleted.
- Last held in 2006, Paper 6 examined the 5 Options which then were transformed into the *T11 Applications of Chemistry* topic (and, for instance, in the Transition elements main topic), which then was examined in Section B of the changed Paper 5. You had to chose 2 questions from the 5 options in Paper 6. Afterwards the syllabus only used 5 exams, which continues to 2024.
- Mass spectroscopy was moved from A2 to AS content.
- NMR and rarely other analytical techniques (T37) are sometimes combined with T36: Organic synthesis, especially in earlier (before 2016) exam papers. Less common more recently.
- One question combined T25: Equilibria with T24: Electrochemistry (2020sP41Q7) in a way that could not be separated.
- Enzymes T8f (2015) was removed and is not found in 2024.
- T24 often has drawing and labelling electrochemical cells questions. Electrophoresis in T37 also requires diagrams. Otherwise, drawing is not a common question type (but is common in Paper 5 for instance).
- Side chains interacting with each other in polymer chains in T11.3 (2014) and in 21.3 Properties of Polymers (2021) is also removed.
- T13.4 (2024) chirality and especially identify the chiral carbon in a given molecule is often assessed when amino acids are examined.
- T23.1 Synthesis of Chiral Drug Molecules (2021) was removed.
- T28.2 (2024) Electrochemical potentials with regards to transition metals is a rare example of a topic appearing twice (mainly in T24). Where the question involves feasibility or direction of a reaction it is in 28.2, if the E_{cell} is instead required, it usually would go into T24.
- Cisplatin's mode of action by binding to DNA in T12.4 (2021) has bee removed from T28.4 (2024).
- One question combined T23 Entropy with T35 Polymerization (2018mP42Q7a). The idea was condensation polymers produce small molecules which increase entropy, addition polymers create a larger molecule from 2 smaller ones, decreasing entropy. Another really rare example of topics being combined in question parts in a way that cannot be separated.
- Generally, if there are 3 steps or more, or 3 parts to an Organic Synthesis it will be placed into T36. If only two parts, then the question part is assigned to the specific organic chemistry topic. The preference therefore is to assign to a specific topic rather than T36.
- 2018sP41Q4 asks about flame tests for Ca and Ba, which corresponds to "describe… the reactions for the elements with oxygen" in T10.
- In some exams 2015 and before, the Question 1 starts off easier and is, at least initially, AS material. But this is much less common in 2016 and after.
- T29 identifying functional groups usually involved one A2 group, like an amide or phenol group, but most of the groups are from T13, but in these cases, these marks cannot be untangled, so are just assigned to T29. In 2014wP41Q5b all the functional groups are from T13, the single exception.
- Section A and B were last seen in the w2015 exam paper.
- For exam papers 2009w to 2014s there are additional marks within questions, so within a 7-mark question there are 8 marks possible (e.g. 2010sP41Q1b). This is separate from an essay style question where there are more marks possible to be awarded than the max because these additional marks are extended into other question parts. They do not have a big impact, but they are at least there and mean that there will be slightly more marks in the total analysis. Specifically, these papers have these extra marks: 09w has 3marks; 10s has 9marks;

10w has 5marks, 11s has 2marks, 11w has 5 marks, 12s has 4marks and 13s, 13w and 14s each have just 1 extra marks.

- Group IV in T9.3 (2015) was discontinued, marks assigned to this are written as topic x9.
- Marks regarding basicity of amines, where they accept H^+ ions, for instance, are sometimes better assigned to T34, but arguably could be also in T7.
- For exam papers downloaded in June 2011 there are problems with how some small parts of the question appear on a pdf viewer, which are not found in the same exam paper or marks scheme downloaded later. This is a rare example indicating that not all exam papers available online are equal. These papers are affected: 10sP41Q5b(iv), 10wP41Q2b.
- In 2016-18 syllabus there is a section titled “Learning outcomes removed from the syllabus content” on page 95, indicating major changes. The group IV T9.3 in 2025 syllabus has been removed, but is not mentioned in this section, but I cannot understand why (possibly a mistake).
- In 2015 T11.2 x-ray crystallography is not found in 2024.
- Drug delivery T11.2 in 2015, including the changes that can happen to a molecule in the body (usually relates to hydrolysis of esters or amides and acidic conditions in stomach), has been removed.
- The largest change to the syllabus was in 2007 (removal of Paper 6, 40marks against 60marks in Paper 5) and in 2016 (removal of section B) are both related to this optional material that then became compulsory, that then was entirely incorporated into the main syllabus.
- Topic 5 in 2010 to 15 seemed to be common when I was assigning topics.
- Comparing the density (and fixed points) of a transition metal and Ca, a typical S block metal, was still in 2021, but removed in 2024.
- Ozone in T16 in 2021 was removed in 2024.
- Partition coefficient moved from T11.2 in 2015 to t25 in 2024.
- Nitrates in water and eutrophication previously in T13 in 2018 was removed.
- Organic synthesis almost never uses T21, it is most often assigned instead to T36. This may be an opportunity to fine tune in future editions.
- 2009s has only 1 time zone, 2009w has 2 and 2010s has 3 time zones.
- 2021 included T4 Ceramics, which was removed in 2022-24.

PAPER 4 Tables of analysis of mark frequencies per topic

Topic Number and Name	9w-22m	9w-15w	16m-22m
1 Atomic structure	0.1	0.2	**0.0**
2 Atoms, molecules and stoichiometry	0.9	1.5	**0.4**
3 Chemical bonding	1.3	1.6	**1.2**
4 States of matter	0.0	0.0	**0.0**
5 Chemical energetics	0.6	1.5	**0.0**
6 Electrochemistry	0.2	0.0	**0.4**
7 Equilibria	0.7	1.7	**0.1**
8 Reaction kinetics	0.0	0.0	**0.0**
9 The Periodic Table: chemical periodicity	1.0	2.4	**0.1**
10 Group 2	0.4	0.0	**0.7**
11 Group 17	0.2	0.5	**0.1**
12 Nitrogen and sulfur	0.6	1.5	**0.0**
13 An introduction to AS Level organic chemistry	1.1	1.3	**1.0**
14 Hydrocarbons	0.9	1.6	**0.4**
15 Halogen compounds	0.6	1.1	**0.2**
16 Hydroxy compounds	0.2	0.0	**0.3**
17 Carbonyl compounds	0.7	1.3	**0.2**
18 Carboxylic acids and derivatives	0.0	0.0	**0.0**
19 Nitrogen compounds	0.0	0.0	**0.0**
20 Polymerisation	0.2	0.3	**0.1**
21 Organic synthesis	0.0	0.0	**0.0**
22 Analytical techniques	1.1	1.2	**1.0**
AS TOTAL	10.8	17.7	6.2
23 Chemical energetics	5.9	2.3	**8.4**
24 Electrochemistry	8.1	8.0	**8.2**
25 Equilibria	7.6	4.3	**9.8**
26 Reaction kinetics	5.5	5.1	**5.8**
27 Group 2	3.7	1.4	**5.3**
28 Chemistry of transition elements	14.5	7.1	**19.7**
29 An introduction to A Level organic chemistry	0.8	1.1	**0.7**
30 Hydrocarbons	2.1	1.1	**2.9**
31 Halogen compounds	0.2	0.0	**0.3**
32 Hydroxy compounds	2.0	2.0	**2.0**
33 Carboxylic acids and derivatives	2.6	1.8	**3.2**
34 Nitrogen compounds	6.7	5.2	**7.8**
35 Polymerisation	2.5	2.4	**2.5**
36 Organic synthesis	11.4	15.8	**8.4**
37 Analytical techniques	6.6	5.0	**7.8**
A2 TOTAL	80.2	62.6	92.8
Chemistry no longer assessed in 2024:	8.8	19.8	**1.1**

Paper 4 ranked by most recent frequency trend (2016m to 2022w)

Topic Number and Name	9w-22m	9w-15w	16m-22m
28 Chemistry of transition elements	14.5	7.1	**19.7**
25 Equilibria	7.6	4.3	**9.8**
23 Chemical energetics	5.9	2.3	**8.4**
36 Organic synthesis	11.4	15.8	**8.4**
24 Electrochemistry	8.1	8.0	**8.2**
34 Nitrogen compounds	6.7	5.2	**7.8**
37 Analytical techniques	6.6	5.0	**7.8**
26 Reaction kinetics	5.5	5.1	**5.8**
27 Group 2	3.7	1.4	**5.3**
33 Carboxylic acids and derivatives	2.6	1.8	**3.2**
30 Hydrocarbons	2.1	1.1	**2.9**
35 Polymerisation	2.5	2.4	**2.5**
32 Hydroxy compounds	2.0	2.0	**2.0**
3 Chemical bonding	1.3	1.6	**1.2**
Chemistry no longer assessed in 2024:	8.8	19.8	**1.1**
13 An introduction to AS Level organic chemistry	1.1	1.3	**1.0**
22 Analytical techniques	1.1	1.2	**1.0**
10 Group 2	0.4	0.0	**0.7**
29 An introduction to A Level organic chemistry	0.8	1.1	**0.7**
2 Atoms, molecules and stoichiometry	0.9	1.5	**0.4**
6 Electrochemistry	0.2	0.0	**0.4**
14 Hydrocarbons	0.9	1.6	**0.4**
16 Hydroxy compounds	0.2	0.0	**0.3**
31 Halogen compounds	0.2	0.0	**0.3**
15 Halogen compounds	0.6	1.1	**0.2**
17 Carbonyl compounds	0.7	1.3	**0.2**
7 Equilibria	0.7	1.7	**0.1**
9 The Periodic Table: chemical periodicity	1.0	2.4	**0.1**
11 Group 17	0.2	0.5	**0.1**
20 Polymerisation	0.2	0.3	**0.1**
1 Atomic structure	0.1	0.2	**0.0**
4 States of matter	0.0	0.0	**0.0**
5 Chemical energetics	0.6	1.5	**0.0**
8 Reaction kinetics	0.0	0.0	**0.0**
12 Nitrogen and sulfur	0.6	1.5	**0.0**
18 Carboxylic acids and derivatives	0.0	0.0	**0.0**
19 Nitrogen compounds	0.0	0.0	**0.0**
21 Organic synthesis	0.0	0.0	**0.0**

Paper 4 and 5 COMBINED Each topic described by frequency

Topic Number and Name	Paper 4 &5 09w-22m	Paper 4 ONLY 16m-22m	P4&5 09w-15w	Paper 4 & 5 16m-22m
1 Atomic structure	0.0	0.0	0.1	0.0
2 Atoms, molecules and stoichiometry	2.6	0.4	4.3	1.8
3 Chemical bonding	0.8	1.2	1.3	0.6
4 States of matter	2.9	0.0	2.3	3.1
5 Chemical energetics	3.1	0.0	2.1	3.6
6 Electrochemistry	3.7	0.4	0.9	5.0
7 Equilibria	4.2	0.1	4.9	3.8
8 Reaction kinetics	1.8	0.0	0.9	2.3
9 The Periodic Table: chemical periodicity	1.8	0.1	2.8	1.3
10 Group 2	1.2	0.7	0.0	1.8
11 Group 17	1.4	0.1	1.3	1.4
12 Nitrogen and sulfur	0.4	0.0	1.2	0.0
13 An introduction to AS Level organic chemistry	0.7	1.0	1.0	0.6
14 Hydrocarbons	1.2	0.4	1.3	1.2
15 Halogen compounds	0.4	0.2	0.8	0.1
16 Hydroxy compounds	0.1	0.3	0.0	0.1
17 Carbonyl compounds	0.4	0.2	1.0	0.1
18 Carboxylic acids and derivatives	0.0	0.0	0.0	0.0
19 Nitrogen compounds	0.0	0.0	0.0	0.0
20 Polymerisation	0.1	0.1	0.2	0.1
21 Organic synthesis	0.6	0.0	0.0	0.8
AS Total	**27.5**	**5.1**	**26.6**	**27.9**
22 Analytical techniques	0.7	1.0	1.0	0.5
23 Chemical energetics	4.9	8.4	4.4	5.1
24 Electrochemistry	8.6	8.2	7.3	9.2
25 Equilibria	6.0	9.8	3.4	7.2
26 Reaction kinetics	10.8	5.8	5.9	13.2
27 Group 2	4.7	5.3	4.7	4.6
28 Chemistry of transition elements	9.9	19.7	6.5	11.6
29 An introduction to A Level organic chemistry	0.5	0.7	0.8	0.4
30 Hydrocarbons	1.3	2.9	0.8	1.6
31 Halogen compounds	0.1	0.3	0.0	0.2
32 Hydroxy compounds	1.3	2.0	1.6	1.1
33 Carboxylic acids and derivatives	1.7	3.2	1.4	1.8
34 Nitrogen compounds	4.3	7.8	4.1	4.3
35 Polymerisation	1.6	2.5	1.9	1.4
36 Organic synthesis	7.2	8.4	12.5	4.6
37 Analytical techniques	4.5	7.8	4.0	4.7
Chemistry no longer assessed in 2024:	4.6	1.1	12.8	0.6
A2 Total	**72.5**	**94.9**	**73.4**	**72.1**

Paper 4 and 5 ranked by most recent frequency trend (2016m to 2022w)

Topic Number and Name	Paper 4 &5 09w-22m	Paper 4 ONLY 16m-22m	Paper 4 & 5 16m-22m
26 Reaction kinetics	8.4	5.8	**13.2**
28 Chemistry of transition elements	10.9	19.7	**11.6**
24 Electrochemistry	8.1	8.2	**9.2**
25 Equilibria	6.0	9.8	**7.2**
23 Chemical energetics	5.8	8.4	**5.1**
6 Electrochemistry	2.8	0.4	**5.0**
37 Analytical techniques	4.9	7.8	**4.7**
27 Group 2	5.4	5.3	**4.6**
36 Organic synthesis	8.1	8.4	**4.6**
34 Nitrogen compounds	4.8	7.8	**4.3**
7 Equilibria	2.6	0.1	**3.8**
5 Chemical energetics	2.5	0.0	**3.6**
4 States of matter	2.1	0.0	**3.1**
8 Reaction kinetics	1.8	0.0	**2.3**
2 Atoms, molecules and stoichiometry	3.6	0.4	**1.8**
10 Group 2	0.8	0.7	**1.8**
33 Carboxylic acids and derivatives	1.9	3.2	**1.8**
30 Hydrocarbons	1.5	2.9	**1.6**
11 Group 17	1.0	0.1	**1.4**
35 Polymerisation	1.7	2.5	**1.4**
9 The Periodic Table: chemical periodicity	1.4	0.1	**1.3**
14 Hydrocarbons	1.0	0.4	**1.2**
32 Hydroxy compounds	1.4	2.0	**1.1**
21 Organic synthesis	0.3	0.0	**0.8**
3 Chemical bonding	1.0	1.2	**0.6**
13 An introduction to AS Level organic chemistry	0.8	1.0	**0.6**
22 Analytical techniques	0.8	1.0	**0.5**
29 An introduction to A Level organic chemistry	0.6	0.7	**0.4**
31 Halogen compounds	0.1	0.3	**0.2**
15 Halogen compounds	0.4	0.2	**0.1**
16 Hydroxy compounds	0.1	0.3	**0.1**
17 Carbonyl compounds	0.5	0.2	**0.1**
20 Polymerisation	0.1	0.1	**0.1**
1 Atomic structure	0.0	0.0	**0.0**
12 Nitrogen and sulfur	0.4	0.0	**0.0**
18 Carboxylic acids and derivatives	0.0	0.0	**0.0**
19 Nitrogen compounds	0.0	0.0	**0.0**

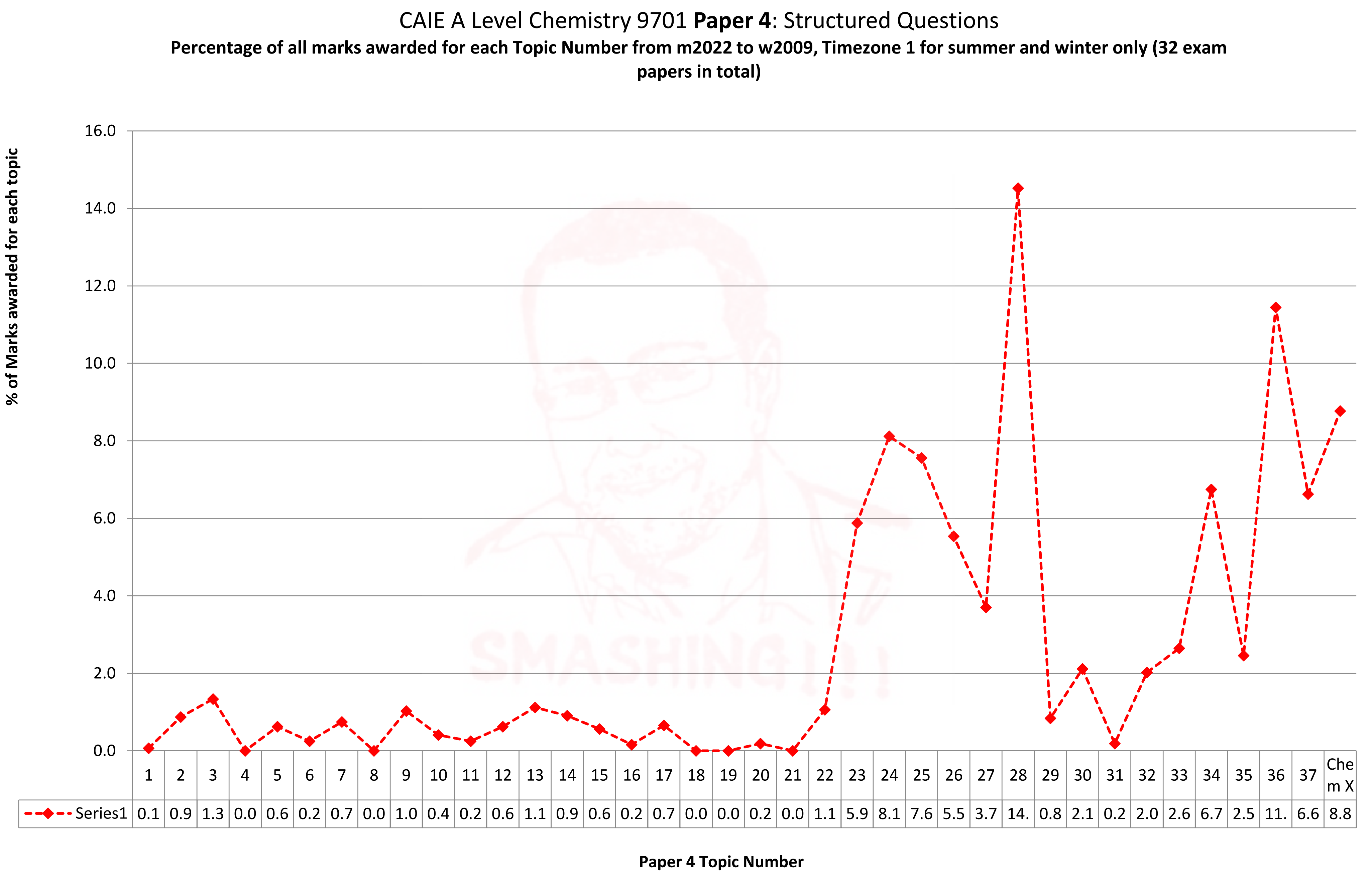
PAPER 5 Tables of analysis of mark frequencies for topics and experiment types

Paper 5 Analysis by TOPIC number (descriptions relate to the subtopic the bulk of the questions deal with):

Topic Number and Name	02s to 23s	02s-06w	07s-13s	13w-23s
26 Rate A2	15.3	6.7	7.7	**20.2**
7 Acid base	7.2	10.1	0.0	**11.2**
24 Electrochemistry	7.9	0.0	3.9	**10.5**
6 Redox	9.2	15.8	7.7	**9.8**
4 States of matter	7.3	10.1	6.2	**7.3**
5 Enthalpy	7.0	14.8	7.7	**7.3**
27 Group 2 (thermal decomposition)	9.4	6.4	15.4	**5.2**
8 Rate AS	6.4	14.4	11.3	**4.6**
9 Periodicity	2.3	0.0	0.0	**3.6**
25 Equilibria	2.3	0.0	0.0	**3.6**
2 Stoichiometry	10.3	21.8	17.2	**3.2**
10 Group 2	1.9	0.0	0.0	**3.0**
11 Group 17 – halide precipitates	3.0	0.0	3.9	**2.9**
14 Organic chemistry	1.3	0.0	0.0	**2.0**
23 Lattice enthalpy	5.7	0.0	15.2	**1.8**
21 Organic synthesis	1.1	0.0	0.0	**1.7**
28 Transition elements	2.1	0.0	3.9	**1.4**
37 Chromatography	0.5	0.0	0.0	**0.8**
1	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0
12	0.0	0.0	0.0	0.0
13	0.0	0.0	0.0	0.0
15	0.0	0.0	0.0	0.0
16	0.0	0.0	0.0	0.0
17	0.0	0.0	0.0	0.0
18	0.0	0.0	0.0	0.0
19	0.0	0.0	0.0	0.0
20	0.0	0.0	0.0	0.0
22	0.0	0.0	0.0	0.0
29	0.0	0.0	0.0	0.0
30	0.0	0.0	0.0	0.0
31	0.0	0.0	0.0	0.0
32	0.0	0.0	0.0	0.0
33	0.0	0.0	0.0	0.0
34	0.0	0.0	0.0	0.0
35	0.0	0.0	0.0	0.0
36	0.0	0.0	0.0	0.0

Paper 5 by EXPERIMENT type:

Experiment type	02s to 23s	02s-06w	07s-13s	**13w-23s**	**Rank**
Rate	23.8	21.1	19.0	**26.9**	**1**
Titration	15.6	19.8	3.9	**19.5**	**2**
Gas Volumes	12.1	10.1	11.8	**13.0**	**3**
States	12.6	5.0	21.6	**11.2**	**4**
Electrolysis	5.9	0.0	3.9	**8.9**	**5**
Thermometric	10.5	14.8	11.6	**8.6**	**6**
Miscellaneous	3.8	0.0	0.0	**6.9**	**7**
Gravimetric	10.9	15.1	24.4	**3.2**	**8**
Thermal Titration	4.7	14.1	3.9	**1.8**	**9**



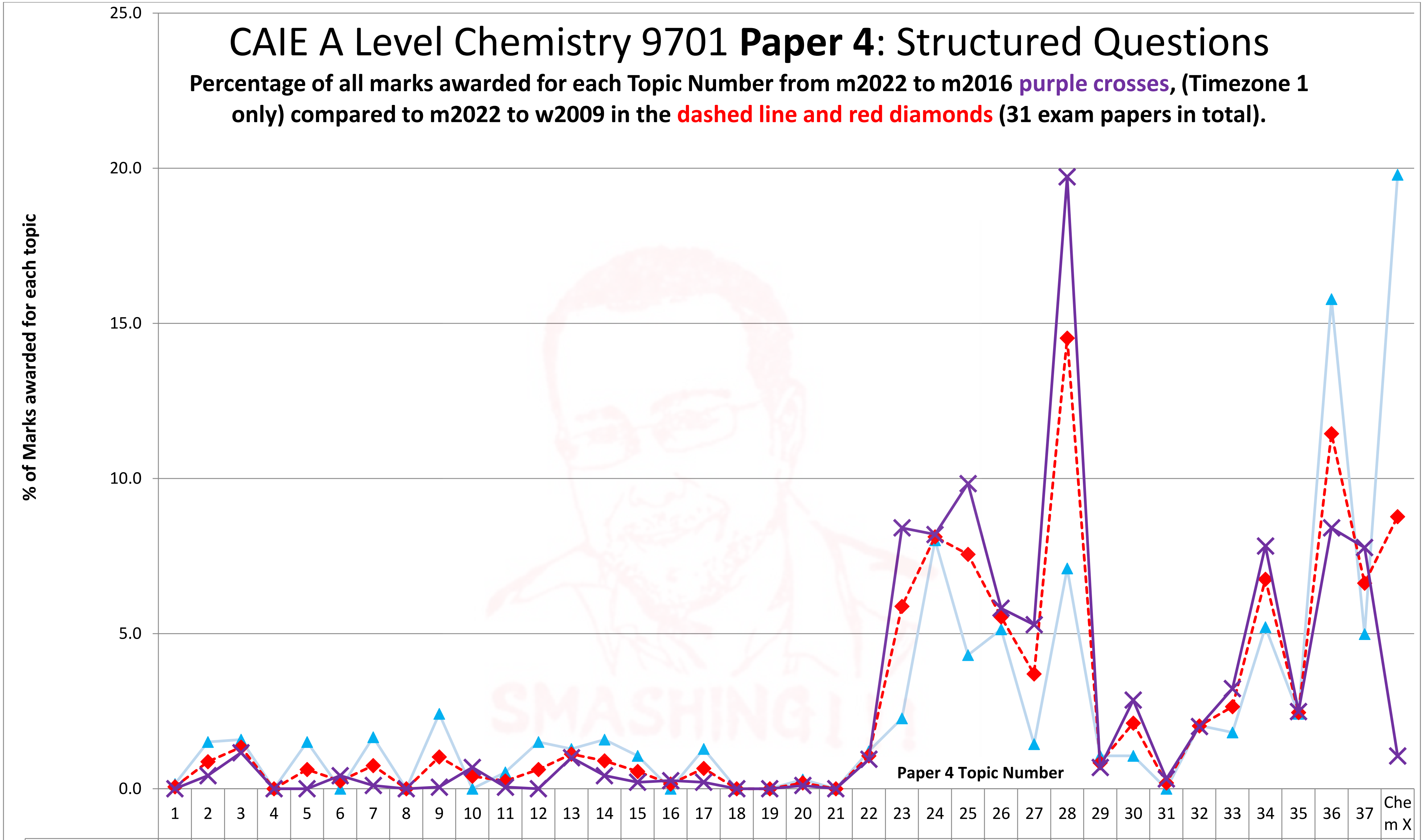
CAIE A Level Chemistry 9701 **Paper 4**: Structured Questions

Percentage of all marks awarded for each Topic Number from m2022 to w2009, Timezone 1 for summer and winter only (32 exam papers in total)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
Series1	0.1	0.9	1.3	0.0	0.6	0.2	0.7	0.0	1.0	0.4	0.2	0.6	1.1	0.9	0.6	0.2	0.7	0.0	0.0	0.2	0.0	1.1	5.9	8.1	7.6	5.5	3.7	14.	0.8	2.1	0.2	2.0	2.6	6.7	2.5	11.	6.6	8.8

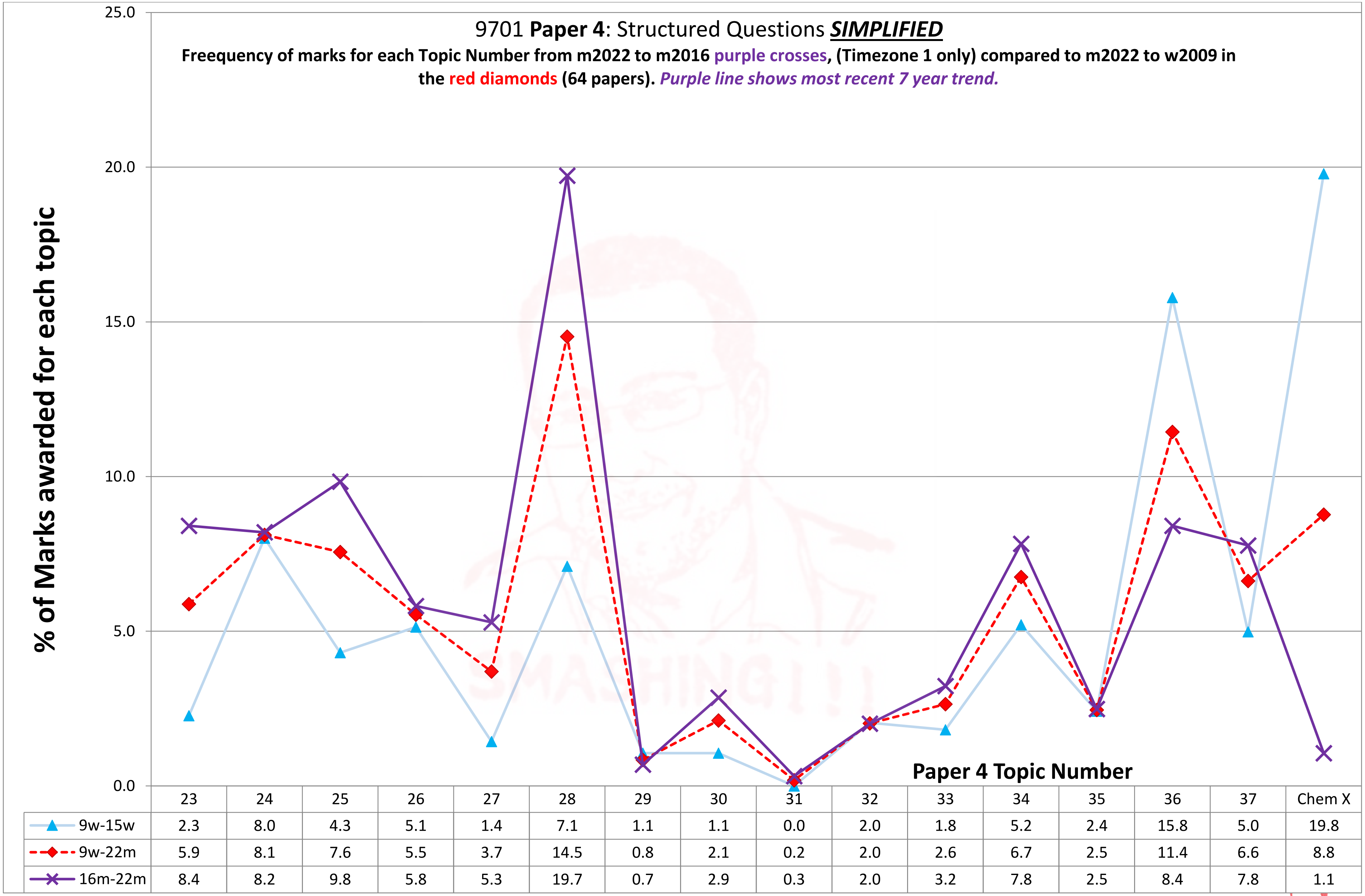
CAIE A Level Chemistry 9701 **Paper 4**: Structured Questions

Percentage of all marks awarded for each Topic Number from m2022 to m2016 purple crosses, (Timezone 1 only) compared to m2022 to w2009 in the dashed line and red diamonds (31 exam papers in total).



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
▲ 9w-15w	0.2	1.5	1.6	0.0	1.5	0.0	1.7	0.0	2.4	0.0	0.5	1.5	1.3	1.6	1.1	0.0	1.3	0.0	0.0
◆ 9w-22m	0.1	0.9	1.3	0.0	0.6	0.2	0.7	0.0	1.0	0.4	0.2	0.6	1.1	0.9	0.6	0.2	0.7	0.0	0.0
✕ 16m-22m	0.0	0.4	1.2	0.0	0.0	0.4	0.1	0.0	0.1	0.7	0.1	0.0	1.0	0.4	0.2	0.3	0.2	0.0	0.0

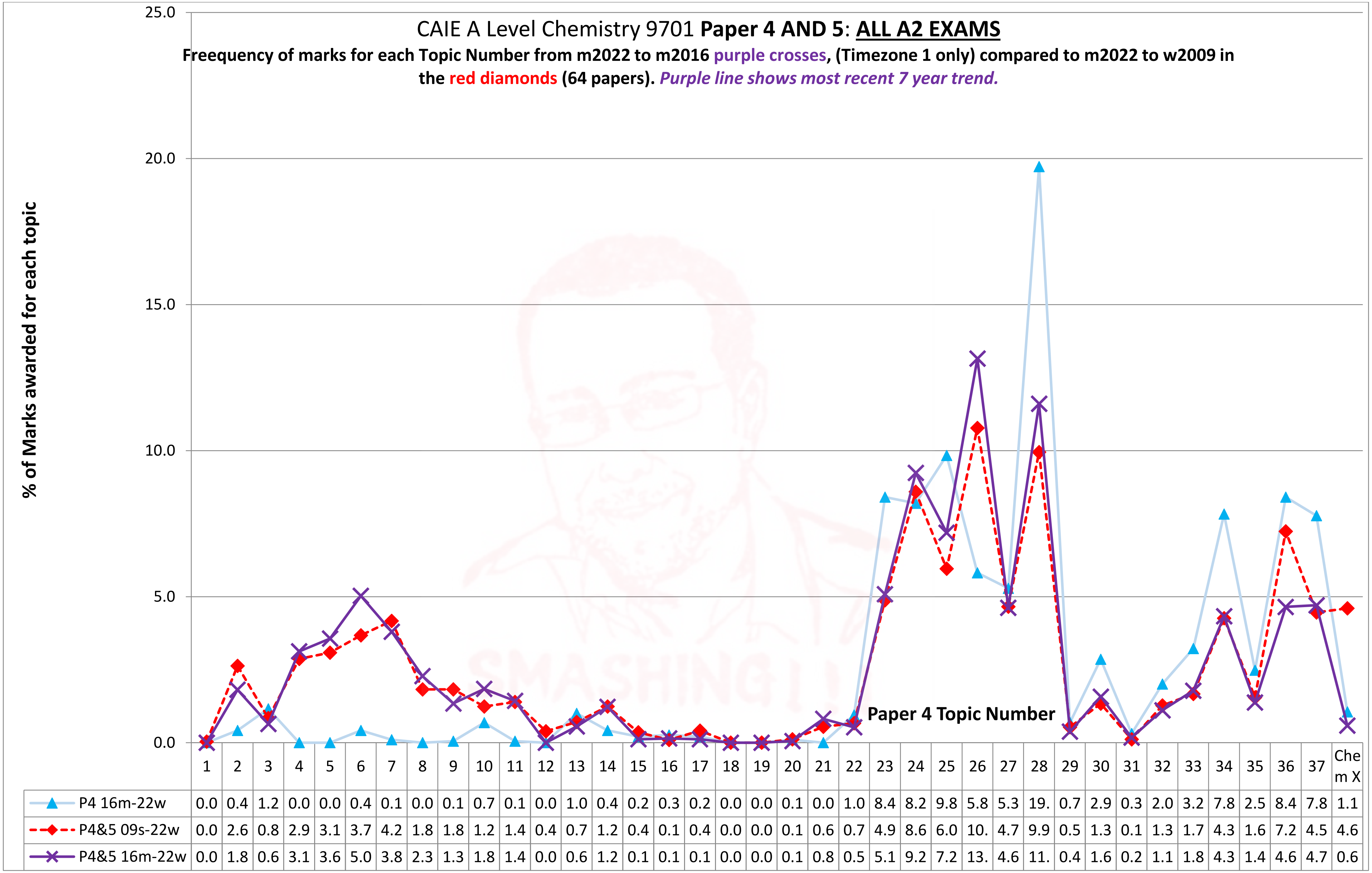
	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
▲ 9w-15w	0.3	0.0	1.2	2.3	8.0	4.3	5.1	1.4	7.1	1.1	1.1	0.0	2.0	1.8	5.2	2.4	15.	5.0	19.
◆ 9w-22m	0.2	0.0	1.1	5.9	8.1	7.6	5.5	3.7	14.	0.8	2.1	0.2	2.0	2.6	6.7	2.5	11.	6.6	8.8
✕ 16m-22m	0.1	0.0	1.0	8.4	8.2	9.8	5.8	5.3	19.	0.7	2.9	0.3	2.0	3.2	7.8	2.5	8.4	7.8	1.1



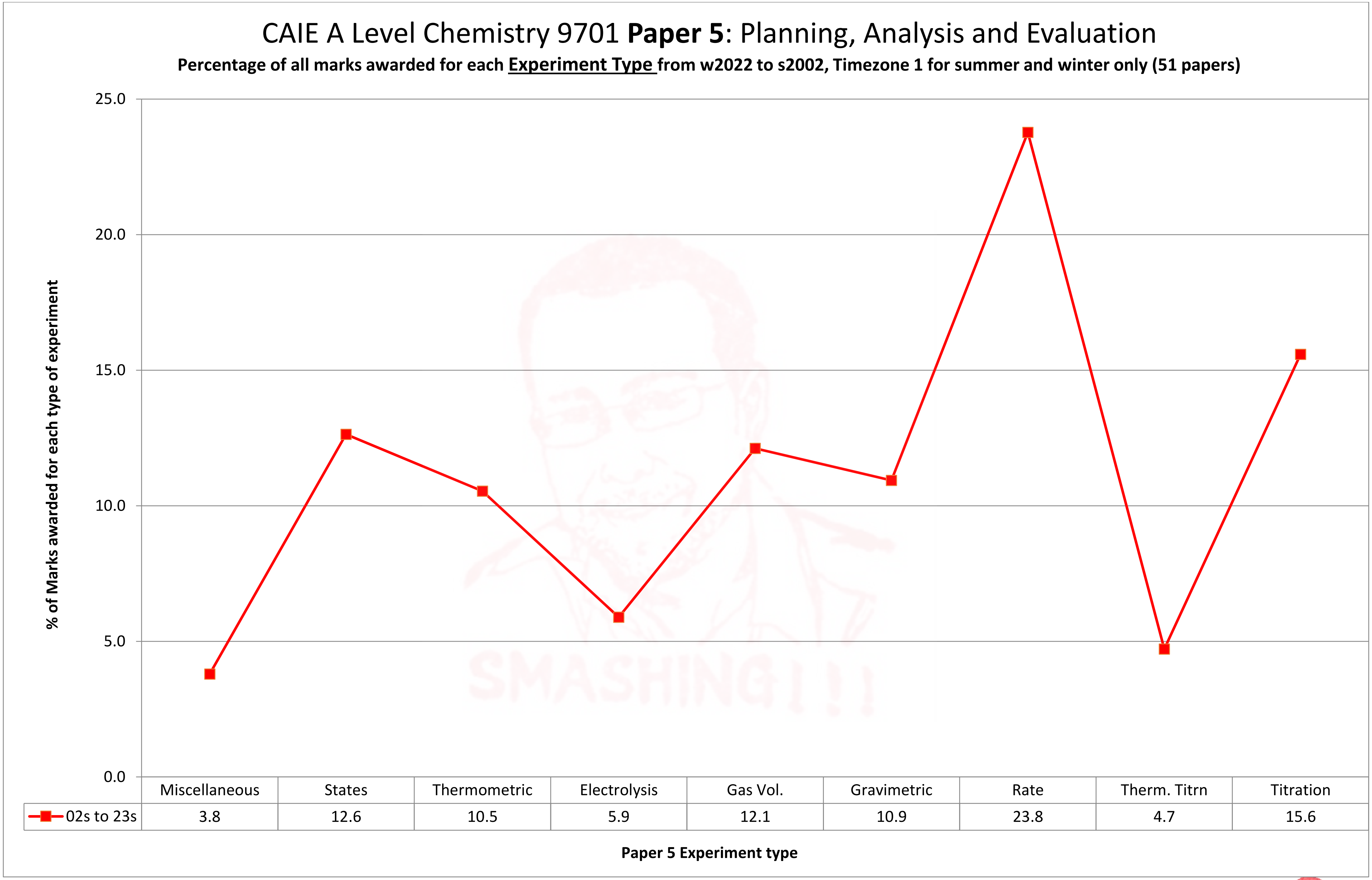
9701 **Paper 4**: Structured Questions ***SIMPLIFIED***

Freequency of marks for each Topic Number from m2022 to m2016 purple crosses, (Timezone 1 only) compared to m2022 to w2009 in the red diamonds (64 papers). ***Purple line shows most recent 7 year trend.***

	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
▲ 9w-15w	2.3	8.0	4.3	5.1	1.4	7.1	1.1	1.1	0.0	2.0	1.8	5.2	2.4	15.8	5.0	19.8
◆ 9w-22m	5.9	8.1	7.6	5.5	3.7	14.5	0.8	2.1	0.2	2.0	2.6	6.7	2.5	11.4	6.6	8.8
× 16m-22m	8.4	8.2	9.8	5.8	5.3	19.7	0.7	2.9	0.3	2.0	3.2	7.8	2.5	8.4	7.8	1.1



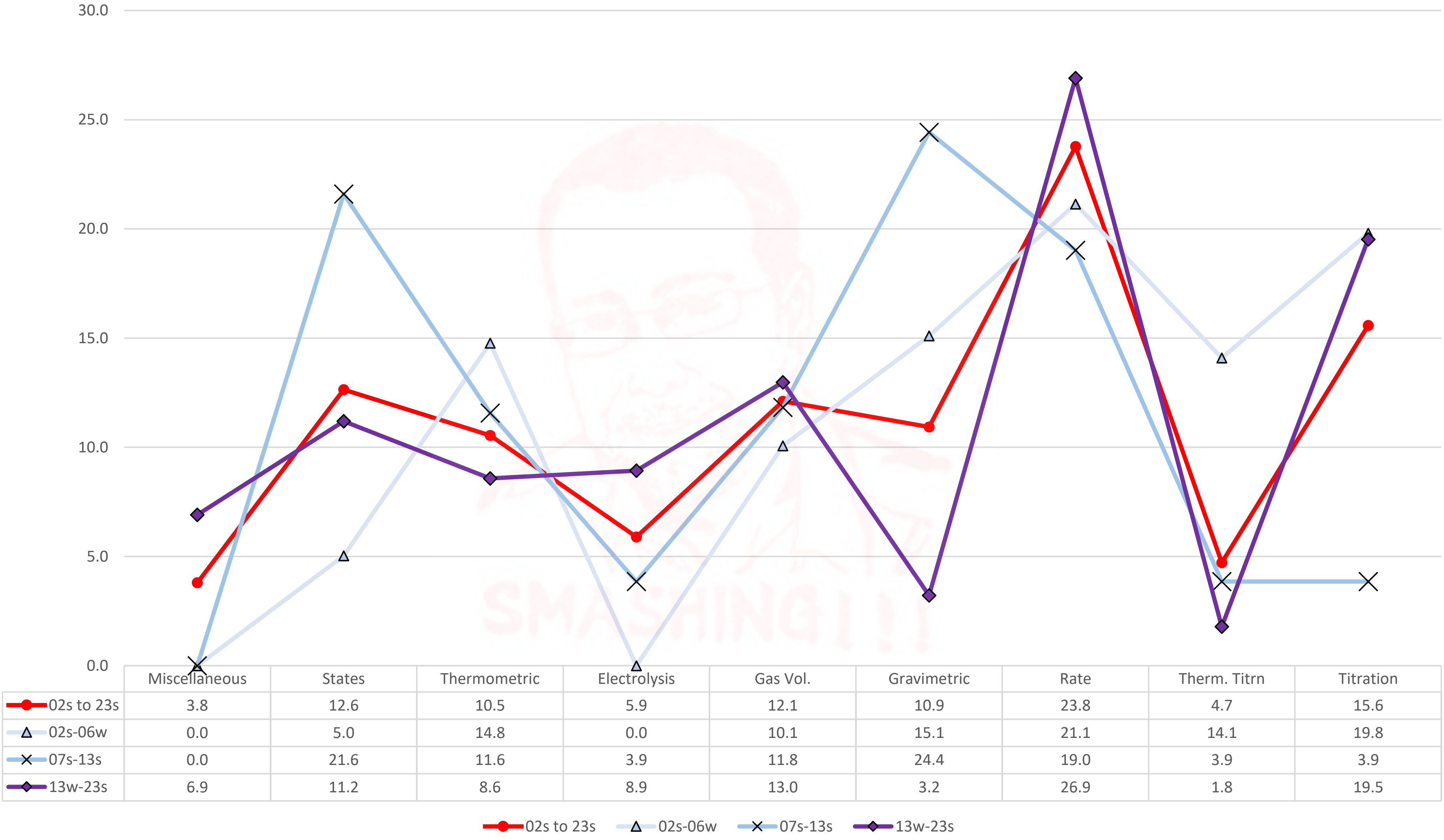
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	Chem X
▲ P4 16m-22w	0.0	0.4	1.2	0.0	0.0	0.4	0.1	0.0	0.1	0.7	0.1	0.0	1.0	0.4	0.2	0.3	0.2	0.0	0.0	0.1	0.0	1.0	8.4	8.2	9.8	5.8	5.3	19.	0.7	2.9	0.3	2.0	3.2	7.8	2.5	8.4	7.8	1.1
◆ P4&5 09s-22w	0.0	2.6	0.8	2.9	3.1	3.7	4.2	1.8	1.8	1.2	1.4	0.4	0.7	1.2	0.4	0.1	0.4	0.0	0.0	0.1	0.6	0.7	4.9	8.6	6.0	10.	4.7	9.9	0.5	1.3	0.1	1.3	1.7	4.3	1.6	7.2	4.5	4.6
✕ P4&5 16m-22w	0.0	1.8	0.6	3.1	3.6	5.0	3.8	2.3	1.3	1.8	1.4	0.0	0.6	1.2	0.1	0.1	0.1	0.0	0.0	0.1	0.8	0.5	5.1	9.2	7.2	13.	4.6	11.	0.4	1.6	0.2	1.1	1.8	4.3	1.4	4.6	4.7	0.6



	Miscellaneous	States	Thermometric	Electrolysis	Gas Vol.	Gravimetric	Rate	Therm. Titrn	Titration
■ 02s to 23s	3.8	12.6	10.5	5.9	12.1	10.9	23.8	4.7	15.6

CAIE A Level Chemistry 9701 **Paper 5**: Planning, Analysis and Evaluation

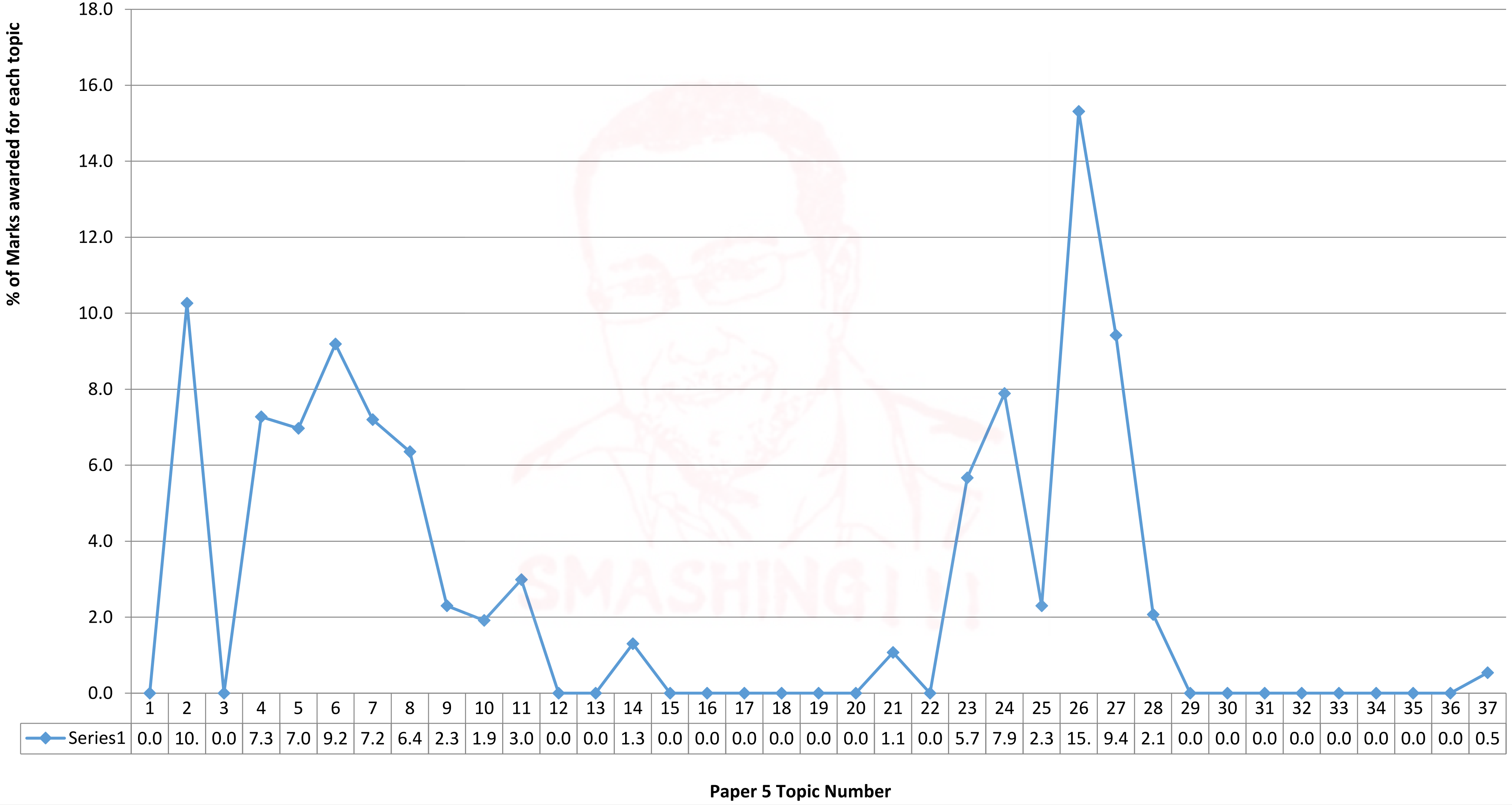
Percentage of all marks awarded for each Experiment Type from w2022 to s2002, Timezone 1 for summer and winter only (51 exam papers in total). ***Purple shows most recent 10 years trend.***



	Miscellaneous	States	Thermometric	Electrolysis	Gas Vol.	Gravimetric	Rate	Therm. Titrn	Titration
02s to 23s	3.8	12.6	10.5	5.9	12.1	10.9	23.8	4.7	15.6
02s-06w	0.0	5.0	14.8	0.0	10.1	15.1	21.1	14.1	19.8
07s-13s	0.0	21.6	11.6	3.9	11.8	24.4	19.0	3.9	3.9
13w-23s	6.9	11.2	8.6	8.9	13.0	3.2	26.9	1.8	19.5

CAIE A Level Chemistry 9701 **Paper 5**: Planning, Analysis and Evaluation

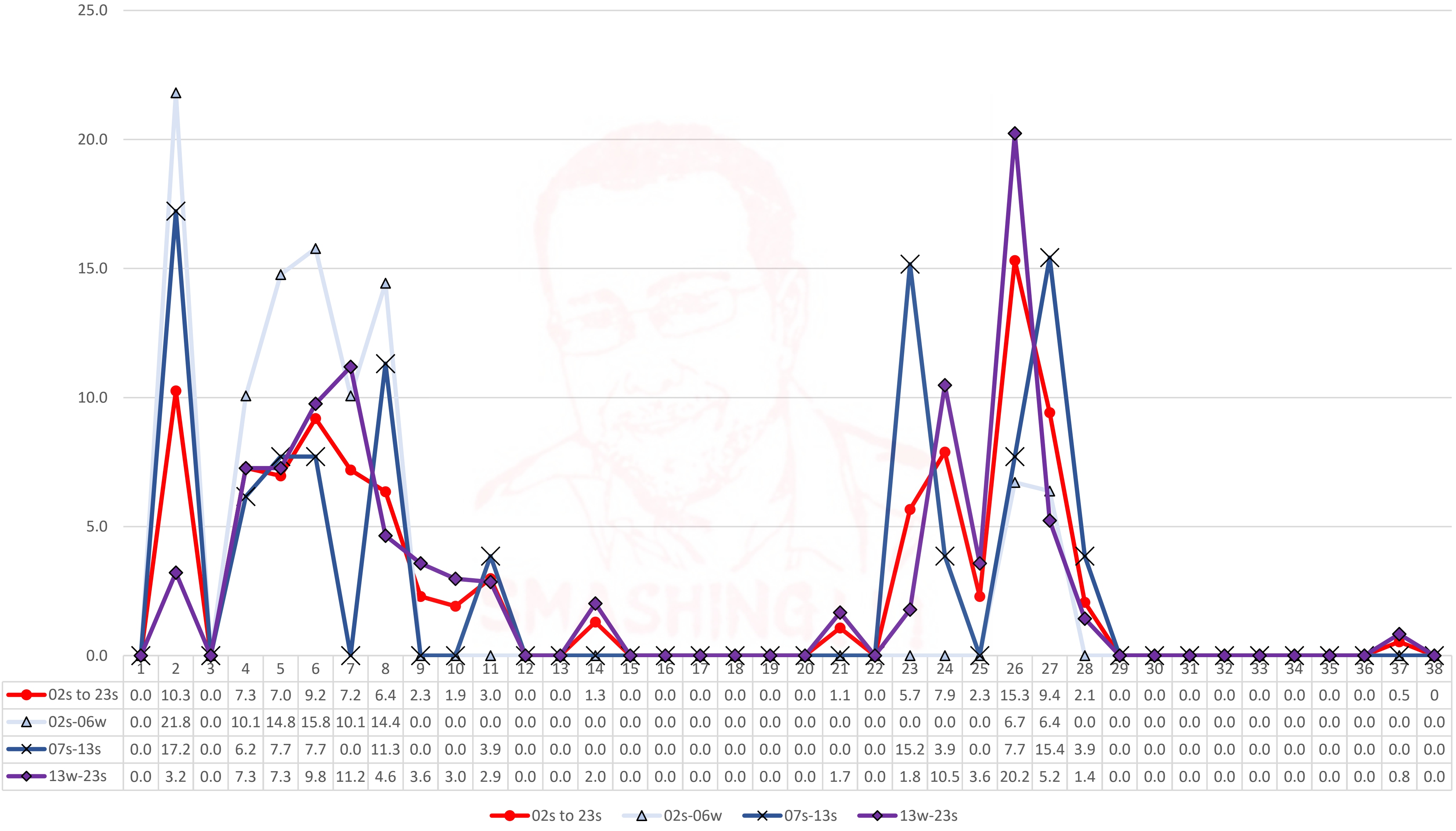
Percentage of all marks awarded for each topic from w2022 to s2002, Timezone 1 for summer and winter only (51 exam papers in total)



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
Series1	0.0	10.	0.0	7.3	7.0	9.2	7.2	6.4	2.3	1.9	3.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	5.7	7.9	2.3	15.	9.4	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5

CAIE A Level Chemistry 9701 **Paper 5**: Planning, Analysis and Evaluation

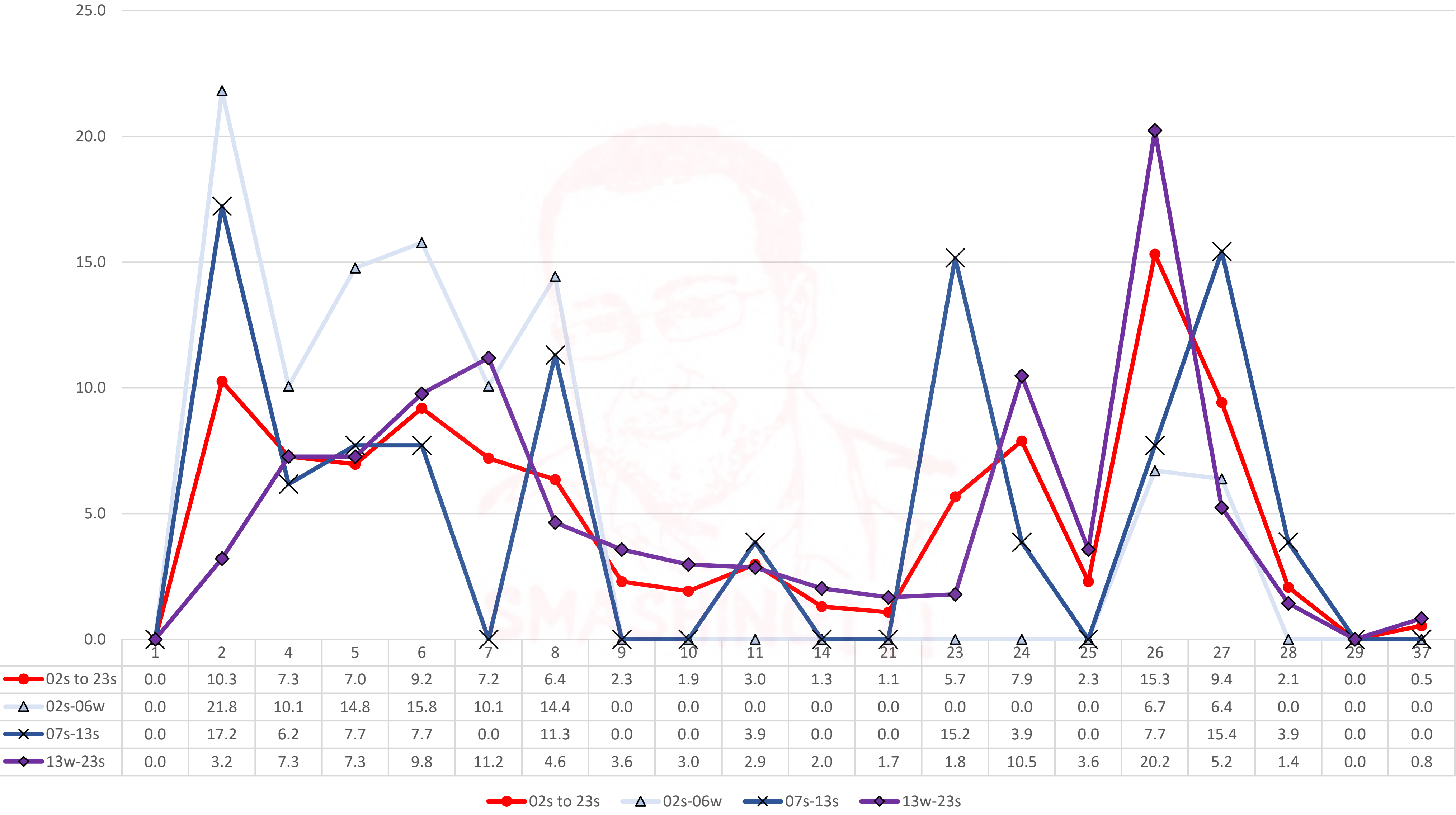
Percentage of all marks awarded for each Topic Number from w2022 to s2002, Timezone 1 for summer and winter only (51 exam papers in total). ***Purple shows most recent 10 years trend.***



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
02s to 23s	0.0	10.3	0.0	7.3	7.0	9.2	7.2	6.4	2.3	1.9	3.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.0	5.7	7.9	2.3	15.3	9.4	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0
02s-06w	0.0	21.8	0.0	10.1	14.8	15.8	10.1	14.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	6.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
07s-13s	0.0	17.2	0.0	6.2	7.7	7.7	0.0	11.3	0.0	0.0	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	15.2	3.9	0.0	7.7	15.4	3.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
13w-23s	0.0	3.2	0.0	7.3	7.3	9.8	11.2	4.6	3.6	3.0	2.9	0.0	0.0	2.0	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.0	1.8	10.5	3.6	20.2	5.2	1.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0

CAIE A Level Chemistry 9701 **Paper 5**: Planning, Analysis and Evaluation - ***SIMPLIFIED***

Percentage of all marks awarded for each Topic Number from w2022 to s2002, Timezone 1 for summer and winter only (51 exam papers in total). ***Purple shows most recent 10 years***



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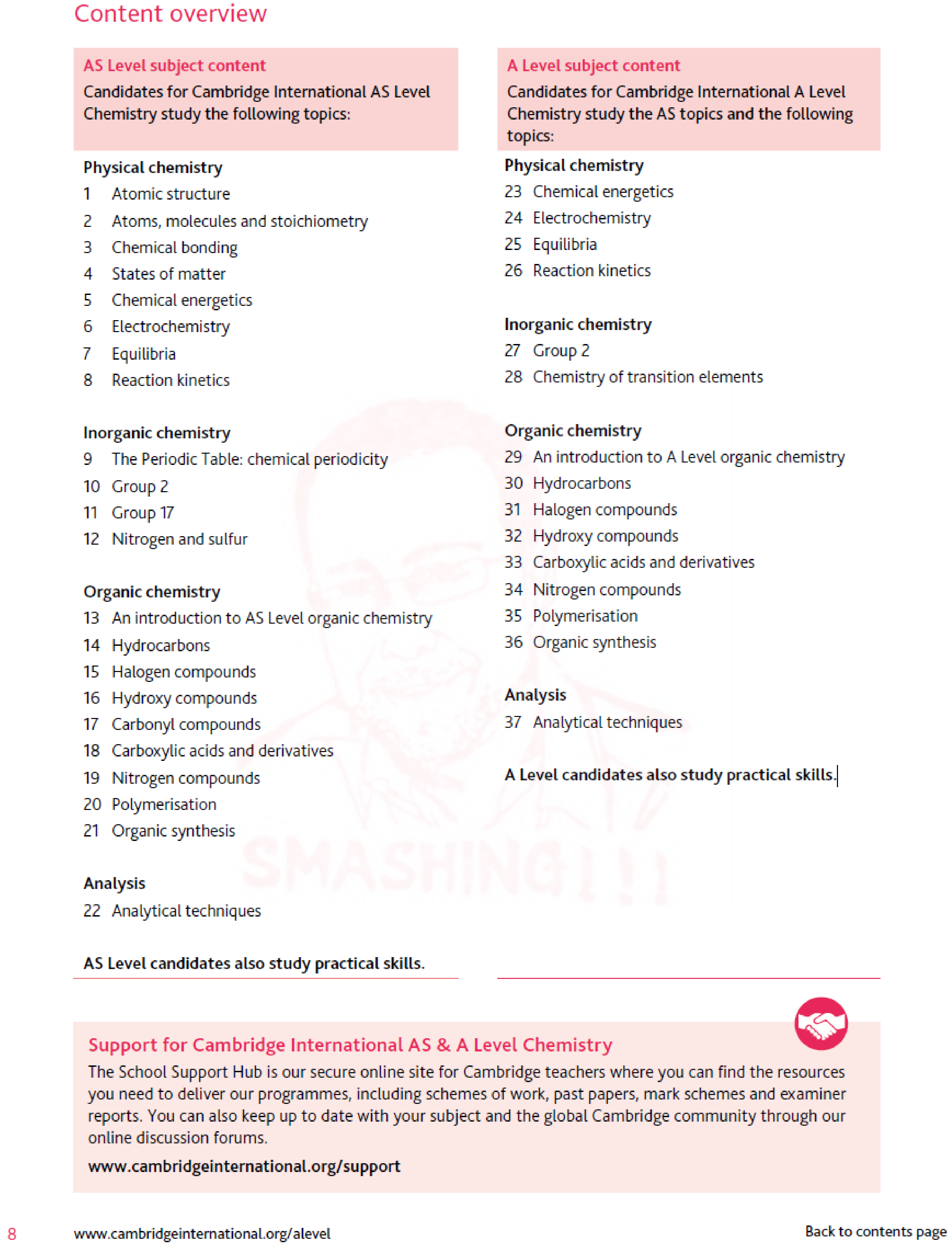
△ 02s-06w	0.0	21.8	10.1	14.8	15.8	10.1	14.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.7	6.4	0.0	0.0	0.0
× 07s-13s	0.0	17.2	6.2	7.7	7.7	0.0	11.3	0.0	0.0	3.9	0.0	0.0	15.2	3.9	0.0	7.7	15.4	3.9	0.0	0.0
◆ 13w-23s	0.0	3.2	7.3	7.3	9.8	11.2	4.6	3.6	3.0	2.9	2.0	1.7	1.8	10.5	3.6	20.2	5.2	1.4	0.0	0.8



Content overview

AS Level subject content

Candidates for Cambridge International AS Level Chemistry study the following topics:

Physical chemistry

1 Atomic structure
2 Atoms, molecules and stoichiometry
3 Chemical bonding
4 States of matter
5 Chemical energetics
6 Electrochemistry
7 Equilibria
8 Reaction kinetics

Inorganic chemistry

9 The Periodic Table: chemical periodicity
10 Group 2
11 Group 17
12 Nitrogen and sulfur

Organic chemistry

13 An introduction to AS Level organic chemistry
14 Hydrocarbons
15 Halogen compounds
16 Hydroxy compounds
17 Carbonyl compounds
18 Carboxylic acids and derivatives
19 Nitrogen compounds
20 Polymerisation
21 Organic synthesis

Analysis

22 Analytical techniques

AS Level candidates also study practical skills.

A Level subject content

Candidates for Cambridge International A Level Chemistry study the AS topics and the following topics:

Physical chemistry

23 Chemical energetics
24 Electrochemistry
25 Equilibria
26 Reaction kinetics

Inorganic chemistry

27 Group 2
28 Chemistry of transition elements

Organic chemistry

29 An introduction to A Level organic chemistry
30 Hydrocarbons
31 Halogen compounds
32 Hydroxy compounds
33 Carboxylic acids and derivatives
34 Nitrogen compounds
35 Polymerisation
36 Organic synthesis

Analysis

37 Analytical techniques

A Level candidates also study practical skills.

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8 www.cambridgeinternational.org/alevel Back to contents page

Past Exam Questions

Topic: Chem 1 Q# 1/ ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Calcium has atomic number 20.

Complete the electronic structures for a

calcium atom, $1s^22s^22p^6$.................................

calcium ion in the +2 oxidation state. $1s^22s^22p^6$.................................

[1]

Topic: **Chem 1 Q# 2/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** Complete the electronic configurations of the following atoms.

oxygen: $1s^2$...

fluorine: $1s^2$...

[1]

Topic: Chem 2 Q# 3/ ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

(ii) Most naturally occurring samples of iron(II) oxide are found as the mineral wüstite.

Wüstite has formula $Fe_{20}O_x$. It contains both Fe^{2+} and Fe^{3+} ions.

90% of the iron is present as Fe^{2+} and 10% is present as Fe^{3+}.

Deduce the value of *x*.

x = ... [1]

Topic: **Chem 2 Q# 4/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

(b) Aluminium is extracted from Al_2O_3 by electrolysis. Al_2O_3 is dissolved in cryolite in this process.

(iii) Cryolite can be made from SiF_4.

The first step in this conversion is the reaction of SiF_4 with H_2O, forming H_2SiF_6 and SiO_2.

Write an equation for this reaction.

.... [1]

[Total: 11]

Topic: **Chem 2 Q# 5/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Sodium oxide, Na_2O, is a white crystalline solid with a high melting point.

(a) Write an equation for the reaction of sodium with oxygen, forming sodium oxide.
Include state symbols.

.... [2]

Topic: **Chem 2 Q# 6/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) Explain why sodium oxide has a high melting point.

....

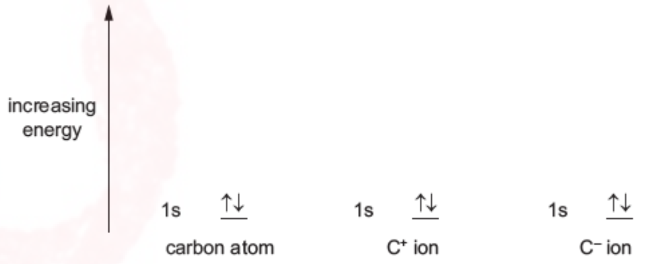
....

....

.... [2]

Topic: **Chem 2 Q# 7/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Complete the diagrams to show the energies of the electrons in a carbon atom, a C^+ ion and a C^- ion.



[2]

Topic: **Chem 2 Q# 8/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Boron forms many useful compounds.

(a) The compound diborane, B_2H_6, can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3, with sodium borohydride, $NaBH_4$.

Balance this equation.

$$\text{.......}BF_3 + \text{.......}NaBH_4 \rightarrow \text{.......}B_2H_6 + \text{.......}NaBF_4$$

[1]

Topic: **Chem 2 Q# 9/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) Alloys of aluminium, titanium and vanadium are used in aerospace and marine equipment, and in medicine.

When a powdered sample of one such alloy is heated with an excess of aqueous NaOH, only the aluminium reacts, according to the following equation.

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \rightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

Reacting 100 g of alloy in this way produced 8.0 dm³ of hydrogen, measured under room conditions.

Calculate the percentage by mass of aluminium in the alloy.

percentage = ... % [3]

[Total: 14]

Topic: **Chem 2 Q# 10/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 The most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

The following two generalisations can be made about the oxides of the elements in Group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(b) 'Red lead' is used as a pigment, and as a metal primer paint to prevent the corrosion of steel. It is an oxide of lead that contains 9.30% oxygen by mass.

Calculate to **3 significant figures** the number of moles of oxygen and lead contained in a 100.0 g sample of red lead. Hence calculate its empirical formula.

empirical formula: .... [2]

Topic: **Chem 2 Q# 11/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) **(i)** Describe what you would observe when a solid sample of anhydrous $Cu(NO_3)_2$ is strongly heated.

....

....

(ii) Write an equation for this reaction.

....

[2] actually [3]

[Total: 10]

Topic: **Chem 2 Q# 12/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) White phosphorus, P_4, is produced commercially by heating calcium phosphate(V) rock with a mixture of silica, SiO_2, and coke in an electric furnace at 1400 °C. Calcium silicate, $CaSiO_3$, and carbon monoxide are the other products.

(i) Balance the following equation which represents the overall process.

$$\_\_\_\ Ca_3(PO_4)_2 + \_\_\_\ SiO_2 + \_\_\_\ C \rightarrow \_\_\_\ P_4 + \_\_\_\ CaSiO_3 + \_\_\_\ CO$$

[2]

Topic: **Chem 2 Q# 13/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) White phosphorus, P_4, is produced commercially by heating calcium phosphate(V) rock with a mixture of silica, SiO_2, and coke in an electric furnace at 1400 °C. Calcium silicate, $CaSiO_3$, and carbon monoxide are the other products.

When heated to 400 °C in the absence of air, white phosphorus is changed into the red form of the element. The following table lists some of the properties of the two forms, which are known as allotropes.

allotrope	electrical conductivity	melting point / °C	solubility in water	solubility in benzene
white	none	44	insoluble	soluble
red	none	500	insoluble	insoluble

(ii) Suggest the type of structure and bonding in each allotrope.

allotrope	type of structure	type of bonding
white		
red		

[4]

(iii) In both allotropes, phosphorus has a valency of 3. Suggest by means of diagrams how the phosphorus atoms might be joined together in each allotrope.

white phosphorus

red phosphorus

[2]

[Total: 11]

Topic: **Chem 2 Q# 14/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(d) When a solution of $CaCl_2$ is added to a solution of the dicarboxylic acid, malonic acid, the salt calcium malonate is precipitated as a white solid. The solid has the following composition by mass: Ca, 28.2%; C, 25.2%; H, 1.4%; O, 45.2%.

(i) Calculate the empirical formula of calcium malonate from these data.

(ii) Suggest the structural formula of malonic acid.

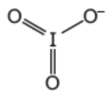
[3]

[Total: 10]

Topic: Chem 3 Q# 15/ ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



Explain, with reference to the qualitative model of electron-pair repulsion, why the IO_3^- anion has a pyramidal shape.

....

....

.... [1]

Topic: **Chem 3 Q# 16/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 When $ClNO_2$ reacts with NO an equilibrium is established.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

In each $ClNO_2$ molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

(a) Draw a 'dot-and-cross' diagram for the $ClNO_2$ molecule.

[2]

Topic: **Chem 3 Q# 17/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

(d) $Ba(NH_2)_2$ contains the NH_2^- ion.

Predict the bond angle of NH_2^-. Explain your answer using the qualitative model of electron-pair repulsion.

bond angle ....

explanation ....

....

....

[3]

[Total: 9]

Topic: **Chem 3 Q# 18/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

(ii) Draw a 'dot-and-cross' diagram to represent the bonding in the hydrogen cyanide molecule. Show the outer shell electrons only.

[1]

(iii) State the hybridisation of the carbon and nitrogen atoms in hydrogen cyanide, and give the H–C–N bond angle.

hybridisation of C ....

hybridisation of N ....

H–C–N bond angle ....
[2]

Topic: **Chem 3 Q# 19/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

(b) Nitrosyl bromide contains a trivalent nitrogen atom.

Draw the 'dot-and-cross' diagram for NOBr. Show outer electrons only.

[2]

Topic: **Chem 3 Q# 20/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(i) Draw 'dot-and-cross' diagrams of these two acids, showing outer shell electrons only.

HOCN, cyanic acid

HNCO, isocyanic acid

[3]

(ii) Suggest the values of the bond angles HNC and NCO in **isocyanic acid**.

HNC .... NCO .... [1]

(iii) Suggest which acid, cyanic or isocyanic, will have the **shorter** C–N bond length. Explain your answer.

....

.... [1]

Topic: **Chem 3 Q# 21/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1(a)/www.SmashingScience.org

(iii) Draw a three-dimensional diagram showing the shape of the chloride. Give the C*l*–Si–C*l* bond angle.

[2]

(iv) Silicon reacts with oxygen to form a high melting point oxide.

- Suggest the formula of the oxide. ....
- Suggest, in terms of structure, why the oxide has a high melting point whereas the chloride has a low boiling point.

....

....

.... [2]

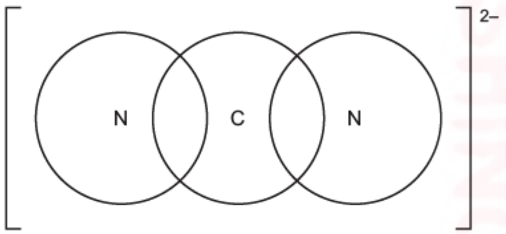
Topic: **Chem 3 Q# 22/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) Calcium cyanamide, $CaCN_2$, can be used as a fertiliser.

(i) Complete the 'dot-and-cross' diagram for the cyanamide ion, CN_2^{2-}.

Use the following key for the electrons.

● electrons from carbon
× electrons from nitrogen
□ added electron(s) responsible for the overall negative charge



[2]

Topic: **Chem 3 Q# 23/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) A compound of fluorine and oxygen contains three atoms in each molecule.

(i) Predict its formula.

.... [1]

(ii) Draw a 'dot-and-cross' diagram to show its bonding.

[1]

(iii) Suggest the shape of this molecule.

.... [1]

Topic: **Chem 3 Q# 24/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) Phosphorus reacts with chlorine to form a variety of chlorides.
PCl_5 is an example of a compound that exists as two structures depending on the conditions.

$$2PCl_5(g) \rightleftharpoons [PCl_4]^+[PCl_6]^-(s)$$

(i) Draw a 'dot-and-cross' diagram to show the bonding in PCl_5. Show the outer electrons only.

(ii) Draw diagrams to suggest the shapes of $[PCl_4]^+$ and $[PCl_6]^-$.

$[PCl_4]^+$ $[PCl_6]^-$

[3]

(c) (i) Phosphorus(III) oxide, P_4O_6, contains no P–P or O–O bonds.
In the P_4O_6 molecule, all oxygen atoms are divalent and all phosphorus atoms are trivalent.

Sketch a structure for P_4O_6.

[1]

Topic: **Chem 3 Q# 25/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** Gaseous ammonia reacts with gaseous hydrogen chloride to form solid ammonium chloride.

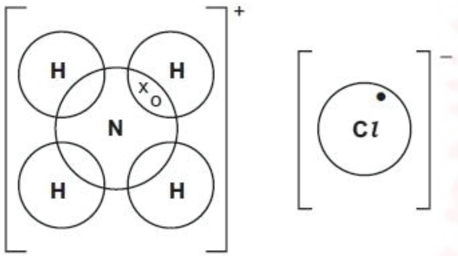
$$NH_3 + HCl \rightarrow NH_4Cl$$

The bonding in ammonium chloride includes ionic, covalent and co-ordinate (dative covalent) bonds.

Complete the following 'dot-and-cross' diagram of the bonding in ammonium chloride. For **each** of the six atoms show **all** the electrons in its outer shell. Three electrons have already been included.

Use the following code for your electrons.

- ● electrons from chlorine
- x electrons from hydrogen
- o electrons from nitrogen



[3]

Topic: **Chem 3 Q# 26/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** **(i)** Describe and explain the trend in the volatilities of the Group IV chlorides CCl_4, $GeCl_4$ and $PbCl_4$.

....

....

....

....

....

.... [3]

Topic: **Chem 3 Q# 27/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(a) **(i)** Suggest a 'dot-and-cross' electronic structure for nitrogen monoxide.

[1]

Topic: **Chem 3 Q# 28/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 Taken together, nitrogen and oxygen make up 99% of the air. Oxygen is by far the more reactive of the two gases, and most of the substances that react with air combine with the oxygen rather than with the nitrogen.

(a) State **one** reason why the molecule of nitrogen, N_2, is so unreactive.

....[1]

Topic: **Chem 3 Q# 29/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) The molecule dichlorocarbene, CCl_2, can be produced under certain conditions. It is highly unstable, reacting with water to produce carbon monoxide and a strongly acidic solution.

(i) Suggest the electron arrangement in CCl_2 and draw a dot-and-cross diagram showing this. Predict the shape of the molecule.

(ii) Construct an equation for the reaction of CCl_2 with water.

....

[3]

[Total: 8]

Topic: **Chem 3 Q# 30/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 **(a)** The Group IV oxides CO_2 and SiO_2 differ widely in their physical properties. Describe these differences and explain them in terms of their structure and bonding.

....

....

....

.... [3]

Topic: Chem 5 Q# 31/ ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Explain what is meant by the term *bond energy*.

....

.... [2]

Topic: **Chem 5 Q# 32/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(e) Ethane reacts with chlorine according to the following equation.

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

One of the steps during this reaction is the following process.

$$Cl^\bullet + CH_3CH_3 \rightarrow HCl + CH_3CH_2^\bullet$$

(iii) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of this step.

ΔH = ... kJ mol^{-1}

(iv) Use the *Data Booklet* to calculate the enthalpy change, ΔH, of the similar reaction:

$$I^\bullet + CH_3CH_3 \rightarrow HI + CH_3CH_2^\bullet$$

ΔH = ... kJ mol^{-1}

(v) Hence suggest why it is **not** possible to make iodoethane by reacting together iodine and ethane.

.... [3]

Topic: **Chem 5 Q# 33/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) When $SiCl_4$ vapour is passed over Si at red heat, Si_2Cl_6 is formed. Si_2Cl_6 contains a Si-Si bond.
The reaction of Si_2Cl_6 and Cl_2 re-forms $SiCl_4$.

$$Si_2Cl_6(g) + Cl_2(g) \rightarrow 2SiCl_4(g)$$

Use bond energy data from the *Data Booklet* to calculate ΔH° for this reaction.

ΔH° = ... kJ mol^{-1} [2]

Topic: **Chem 5 Q# 34/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(ii) The enthalpy change of formation of nitrogen monoxide is +90 kJ mol^{-1}. What is the enthalpy change for the following reaction?

$2NO(g) \rightarrow N_2(g) + O_2(g)$ ΔH_r = ... kJ mol^{-1} [1]

(iv) Using bond enthalpy values from the *Data Booklet* and your answer in **(ii)** above, calculate a value for the bond energy of nitrogen monoxide.

bond energy = ... kJ mol^{-1} [2]

Topic: **Chem 5 Q# 35/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 **(a)** The halogens chlorine and bromine react readily with hydrogen.

$$X_2(g) + H_2(g) \longrightarrow 2HX(g) \qquad [X = Cl \text{ or } Br]$$

(iii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^{\ominus}$ for this reaction when

$X = Cl$,

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

$X = Br$.

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

(iv) What is the major reason for the difference in these two $\Delta H^{\ominus}$ values?

.... [5]

(b) Some halogens also react readily with methane.

$$CH_4(g) + X_2(g) \rightarrow CH_3X(g) + HX(g)$$

(ii) Use bond energy data from the *Data Booklet* to calculate the $\Delta H^{\ominus}$ of this reaction for the situation where X is iodine, I.

$\Delta H^{\ominus}$ = ... kJ mol^{-1}

(iii) Hence suggest why it is not possible to make iodomethane, CH_3I, by this reaction.

.... [3]15

Topic: **Chem 5 Q# 36/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2 (Cl-S-Cl).

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

Use data from the *Data Booklet* to calculate the enthalpy change, ΔH, for this reaction. The eight sulfur atoms in the S_8 molecule are all joined in a single ring by single bonds.

ΔH = ...kJ mol^{-1} [2]

Topic: Chem 6 Q# 37/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions, I^-, react with acidified H_2O_2(aq) to form iodine, I_2, and water. This reaction mixture is shaken with cyclohexane, C_6H_{12}, to extract the I_2. Cyclohexane is immiscible with water.

(i) Identify the role of H_2O_2(aq) in its reaction with I^- ions in acidic conditions.

Write an ionic equation for the reaction.

role ....

ionic equation ....

.... [2]

Topic: **Chem 6 Q# 38/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions, I^-, react with acidified H_2O_2(aq) to form iodine, I_2, and water. This reaction mixture is shaken with cyclohexane, C_6H_{12}, to extract the I_2. Cyclohexane is immiscible with water.

(b) The Group 1 iodides all form stable ionic lattices and are soluble in water.

(c) The concentration of Cu^{2+}(aq) in a solution can be determined by the reaction of Cu^{2+} ions with I^- ions.

reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The I_2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}$, using a suitable indicator.

reaction 2 $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(i) A 25.0 cm³ portion of a Cu^{2+}(aq) solution reacts with an excess of I^-(aq).
The end-point of the titration occurs when 22.30 cm³ of 0.150 mol dm⁻³ $S_2O_3^{2-}$(aq) is added.

Calculate the concentration of Cu^{2+}(aq) in the original solution.

concentration of Cu^{2+}(aq) = ... mol dm⁻³ [2]

(ii) Identify a suitable indicator for the titration.

.... [1]

Topic: **Chem 6 Q# 39/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 5b/www.SmashingScience.org

A three-step mechanism for this reaction is shown.

step 1 $ClO^- + H_2O \rightarrow HClO + OH^-$

step 2 $I^- + HClO \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(iii) Identify a step that involves a redox reaction. Explain your answer.

....

.... [1]

Topic: **Chem 6 Q# 40/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

(a) Using oxidation numbers, explain why this reaction is a redox reaction.

....

....

.... [2]

Topic: Chem 7 Q# 41/ ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c) Methylamine, CH_3NH_2, is a monodentate ligand.

(e) Methylamine is a Brønsted-Lowry base.

Write an equation showing how methylamine dissolves in water to give an alkaline solution.

.... [1]

Topic: **Chem 7 Q# 42/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(b) The drug named ketamine readily reacts with protons as shown.

ketamine + $H^+ \rightarrow$ [ketamine-H]$^+$

(i) State the role of ketamine in this reaction.

.... [1]

Topic: **Chem 7 Q# 43/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) Calcium nitrate, $Ca(NO_3)_2$, is used in fertilisers and can be prepared by an acid-base reaction.

Write an equation for the preparation of calcium nitrate by an acid-base reaction.

.... [1]

Topic: **Chem 7 Q# 44/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the ΔH_f° values for some compounds.

compound	ΔH_f° / kJ mol⁻¹
$Cu_2O(s)$	–168.6
$CuO(s)$	–157.3
$Cu(NO_3)_2(s)$	–302.9
$NO_2(g)$	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable ΔH_f° values from the table to calculate the ΔH° for this reaction.

$$Cu(NO_3)_2(s) \rightarrow CuO(s) + 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

ΔH° = ... kJ mol⁻¹

(ii) Copper(I) oxide can be produced from copper(II) oxide.

- Use suitable ΔH_f° values from the table to calculate ΔH° for the reaction.

$$2CuO(s) \rightleftharpoons Cu_2O(s) + \tfrac{1}{2}O_2(g)$$

ΔH° = ... kJ mol^{-1}

- Hence suggest whether a low or a high temperature of oxidation would favour the production of copper(I) oxide. Explain your reasoning.

....

.... [4]

Topic: **Chem 7 Q# 45/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 In a world with a rapidly increasing population, access to clean drinking water is critical. For many countries, groundwater sources, rather than stored rainwater or river-water, are vital. *Groundwater* is water that exists in the pore spaces and fractures in rock and sediment beneath the Earth's surface. The World Health Organisation (WHO) provides maximum recommended concentrations for different ions present in drinking water.

(a) The geological nature of the soil determines the chemical composition of the groundwater. The table shows some ions which may contaminate groundwater.

ion present	WHO maximum permitted concentration / mg dm^{-3}
Ba^{2+}	0.30
Cl^-	250.00
NO_3^-	50.00
Pb^{2+}	0.01
Na^+	20.00
SO_4^{2-}	500.00

(i) Nitrate, NO_3^-, ions are difficult to remove from groundwater.
What is the reason for this?

....

(ii) State which ions in the table above are likely to be removed from the water by treatment with powdered limestone, $CaCO_3$, giving reasons for each of your answers.

....

....

.... [4]

(b) Nitrates and phosphates can enter water courses such as rivers or streams as a result of human activity. Both of these ions are nutrients for algae.

(i) What is the origin of these nitrates?

....

(ii) Suggest an origin for the phosphates found in water courses.

....

(iii) What effect do nitrates and phosphates have on water courses?

....

.... [3]

Topic: **Chem 7 Q# 46/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** **(i)** Using the symbol **HZ** to represent a Brønsted-Lowry acid, write equations which show the following substances acting as Brønsted-Lowry bases.

NH_3 + →

CH_3OH + →

(ii) Using the symbol **B**$^-$ to represent a Brønsted-Lowry base, write equations which show the following substances acting as Brønsted-Lowry acids.

NH_3 + →

CH_3OH + →

[4]

(b) State briefly what is meant by the following terms.

(i) reversible reaction

....

(ii) dynamic equilibrium

....

.... [2]

Topic: **Chem 7 Q# 47/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** State briefly what is meant by the following terms.

(i) reversible reaction

....

(ii) dynamic equilibrium

....

.... [2]

Topic: Chem 9 Q# 48/ ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1(a)/www.SmashingScience.org

(ii) Silicon forms a low boiling point chloride which reacts with water.

Write an equation to show the reaction of the chloride with water.

.... [1]

Topic: **Chem 9 Q# 49/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Complete the table to show the number of **unpaired** electrons in the outer shell of each of the gaseous atoms, Na to Ar.

	Na	Mg	A*l*	Si	P	S	C*l*	Ar
number of unpaired electrons								

[3]

(b) **(i)** Complete the table for the reactions of two Period 3 chlorides with water.

Period 3 chloride	observations	pH of solution formed
$SiCl_4$		
PCl_5		

[3]

(ii) Write an equation for the reaction between $SiCl_4$ and H_2O.

.... [1]

[Total: 7]

Topic: **Chem 9 Q# 50/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** Write down what you would see, and write equations for the reactions that occur, when silicon(IV) chloride and phosphorus(V) chloride are separately mixed with water.

silicon(IV) chloride

....

....

phosphorus(V) chloride

....

.... [4]

Topic: **Chem 9 Q# 51/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) Write equations, including state symbols, for the reactions, if any, of the following two oxides with water. Suggest values for the pH of the resulting solutions.

oxide	equation	pH of resulting solution
Na_2O		
MgO		

[3]

[Total: 12]

Topic: **Chem 9 Q# 52/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** State and explain the variation in the oxidation numbers of the chlorides of the elements Na, Mg, A*l* and Si.

....

....

....

....[2]

(b) Describe the reaction of phosphorus(V) chloride with water, and write an equation for the reaction.

....

....[2]

(c) When microwave radiation is passed through phosphorus(III) chloride, PCl_3, at low pressure, a new chloride of phosphorus, **B**, is formed.
B contains 69.6% by mass of chlorine and 30.4% by mass of phosphorus, and its M_r is approximately 200.

(i) Calculate the empirical and molecular formulae of **B**.

....

(ii) Assuming phosphorus and chlorine show their typical valencies, draw the displayed formula of **B**, showing all bonds and lone pairs.

....

(iii) Calculate the oxidation number of phosphorus in **B**.

....

(iv) One mole of **B** reacts with four moles of water.
Suggest the structure of the phosphorus-containing product of this reaction.

.... [6]

[Total: 10]

Topic: **Chem 9 Q# 53/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** Write a balanced equation for the reaction of each of the following chlorides with water.

phosphorus(V) chloride ....

silicon(IV)chloride .... [2]

Topic: **Chem 9 Q# 54/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 **(a)** Phosphorus and sulfur are two non-metallic elements on the right hand side of the Periodic Table.
For each of these elements describe the observations you would make when it burns in air, and write a balanced equation for the reaction.

phosphorus

observation ....

equation ....

sulfur

observation ....

equation .... [4]

Topic: **Chem 9 Q# 55/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) Lead(II) oxide reacts with both acids and bases.

(i) What is the name given to oxides that have this property?

....

(ii) Write a balanced equation for the reaction between PbO and NaOH.

.... [2]

Topic: Chem 10 Q# 56/ ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(b) **(i)** Write an equation for the reaction between BaO and H_2O.
Include state symbols.

.... [1]

Topic: **Chem 10 Q# 57/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 The elements in Group 2 include magnesium, calcium, strontium and barium.

(a) (i) Write an equation for the change representing the first ionisation energy of magnesium. Include state symbols.

.... [1]

(ii) Write an equation for the reaction of strontium with cold water. Include state symbols.

.... [1]

(iii) Describe and explain the trend in reactivity observed in the reactions of these Group 2 metals with cold water.

....

....

.... [1]

(b) The Group 2 metal nitrates decompose when heated.

(i) Describe fully what is seen when anhydrous calcium nitrate is heated in a test-tube and decomposition occurs.

....

.... [1]

(ii) Write an equation for the decomposition of calcium nitrate.

.... [1]

Topic: **Chem 10 Q# 58/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Describe what you would see when calcium and barium are heated separately with oxygen.

calcium ....

barium ....
[2]

(c) Magnesium carbonate was heated in an open test-tube. It was difficult to see whether a thermal decomposition reaction took place.

Explain why.

....

....

.... [2]

[Total: 7]

Topic: **Chem 10 Q# 59/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1(a)/www.SmashingScience.org

(b) Element **A** is in the same period as silicon. Element **A** reacts with dilute nitric acid to form a nitrate. This nitrate decomposes on heating to form an oxide.

(i) Write an equation for the decomposition of the nitrate.

.... [2]

(ii) The oxide of element **A** has a high melting point.

Suggest the structure and bonding present in the oxide of **A**.

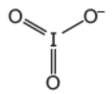
.... [1]

[Total: 9]

Topic: Chem 11 Q# 60/ ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



(b) The reaction of iodine and hot aqueous sodium hydroxide is similar to that of chlorine and hot aqueous sodium hydroxide. Sodium iodate, $NaIO_3$, is formed as one of the products.

Suggest an equation for the reaction of iodine and hot aqueous sodium hydroxide.

.... [1]

Topic: **Chem 11 Q# 61/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(d) Describe how the colours of the silver halides, and their relative solubilities in $NH_3(aq)$, can be used to distinguish between solutions of the halide ions Cl^-, Br^- and I^-.

....

....

....

....

....

....

.... [4]

Topic: **Chem 11 Q# 62/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 **(a)** The halogens chlorine and bromine react readily with hydrogen.

$$X_2(g) + H_2(g) \rightarrow 2HX(g) \qquad [X = Cl \text{ or } Br]$$

(i) Describe how you could carry out this reaction using chlorine.

....

(ii) Describe **two** observations you would make if this reaction was carried out with bromine.

....

.... [3]

Topic: **Chem 12 Q# 63/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) Acid rain can have a major impact on natural waters, particularly lakes. In recent years there has been a worldwide effort to reduce the amount of acid rain produced.

(i) Write equations to show the production of acid rain from sulfur dioxide, SO_2.

....

....

(ii) The use of fossil fuels is one major source of sulfur dioxide. Name another major industrial source.

....

[2]

[Total: 9]

Topic: **Chem 12 Q# 64/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Because of the lack of reactivity of the nitrogen molecule, extreme conditions need to be used to synthesise ammonia from nitrogen in the Haber process.

(a) Suggest an explanation for the lack of reactivity of the nitrogen molecule, N_2.

....

....

[1]

(b) Under conditions of high temperature, nitrogen and oxygen react together to give oxides of nitrogen.

(i) Write an equation for a possible reaction between nitrogen and oxygen.

....

(ii) State **two** situations, one natural and one as a result of human activities, in which nitrogen and oxygen react together.

....

....

(iii) What is the main environmental effect of the presence of nitrogen oxides in the atmosphere?

....

[4]

Topic: **Chem 12 Q# 65/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(iii) Explain why nitrogen monoxide is formed in the car engine.

.... [1]

Topic: **Chem 12 Q# 66/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 The combustion of fuels in motor vehicles, trains, aeroplanes and power stations produces the pollutant gas NO_2.

(a) Write an equation to show how NO_2 is formed in these situations.

....[1]

(b) **(i)** How is the NO_2 removed from the exhaust gases of motor vehicles?

....

(ii) Write an equation for this process.

....

[2]

Topic: **Chem 12 Q# 67/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 Taken together, nitrogen and oxygen make up 99% of the air. Oxygen is by far the more reactive of the two gases, and most of the substances that react with air combine with the oxygen rather than with the nitrogen.

(a) State **one** reason why the molecule of nitrogen, N_2, is so unreactive.

....[1]

Despite the apparent lack of reactivity of N_2, nitrogen atoms have been found to form bonds with almost all of the elements in the Periodic Table. Lithium metal reacts with nitrogen gas at room temperature to give lithium nitride, Li_3N. Magnesium produces magnesium nitride, Mg_3N_2, as well as magnesium oxide, when heated in air.

(c) Lithium reacts readily with nitrogen, and because of this Li_3N has been considered as a possible intermediate in the 'fixing' of nitrogen to make ammonia-based fertilisers.

$$N_2(g) \xrightarrow{+\,Li} Li_3N \xrightarrow{+\,H_2O} NH_3 + \mathbf{A}$$

(i) Construct an equation for the reaction between Li_3N and H_2O, and hence identify compound **A**.

....

(ii) Using your knowledge of the Haber process, consider **one** advantage and **one** disadvantage of using lithium as a means of fixing nitrogen, rather than the Haber process.

advantage of the lithium method

....

disadvantage of the lithium method

....[3]

(d) Another possible advantage of Li_3N is that it contains a large percentage by mass of nitrogen. Another fertiliser that contains a large percentage by mass of nitrogen is urea, NH_2CONH_2.

(i) Calculate and compare the percentages by mass of nitrogen in Li_3N and NH_2CONH_2.

....

....

....

(ii) What *class* of organic compound is urea?

....

(iii) Write an equation for the production of ammonia by the reaction between urea and water.

....

(iv) Urea can be applied directly to the soil either before or during the growing of crops.
What would be a major **disadvantage** of using lithium nitride in this way?

....

....[5]

[Total: 12]

Topic: Chem 13 Q# 68/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(iii) Alanine exists as a pair of optical isomers. The structure of one optical isomer is shown in Fig. 5.2.

Draw the three-dimensional structure of the other optical isomer of alanine.

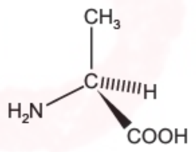
optical isomer 1	optical isomer 2
	

Fig. 5.2

[1]

Topic: **Chem 13 Q# 69/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Compounds **F** and **J** are shown in Fig. 4.1.

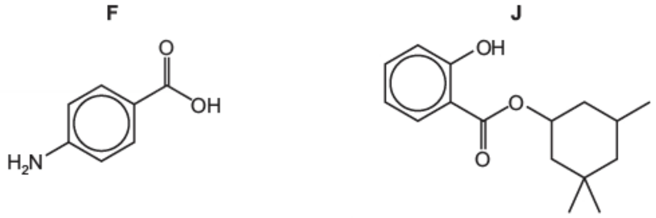


Fig. 4.1

(ii) State the number of chiral centres in a molecule of **F** and in a molecule of **J**.

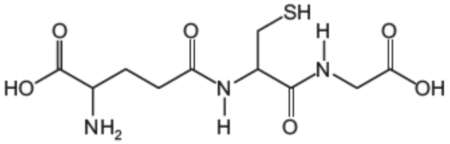
number of chiral centres in: **F** = ... **J** = ...

[1]

Topic: **Chem 13 Q# 70/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) Glutathione is a naturally occurring compound found in plants.

glutathione

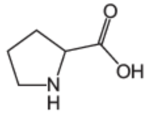


(i) On the diagram of glutathione, label each chiral centre with an asterisk (*). [1]

Topic: **Chem 13 Q# 71/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

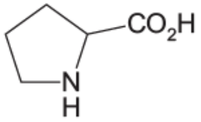
7 Proline (Pro) is a naturally occurring amino acid.

proline



(a) Proline is often found bonded to glycine (Gly) in a protein.

(vii) Identify with an asterisk (*) the chiral centre in proline.

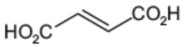


[1]

Topic: **Chem 13 Q# 72/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

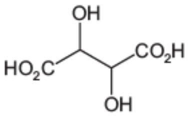
6 Fumaric acid is a naturally occurring dicarboxylic acid.

fumaric acid

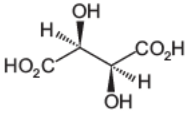


(c) Fumaric acid reacts with cold, dilute, acidified manganate(VII) to form compound **P**.

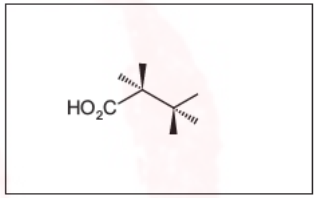
P

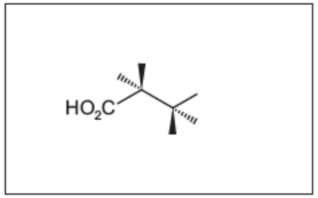


Only three stereoisomers of **P** exist. One of the stereoisomers is shown.



Complete the three-dimensional diagrams in the boxes to show the **other** two stereoisomers of **P**.





[2]

Topic: **Chem 13 Q# 73/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

(b) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

(ii) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of 2-aminopropanoic acid. State the type of stereoisomerism shown.

type of stereoisomerism ....

[2]

Topic: **Chem 13 Q# 74/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(e) Compound **V** is a carboxylic acid which contains a chiral centre. It also has the molecular formula $C_5H_{10}O_2$.

(i) Explain what is meant by the term *chiral centre*.

....

.... [1]

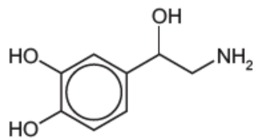
(ii) Suggest a structure for **V**.

[1]

[Total: 11]

Topic: **Chem 13 Q# 75/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 Noradrenaline is a hormone found in humans.



noradrenaline

(a) Give the molecular formula of noradrenaline.

.... [1]

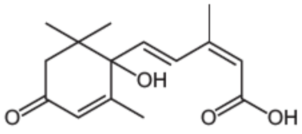
(b) State whether or not noradrenaline shows stereoisomerism. Explain your answer.

....

.... [1]

Topic: **Chem 13 Q# 76/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Abscisic acid, $C_{15}H_{20}O_4$, is a plant hormone.

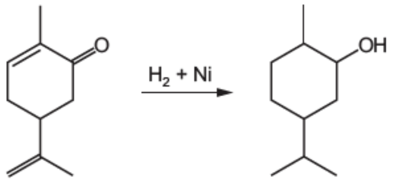


abscisic acid, $C_{15}H_{20}O_4$

(a) On the diagram of abscisic acid, use an asterisk (*) to label each chiral carbon atom. [1]

Topic: **Chem 13 Q# 77/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



carvone **X**

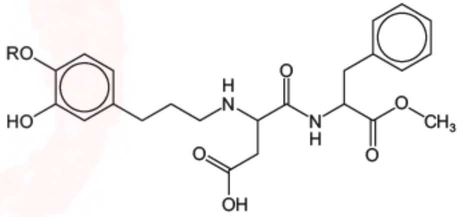
(a) **(i)** State the type of stereoisomerism carvone can show. Explain your answer.

....

.... [1]

Topic: **Chem 13 Q# 78/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 The compound *Advantame* is a sweetener that tastes approximately 25 000 times sweeter than sucrose.



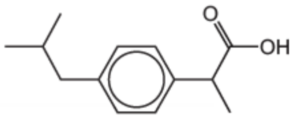
Advantame

(a) *Advantame* is optically active.

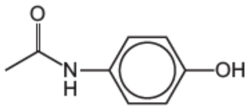
On the diagram of *Advantame*, circle all the chiral carbon atoms. [1]

Topic: **Chem 13 Q# 79/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(b) Ibuprofen contains a chiral centre and shows stereoisomerism.

(i) State what is meant by the term *chiral centre*.

....

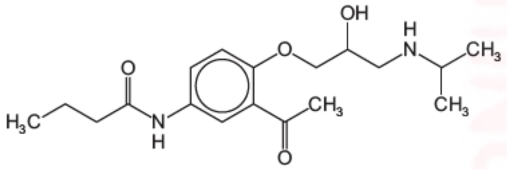
.... [1]

(ii) Draw the two stereoisomers of ibuprofen.

[2]

Topic: **Chem 13 Q# 80/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

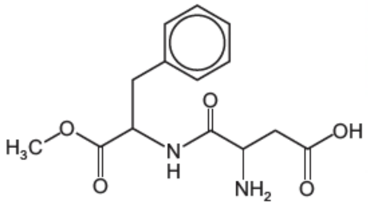
(b) On the diagram of acebutolol below, draw a **circle** around any chiral carbon atoms.



[1]

Topic: **Chem 13 Q# 81/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 (a) Aspartame is an artificial sweetener that has the structure shown below.

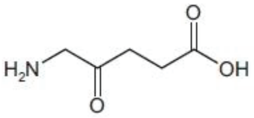


aspartame

(i) Draw a circle around each chiral centre in aspartame. [1]

Topic: **Chem 13 Q# 82/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



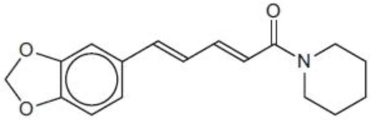
aminolaevulinic acid

Name the **three** functional groups in aminolaevulinic acid.

.... [2]

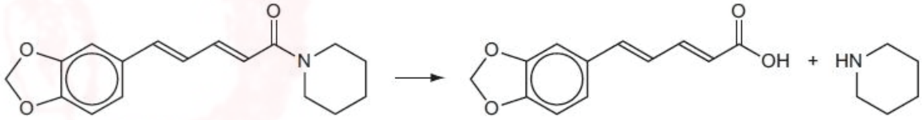
Topic: **Chem 13 Q# 83/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:



piperine piperic acid piperidine

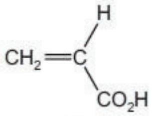
(b) **(i)** How many stereoisomers are there with the same structural formula as piperic acid (including piperic acid itself)?

....

(ii) Draw the skeletal structure of a stereoisomer of piperic acid, different to the one shown above.

[2]

Topic: **Chem 13 Q# 84/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org



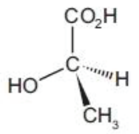
K

(b) *Acrylic acid* is the common name for compound **K**.
Suggest the systematic (chemical) name of **K**.

.... [1]

Topic: **Chem 13 Q# 85/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(ii) The structure of lactic acid is shown.



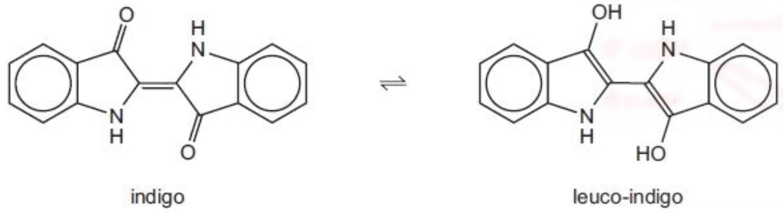
(b) Lactic acid exists in two stereoisomeric forms. Draw the other form in the box.

[1]

Topic: **Chem 13 Q# 86/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.



indigo

leuco-indigo

(a) **(i)** Give the molecular formula of indigo.

.... [1]

Topic: **Chem 13 Q# 87/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** questions in the spaces provided.

1 **(a)** The halogens chlorine and bromine react readily with hydrogen.

$$X_2(g) + H_2(g) \longrightarrow 2HX(g) \qquad [X = Cl \text{ or } Br]$$

(b) Some halogens also react readily with methane.

$$CH_4(g) + X_2(g) \longrightarrow CH_3X(g) + HX(g)$$

(i) What conditions are needed to carry out this reaction when X is bromine, Br?

.... [1]

(c) Halogenoalkanes can undergo *homolytic fission* in the upper atmosphere.

(i) Explain the term *homolytic fission*.

....

....

(ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl. Explain your answer.

....

....

....

[3]

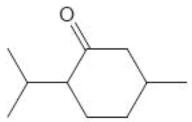
(d) The reaction between propane and chlorine produces a mixture of many compounds, four of which are structural isomers with the molecular formula $C_3H_6Cl_2$.
Draw the structural or skeletal formulae of these isomers, and indicate any chiral atoms with an asterisk (*).

[3]

[Total: 18]

Topic: **Chem 13 Q# 88/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Menthone, $C_{10}H_{18}O$, is a cyclic ketone that occurs in oil of peppermint.



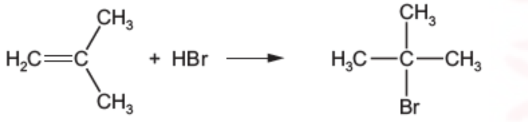
menthone

(a) Use asterisks (*) on the formula above to identify any chiral centres in the molecule of menthone. [2]

Topic: Chem 14 Q# 89/ ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) Halogenoalkanes can be formed from the reaction of an alkene with a hydrogen halide.

Methylpropene reacts with hydrogen bromide to form 2-bromo-2-methylpropane.



$$H_2C{=}C(CH_3)_2 + HBr \longrightarrow H_3C{-}C(CH_3)(Br){-}CH_3$$

methylpropene 2-bromo-2-methylpropane

(i) Draw the mechanism of this reaction. Include all relevant curly arrows, dipoles and charges.

[3]

(ii) 1-bromo-2-methylpropane is also formed in this reaction.

Explain why 2-bromo-2-methylpropane will be the **major** product in this reaction.

....

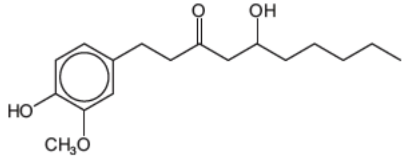
....

.... [1]

Topic: **Chem 14 Q# 90/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

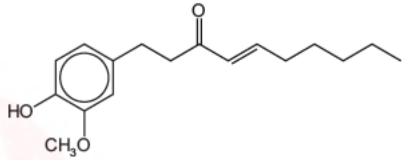
8 The root of the ginger plant contains compounds with medicinal and flavouring properties. Three of the more important compounds are gingerol, shogaol and zingerone.

(a) The structure of gingerol is shown. The CH_3O– group in gingerol is unreactive.



gingerol

(b) The structure of shogaol is shown.



shogaol

(i) State the *type of reaction* needed to convert gingerol into shogaol.

.... [1]

(ii) State the reagents and conditions needed to convert gingerol into shogaol.

reagents ....

conditions ....

[1]

(iii) Shogaol reacts with hot, concentrated acidified manganate(VII) ions to form two organic products, **Q** and **R**.

Draw the structures of **Q** and **R**.

Q **R**

[2]

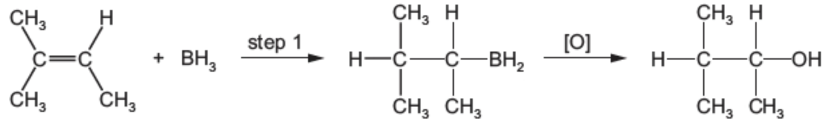
Topic: **Chem 14 Q# 91/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Boron forms many useful compounds.

(a) The compound diborane, B_2H_6, can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3, with sodium borohydride, $NaBH_4$.

(c) Borane, BH_3, is used to synthesise alcohols from alkenes.
The reaction occurs in two steps.

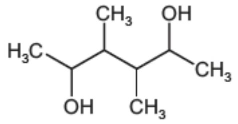
The BH_2 group from BH_3 bonds to the **least** substituted carbon atom of the double bond, and the remaining H from BH_3 bonds to the other carbon.



(i) Suggest the *type of reaction* in step 1.

.... [1]

(ii) The diol **Y** can be prepared by the same method.



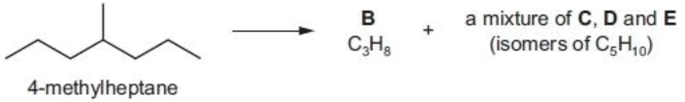
Y

Draw the structure of the **diene** which could be used to prepare diol **Y**.

[1]

Topic: **Chem 14 Q# 92/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Long chain alkanes such as 4-methylheptane can be 'cracked' to produce shorter chain hydrocarbons.



(i) State the conditions necessary for this reaction to take place.

.... [1]

(ii) Suggest the structure of **B**.

B

[1]

Topic: **Chem 14 Q# 93/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) Propene, $CH_3CH{=}CH_2$, reacts with bromine to give 1,2-dibromopropane.

(i) How is this reaction usually carried out?

.... [1]

(ii) State the *type of reaction* that is occurring here.

.... [1]

(iii) Draw the mechanism of this reaction, including the structures of any intermediates, and any dipoles, lone pairs and curly arrows to show the movements of electrons.

[2]

[Total: 10]

Topic: **Chem 14 Q# 94/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 In recent years there has been worldwide interest in the possible extraction of 'shale gas' (a form of natural gas) as an important energy source.

(a) One of the problems associated with using shale gas is its variable composition.
Table 1 shows the percentage composition of shale gas from four different sources **J**, **K**, **L** and **M**.

source	CH_4	C_2H_x	C_3H_y	CO_2	N_2
J	80.3	8.1	2.3	1.4	7.9
K	82.1	14.0	3.5	0.1	0.3
L	88.0	0.8	0.7	10.4	0.1
M	77.5	4.0	0.9	3.3	14.3

In the formulae above, ***x*** and ***y*** are variables.

Table 1

(i) Draw the structures of **three** possible compounds with the formula C_3H_y.

[2]

(ii) Which source of shale gas, **J**, **K**, **L** or **M**, will provide the most energy when burned? Explain your answer.

....

.... [1]

(iii) Suggest **two** methods by which carbon dioxide can be removed from shale gas.

1 ....

....

2 ....

....

[2]

(b) **Table 2** shows a comparison of the relative amounts of pollutants produced when shale gas, fuel oil and coal are burned to produce **the same amount of energy**.

air pollutant	shale gas	fuel oil	coal
CO_2	117	164	208
CO	0.040	0.033	0.208
NO_2	0.092	0.548	0.457
SO_2	0.001	1.12	2.59
particulates	0.007	0.84	2.74

Table 2

(i) Suggest why shale gas produces the smallest amount of CO_2.

....

.... [1]

(ii) Explain which of the three fuels, shale gas, fuel oil or coal, is the **largest** contributor to 'acid rain'.

fuel ....

....

.... [1]

(iii) Suggest a reason why fuel oil and coal produce more NO_2 than shale gas.

....

.... [1]

(iv) State **one** environmental consequence of raised levels of

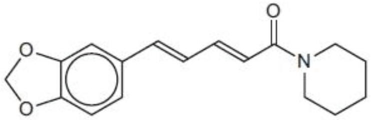
- CO, ...
- CO_2. ....

[2]

[Total: 10]

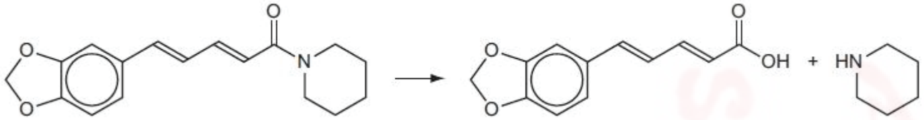
Topic: **Chem 14 Q# 95/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:



piperine piperic acid piperidine

(iii) Suggest structures for the compounds that would be formed when piperic acid is treated with an **excess** of hot concentrated acidified $KMnO_4$.

[2]

Topic: **Chem 14 Q# 96/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 The combustion of fuels in motor vehicles, trains, aeroplanes and power stations produces the pollutant gas NO_2.

(c) Suggest whether the production of the pollutant NO_2 would be reduced if fossil fuels were replaced by hydrogen as a fuel for combustion. Explain your answer.

....

....[1]

Topic: Chem 15 Q# 97**/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org
NOT WITH Q# 6 part b

6 The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

The answer mentioned below from (b)(i) “The reaction mechanism is an Sn1”

(c) **(i)** Use your answers in **(b)(i)** to help you to draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions, including the following.

- all relevant lone pairs and dipoles
- curly arrows to show the movement of electron pairs
- the structures of any transition state or intermediate

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane.

Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

....

.... [1]

Topic: **Chem 15 Q# 98/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 In aqueous solution, 2-chloro-2-methylpropane, $(CH_3)_3CCl$, reacts with sodium hydroxide, NaOH. This is a nucleophilic substitution reaction.

$$(CH_3)_3CCl(aq) + NaOH(aq) \rightarrow (CH_3)_3COH(aq) + NaCl(aq)$$

(a) Show the mechanism for this reaction. Include all necessary curly arrows, lone pairs and relevant dipoles.

[3]

Topic: **Chem 15 Q# 99/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) **(i)** Describe and explain the trend in bond energies of the C–X bond in halogenoalkanes, where X = F, C*l*, Br or I.

....

....

(ii) Describe the relationship between the reactivity of halogenoalkanes, RX, and the bond energies of the C–X bond.

....

.... [3]

(e) Ethane reacts with chlorine according to the following equation.

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

(i) State the conditions needed for this reaction.

....

(ii) State the *type of reaction* occurring here.

....

One of the steps during this reaction is the following process.

$$Cl^\bullet + CH_3CH_3 \rightarrow HCl + CH_3CH_2^\bullet$$

(vi) Complete the following equations of some possible steps in the formation of chloroethane.

$Cl_2 \rightarrow$ ....

$Cl^\bullet + CH_3CH_3 \rightarrow HCl + CH_3CH_2^\bullet$

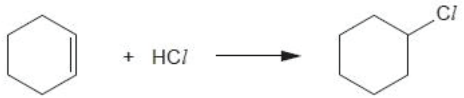
$CH_3CH_2^\bullet +$ .... $\rightarrow$ .... + ...

.... + ... $\rightarrow CH_3CH_2Cl$ [5]

[Total: 19]

Topic: **Chem 15 Q# 100/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d) Chlorocyclohexane can be prepared by bubbling HC*l*(g) through a solution of cyclohexene.



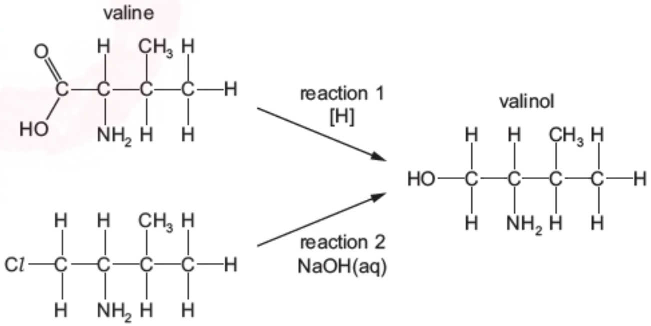
Suggest the mechanism of this 2-stage reaction by means of a diagram. Include all whole or partial charges, and represent the movements of electron pairs by curly arrows.

[3]

[Total: 12]

Topic: Chem 16 Q# 101/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(a) **(i)** Write an equation for reaction 1, using [H] to represent the reducing agent.

.... [1]

(ii) Suggest a suitable reagent for reaction 1.

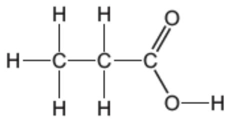
.... [1]

(iii) Name the mechanism for reaction 2.

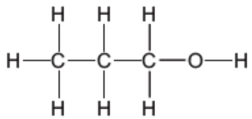
.... [1]

Topic: **Chem 16 Q# 102/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

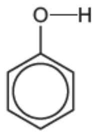
7 The three substances shown all have some acidic properties.



propanoic acid



propan-1-ol



phenol

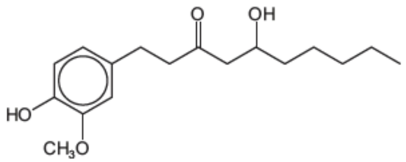
(a) Write an equation for the reaction between propan-1-ol and sodium metal.

.... [1]

Topic: **Chem 16 Q# 103/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 The root of the ginger plant contains compounds with medicinal and flavouring properties. Three of the more important compounds are gingerol, shogaol and zingerone.

(a) The structure of gingerol is shown. The $CH_3O–$ group in gingerol is unreactive.



gingerol

Gingerol reacts with acidified potassium dichromate(VI).

State the *type of reaction* and the functional group change which occurs during this reaction.

type of reaction ....

functional group change

from .... to .... [1]

Topic: Chem 17 Q# 104/ ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(b) The drug named ketamine readily reacts with protons as shown.

ketamine + H^+ → $[\text{ketamine-H}]^+$

Ketamine gives an orange precipitate with 2,4-dinitrophenylhydrazine (2,4-DNPH).

(ii) Suggest the functional group in the ketamine molecule responsible for this observation.

.... [1]

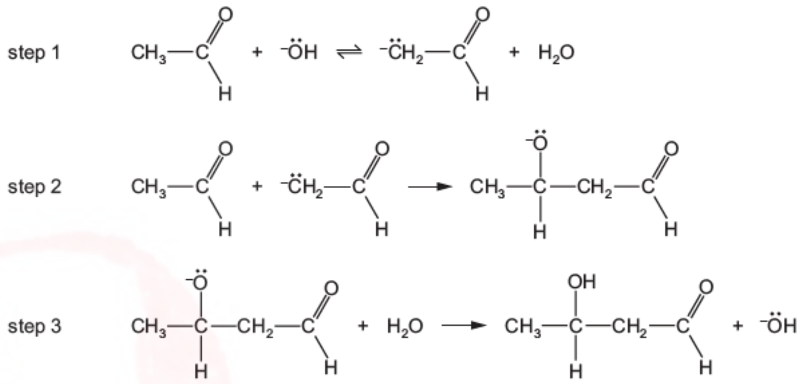
Topic: **Chem 17 Q# 105/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

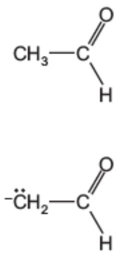
(b) **(i)** A three-step mechanism has been proposed for the reaction in **(a)**.



(c) Name the mechanism occurring in steps 2 and 3.

.... [1]

(d) Using the diagram below, show the mechanism for step 2 showing the relevant curly arrows and dipoles.



[2]

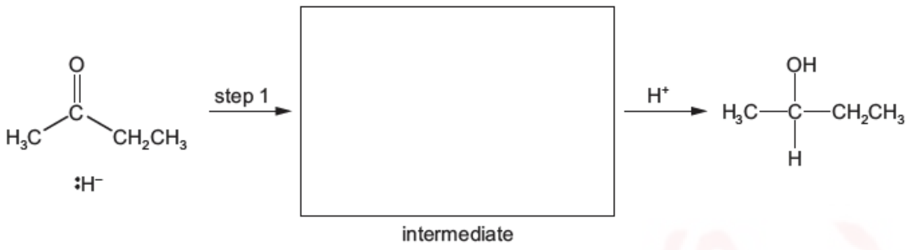
Topic: **Chem 17 Q# 106/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Boron forms many useful compounds.

(a) The compound diborane, B_2H_6, can be used as a rocket fuel.
It can be prepared by the reaction of boron trifluoride, BF_3, with sodium borohydride, $NaBH_4$.

(b) Primary and secondary alcohols can be formed by the reaction of carbonyl compounds with $NaBH_4$, which is a source of hydride ions, H^-.

Complete the mechanism for the reaction of butanone with hydride ions, H^-, and draw the intermediate in the box. Include all necessary curly arrows and relevant dipoles.

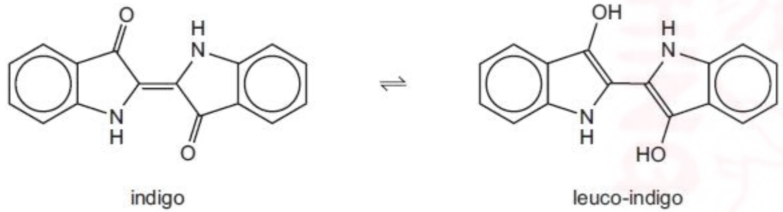


[3]

Topic: **Chem 17 Q# 107/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.



[1]

(b) **(i)** What *type of reaction* is the conversion of indigo into leuco-indigo?

....

(ii) Suggest a laboratory reagent for this reaction.

.... [2]

Topic: **Chem 17 Q# 108/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** The reaction producing tri-iodomethane (iodoform) can be used as a test for the presence of certain groups within a molecule.

(i) State the reagents and conditions used for this reaction.

....

(ii) Write the structural formula of **one** functional group that would give a positive result with this iodoform reaction.

....

(iii) What do you observe in a positive test?

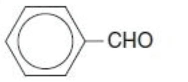
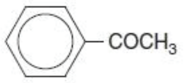
....

....

Topic: **Chem 17 Q# 109/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** The reaction producing tri-iodomethane (iodoform) can be used as a test for the presence of certain groups within a molecule.

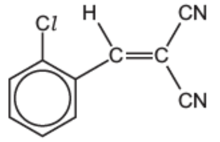
(iv) In the following table place a tick (✓) in the column against each compound that would give a positive result with this test, and a cross (✗) against each compound that would give a negative result.

compound	result
CH_3OH	
CH_3CH_2OH	
CH_3CHO	
CH_3CO_2H	
	
	

[6]

Topic: Chem 20 Q# 110/ ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **P** contains several functional groups.



P

(b) Compound **P** can be polymerised.

Draw a section of the polymer of **P** showing **two** repeat units.
Name the type of polymerisation.

type of polymerisation .... [2]

Topic: **Chem 20 Q# 111/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 In today's world we make use of a wide range of different polymers. These polymers are often substitutes for traditional materials, but may have more useful properties.

(c) One suggestion for the disposal of polymers is to use them as a fuel to provide energy for small-scale power stations or district heating schemes.
Identify one polymer which would be **unsuitable** for this use, explaining the reason behind this.

polymer ....

reason ....

....

.... [2]

Topic: **Chem 20 Q# 112/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 In today's world, many traditional materials have been replaced by different sorts of polymers. This includes rigid polymers such as those used in car bodies to replace steel and flexible polymers like those used in textiles to replace cotton or wool.

(a) **(i)** To form a polymer, what is the **minimum** number of functional groups that the monomer must possess?

....

(ii) Illustrate your answer to **(i)** with the structure of a possible monomer.

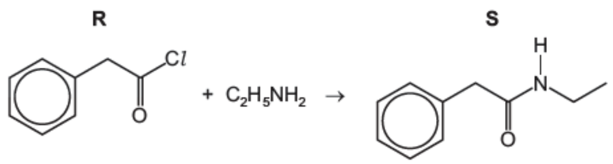
[2]

Topic: Chem 22 Q# 113/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 Compound **T** is made by a three-stage synthesis.

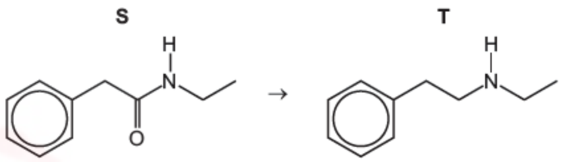
(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

stage 2



(c) In stage 3, compound **S** reacts with a suitable reagent to form compound **T**.

stage 3



(d) The relative abundance of the molecular ion peak in the mass spectrum of ethylamine is 62.

(i) Calculate the relative abundance of the M+1 peak in the mass spectrum of ethylamine.

relative abundance = ... [1]

(ii) The mass spectrum of compound **T** contains several fragments. The *m*/*e* values of two of these fragments are 29 and 91.

Draw the structures of the ions responsible for these peaks.

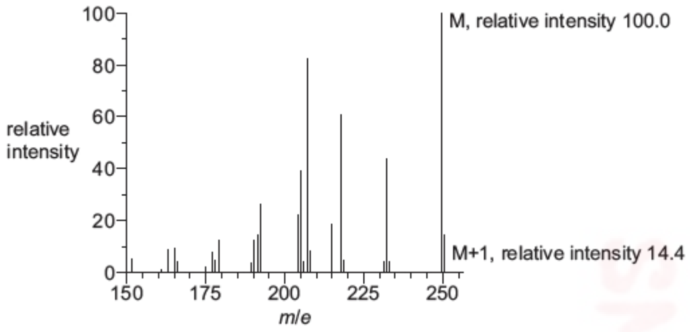
m/*e*	structure of ion
29	
91	

[2]

Topic: **Chem 22 Q# 114/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(d) Compound **J**, $C_xH_yO_z$, is also found in some cereals.

Part of the mass spectrum of **J** is shown. The M and M+1 peaks are labelled, along with their relative intensities.



(i) Calculate the number of carbon atoms, *x*, present in **J**.

x = ... [2]

(ii) The mass spectrum has a peak at *m*/*e* = 205.

Suggest the identity of the fragment lost from **J** to form this peak.

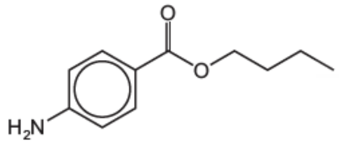
.... [1]

[Total: 12]

Topic: **Chem 22 Q# 115/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 The structure of butamben is shown.

butamben



(a) Butamben can act as a base.

(d) The mass spectrum of butamben includes peaks at *m*/*e* 92 and 57.

Identify the fragments responsible for these peaks.

m/*e* 92 = ...

m/*e* 57 = ...

[1]

[Total: 10]

Topic: **Chem 22 Q# 116/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** The mass spectrum of compound **X**, $C_5H_{10}O_2$, is recorded.

The peak heights of the M and M+1 peaks are 22.65 and 1.25 respectively.

(i) Use these data to show that there are five carbon atoms present in one molecule of **X**.

Show your working.

[1]

(ii) The mass spectrum has a peak at *m*/*e* = 57.

Complete the equation to show the fragmentation of **X** to produce this peak.

$[C_5H_{10}O_2]^+ \rightarrow$ .... + ...

[2]

Topic: **Chem 22 Q# 117/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(b) The drug named ketamine readily reacts with protons as shown.

$$\text{ketamine} + H^+ \rightarrow [\text{ketamine-H}]^+$$

Ketamine gives an orange precipitate with 2,4-dinitrophenylhydrazine (2,4-DNPH).

The mass spectrum of ketamine is determined. Two peaks close to the molecular ion peak, M, are observed with the relative abundances shown in the table.

peak	m/e	relative abundance
M	237	100.0
M+1	238	14.3
M+2	239	33.3

(iii) Use the numbers in the table to show that there are 13 carbon atoms in a ketamine molecule.

[1]

In addition to carbon and hydrogen atoms, each molecule of ketamine contains **one** atom of each of **three** different elements. These are called heteroatoms. One of these heteroatoms is a halogen.

(iv) Use the figures in the table to suggest the identity of this halogen. Explain your answer.

....

.... [1]

(v) Another peak in the mass spectrum of ketamine has an m/e value of 240.

Predict the relative abundance of this peak.

relative abundance = ... [1]

(vi) Use the information in **(b)** to complete the molecular formula of ketamine by working out the identities of the **three** different heteroatoms and the number of hydrogen atoms present.

$C_{13}H$

[1]

Topic: **Chem 22 Q# 118/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

---

(b) **(i)** The mass spectrum of a halogenoalkane containing one chlorine atom **or** bromine atom will show an additional peak at M+2.

State the isotopes of chlorine and bromine responsible for M+2 peaks.

chlorine .... bromine ....

[1]

(ii) The mass spectrum of bromochloromethane, CH_2BrCl, has a molecular ion peak, M, at an *m*/*e* value of 128. It also has M+2 and M+4 peaks.

Suggest the identity of the molecular ions that give rise to these peaks.

M peak ....

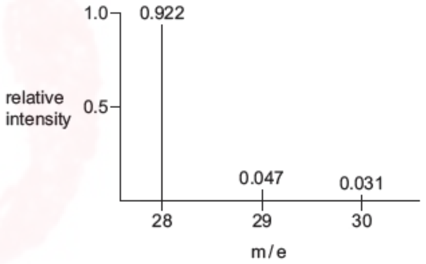
M+2 peak ....

M+4 peak ....

[2]

Topic: **Chem 22 Q# 119/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** **(i)** The mass spectrum of silicon is shown.

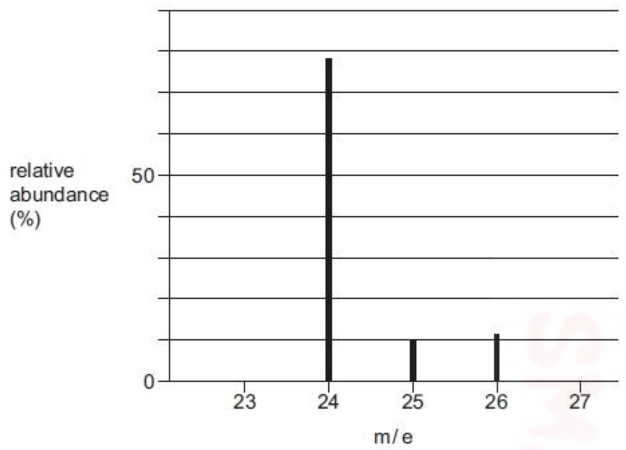


Calculate the A_r of silicon. Give your answer to **two** decimal places.

A_r = ... [1]

Topic: **Chem 22 Q# 120/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** The mass spectrum of the element magnesium is shown below.



(i) From the mass spectrum, complete the table with the relative abundances of the three isotopes.

isotope	relative abundance
^{24}Mg	
^{25}Mg	
^{26}Mg	

[1]

(ii) Use your values in **(i)** to calculate the relative atomic mass, A_r, of magnesium to **two** decimal places.

A_r (Mg) = ... [1]

Topic: **Chem 22 Q# 121/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Natural phosphorus consists of one isotope, ^{31}P. Chlorine exists naturally as two isotopes, ^{35}Cl and ^{37}Cl, in the relative abundance ratio of 3 : 1.

(i) The mass spectrum of PCl_3 contains several peaks corresponding to a number of molecular fragments.

Suggest the isotopic composition of the fragments with the following mass numbers.

mass number	isotopic composition
101	
103	
105	

(ii) Predict the relative ratios of the peak heights of the three peaks corresponding to these fragments.

....

[4]

Topic: **Chem 22 Q# 122/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) Propene was treated with bromine in the presence of chloride ions and the product analysed using mass spectrometry.

A group of peaks was found in the range *m*/*e* 156–160 with the following relative heights.

m/*e*	relative height
156	3
158	4
160	1

(i) Identify the species responsible for each of these peaks.

156 ....

158 ....

160 ....

A large peak was present in the spectrum with a *m*/*e* value of less than 20.

(ii) Suggest the *m*/*e* value for the peak and the species that produced it.

m/*e* ....

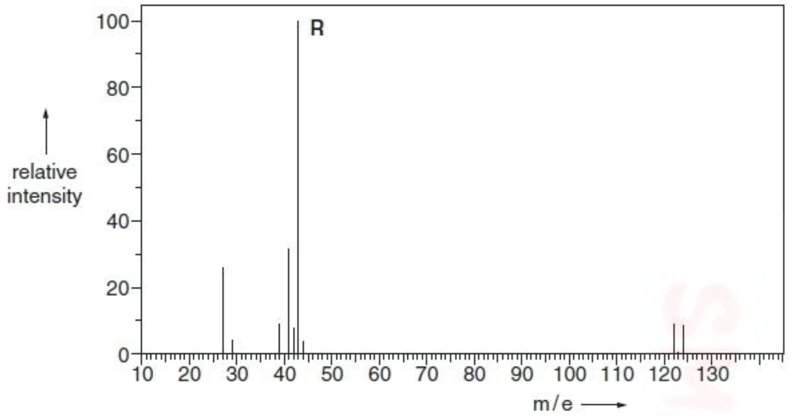
species ....

[4]

[Total: 10]

Topic: **Chem 22 Q# 123/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) The mass spectrum shown was obtained from a compound of formula C_pH_qX, where X represents a halogen atom.



(i) Deduce the identity of *X*, giving a reason.

X is ....

....

(ii) If the relative heights of the M and M+1 peaks are 9 and 0.3 respectively, calculate the value of *p*. Use this value and the m / e value of the molecular ion to calculate the value of *q*, and hence the molecular formula of the compound. Show your working.

(iii) Suggest a formula for the ion responsible for the peak labelled **R**.

.... [4]

(d) In the fragmentation of alcohols which occurs in a mass spectrometer, small stable, neutral molecules are sometimes produced. Suggest the identity of **two** such molecules, each with an M_r less than 30.

(i) .... **(ii)** .... [2]

[Total: 10]

Topic: Chem 23 Q# 124/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Silicon is the second most abundant element by mass in the Earth's crust.

(a) In industry, silicon is extracted from SiO_2 by reaction with carbon at over 2000 °C.

reaction 1 $SiO_2(s) + 2C(s) \rightarrow Si(l) + 2CO(g)$

(i) Explain why the entropy change, ΔS, of reaction 1 is positive.

....

.... [1]

(ii) Reaction 1 is highly endothermic.

Suggest the effect of an increase in temperature on the feasibility of this reaction. Explain your answer.

....

....

.... [2]

(b) Silicon is purified by first heating it in a stream of $HCl(g)$ to form $SiHCl_3$. The $SiHCl_3$ formed is then distilled to remove other impurities.

reaction 2 $Si(s) + 3HCl(g) \rightarrow SiHCl_3(g) + H_2(g)$

(i) Table 2.1 shows some standard entropy data.

Table 2.1

compound	standard entropy, S° / J K^{-1} mol^{-1}
Si(s)	19
$HCl(g)$	187
$SiHCl_3(g)$	314
$H_2(g)$	131

Use the data in Table 2.1 to calculate ΔS° for reaction 2.

ΔS° = ... J K^{-1} mol^{-1} [2]

(ii) Reaction 3 is the reverse of reaction 2 and is used to obtain pure silicon.

reaction 3 $SiHCl_3(g) + H_2(g) \rightarrow Si(s) + 3HCl(g)$ $\Delta H = +219.3\,kJ\,mol^{-1}$

Use this information and your answer to **(b)(i)** to calculate the temperature, in K, at which reaction 3 becomes feasible.
Show your working.

[If you were unable to answer **(b)(i)**, you should use $\Delta S^{\circ} = -150\,J\,K^{-1}mol^{-1}$ for reaction 2.
This is not the correct answer to **(b)(i)**.]

temperature = ... K [2]

Topic: **Chem 23 Q# 125/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) The Group 1 iodides all form stable ionic lattices and are soluble in water.

(i) Define enthalpy change of solution.

....

....

.... [1]

(ii) Use the data in Table 1.1 to calculate the enthalpy change of solution of potassium iodide, KI.

Table 1.1

process	enthalpy change, ΔH/kJ mol^{-1}
$K^+(g) + I^-(g) \rightarrow KI(s)$	–629
$K^+(g) \rightarrow K^+(aq)$	–322
$I^-(g) \rightarrow I^-(aq)$	–293

enthalpy change of solution = ... kJ mol^{-1} [1]

(iii) Suggest the trend in the magnitude of the lattice energies of the Group 1 iodides, LiI, NaI, KI.
Explain your answer.

....

....

....

.... [2]

Topic: **Chem 23 Q# 126/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Define the term *electron affinity*.

....

.... [2]

(b) Write an equation for the process corresponding to the **second** ionisation energy of calcium.
Include state symbols.

.... [1]

Some data relating to calcium and oxygen are listed. Select relevant data from this list for your answers to parts **(c)**, **(d)** and **(e)**.

process	value / kJ mol^{-1}
first ionisation energy of oxygen	+1310
second ionisation energy of oxygen	+3390
first electron affinity of oxygen	–142
second electron affinity of oxygen	+844
enthalpy change for $\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}(g)$	+951
enthalpy change for $Ca(s) \rightarrow Ca^{2+}(g) + 2e^-$	+1933
lattice energy of CaO(s)	–3517

(c) Oxygen exists as O_2 molecules.

Use the data in this question to calculate a value for the bond energy of the O=O bond.
Show all your working.

bond energy = ... kJ mol^{-1} [3]

(d) **(i)** Suggest why the first electron affinity of oxygen is negative.

....

.... [1]

(ii) Suggest why the second electron affinity of oxygen is positive.

....

.... [1]

(e) Calculate the enthalpy of formation of calcium oxide, CaO(s).

enthalpy of formation = ... kJ mol^{-1} [2]

(f) The lattice energy of lithium fluoride, LiF(s), is –1022 kJ mol^{-1}.

Identify the factor that causes the lattice energy of calcium oxide to be more exothermic than that of lithium fluoride. Explain why this factor causes the difference in lattice energies.

....

.... [2]

[Total: 12]

Topic: **Chem 23 Q# 127/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

(e) The standard entropies, S°, of three species are given in the table.

species	S°/ J K^{-1} mol^{-1}
$H_2O(l)$	+70
$H_2(g)$	+131
$O_2(g)$	+205

(i) Calculate ΔS° for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$.

ΔS° = ... J K^{-1} mol^{-1} [1]

(ii) ΔH° for the reaction $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ is +572 kJ mol^{-1}.

Calculate ΔG° for this reaction at 298 K.

ΔG° = ... kJ mol^{-1} [2]

(iii) Predict the effect of increasing temperature on the spontaneity of this reaction. Explain your answer.

....

.... [1]

Topic: **Chem 23 Q# 128/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 When dilute sulfuric acid is electrolysed, water is split into hydrogen and oxygen.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

A current of **x** A is passed through the solution for 14.0 minutes. 462 cm^3 of hydrogen are produced at the cathode, measured under room conditions.

(a) Calculate the number of hydrogen molecules produced during the electrolysis.

number of hydrogen molecules = ... [2]

(b) Calculate the total number of electrons transferred to produce this number of hydrogen molecules.

total number of electrons = ... [1]

(c) Calculate the quantity of charge, in coulombs, of the total number of electrons calculated in **(b)**.

quantity of charge = ... C [1]

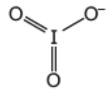
(d) Calculate the current, **x**, passed during this experiment.

x = ... A [1]

Topic: **Chem 23 Q# 129/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



(f) NH_4IO_3 is an unstable compound that readily decomposes when warmed. The decomposition reaction is shown.

$$NH_4IO_3(s) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) + \tfrac{1}{2}I_2(g) + 2H_2O(l) \qquad \Delta H = -154.6\,kJ\,mol^{-1}$$

(i) Use the data in the table to calculate the entropy change of reaction, ΔS, of the decomposition of $NH_4IO_3(s)$.

compound	S / J K^{-1} mol^{-1}
$NH_4IO_3(s)$	42
$N_2(g)$	192
$O_2(g)$	205
$I_2(g)$	261
$H_2O(l)$	70

ΔS = ... J K^{-1} mol^{-1} [2]

(ii) This reaction is feasible at all temperatures.

Explain why, using the data in **(f)** and your answer to **(f)(i)**.

....

....

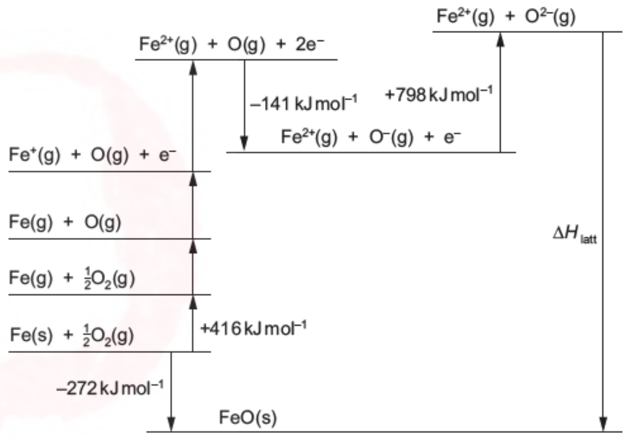
.... [1]

Topic: **Chem 23 Q# 130/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Iron(II) compounds are generally only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

(i) Use data from the *Data Booklet* and this Born–Haber cycle to calculate the lattice energy, ΔH_{latt}, of FeO(s) in kJ mol^{-1}.



ΔH_{latt}FeO(s) = ... kJ mol^{-1} [2]

(iii) State and explain how the lattice energy of FeO(s) compares to the lattice energy of CaO(s).

....

....

....

....

.... [2]

Topic: **Chem 23 Q# 131/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** The lattice energies of three ionic compounds are given.

compound	lattice energy / kJ mol^{-1}
LiF(s)	–1022
CaO(s)	–3513
SrO(s)	–3310

(i) Define the term *lattice energy*.

....

....

.... [2]

(ii) Explain why the lattice energy of CaO is more exothermic than the lattice energy of LiF.

....

....

.... [1]

(iii) Use the data in the table to estimate approximate values for the lattice energies of magnesium oxide and barium oxide.

ΔH_{latt}MgO(s) = ... kJ mol^{-1}

ΔH_{latt}BaO(s) = ... kJ mol^{-1}
[1]

(c) Use the following data and relevant data from the *Data Booklet* to calculate a value for the lattice energy of magnesium fluoride, MgF$_2$(s).

You might find it helpful to construct an energy cycle.
Show your working.

electron affinity of F(g) = –348 kJ mol^{-1}
enthalpy change of atomisation of Mg(s) = +147 kJ mol^{-1}
enthalpy change of formation of MgF$_2$(s) = –1102 kJ mol^{-1}

ΔH_{latt}MgF$_2$(s) = ... [3]

(d) **(i)** Define the term *electron affinity*.

....

.... [2]

(ii) The electron affinity of carbon, C(g), is –120 kJ mol^{-1}.

Suggest an explanation for the difference between the electron affinity of fluorine and the electron affinity of carbon.

....

....

....

.... [1]

[Total: 15]

Topic: **Chem 23 Q# 132/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) Silver chloride, AgC*l*, is sparingly soluble in water. The equation for the enthalpy change of solution is shown.

$$\text{AgC}l\text{(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{C}l^-\text{(aq)} \qquad \Delta H^\circ_{\text{sol}} = +65.5\,\text{kJ mol}^{-1}$$

Standard entropies are shown in the table.

species	AgC*l*(s)	Ag⁺(aq)	C*l*⁻(aq)
S°/J K^{-1} mol^{-1}	+96.2	+72.7	+56.5

(i) Calculate the standard entropy change of solution, ΔS°.

ΔS° = ... J K^{-1} mol^{-1} [1]

(ii) Explain, with the aid of a calculation, why AgC*l* is insoluble in water at 25 °C.

You should use data from this question and your answer to **(b)(i)**.

....

.... [3]

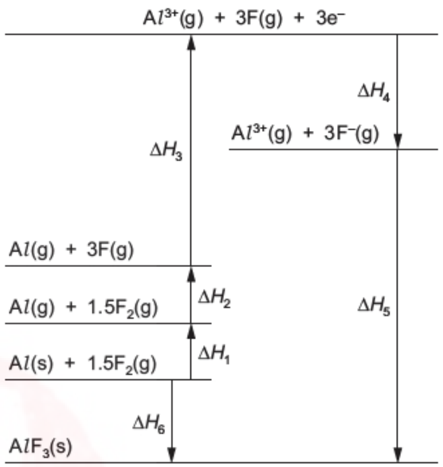
[Total: 10]

Topic: **Chem 23 Q# 133/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Gold is an unreactive metal that can only be oxidised under specific conditions.

(c) A*l*F$_3$ is an ionic compound.

The Born–Haber cycle for the formation of A*l*F$_3$ is shown.



(i) Name the enthalpy changes labelled ΔH_4 and ΔH_6.

ΔH_4 = ...

ΔH_6 = ...

[2]

(ii) Use the data in the table and data from the *Data Booklet* to calculate the lattice energy of A*l*F$_3$.

process	enthalpy change /kJ mol^{-1}
$\text{A}l\text{(s)} \rightarrow \text{A}l\text{(g)}$	+326
$\text{A}l\text{(g)} \rightarrow \text{A}l^{3+}\text{(g)}$	+5137
$\text{F(g)} \rightarrow \text{F}^-\text{(g)}$	–328
$\text{A}l\text{(s)} + 1.5\text{F}_2\text{(g)} \rightarrow \text{A}l\text{F}_3\text{(s)}$	–1504

lattice energy of A*l*F$_3$ = ... kJ mol^{-1} [2]

(iii) Scandium fluoride, ScF_3, is an ionic compound.

Use data from the *Data Booklet* to suggest how the lattice energy of AlF_3 compares with the lattice energy of ScF_3.

Explain your answer.

....

....

.... [2]

Topic: **Chem 23 Q# 134/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Explain what is meant by the term *entropy of a system*.

....

.... [1]

(b) State and explain whether the entropy change of each of the following processes is positive or negative. Do not consider the entropy change of the surroundings.

- liquid water at 80 °C is cooled to 60 °C

The entropy change is .... because ....

....

- solid calcium chloride is added to water and the mixture is stirred

The entropy change is .... because ....

....

- the change corresponding to the lattice energy of calcium chloride, ΔH_{latt} $CaCl_2(s)$, takes place

The entropy change is .... because ....

....
[3]

(c) The reaction $ZnCO_3(s) \rightarrow ZnO(s) + CO_2(g)$ is not spontaneous at room temperature.

(i) Give the full name for the term ΔG°.

.... [1]

(ii) Describe how the temperature at which the reaction becomes spontaneous can be calculated. Include an equation in your answer.

equation ....

....

....

....
[2]

Topic: **Chem 23 Q# 135/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** Complete the table by placing **one** tick (✓) in each row to indicate the sign of each type of energy change under standard conditions.

energy change	always positive	always negative	either negative or positive
bond energy			
enthalpy change of formation			

[1]

(b) Explain what is meant by the term *enthalpy change of atomisation*.

....

.... [1]

(c) The overall reaction for the atomisation of liquid bromine molecules, $Br_2(l)$, is shown.

$$Br_2(l) \rightarrow 2Br(g)$$

This happens via a two-step process.

- Construct a **labelled** energy cycle to represent this atomisation process, including state symbols.
- Use your cycle and relevant data from the *Data Booklet* to calculate the enthalpy change of vaporisation of $Br_2(l)$, ΔH°_{vap}.
  The enthalpy change of atomisation of bromine, ΔH_{at}, = +112 kJ mol^{-1}.

ΔH°_{vap} = ... kJ mol^{-1} [3]

(d) Suggest how the $\Delta H^{\ominus}_{vap}$ of iodine, $I_2(l)$, would compare to that of bromine, $Br_2(l)$. Explain your answer.

....

.... [1]

(e) **(i)** Explain what is meant by the term *enthalpy change of hydration*.

....

.... [1]

(ii) Suggest why the enthalpy change of hydration of $Br^-(g)$ is **more** exothermic than that of $I^-(g)$.

....

....

.... [2]

[Total: 9]

Topic: **Chem 23 Q# 136/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** The following table lists the solubilities of the hydroxides and carbonates of some of the Group 2 elements, **M**, at 25 °C.

element **M**	solubility / mol dm^{-3}	
	$M(OH)_2$	MCO_3
Mg	2.0×10^{-4}	1.5×10^{-3}
Ca	1.5×10^{-2}	1.3×10^{-4}
Sr	3.4×10^{-2}	7.4×10^{-5}
Ba	1.5×10^{-1}	9.1×10^{-5}

(c) The equation for the formation of the gaseous hydroxide ion is shown.

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) + e^- \rightarrow OH^-(g) \qquad \Delta H = \Delta H^{\ominus}_f(OH^-(g))$$

Use data in the table and from the *Data Booklet* to calculate $\Delta H^{\ominus}_f(OH^-(g))$. You might find it useful to construct a Born-Haber cycle.

enthalpy change	$\Delta H^{\ominus}$ / kJ mol^{-1}
atomisation of Mg(s)	+148
formation of $Mg(OH)_2(s)$	–925
lattice energy of $Mg(OH)_2(s)$	–2993

$\Delta H^{\ominus}_f(OH^-(g))$ = ... kJ mol^{-1}
[3]

Topic: **Chem 23 Q# 137/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** State **one** natural and **one** man-made occurrence of oxides of nitrogen.

....

.... [1]

(b) Under conditions of high pressure and a catalyst, nitrogen monoxide, NO, forms two other oxides of nitrogen, dinitrogen monoxide, N_2O, and dinitrogen trioxide, N_2O_3.

$$\ldots\ NO(g) \rightarrow \ldots\ N_2O(g) + \ldots\ N_2O_3(g) \qquad \Delta H^{\ominus} = -195.2\,kJ\,mol^{-1} \quad \Delta G^{\ominus} = -102.8\,kJ\,mol^{-1}$$

(i) Balance the equation above for the formation of N_2O and N_2O_3 from NO. [1]

(ii) State how the oxidation number of nitrogen changes during this reaction.

$NO \rightarrow N_2O$ from .... to ....

$NO \rightarrow N_2O_3$ from .... to ....

[1]

(iii) Calculate the entropy change for the reaction at 298 K. Include the units in your answer.

$\Delta S^{\ominus}$ = ...

units = ...
[2]

(iv) State whether the sign of $\Delta S^{\ominus}$ calculated in **(iii)** agrees with that predicted from your balanced equation in **(i)**. Explain your answer.

....

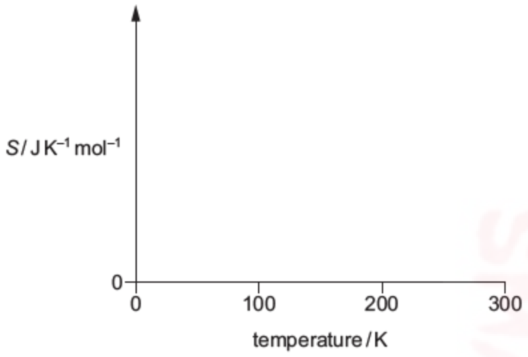
.... [1]

Topic: **Chem 23 Q# 138/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Entropy is a measure of the disorder of a system.

(a) Assume the entropy, S, for H_2O is zero at 0 K.

Sketch a graph on the axes to show how the entropy changes for H_2O between 0 K and 300 K.



[2]

(b) Place **one tick** (✓) in **each row** of the table to show the sign of the entropy changes, ΔS.

	ΔS is negative	ΔS is positive
solid dissolving in water		
water boiling to steam		

[1]

(c) The equation for a reaction that produces methanol is shown.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(g) + H_2O(g)$$

Use relevant bond energies from the *Data Booklet* to calculate the enthalpy change, ΔH, for this gas phase reaction.

ΔH = ... kJ mol⁻¹ [2]

(d) At 298 K, both products of this reaction are liquid.

$$CO_2(g) + 3H_2(g) \rightarrow CH_3OH(l) + H_2O(l) \qquad \Delta H^\circ = -131\,\text{kJ mol}^{-1}$$

Standard entropies are shown in the table.

substance	$CO_2(g)$	$H_2(g)$	$CH_3OH(l)$	$H_2O(l)$
S° / J K⁻¹ mol⁻¹	+214	+131	+127	+70

(i) Calculate the standard entropy change, ΔS°, for this reaction.

ΔS° = ... J K⁻¹ mol⁻¹ [2]

(ii) Calculate the standard Gibbs free energy change, ΔG°, for this reaction at 298 K.

ΔG° = ... kJ mol⁻¹ [2]

(iii) Predict the effect of increasing the temperature on the feasibility of this reaction.

....

.... [1]

Topic: **Chem 23 Q# 139/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Sodium oxide, Na_2O, is a white crystalline solid with a high melting point.

(d) Use the data below, and other suitable data from the *Data Booklet*, to calculate the lattice energy of sodium oxide, $\Delta H^{\ominus}_{latt}$ $Na_2O(s)$.

energy change	value / kJ mol^{-1}
standard enthalpy change of formation of sodium oxide, $\Delta H^{\ominus}_f$ $Na_2O(s)$	–416
standard enthalpy change of atomisation of sodium, $\Delta H^{\ominus}_{at}$ Na(s)	+109
electron affinity of O(g)	–142
electron affinity of $O^-(g)$	+844

$\Delta H^{\ominus}_{latt}$ $Na_2O(s)$ = ... kJ mol^{-1} [4]

(e) State how $\Delta H^{\ominus}_{latt}$ $Na_2S(s)$ differs from $\Delta H^{\ominus}_{latt}$ $Na_2O(s)$.
Indicate this by placing a tick (✓) in the appropriate box in the table.

$\Delta H^{\ominus}_{latt}$ $Na_2S(s)$ is more exothermic than $\Delta H^{\ominus}_{latt}$ $Na_2O(s)$	$\Delta H^{\ominus}_{latt}$ $Na_2S(s)$ is the same as $\Delta H^{\ominus}_{latt}$ $Na_2O(s)$	$\Delta H^{\ominus}_{latt}$ $Na_2S(s)$ is less exothermic than $\Delta H^{\ominus}_{latt}$ $Na_2O(s)$

Explain your answer.

....

....

.... [2]

[Total: 15]

Topic: **Chem 23 Q# 140/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

The table lists the standard enthalpy changes of formation, $\Delta H^{\ominus}_f$, for some compounds and aqueous ions.

species	$\Delta H^{\ominus}_f$ / kJ mol^{-1}
$Ba^{2+}(aq)$	–538
$OH^-(aq)$	–230
$CO_2(g)$	–394
$BaCO_3(s)$	–1216
$H_2O(l)$	–286

(b) **(i)** Reaction 1 occurs when $CO_2(g)$ is bubbled through an aqueous solution of $Ba(OH)_2$.

Use the data in the table to calculate the standard enthalpy change for reaction 1, $\Delta H^{\ominus}_{r1}$.

$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$ reaction 1

$\Delta H^{\ominus}_{r1}$ = ... kJ mol^{-1} [2]

If $CO_2(g)$ is bubbled through an aqueous solution of $Ba(OH)_2$ for a long time, the precipitated $BaCO_3(s)$ dissolves, as shown in reaction 2.

$BaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ba(HCO_3)_2(aq)$ reaction 2

The standard enthalpy change for reaction 2, $\Delta H^{\ominus}_{r2}$, = –26 kJ mol^{-1}.

(ii) Use this information and the data in the table to calculate the standard enthalpy change of formation of the $HCO_3^-(aq)$ ion.

$\Delta H^{\ominus}_f$ $HCO_3^-(aq)$ = ... kJ mol^{-1} [2]

(iii) The overall process is shown by reaction 3.

Use your answer to **(ii)**, and the data given in the table, to calculate the standard enthalpy change for reaction 3, ΔH°_{r3}.

$Ba(OH)_2(aq) + 2CO_2(g) \rightarrow Ba(HCO_3)_2(aq)$ reaction 3

ΔH°_{r3} = ... kJ mol^{-1} [1]

(iv) How would the value of ΔH°_{r3} compare with the value of ΔH°_{r4} for the similar reaction with $Ca(OH)_2(aq)$ as shown in reaction 4?
Explain your answer.

$Ca(OH)_2(aq) + 2CO_2(g) \rightarrow Ca(HCO_3)_2(aq)$ reaction 4

....

....

.... [2]

(c) The standard entropy change for reaction 1 is ΔS°_{r1}.

Suggest, with a reason, how the standard entropy change for reaction 3 might compare with ΔS°_{r1}.

....

....

.... [2]

[Total: 13]

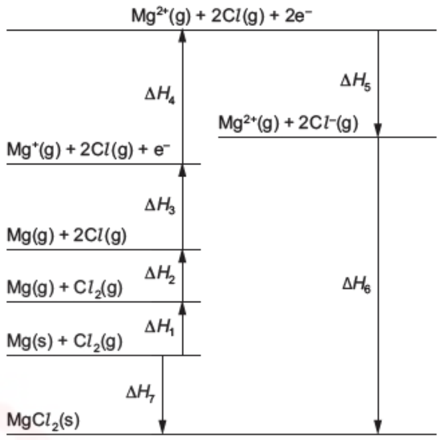
Topic: **Chem 23 Q# 141/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Complete the table using ticks (✓) to indicate whether the sign of each type of energy change, under standard conditions, is always positive, always negative or could be either positive or negative.

energy change	always positive	always negative	either positive or negative
electron affinity			
enthalpy change of atomisation			
ionisation energy			
lattice energy			

[2]

(b) The Born-Haber cycle for magnesium chloride is shown.



(i) Explain why ΔH_4 is greater than ΔH_3.

....

.... [1]

(ii) What names are given to the enthalpy changes ΔH_6 and ΔH_7?

ΔH_6 ....

ΔH_7 ....

[1]

(c) Chlorine is in Group 17.

Suggest the trend in the first electron affinity of the elements in Group 17. Explain your answer.

....

....

.... [2]

(d) The equation for the formation of magnesium oxide from its elements is shown.

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) \qquad \Delta H^{\ominus} = -602\,\text{kJ mol}^{-1}$$

substance	$S^{\ominus}$/J K^{-1} mol^{-1}
Mg(s)	32.7
O_2(g)	205
MgO(s)	26.9

Use the equation and the data given in the table to calculate $\Delta G^{\ominus}$ for the reaction at 25 °C.

$\Delta G^{\ominus}$ = ... units ....

[4]

[Total: 10]

Topic: **Chem 23 Q# 142/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, $\Delta G^{\ominus}$. This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

(d) The solubility of Group 2 sulfates decreases down the Group.

Explain this trend.

....

....

....

.... [2]

[Total: 11]

Topic: **Chem 23 Q# 143/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 The spontaneity (feasibility) of a chemical reaction depends on the standard Gibbs free energy change, $\Delta G^{\ominus}$. This is related to the standard enthalpy and entropy changes by the equation shown.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

(a) State and explain whether the following processes will lead to an increase or decrease in entropy.

(i) the reaction of magnesium with hydrochloric acid

entropy change ....

explanation ....

[1]

(ii) solid potassium chloride dissolving in water

entropy change ....

explanation ....

[1]

(iii) steam condensing to water

entropy change ....

explanation ....

[1]

(b) Magnesium carbonate can be decomposed.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +117\,\text{kJ mol}^{-1}$$

Standard entropies are shown in the table.

substance	$MgCO_3$(s)	MgO(s)	CO_2(g)
$S^{\ominus}$/J mol^{-1} K^{-1}	+65.7	+26.9	+214

(i) Calculate $\Delta G^{\ominus}$ for this reaction at 298 K.
Include a relevant sign and give your answer to **three** significant figures.

$\Delta G^{\ominus}$ = ... kJ mol^{-1} [3]

(ii) Explain, with reference to $\Delta G^{\ominus}$, why this reaction becomes more feasible at higher temperatures.

....

.... [1]

(c) On heating, sodium hydrogencarbonate decomposes into sodium carbonate as shown.

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad \Delta H^\ominus = +130\,kJ\,mol^{-1}$$
$$\Delta S^\ominus = +316\,J\,mol^{-1}\,K^{-1}$$

Calculate the **minimum** temperature at which this reaction becomes spontaneous (feasible).
Show your working.

temperature = ... K [2]

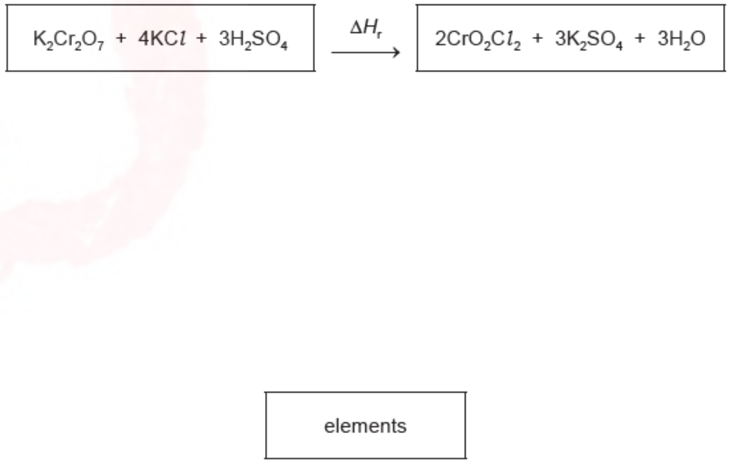
Topic: **Chem 23 Q# 144/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** Chromyl chloride, CrO_2Cl_2, can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

Use the following data to complete the Hess' Law cycle and calculate the enthalpy change of the reaction, ΔH_r.

compound	enthalpy change of formation, $\Delta H_f^\ominus$/ kJ mol^{-1}
$K_2Cr_2O_7$	–2061
KCl	–437
H_2SO_4	–814
CrO_2Cl_2	–580
K_2SO_4	–1438
H_2O	–286



ΔH_r = ... kJ mol^{-1} [2]

Topic: **Chem 23 Q# 145/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** Chromyl chloride, CrO_2Cl_2, can be prepared by heating a mixture of potassium dichromate(VI) and potassium chloride with concentrated sulfuric acid.

$$K_2Cr_2O_7 + 4KCl + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + 3K_2SO_4 + 3H_2O$$

(b) There are two isomeric complex ions with the formula $[Cr(NH_3)_4Cl_2]^+$. One is green and the other is violet.

(i) Suggest the *type of isomerism* shown by these complex ions.

.... [1]

(ii) Explain why these two complex ions

- are coloured, ...

....

....

....

- have **different** colours. ....

....

....

.... [4]

[Total: 7]

Topic: **Chem 23 Q# 146/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) **(i)** Predict the sign of $\Delta S^\ominus$ for this reaction. Explain your answer.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g) \qquad \Delta H^\ominus = +241\,kJ\,mol^{-1}$$

....

.... [1]

The free energy change, $\Delta G^\ominus$, for this reaction at 1000 K is $+51\,kJ\,mol^{-1}$.

(ii) Calculate the value of $\Delta S^\ominus$ for this reaction, stating its units.

$\Delta S^\ominus$ = ... units .... [2]

(d) How would the value of $\Delta G^\ominus$, and hence the spontaneity (feasibility) of this reaction change as the temperature increases? Explain your answer.

....

....

.... [2]

[Total: 10]

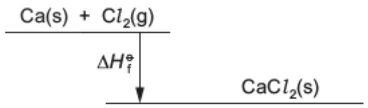
Topic: **Chem 23 Q# 147/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Calcium metal reacts with chlorine gas to form calcium chloride, $CaCl_2$.

(i) Write an equation, including state symbols, to represent the lattice energy of calcium chloride, $CaCl_2$.

.... [1]

(ii) Complete a fully labelled Born-Haber cycle that could be used to calculate the lattice energy, $\Delta H^\ominus_{latt}$, for calcium chloride.



[2]

(iii) Use your answer to **(ii)** and the following data, together with relevant data from the *Data Booklet*, to calculate a value for $\Delta H^\ominus_{latt}$ for calcium chloride.

standard enthalpy change of formation of $CaCl_2(s)$, $\Delta H^\ominus_f$	$-796\,kJ\,mol^{-1}$
standard enthalpy change of atomisation of Ca(s), $\Delta H^\ominus_{at}$	$+178\,kJ\,mol^{-1}$
electron affinity of chlorine atoms	$-349\,kJ\,mol^{-1}$

$\Delta H^\ominus_{latt}$ = ... $kJ\,mol^{-1}$ [3]

(b) Entropy is a measure of the disorder of a system.

Describe and explain what happens to the entropy of a gas when the temperature is increased.

....

....

.... [2]

(c) The table shows four reactions.

(i) For each reaction, predict the sign of the entropy change, $\Delta S^\ominus$. If you predict no entropy change, write 'no change' in the table below. The first one has been done for you.

reaction	sign of $\Delta S^\ominus$
$CO(g) + O_2(g) \rightarrow CO_2(g)$	negative
$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$	
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_5O(s)$	
$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + CO_2(g) + H_2O(l)$	

[2]

(ii) Explain why the entropy change for the first process is negative.

....

.... [1]

(d) Calculate the standard entropy change, $\Delta S^\ominus$, for this reaction.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Standard entropies, $S^\ominus$, in $JK^{-1} mol^{-1}$ are given.

$N_2(g)$	$H_2(g)$	$NH_3(g)$
+192	+131	+193

$\Delta S^\ominus$ .... $JK^{-1} mol^{-1}$ [2]

(e) Whether or not a chemical reaction is spontaneous (feasible) can be deduced by calculating the change in free energy, $\Delta G^\ominus$, at a given temperature.

$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ $\Delta H^\ominus = +117\,kJ\,mol^{-1}$
$\Delta S^\ominus = +175\,JK^{-1} mol^{-1}$

(i) Calculate the value of $\Delta G^\ominus$ at 298K for the above reaction.

[2]

(ii) Use your answer to **(i)** to explain whether or not this reaction is spontaneous at 298K.

....

.... [1]

[Total: 16]

Topic: **Chem 23 Q# 148/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) **(i)** What is meant by the term *standard enthalpy change of hydration*, $\Delta H^\ominus_{hyd}$?

....

....

.... [2]

(ii) Use the following data to calculate the lattice energy, $\Delta H^\ominus_{latt}$, of calcium nitrate, $Ca(NO_3)_2(s)$. You may find it helpful to construct an energy cycle.

enthalpy change	value
$\Delta H^\ominus_{hyd}$ $(Ca^{2+}(g))$	$-1650\,kJ\,mol^{-1}$
$\Delta H^\ominus_{hyd}$ $(NO_3^-(g))$	$-314\,kJ\,mol^{-1}$
enthalpy change of solution for $Ca(NO_3)_2(s)$	$-19\,kJ\,mol^{-1}$

$\Delta H^\ominus_{latt}$ $Ca(NO_3)_2(s)$ = ... $kJ\,mol^{-1}$ [3]

(e) The standard enthalpy change of hydration for Ba^{2+}, $\Delta H^{\circ}_{hyd}(Ba^{2+}(g))$, is –1305 kJ mol^{-1}.

Suggest an explanation for why the ΔH°_{hyd} of the Ba^{2+} ion is **less** exothermic than the ΔH°_{hyd} of the Ca^{2+} ion.

....

....

.... [2]

[Total: 12]

Topic: **Chem 23 Q# 149/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

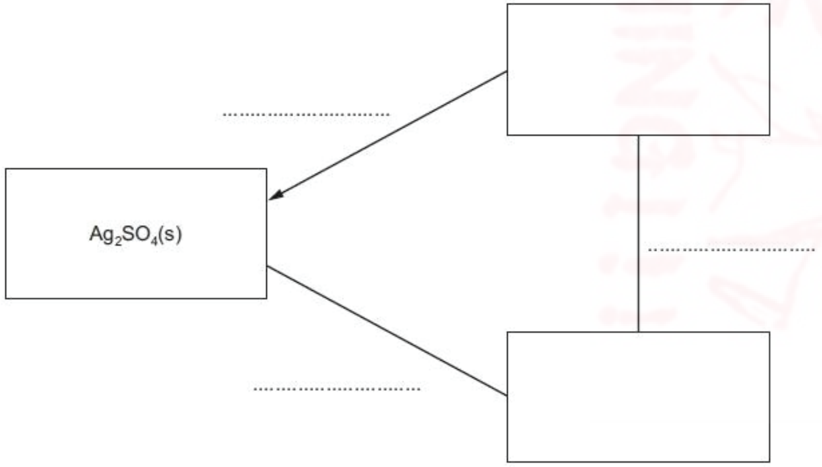
4 **(a)** Silver sulfate, Ag_2SO_4, is sparingly soluble in water. The concentration of its saturated solution is 2.5×10^{-2} mol dm^{-3} at 298 K.

(b) Using Ag_2SO_4 as an example, complete the following Hess' Law energy cycle relating the

- lattice energy, ΔH°_{latt},
- enthalpy change of solution, ΔH°_{sol}, and
- enthalpy change of hydration, ΔH°_{hyd}.

On your diagram:

- include the relevant species in the two empty boxes,
- label each enthalpy change with its appropriate symbol,
- complete the remaining two arrows showing the correct direction of enthalpy change.



[4]

Topic: **Chem 23 Q# 150/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(e) **(i)** What is meant by the term *lattice energy*?

....

....

(ii) Explain why the lattice energy of calcium phosphate is **less** exothermic than that of magnesium phosphate.

....

.... [3]

Topic: **Chem 23 Q# 151/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

Section A

Answer **all** the questions in the spaces provided.

1 **(a)** **(i)** What is meant by the term *lattice energy*?

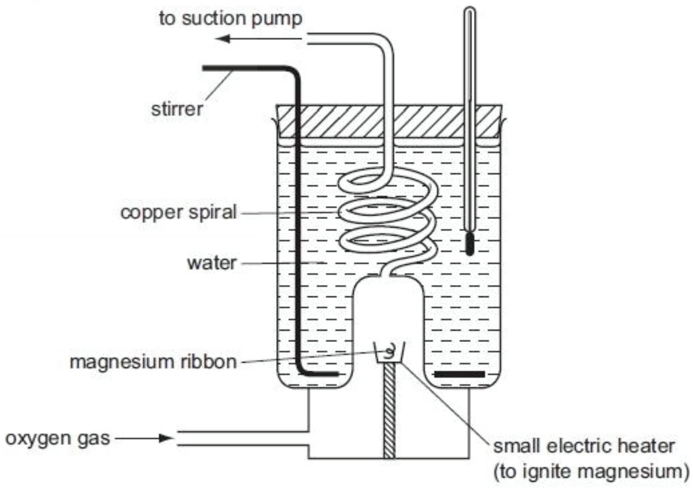
....

....

(ii) Write an equation to represent the lattice energy of MgO.

.... [3]

(b) The apparatus shown in the diagram can be used to measure the enthalpy change of formation of magnesium oxide, $\Delta H^{\circ}_{f}(MgO)$.



List the measurements you would need to make using this apparatus in order to calculate $\Delta H_f^{\ominus}(MgO)$.

....

....

....

.... [3]

Topic: **Chem 23 Q# 152/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Taken together, nitrogen and oxygen make up 99% of the air. Oxygen is by far the more reactive of the two gases, and most of the substances that react with air combine with the oxygen rather than with the nitrogen.

Despite the apparent lack of reactivity of N_2, nitrogen atoms have been found to form bonds with almost all of the elements in the Periodic Table. Lithium metal reacts with nitrogen gas at room temperature to give lithium nitride, Li_3N. Magnesium produces magnesium nitride, Mg_3N_2, as well as magnesium oxide, when heated in air.

(b) Calculate the lattice energy of magnesium nitride using the following data, in addition to relevant data from the *Data Booklet*.

enthalpy change	value/kJ mol^{-1}
atomisation of Mg(s)	+148
total of electron affinities for the change $N(g) \longrightarrow N^{3-}(g)$	+2148
enthalpy of formation of $Mg_3N_2(s)$	–461

lattice energy = ...kJ mol^{-1} [3]

Topic: **Chem 23 Q# 153/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Calcium chloride, $CaCl_2$, is an important industrial chemical used in refrigeration plants, for de-icing roads and for giving greater strength to concrete.

(a) Show by means of an equation what is meant by the lattice energy of calcium chloride.

.... [1]

(b) Suggest, with an explanation, how the lattice energies of the following salts might compare in magnitude with that of calcium chloride.

(i) calcium fluoride, CaF_2

....

....

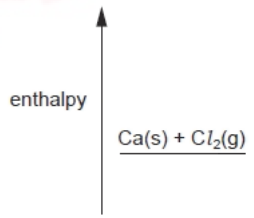
(ii) calcium sulfide, CaS

....

.... [3]

(c) Use the following data, together with additional data from the *Data Booklet*, to calculate the lattice energy of $CaCl_2$.

standard enthalpy change of formation of $CaCl_2$	–796 kJ mol^{-1}
standard enthalpy change of atomisation of Ca(s)	+178 kJ mol^{-1}
electron affinity per mole of chlorine atoms	–349 kJ mol^{-1}



lattice energy = ... kJ mol^{-1} [3]

Topic: Chem 24 Q# 154/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Titanium is a transition element in Period 4. It is commonly found as TiO_2 in minerals.

(c) Acidified $Ti^{3+}(aq)$ reacts with oxygen dissolved in water as shown.

$$4Ti^{3+} + O_2 + 2H_2O \rightarrow 4TiO^{2+} + 4H^+ \qquad \Delta G^\ominus = -436.1\,kJ\,mol^{-1}$$

The standard reduction potential, $E^\ominus$, of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ is +1.23 V.

(i) Calculate the standard reduction potential, $E^\ominus$, in V, of the $TiO^{2+}(aq)/Ti^{3+}(aq)$ half-cell.
Show your working.

$E^\ominus$ = ... V [3]

Topic: **Chem 24 Q# 155/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Silicon is the second most abundant element by mass in the Earth's crust.

(c) Silicon can also be produced by electrolysis of SiO_2 dissolved in molten $CaCl_2$.
The relevant half-equation for the cathode is shown.

$$SiO_2 + 4e^- \rightarrow Si + 2O^{2-}$$

Calculate the time, in seconds, required to produce 1.00 g of Si by this electrolysis, using a current of 6.00 A.
Assume no other substances are produced at the cathode.

time = ... s [2]

[Total: 9]

Topic: **Chem 24 Q# 156/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) **(i)** Define the term *standard cell potential*, $E^\ominus_{cell}$.

....

....

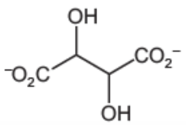
.... [2]

(ii) Draw a fully labelled diagram of the apparatus that can be used to measure the cell potential of a cell composed of a Cu(II)/Cu electrode and an Fe(III)/Fe(II) electrode. Include all necessary reactants.

[3]

(d) When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions are mixed the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an $Fe^{3+}(aq)$ catalyst.
The overall equation for this reaction is shown.

tartrate ions



$$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

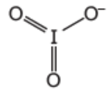
(ii) Use the overall equation to deduce the half-equation for the oxidation of tartrate ions, $C_4H_4O_6^{2-}$, to carbon dioxide, CO_2, and methanoate ions, HCO_2^-.

$C_4H_4O_6^{2-}$ + ... $\rightleftharpoons$ .... [1]

Topic: **Chem 24 Q# 157/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



(c) The decomposition of hydrogen peroxide, H_2O_2, is catalysed by acidified IO_3^-.

H_2O_2 reduces acidified IO_3^- as shown.

$$5H_2O_2 + 2H^+ + 2IO_3^- \rightarrow I_2 + 5O_2 + 6H_2O$$

This reaction is followed by the oxidation of I_2 by H_2O_2.

half-equation	E°/V
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons \frac{1}{2}I_2 + 3H_2O$	+1.19
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68

(i) Use the data to show that the separate reactions of H_2O_2 with IO_3^- and with I_2 are both feasible under standard conditions.

In your answer, give the equation for the reaction of H_2O_2 with I_2.

....

....

....

....

....

.... [3]

(ii) Write the overall equation for the decomposition of H_2O_2 catalysed by acidified IO_3^-.

.... [1]

Topic: **Chem 24 Q# 158/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Iron(II) compounds are generally only stable in neutral, non-oxidising conditions.

It is difficult to determine the lattice energy of FeO experimentally.

(b) Heating of FeO results in the formation of Fe_3O_4, as shown.

reaction 1 $4FeO \rightarrow Fe + Fe_3O_4$

Each formula unit of Fe_3O_4 contains one Fe^{2+} and two Fe^{3+} ions.

(i) Show how reaction 1 can be described as a disproportionation reaction.

....

....

.... [1]

Fe_3O_4(l) can be electrolysed using inert electrodes to form Fe.

(ii) Write the half-equation for the reaction that occurs at the anode during the electrolysis of Fe_3O_4(l).

.... [1]

(iii) Calculate the maximum mass of iron metal formed when Fe_3O_4(l) is electrolysed for six hours using a current of 50A.

Assume the one Fe^{2+} and two Fe^{3+} ions are discharged at the same rate.

mass of iron = ... g [3]

(c) $LiFePO_4$ can be used in lithium-ion rechargeable batteries.

When the cell is charging, lithium reacts with a graphite electrode to form LiC_6.

When the cell is discharging, the half-equations for the two processes that occur are as follows.

anode half-equation $LiC_6 \rightarrow 6C + Li^+ + e^-$

cathode half-equation $Li^+ + FePO_4 + e^- \rightarrow LiFePO_4$

(i) State one possible advantage of developing cells such as lithium-ion rechargeable batteries.

.... [1]

(ii) Use the cathode half-equation to determine the change, if any, in oxidation states of lithium and iron at the **cathode** during discharging.

metal	change in oxidation state during discharging	
	from	to
lithium		
iron		

[1]

(iii) Write the equation for the overall reaction that occurs when this cell is discharging.

.... [1]

Topic: **Chem 24 Q# 159/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Identify the substances liberated at the anode and at the cathode during the electrolysis of aqueous sodium sulfate, $Na_2SO_4(aq)$.

anode ....

cathode ....
[1]

(b) When molten sodium chloride is electrolysed, chlorine is liberated at the anode and sodium is liberated at the cathode.

A sample of molten sodium chloride is electrolysed for 1.50 hours using a current of 4.50A.

Calculate the volume of chlorine and the mass of sodium that are liberated under room conditions.

volume of chlorine = ... dm^3

mass of sodium = ... g
[4]

(c) The equation representing the standard electrode potential, E°, for the reduction of $MnO_4^-(aq)$ to $Mn^{2+}(aq)$ in acid solution is given.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^\circ = +1.52\,V$$

(i) Draw a diagram of the apparatus that would be used to measure the E° value of this half-cell. Your diagram should be fully labelled to identify all apparatus, substances and conditions.

[4]

(ii) Use the *Data Booklet* to identify a substance that could be used to oxidise Mn^{2+} ions to MnO_4^- ions under standard conditions.

Write an equation for the reaction.

....

....

.... [2]

[Total: 11]

9 **(a)** Manganese(IV) oxide, MnO_2, catalyses the decomposition of hydrogen peroxide, H_2O_2, as shown.

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

The mechanism involves the formation of the intermediate species, Mn^{2+}, in the first step which is subsequently used up in the second step.

State and use relevant electrode potentials, $E^\ominus$, to construct **two** equations to show how MnO_2 can catalyse this reaction.

....

....

....

....

....

equation 1 ....

equation 2 ....

[3]

---

3 The overall reaction for photosynthesis is shown.

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$$

Water is oxidised in this process according to the following half-equation.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad \text{half-equation 1}$$

(a) **(i)** Use these equations to deduce the half-equation for the reduction of carbon dioxide in this process.

[2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard electrode potential, $E^\ominus$, of $O_2(g)$ in half-equation 1 under standard conditions. Include all necessary chemicals.

[4]

(iii) For the cell drawn in **(a)(ii)**, use the *Data Booklet* to calculate the $E^\ominus_{cell}$ and deduce which electrode is positive.

$E^\ominus_{cell}$ = ... V

identity of the positive electrode = ...

[1]

[Total: 7]

Topic: **Chem 24 Q# 162/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Gold is an unreactive metal that can only be oxidised under specific conditions.

(a) The standard electrode potential, E°, of $Au^{3+}(aq)/Au(s)$ is +1.50 V.

(i) Define the term *standard electrode potential*.

....

....

.... [2]

(ii) Draw a fully labelled diagram of the apparatus that should be used to measure the standard cell potential, E°_{cell}, of $Au^{3+}(aq)/Au(s)$ and $HNO_3(aq)/NO(g)$.

Include all necessary chemicals.

[4]

Some relevant half-equations and their standard electrode potentials are given.

	half-equation	E°/V
1	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
2	$[AuCl_4]^-(aq) + 3e^- \rightleftharpoons Au(s) + 4Cl^-(aq)$	+1.00
3	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96

(iii) Write an ionic equation to show the spontaneous reaction that occurs when an electric current is drawn from the cell in **(a)(ii)**.

.... [1]

(iv) Calculate the E°_{cell} of the reaction in **(a)(iii)**.

E°_{cell} = ... V [1]

(v) Gold can be oxidised by a mixture of concentrated hydrochloric acid and concentrated nitric acid, known as *aqua regia*. Concentrated hydrochloric acid is 12 mol dm^{-3}. Concentrated nitric acid is 16 mol dm^{-3}.

Explain why *aqua regia* is able to dissolve gold.

In your answer, state and explain what effect the use of concentrated hydrochloric acid and concentrated nitric acid have on the E values of half-equations 2 and 3.

....

....

....

....

....

.... [3]

Topic: **Chem 24 Q# 163/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Group 2 metals form stable carbonates and sulfates.

(b) Aluminium is extracted from Al_2O_3 by electrolysis. Al_2O_3 is dissolved in cryolite in this process.

(i) The half-equation for the reaction at the anode is shown.

$$O^{2-} + C \rightarrow CO + 2e^-$$

Use this half-equation to write the ionic equation for the electrolysis of Al_2O_3.

.... [1]

(ii) Aluminium oxide is electrolysed for 3.0 hours using carbon electrodes and a current of 3.5×10^5 A.

Calculate the mass of aluminium that is formed.

mass of aluminium = ... g [3]

Topic: **Chem 24 Q# 164/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 An electrochemical cell is constructed using two half-cells.

- an Sn^{4+}/Sn^{2+} half-cell
- an Al^{3+}/Al half-cell

(a) State the material used for the electrode in each half-cell.

- Sn^{4+}/Sn^{2+} half-cell ....
- Al^{3+}/Al half-cell ....

[1]

(b) The cell is operated at 298 K.

The Al^{3+}/Al half-cell has standard concentrations.

The Sn^{4+}/Sn^{2+} half-cell has $[Sn^{4+}] = 0.300\,mol\,dm^{-3}$ and $[Sn^{2+}] = 0.150\,mol\,dm^{-3}$.

(i) Use the Nernst equation to calculate the electrode potential, E, of the Sn^{4+}/Sn^{2+} half-cell under these conditions.

E = ... V [2]

(ii) Calculate the E_{cell} under these conditions.

E_{cell} = ... V [1]

(iii) Write an equation for the overall cell reaction that occurs.

.... [2]

(c) Aluminium is produced industrially by electrolysis of a melt containing large amounts of Al^{3+} ions.

Calculate the mass of aluminium that is obtained when a current of 300 000 A is passed for 24 hours. Give your answer to **three** significant figures.

mass = ... units = ...

[4]

(d) Explain why chromium metal cannot be obtained by the electrolysis of dilute aqueous chromium(II) sulfate. Your answer should include data from the *Data Booklet*.

....

....

....

.... [2]

[Total: 12]

Topic: **Chem 24 Q# 165/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Chlorate(V) ions are powerful oxidising agents.

(a) The reduction of chlorate(V) ions, ClO_3^-, with SO_2 forms chlorine dioxide, ClO_2, and sulfate ions, SO_4^{2-}, as the only products.

Construct an equation for this reaction.

.... [1]

(b) **(i)** Chlorine dioxide, ClO_2, disproportionates with hydroxide ions, $OH^-(aq)$, to form a mixture of ClO_2^- and ClO_3^- ions.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

Explain, using this reaction as an example, what is meant by *disproportionation*.

....

.... [1]

(ii) Deduce the ionic half-equations for the reaction in **(b)(i)**.

....

.... [2]

(c) A lithium-iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell consists of a lithium electrode and an inert electrode immersed in body fluids. When current flows lithium is oxidised and iodine is reduced.

(i) Use the *Data Booklet* to write half-equations for the reactions taking place at the two electrodes. Hence write the overall equation for when a current flows.

- ....
- ....

overall equation ....

[2]

(ii) Use the *Data Booklet* to calculate the $E^\ominus_{cell}$ for this cell.

$E^\ominus_{cell}$ = ... V [1]

(iii) A current of 2.5×10^{-5} A is drawn from this cell.

Calculate the time taken for 0.10 g of lithium electrode to be used up. Assume the current remains constant throughout this period.

time = ... s [3]

[Total: 10]

Topic: **Chem 24 Q# 166/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(e) In a methanol-oxygen fuel cell, $CH_3OH(l)$ and $O_2(g)$ are in contact with two inert electrodes immersed in an acidic solution.

The half-equation for the reaction at the methanol electrode is shown.

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^- \qquad E^\ominus = -0.02\,V$$

(i) Use the *Data Booklet* to write an equation for the overall cell reaction.

....

....

.... [1]

(ii) Use $E^\ominus$ values to calculate the $E^\ominus_{cell}$ for this reaction.

$E^\ominus_{cell}$ = ... V [1]

[Total: 12]

3 **(a)** Complete the table, identifying the substance liberated at each electrode during electrolysis with inert electrodes.

electrolyte	substance liberated at the anode	substance liberated at the cathode
$AgNO_3$(aq)		
concentrated $NaCl$(aq)		
$CuSO_4$(aq)		

[3]

(b) Molten calcium iodide, CaI_2, is electrolysed in an inert atmosphere with inert electrodes.

(i) Write ionic equations for the reactions occurring at the electrodes.

- ....
- .... [2]

(ii) The electrolysis of molten CaI_2 is a redox process.

Identify the ion that is oxidised and the ion that is reduced, explaining your answer by reference to oxidation numbers.

....

....

.... [2]

(iii) Describe **two** visual observations that would be made during this electrolysis.

1 ....

2 .... [1]

(c) An oxide of iron dissolved in an inert solvent is electrolysed for 2.00 hours using a current of 0.800A. The electrolysis products are iron and oxygen. The mass of iron produced is 1.11 g.

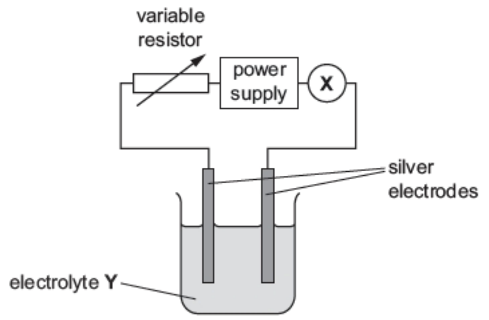
Calculate the oxidation number of Fe in the oxide of iron. Show **all** your working.

oxidation number of Fe = ... [3]

[Total: 11]

---

6 The apparatus shows a cell which can be used to determine a value of the Avogadro constant, L.



(a) **(i)** Name component **X**.

.... [1]

(ii) Suggest a suitable electrolyte **Y**.

.... [1]

(b) In an experiment, a current of 0.200A was passed through the cell for 40.0 minutes. The mass of the silver cathode increased by 0.500 g.

The charge on the electron is -1.60×10^{-19} C.

Calculate the:

- number of moles of silver deposited on the cathode
- number of coulombs of charge passed
- number of electrons passed
- number of electrons needed to deposit 1 mol of silver at the cathode.

[3]

[Total: 5]

Topic: **Chem 24 Q# 169/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Describe the trend in the reactivity of the halogens Cl_2, Br_2 and I_2 as oxidising agents. Explain this trend using values of E° (X_2/X^-) from the *Data Booklet*.

....

....

....

....

.... [2]

(b) **(i)** Write an equation for the reaction between chlorine and water.

.... [1]

(ii) Use standard electrode potential, E°, data from the *Data Booklet* to calculate the E°_{cell} for the following reaction.

$$Cl_2 + 2OH^- \rightleftharpoons Cl^- + ClO^- + H_2O$$

E°_{cell} = ... V [2]

(iii) The [OH⁻] was increased and the E_{cell} was measured.

Indicate how the value of the E_{cell} measured would compare to the E°_{cell} calculated in **(ii)** by placing **one** tick (✓) in the table.

E_{cell} becomes less positive than E°_{cell}.	
E_{cell} stays the same as E°_{cell}.	
E_{cell} becomes more positive than E°_{cell}.	

Explain your answer.

....

....

....

[2]

(c) A half-equation involving bromate(V) ions, BrO_3^-, and bromide ions is shown.

$$BrO_3^-(aq) + 3H_2O(l) + 6e^- \rightleftharpoons Br^-(aq) + 6OH^-(aq) \qquad E^\circ = +0.58\,V$$

(i) An alkaline solution of chlorate(I), ClO^-, can be used to oxidise bromide ions to bromate(V) ions.

Use the *Data Booklet* and the half-equation shown to write an equation for this reaction.

.... [1]

(ii) Calculate the E°_{cell} for the reaction in **(i)**.

E°_{cell} = ... V [1]

(iii) When a concentrated solution of bromic(V) acid, $HBrO_3$, is warmed, it decomposes to form bromine, oxygen and water only.

Write an equation for this reaction. The use of oxidation numbers may be helpful.

.... [1]

[Total: 10]

3 **(a)** Define the term *standard cell potential*.

....

....

.... [2]

(b) **(i)** Draw a fully labelled diagram of the experimental set-up you could use to measure the standard electrode potential of the $Pb^{2+}(aq)/Pb(s)$ electrode. Include the necessary chemicals.

[4]

(ii) The $E^\ominus$ for a $Pb^{2+}(aq)/Pb(s)$ electrode is –0.13 V.

Suggest how the E for this electrode would differ from its $E^\ominus$ value if the concentration of $Pb^{2+}(aq)$ ions is reduced. Indicate this by placing a tick (✓) in the appropriate box in the table.

more negative	no change	less negative

Explain your answer.

....

....

.... [2]

(c) Car batteries are made up of rechargeable lead-acid cells. Each cell consists of a negative electrode made of Pb metal and a positive electrode made of PbO_2. The electrolyte is $H_2SO_4(aq)$.

When a lead-acid cell is in use, Pb^{2+} ions are precipitated out as $PbSO_4(s)$ at the negative electrode.

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

(i) Calculate the mass of Pb that is converted to $PbSO_4$ when a current of 0.40 A is delivered by the cell for 80 minutes.

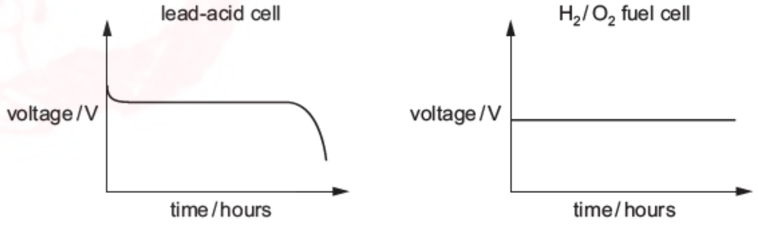
mass of Pb = ... g [2]

(ii) Complete the half-equation for the reaction taking place at the positive electrode.

$PbO_2(s)$ + $SO_4^{2-}(aq)$ + ... + ... → $PbSO_4(s)$ + ...

[1]

(d) The diagrams show how the voltage across two different cells changes with time when each cell is used to provide an electric current.



Suggest a reason why

- the voltage of the lead-acid cell changes after several hours,

....

....

- the voltage of the fuel cell remains constant.

....

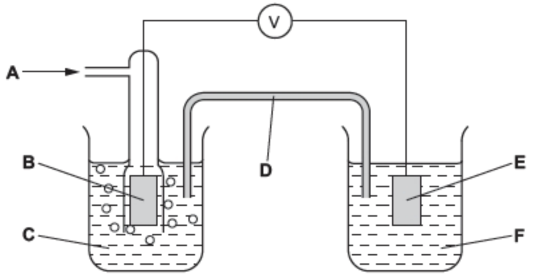
....

[2]

[Total: 13]

Topic: **Chem 24 Q# 171/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** The diagram shows the apparatus used to measure the standard electrode potential, *E*°, of $Fe^{3+}(aq)/Fe^{2+}(aq)$.



(i) Identify what the letters **A** to **F** represent.

A .... D ....

B .... E ....

C .... F ....

[3]

(ii) Label the diagram to show

- which is the positive electrode,
- the direction of electron flow in the external circuit.

Use the *Data Booklet* to help you.

[1]

(b) In another experiment, an $Fe^{3+}(aq)/Fe^{2+}(aq)$ half-cell was connected to a $Cu^{2+}(aq)/Cu(s)$ half-cell.

Determine the standard cell potential, E°_{cell}, when these two half-cells are connected by a wire and the circuit is completed.
Use the *Data Booklet* to help you.

E°_{cell} = ... V [1]

(c) **(i)** The *E*° of $Ni^{2+}(aq)/Ni(s)$ is –0.25 V.

State and explain how the electrode potential changes if the concentration of $Ni^{2+}(aq)$ is decreased.

....

....

.... [1]

(ii) The *E*° of $Cr^{3+}(aq)/Cr^{2+}(aq)$ is –0.41 V.

Calculate the electrode potential when $[Cr^{3+}(aq)]$ is 0.60 mol dm^{-3} and $[Cr^{2+}(aq)]$ is 0.15 mol dm^{-3}. Use the Nernst equation.

$$E = E^{\circ} + \frac{0.059}{z} \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

E = ... V [2]

[Total: 8]

Topic: **Chem 24 Q# 172/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Cobalt is a transition element that forms complex ions with oxidation states +2 and +3.

(c) Define the term *standard electrode potential*.

....

....

.... [2]

(d) An electrochemical cell was set up to measure the standard electrode potential, $E^{\ominus}_{cell}$, of a cell made of a Co^{2+}/Co half-cell and a Fe^{3+}/Fe^{2+} half-cell.

(i) Complete the table with the substance used to make the electrode in each of these half-cells.

half-cell	electrode
Co^{2+}/Co	
Fe^{3+}/Fe^{2+}	

[1]

(ii) Write the equation for the overall cell reaction.

.... [1]

(iii) Use the *Data Booklet* to calculate the $E^{\ominus}_{cell}$.

$E^{\ominus}_{cell}$ = ... V [1]

(e) The electrochemical cell in **(d)** was set up again but this time the concentration of $Co^{2+}(aq)$ was $0.050\,mol\,dm^{-3}$.

The Nernst equation can be used to calculate the value of an electrode potential at different concentrations.

$E = E^{\ominus} + (0.059/z)\log[Co^{2+}(aq)]$ Nernst equation

(i) Use the *Data Booklet* and the Nernst equation to calculate the value of E for the Co^{2+}/Co half-cell in this experiment.

E for Co^{2+}/Co = ... V [1]

(ii) Suggest how this change will affect the overall cell potential, E_{cell}, compared to $E^{\ominus}_{cell}$ in **(d)(iii)**.
Circle your answer.

less positive no change more positive

[1]

(f) Iron(III) ions can oxidise vanadium metal.

Construct an equation for the reaction of an excess of iron(III) ions with vanadium metal.
Use of the *Data Booklet* will be helpful.

.... [2]

[Total: 14]

---

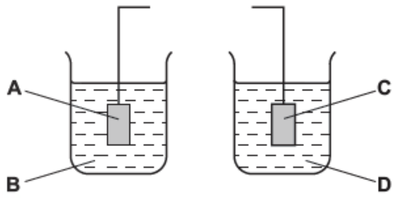
4 (a) (i) Define the term *standard cell potential*, $E^{\ominus}_{cell}$.

....

....

.... [1]

The following incomplete diagram shows the apparatus that can be used to measure the $E^{\ominus}_{cell}$ for a cell composed of the Fe^{3+}/Fe^{2+} and Ag^{+}/Ag half-cells.



(ii) Complete the diagram, labelling the components you add. [1]

(iii) Identify the components **A**-**D**.

A ....

B ....

C ....

D ....

[3]

(b) (i) Use $E^{\ominus}$ values to write an equation for the cell reaction that takes place if the two electrodes in **(a)** are connected by a wire and the circuit is completed.

....

.... [1]

(ii) Another electrochemical cell was set up using $0.31\,mol\,dm^{-3}$ $Ag^{+}(aq)$ instead of the standard Ag solution.

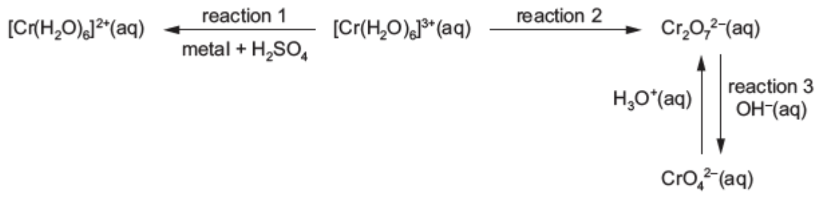
Use the Nernst equation, $E = E^{\ominus} + 0.059\log[Ag^{+}(aq)]$, and the relevant $E^{\ominus}$ values to calculate the new E_{cell} in this experiment.

E_{cell} = ... V [2]

[Total: 8]

Topic: **Chem 24 Q# 174/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 Some reactions of chromium ions are shown below.



(a) **(i)** Use the *Data Booklet* to suggest a suitable metal to carry out reaction 1.

.... [1]

(ii) Use $E^\ominus$ values to explain your answer to **(i)** by calculating the $E^\ominus_{cell}$.

....

....

.... [2]

(b) A student suggested that reaction 2 could be carried out using acidified hydrogen peroxide solution.

Use the *Data Booklet* to show whether or not this reaction is feasible.

....

....

.... [2]

(c) Explain using oxidation numbers whether or not reaction 3 is a redox reaction.

....

....

.... [2]

(d) The student used an acidified solution of $Cr_2O_7^{2-}$(aq) to electroplate a steel box with chromium metal.

Calculate how long it would take for a current of 0.125A to deposit 0.0312g of chromium metal.

time = ... [3]

[Total: 10]

Topic: **Chem 24 Q# 175/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **X** is a metallic element.

(a) **(i)** Draw a fully labelled diagram to show how the standard electrode potential, $E^\ominus$, of $\mathbf{X}^{2+}$(aq)/**X**(s) could be measured.

[4]

(ii) What are the conditions needed for the value measured to be a **standard** electrode potential?

.... [1]

(iii) State the charge carriers that transfer current through

the solutions, ... the wire. .... [1]

(b) An electrochemical cell was set up consisting of an $\mathbf{X}^{2+}$(aq) / **X**(s) half-cell (E° = –0.40 V) and an Ag^+(aq) / Ag(s) half-cell (E° = +0.80 V).

(i) Write an equation for the reaction that would take place if the electrodes of this cell were connected by a wire.

.... [1]

When the current was allowed to pass for a period of time,

- the Ag electrode gained 1.30 g in mass,
- the electrode made of metal **X** lost 0.67 g in mass.

(ii) Calculate the A_r of metal **X**; hence suggest an identity for **X**.
Show all your working. Use of the *Data Booklet* is relevant to this question.

A_r = ...

X is ....
[4]

[Total: 11]

(e) **(i)** State the relationship between the Faraday constant and the Avogadro constant.

.... [1]

(ii) When a current of 1.2A was passed through dilute sulfuric acid for 30 minutes, it was found that 130 cm^3 of oxygen, measured at 25 °C and 1 atm, was collected at the anode. The following reaction takes place.

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

Use these data and data from the *Data Booklet* to calculate a value for the Avogadro constant, *L*, by calculating

- the number of moles of oxygen produced,
- the number of moles of electrons needed for this,
- the number of coulombs passed,
- the number of electrons passed,
- the number of electrons in one mole of electrons (*L*).

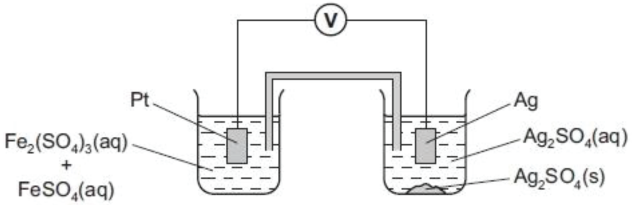
L = ... mol^{-1}
[4]

[Total: 15]

Topic: **Chem 24 Q# 177/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Silver sulfate, Ag_2SO_4, is sparingly soluble in water. The concentration of its saturated solution is 2.5×10^{-2} mol dm^{-3} at 298 K.

(c) An electrochemical cell is set up as follows.



(i) Use the *Data Booklet* to calculate the value of E°_{cell} under standard conditions, stating which electrode is the positive one.

E°_{cell} = ... positive electrode: .... [1]

(ii) How would the actual E_{cell} of the above cell compare to the E°_{cell} under standard conditions? Explain your answer.

[1]

(iii) How would the E_{cell} of the above cell change, if at all, if a few cm^3 of concentrated $Na_2SO_4(aq)$ were added to

- the beaker containing $Fe^{3+}(aq) + Fe^{2+}(aq)$,

- the beaker containing $Ag_2SO_4(aq)$?

[2]

(iv) Explain any changes in E_{cell} you have stated in **(iii)**.

[1]

Topic: **Chem 24 Q# 178/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) **(i)** Use E° values from the *Data Booklet* to predict the relative oxidising abilities of fluorine and chlorine.

[2]

(ii) Predict the *type of reaction* that would occur between the interhalogen compound chlorine fluoride, ClF, and potassium bromide solution.

[1]

(iii) Construct an equation for this reaction.

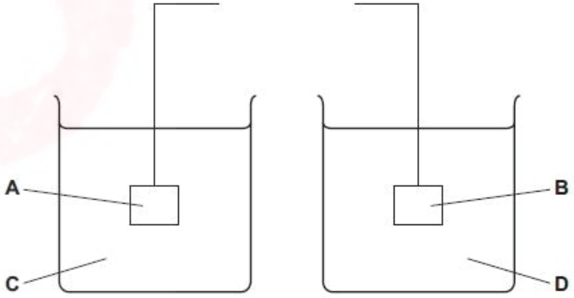
[1]

[Total: 8]

Topic: **Chem 24 Q# 179/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) The following diagram shows the apparatus used to measure the standard electrode potential, E°, of a cell composed of a Cu(II)/Cu electrode and an Fe(II)/Fe electrode.

(i) Finish the diagram by adding components to show the complete circuit. Label the components you add.



(ii) In the spaces below, identify or describe what the four letters **A**-**D** represent.

A ....

B ....

C ....

D ....

(iii) Use the *Data Booklet* to calculate the $E^\ominus$ for this cell.

....

(iv) Predict how the size of the overall cell potential would change, if at all, as the concentration of solution **C** is increased.
Explain your reasoning.

....

....

.... [8]

Topic: **Chem 24 Q# 180/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** What is meant by the term *standard electrode potential*, SEP?

....

.... [2]

(b) Draw a fully labelled diagram of the apparatus you could use to measure the SEP of the Fe^{3+}/Fe^{2+} electrode.

[5]

(c) The reaction between Fe^{3+} ions and I^- ions is an equilibrium reaction.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

(i) Use the *Data Booklet* to calculate the $E^\ominus_{cell}$ for this reaction.

....

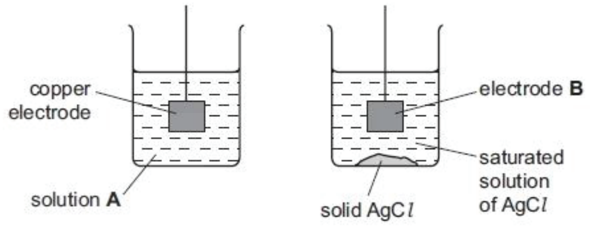
(ii) Hence state, with a reason, whether there will be more products or more reactants at equilibrium.

....

.... [2]

Topic: **Chem 24 Q# 181/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** The diagram below shows an incomplete experimental set-up needed to measure the E_{cell} of a cell composed of the standard Cu^{2+}/Cu electrode and an Ag^+/Ag electrode.



(i) State the chemical composition of

solution **A**, ...

electrode **B**. ....

(ii) Complete the diagram to show the whole experimental set-up.

[4]

(b) The above cell is not under standard conditions, because the $[Ag^+]$ in a saturated solution of AgC*l* is much less than $1.0\,mol\,dm^{-3}$. The $E_{electrode}$ is related to $[Ag^+]$ by the following equation.

equation 1 $$E_{electrode} = E^\ominus_{electrode} + 0.06\log[Ag^+]$$

(i) Use the *Data Booklet* to calculate the $E^\ominus_{cell}$ if the cell was operating under standard conditions.

$E^\ominus_{cell}$ = ... V

In the above experiment, the E_{cell} was measured at +0.17V.

(ii) Calculate the value of $E_{electrode}$ for the Ag^+/Ag electrode in this experiment.

....

(iii) Use equation 1 to calculate $[Ag^+]$ in the saturated solution.

$[Ag^+]$ = ... $mol\,dm^{-3}$
[3]

(c) **(i)** Write an expression for K_{sp} of silver sulfate, Ag_2SO_4, including units.

K_{sp} = ... units ....

Using a similar experimental set-up to that illustrated opposite, it is found that $[Ag^+]$ in a saturated solution of Ag_2SO_4 is 1.6×10^{-2} mol dm^{-3}.

(ii) Calculate the value of K_{sp} of silver sulfate.

K_{sp} = ...

[3]

Topic: **Chem 24 Q# 182/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) Iron(III) chloride, $FeCl_3$, is used to dissolve unwanted copper from printed circuit boards (PCBs) by the following reaction.

$$2FeCl_3(aq) + Cu(s) \rightarrow 2FeCl_2(aq) + CuCl_2(aq)$$

A solution in which $[Fe^{3+}(aq)]$ was originally equal to 1.50 mol dm^{-3} was re-used several times to dissolve copper from the PCBs, and was then titrated as follows.

A 2.50 cm^3 sample of the partially-used-up solution was acidified and titrated with 0.0200 mol dm^{-3} $KMnO_4$.
This oxidised any $FeCl_2$ in the solution back to $FeCl_3$.
It was found that 15.0 cm^3 of $KMnO_4(aq)$ was required to reach the end point.

(i) Construct an ionic equation for the reaction between Fe^{2+} and MnO_4^- in acid solution.

....

(ii) State here the $Fe^{2+} : MnO_4^-$ ratio from your equation in **(i)**. ....

(iii) Calculate the number of moles of MnO_4^- used in the titration.

(iv) Calculate the number of moles of Fe^{2+} in 2.50 cm^3 of the partially-used-up solution.

(v) Calculate the $[Fe^{2+}]$ in the partially-used-up solution.

(vi) Calculate the mass of copper that could still be dissolved by 100 cm^3 of the partially-used-up solution.

mass of copper = ... g

[6]

(d) Calcium forms three calcium silicides, Ca_2Si, CaSi and $CaSi_2$. The first of these reacts with water as follows.

$$\text{.........}Ca_2Si + \text{........}H_2O \rightarrow \text{.......}Ca(OH)_2 + \text{......}SiO_2 + \text{.....}H_2$$

(i) Balance this equation. You may find the use of oxidation numbers helpful.

(ii) During this reaction, state

which element(s) have been oxidised, ...

which element(s) have been reduced. ....

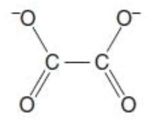
[2]

[Total: 14]

Topic: **Chem 24 Q# 183/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

The structure of the ethanedioate ion is as follows.



(i) Calculate the oxidation number of carbon in this ion. .... [1]

(iv) In sunlight the complex decomposes into potassium ethanedioate, iron(II) ethanedioate and carbon dioxide.

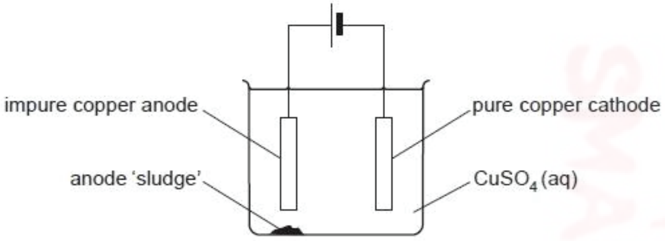
Use oxidation numbers to help you balance the following equation for this decomposition.

$K_3Fe(C_2O_4)_3 \rightarrow$ ....$K_2C_2O_4$ + ...FeC_2O_4 + ...CO_2 - - [2]

[Total: 14]

Topic: **Chem 24 Q# 184/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.



The impure copper anode contains small quantities of metallic nickel, zinc and silver, together with inert oxides and carbon resulting from the initial reduction of the copper ore with coke. The copper goes into solution at the anode, but the silver remains as the metal and falls to the bottom as part of the anode 'sludge'. The zinc also dissolves.

(a) **(i)** Write a half equation including state symbols for the reaction of copper at the anode.

....

(ii) Use data from the *Data Booklet* to explain why silver remains as the metal.

....

(iii) Use data from the *Data Booklet* to predict what happens to the nickel at the anode.

....

....

(iv) Write a half equation including state symbols for the main reaction at the cathode.

....

(v) Use data from the *Data Booklet* to explain why zinc is not deposited on the cathode.

....

....

(vi) Suggest why the blue colour of the electrolyte slowly fades as the electrolysis proceeds.

....

....

[7]

(b) Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution.
When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.

(i) Calculate the following, using appropriate data from the *Data Booklet*.

- number of moles of copper produced at the cathode

- number of moles of electrons needed to produce this copper

- number of moles of electrons that passed through the cell

(ii) Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode.

[4]

(c) Nickel often occurs in ores along with iron. After the initial reduction of the ore with coke, a nickel-iron alloy is formed.
Use data from the *Data Booklet* to explain why nickel can be purified by a similar electrolysis technique to that used for copper, using an impure nickel anode, a pure nickel cathode, and nickel sulfate as the electrolyte. Explain what would happen to the iron during this process.

....

....

....

....[2]

Topic: **Chem 24 Q# 185/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) When sulfur is heated under pressure with chlorine, the major product is SCl_2 (Cl-S-Cl).

$$S_8(g) + 8Cl_2(g) \rightarrow 8SCl_2(g)$$

(c) Under suitable conditions, SCl_2 reacts with water to produce a yellow precipitate of sulfur and a solution **A**. Solution **A** contains a mixture of $SO_2(aq)$ and compound **B**.

(i) What is the oxidation number of sulfur in SCl_2? ....

(ii) Work out how the oxidation number of sulfur changes during the reaction of SCl_2 with water.

....

....

(iii) Suggest the identity of compound **B**. ....

(iv) Construct an equation for the reaction between SCl_2 and water.

....

(v) What would you observe when each of the following reagents is added to separate samples of solution **A**?

$AgNO_3(aq)$ ....

$K_2Cr_2O_7(aq)$ ....

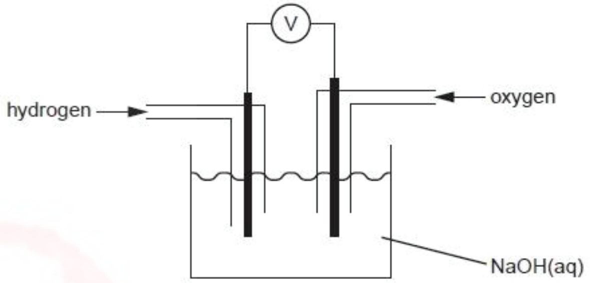
[7]

[Total: 11]

Topic: **Chem 24 Q# 186/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Although standard electrode potentials are measured for solutions where the concentrations of ions are 1.0 mol dm^{-3}, cells used as sources of battery power tend to operate with more concentrated solutions. This question concerns the electrode reactions involved in the hydrogen-oxygen fuel cell and the lead-acid car battery.

(a) In the hydrogen-oxygen fuel cell, $H_2(g)$ and $O_2(g)$ are fed onto two inert electrodes dipping into NaOH(aq).



The following reactions take place.

left hand electrode (cathode): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

right hand electrode (anode): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(i) Use the *Data Booklet* to calculate $E^\ominus_{cell}$ for this reaction.

....

(ii) Construct an equation for the overall reaction.

....

(iii) By using **one** of the phrases *more positive*, *more negative* or *no change*, deduce the effect of increasing $[OH^-(aq)]$ on the electrode potential of

- the left hand electrode ....
- the right hand electrode ....

(iv) Hence deduce whether the overall E_{cell} is likely to *increase*, *decrease* or *remain the same*, when $[OH^-(aq)]$ increases. Explain your answer.

....

....

(v) Suggest **one** other reason why a high [NaOH(aq)] is used in the fuel cell.

....

[6]

(b) In the cells of a lead-acid car battery the following reactions take place.

cathode: $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

anode: $PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$

(i) Use the *Data Booklet* to calculate $E^{\ominus}_{cell}$ for this reaction.

....

(ii) Construct an equation for the overall reaction.

....

The electrolyte in a lead-acid cell is $H_2SO_4(aq)$. Most of the $Pb^{2+}(aq)$ ions that are produced at the electrodes are precipitated as the highly insoluble $PbSO_4(s)$.

(iii) Construct an equation for the overall cell reaction in the presence of H_2SO_4.

....

(iv) By considering the effect of decreasing $[Pb^{2+}(aq)]$ on the electrode potentials of the cathode and the anode, deduce the effect of the presence of $H_2SO_4(aq)$ in the electrolyte on the overall E_{cell}.
State whether the E_{cell} will *increase*, *decrease* or *remain the same*.

Overall E_{cell} will ....

Explain your answer.

....

....

[5]

[Total: 11]

(d) Tin forms an oxide, **A**, that contains the metal in both oxidation states II and IV. The formula of **A** can be found by the following method.

- A sample of **A** was dissolved in $H_2SO_4(aq)$, producing solution **B**, which was a mixture of tin(II) sulfate and tin(IV) sulfate.
- A 25.0 cm^3 sample of solution **B** was titrated with 0.0200 mol dm^{-3} $KMnO_4$. 13.5 cm^3 of $KMnO_4$ was required to reach the end-point.
- Another 25.0 cm^3 sample of solution **B** was stirred with an excess of powdered zinc. This converted all the tin into tin(II). The excess of zinc powder was filtered off and the filtrate was titrated with 0.0200 mol dm^{-3} $KMnO_4$, as before.
This time 20.3 cm^3 of $KMnO_4$ was required to reach the end-point.

The equation for the reaction occurring during the titration is as follows.

$$2MnO_4^- + 16H^+ + 5Sn^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 5Sn^{4+}$$

(i) Write a balanced equation for the reaction between Zn and Sn^{4+}.

....

(ii) Use the *Data Booklet* to calculate the $E^{\ominus}$ values for the reactions between

- Zn and Sn^{4+}, ...
- MnO_4^- and Sn^{2+}..

(iii) Use the results of the two titrations to calculate

- the number of moles of Sn^{2+} in the first titration sample,

....

....

- the number of moles of Sn^{2+} in the second titration sample.

....

....

(iv) Use the results of your calculation in **(iii)** to deduce the Sn^{2+}/ Sn^{4+} ratio in the oxide **A**, and hence suggest the formula of **A**.

....

....

....

[8]

(e) A major use of tin is to make 'tin plate', which is composed of thin sheets of mild steel electroplated with tin, for use in the manufacture of food and drinks cans. A tin coating of 1.0×10^{-5} m thickness is often used.

(i) Calculate the volume of tin needed to coat a sheet of steel 1.0 m × 1.0 m to this thickness, on one side only.

....

....

(ii) Calculate the number of moles of tin that this volume represents.
[The density of tin is 7.3 g cm^{-3}.]

....

....

....

(iii) The solution used for electroplating contains Sn^{2+} ions. Calculate the quantity of electricity in coulombs needed to deposit the amount of tin you calculated in **(ii)**.

....

....

.... [4]

[Total: 19]

Topic: Chem 25 Q# 188**/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(c) A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction 1 $CH_3CHClCOOH + NH_3 \rightarrow CH_3CHClCOO^- + NH_4^+$

(i) Identify the conjugate acid–base pairs in reaction 1.

conjugate acid–base pair I .... and ....

conjugate acid–base pair II .... and .... [1]

Topic: **Chem 25 Q# 189/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 2-Chloropropanoic acid, $CH_3CHClCOOH$, is used in many chemical syntheses.

(a) (i) An equilibrium is set up when $CH_3CHClCOOH$ is added to water.

Write the equation for this equilibrium.

.... [1]

(ii) 0.150 mol of $CH_3CHClCOOH$ dissolves in 250 cm^3 of distilled water to produce a solution of pH 1.51.

Calculate the pK_a of $CH_3CHClCOOH$.

pK_a = ... [2]

(iii) An equal concentration of aqueous propanoic acid has pH 2.55.

Explain the difference in the pH of solutions of equal concentration of $CH_3CHClCOOH$ and propanoic acid.

....

....

....

.... [2]

Topic: **Chem 25 Q# 190/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(e) An orange precipitate of HgI_2 forms when Hg^{2+} ions are added to KI(aq).
The solubility of HgI_2 at 25 °C is 1.00×10^{-7} g dm^{-3}.

Calculate the solubility product, K_{sp}, of HgI_2.
Include units in your answer.

[M_r: HgI_2, 454.4]

value of K_{sp} = ...

units = ... [3]

Topic: **Chem 25 Q# 191/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Iodine is found naturally in compounds in many different oxidation states.

(a) Iodide ions, I^-, react with acidified $H_2O_2(aq)$ to form iodine, I_2, and water.
This reaction mixture is shaken with cyclohexane, C_6H_{12}, to extract the I_2.
Cyclohexane is immiscible with water.

(ii) 15.0 cm^3 of C_6H_{12} is shaken with 20.0 cm^3 of an aqueous solution containing I_2 until no further change is seen.
It is found that 0.390 g of I_2 is extracted into the C_6H_{12}.
The partition coefficient of I_2 between C_6H_{12} and water, K_{pc}, is 93.8.

Calculate the mass of I_2 that remains in the aqueous layer.
Show your working.

mass of I_2 in aqueous layer = ... g [2]

(iii) Suggest how the value of K_{pc} of I_2 between hexan-2-one, $CH_3(CH_2)_3COCH_3$, and water compares to the value given in **(a)(ii)**.
Explain your answer.

....

....

....

.... [2]

Topic: **Chem 25 Q# 192/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Solution **Y** is hydrochloric acid, $HCl(aq)$. Solution **Z** is aqueous 4-chlorobutanoic acid, $Cl(CH_2)_3CO_2H(aq)$. The pK_a of $Cl(CH_2)_3CO_2H(aq)$ is 4.52. The pH of both solutions is 4.00.

(a) **(i)** Write an expression for the K_a of $Cl(CH_2)_3CO_2H(aq)$.

K_a =

[1]

(ii) Write a mathematical expression to describe the relationship between K_a and pK_a.

.... [1]

(iii) Calculate [H$^+$] in solutions **Y** and **Z**.

[H$^+$] = ... mol dm^{-3} [1]

(iv) Calculate the ratio $\dfrac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}}$.

$\dfrac{[HCl] \text{ dissolved in solution } \mathbf{Y}}{[Cl(CH_2)_3CO_2H] \text{ dissolved in solution } \mathbf{Z}}$ = ... [2]

(b) A buffer solution of pH 5.00 is produced by adding sodium propanoate to 5.00 g of propanoic acid in 100 cm^3 of distilled water.

Calculate the mass of sodium propanoate that must be used to produce this buffer solution.
The K_a of propanoic acid is 1.35×10^{-5} mol dm^{-3}.

[M_r: propanoic acid, 74.0; sodium propanoate, 96.0]

mass of sodium propanoate = ... g [3]

(c) Some dilute sulfuric acid is mixed with a small sample of the buffer solution described in **(b)**.
The final pH of the mixture is close to 1.

Explain this observation.

....

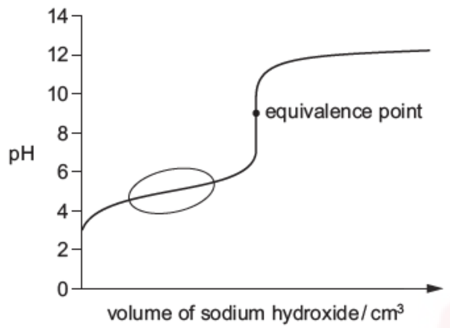
....

....

.... [2]

Topic: **Chem 25 Q# 193/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** The sketch graph for the titration of ethanoic acid, CH_3CO_2H, with sodium hydroxide is shown.



(i) In the region circled on the graph, identify the **two** organic species that are present in the solution. Explain why the pH of the mixture only changes slowly and gradually in this region when sodium hydroxide is being added.

two species present ....

....

....

....

.... [3]

(ii) The equivalence point in this acid-base titration is where the two solutions have been mixed in exactly equal molar proportion.

Suggest why the pH is greater than 7 at the equivalence point in this titration.

....

....

....

.... [1]

Topic: **Chem 25 Q# 194/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b) An impure sample of ammonium vanadate(V), NH_4VO_3, with mass 0.150 g, is dissolved in an excess of dilute acid.

In this solution all vanadium is present as VO_2^+ ions. An excess of zinc powder is added to the solution and all the VO_2^+ ions are reduced to V^{2+} ions. The mixture is filtered to remove any remaining zinc powder.

$$VO_2^+ + 4H^+ + 3e^- \rightarrow V^{2+} + 2H_2O$$

When the resulting solution is titrated, 20.10 cm³ of 0.0250 mol dm⁻³ acidified MnO_4^- oxidises all V^{2+} ions back to VO_2^+ ions.

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$$

Calculate the percentage by mass of NH_4VO_3 in the 0.150 g impure sample of NH_4VO_3.

Give your answer to **three** significant figures.

[M_r: NH_4VO_3, 116.9]

percentage by mass of NH_4VO_3 = ... % [3]

Topic: **Chem 25 Q# 195/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** The carbonates and hydroxides of Group 2 elements show similar trends in thermal stability.

(b) Calcium hydroxide is slightly soluble in water.

(i) Write an equation to show the dissociation of calcium hydroxide, $Ca(OH)_2(s)$, in aqueous solution. Include state symbols.

.... $\rightleftharpoons$ .... [1]

(ii) Calculate the solubility, in mol dm⁻³, of $Ca(OH)_2$.
[K_{sp}: $Ca(OH)_2$, 5.02×10^{-6} mol³ dm⁻⁹]

solubility = ... mol dm⁻³ [2]

(iii) Suggest how the solubility of $Ca(OH)_2$ in aqueous NaOH compares to its solubility in water.

Explain your reasoning.

....

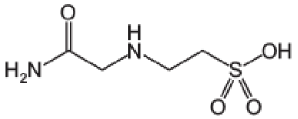
....

.... [1]

Topic: **Chem 25 Q# 196/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(f) The weak acid **ACES** is a compound that can be used to make a buffer solution for electrophoresis experiments.

ACES



The anion of the sodium salt of **ACES**, $C_4H_9N_2O_4SNa$, is a strong base.

A buffer solution is prepared by the following steps.

- 3.50 g of $C_4H_9N_2O_4SNa$ is dissolved in 100 cm^3 of distilled water.
- 50.0 cm^3 of 0.200 mol dm^{-3} dilute hydrochloric acid is added to the solution.
- The resulting mixture is transferred to a 250.0 cm^3 volumetric flask, and the solution made up to the mark.

$C_4H_9N_2O_4SNa$ reacts with HCl with a 1 : 1 stoichiometry.

The pK_a of **ACES** is 6.88 at 298 K.

Calculate the pH of the buffer solution formed at 298 K.

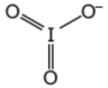
[M_r: $C_4H_9N_2O_4SNa$, 204.1]

pH = ... [4]

Topic: **Chem 25 Q# 197/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



(e) $Pb(IO_3)_2$ is only sparingly soluble in water at 25 °C.

The solubility product, K_{sp}, of $Pb(IO_3)_2$ is 3.69×10^{-13} $mol^3 dm^{-9}$ at 25 °C.

(i) Write an expression for the solubility product of $Pb(IO_3)_2$.

K_{sp} =

[1]

(ii) Calculate the solubility, in mol dm^{-3}, of $Pb(IO_3)_2$ at 25 °C.

solubility = ... mol dm^{-3} [2]

4 **(a)** **(i)** Give the mathematical expression for each of the terms pH and K_w.

pH = ...

K_w = ...
[2]

(ii) Calculate the pH of 0.027 mol dm^{-3} NaOH(aq).

pH = ... [1]

(b) The K_a value of chloric(I) acid, HC*l*O, is 3.72 × 10^{-8} mol dm^{-3}.

Calculate the pH of 0.010 mol dm^{-3} HC*l*O(aq).

pH = ... [1]

(c) Water and octan-1-ol form two layers when mixed.

Ethanamide is more soluble in water than it is in octan-1-ol. When 1.00 g of ethanamide is added to 50.0 cm^3 of water and this is then shaken with 50.0 cm^3 of octan-1-ol, it is found that the water layer contains 0.935 g of ethanamide at equilibrium.

(i) Calculate the partition coefficient, K_{pc}, for ethanamide in water and octan-1-ol.

K_{pc} = ... [1]

(ii) The 50.0 cm^3 of water containing 0.935 g of ethanamide is then shaken with 100.0 cm^3 of pure octan-1-ol under the same conditions.

Calculate the mass of ethanamide that is dissolved in the 100.0 cm^3 of octan-1-ol at equilibrium.

mass of ethanamide = ... g
[2]

[Total: 7]

---

8 **(a)** Explain what is meant by the term *buffer solution*.

....

....

.... [2]

(b) **(i)** Write an expression for the acid dissociation constant, K_a, for ammonium ions, NH_4^+(aq).

K_a =

[1]

(ii) Write **two** equations to describe how a solution containing ammonium ions, NH_4^+(aq), and ammonia, NH_3(aq), can act as a buffer.

....

.... [2]

(iii) The numerical value of K_a for NH_4^+(aq) is 5.6 × 10^{-10} at 298 K.
A buffer solution was prepared by adding 0.80 dm^3 of 0.25 mol dm^{-3} ammonia, an excess, to 0.20 dm^3 of 0.20 mol dm^{-3} hydrochloric acid.

Calculate the pH of the buffer solution formed at 298 K.

pH = ... [3]

[Total: 8]

Topic: **Chem 25 Q# 200/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Silver carbonate, Ag_2CO_3, is sparingly soluble in water. The numerical value of the solubility product, K_{sp}, for silver carbonate is 6.3×10^{-12} at 25 °C.

(i) Write an expression for the solubility product, K_{sp}, of Ag_2CO_3, and state its units.

K_{sp} =

units = ... [2]

(ii) Calculate the equilibrium concentration of Ag^+ in a saturated solution of Ag_2CO_3 at 25 °C.

$[Ag^+]$ = ... mol dm^{-3} [1]

(iii) Solid Ag_2CO_3 is stirred at 25 °C with 0.050 mol dm^{-3} $AgNO_3$ until no more Ag_2CO_3 dissolves.

Calculate the concentration of carbonate ions, $[CO_3^{2-}]$, in this solution.

$[CO_3^{2-}]$ = ... mol dm^{-3} [1]

(iv) An electrochemical cell is set up to measure the electrode potential, *E*, for the Ag^+/Ag half-cell using the saturated Ag_2CO_3(aq) with a standard hydrogen electrode.

Use the *Data Booklet*, your answer to **(a)(ii)**, and the Nernst equation to calculate the electrode potential, *E*, for this Ag^+/Ag half-cell.

E for Ag^+/Ag half-cell = ... V [2]

Topic: **Chem 25 Q# 201/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b) **(i)** The numerical values of K_a for methanoic acid, HCO_2H, and pyruvic acid, CH_3COCO_2H, are given.

acid	K_a
HCO_2H	1.78×10^{-4}
CH_3COCO_2H	4.07×10^{-3}

An equilibrium mixture containing the two acid-base pairs is formed.

$$HCO_2^- + CH_3COCO_2H \rightleftharpoons HCO_2H + CH_3COCO_2^-$$

Use the K_a values to calculate the equilibrium constant, K_{eq}, for this equilibrium.

K_{eq} = ... [1]

(ii) Use your value of K_{eq} to predict the position of this equilibrium. Indicate this by placing a tick (✓) in the appropriate box in the table. Explain your answer.

equilibrium lies to the left	equilibrium lies in the middle	equilibrium lies to the right

....

.... [1]

(iii) Ethanedioic acid, HO_2CCO_2H, has two dissociation constants, K_{a1} and K_{a2}, whose pK_a values are 1.23 and 4.19.

Suggest equations to show the two dissociations that give rise to these pK_a values.

pK_{a1} 1.23 ....

pK_{a2} 4.19 ....
[2]

(iv) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

.... [1]

(f) Deuterium oxide, D_2O, where D is ^2H, can be used as a solvent in proton NMR spectroscopy.

(g) The ionic product, K_w, for D_2O has a value of $1.35 \times 10^{-15}\,mol^2\,dm^{-6}$ at 298 K.

(i) Write the expression for the K_w of D_2O.

K_w =

[1]

(ii) Calculate the pH of pure, neutral D_2O at 298 K.
Assume $[D^+]$ is equivalent to $[H^+]$ for pH calculations.

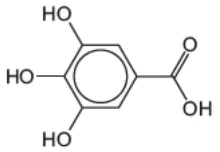
pH = ... [2]

[Total: 23]

Topic: **Chem 25 Q# 202/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(b) A buffer solution was prepared by dissolving 2.04 g of gallic acid in 250 cm³ of a solution containing $0.0600\,mol\,dm^{-3}$ of gallate ions, $C_7H_5O_5^-$.

$$C_7H_6O_5 \rightleftharpoons C_7H_5O_5^- + H^+ \qquad K_a = 3.89 \times 10^{-5}\,mol\,dm^{-3} \text{ at } 298\,K$$

(i) Define the term *buffer solution*.

....

....

.... [2]

(ii) Calculate the pH of this buffer solution.

pH = ... [3]

(iii) Write **two** equations to show how a solution containing gallic acid, $C_7H_6O_5$, and gallate ions, $C_7H_5O_5^-$, acts as a buffer.

....

....

....

.... [2]

Topic: **Chem 25 Q# 203/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Gold is an unreactive metal that can only be oxidised under specific conditions.

(d) AlF_3 is sparingly soluble in water. The concentration of its saturated solution at 298 K is $6.5 \times 10^{-2}\,mol\,dm^{-3}$.

(i) Write an expression for the solubility product, K_{sp}, of AlF_3.

K_{sp} = ... [1]

(ii) Calculate the numerical value of K_{sp} for AlF_3 at 298 K.

K_{sp} = ...
[1]

Topic: **Chem 25 Q# 204/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Silver sulfide, Ag_2S, is very insoluble in water.

(a) **(i)** Write an expression for the solubility product, K_{sp}, of $Ag_2S(s)$.

K_{sp} =

[1]

(ii) The solubility of $Ag_2S(s)$ in water at 298 K is 1.16×10^{-17} mol dm^{-3}.

Calculate the numerical value of the solubility product, K_{sp}, of $Ag_2S(s)$ at 298 K.

K_{sp} = ... [2]

(iii) Calculate the minimum volume of water needed to dissolve 1.00 g of $Ag_2S(s)$ under standard conditions.

volume = ... dm^3 [2]

(b) Bromic(I) acid, HOBr(aq), is a weak acid. Its K_a is 2.0×10^{-9} mol dm^{-3}.

(i) Calculate the pH of 0.20 mol dm^{-3} HOBr(aq).

pH = ... [2]

(ii) 5.0 cm^3 of 0.20 mol dm^{-3} potassium hydroxide, KOH, are added to 20.0 cm^3 of 0.20 mol dm^{-3} HOBr(aq).

Calculate the pH of the buffer solution produced.

pH = ... [2]

[Total: 9]

Topic: **Chem 25 Q# 205/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(d) When concentrated sulfuric acid is added to water, dissociation takes place in two stages.

stage 1 $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

stage 2 $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_{a2} = 1.0 \times 10^{-2}$ mol dm^{-3}

K_{a2} is the acid dissociation constant for stage 2.

(i) Write the expression for the acid dissociation constant K_{a2}.

K_{a2} =

[1]

(ii) H_2SO_4 is considered a strong acid whereas HSO_4^- is considered a weak acid.

Suggest how the magnitude of the acid dissociation constant for stage 1 compares to K_{a2}.

.... [1]

(e) Benzoic acid, $C_6H_5CO_2H$, is a weak acid. A solution of 0.0250 mol dm^{-3} benzoic acid has a pH of 2.90.

Calculate the K_a of benzoic acid.

K_a = ... mol dm^{-3}
[2]

3 **(a)** **(i)** Use mathematical expressions to define the following terms.

- pH = ...

  ....

- K_a for a weak acid, HA = ...

  .... [2]

(ii) Write equations to show how a buffer solution consisting of a mixture of HA(aq) and NaA(aq) controls pH when an acid or an alkali is added.

....

....

.... [2]

(b) When chlorine dissolves in water the following reaction occurs.

$$Cl_2(g) + H_2O(l) \rightarrow HClO(aq) + H^+(aq) + Cl^-(aq)$$

When solutions of chlorine are used for water purification, the pH of the solution of chlorine is kept near to pH 7 by the addition of a base.

Chlorine is dissolved in water to produce 1000 cm^3 of a solution containing 0.170 mol of HC*l*O and 0.170 mol of HC*l*.

A buffer solution is then prepared by adding 0.200 mol of NaOH(s) to this solution. The NaOH reacts initially with the HC*l*.

Calculate the pH of the buffer solution.

[HC*l*O is a weak acid with $K_a = 2.9 \times 10^{-8}$ mol dm^{-3}.]

pH = ... [3]

[Total: 7]

---

2 **(a)** The following table lists the solubilities of the hydroxides and carbonates of some of the Group 2 elements, **M**, at 25 °C.

element **M**	solubility / mol dm^{-3}	
	$M(OH)_2$	MCO_3
Mg	2.0×10^{-4}	1.5×10^{-3}
Ca	1.5×10^{-2}	1.3×10^{-4}
Sr	3.4×10^{-2}	7.4×10^{-5}
Ba	1.5×10^{-1}	9.1×10^{-5}

(b) **(i)** Calculate the value of the solubility product, K_{sp}, of magnesium hydroxide at 25 °C.

K_{sp} = ... [2]

(ii) State what would be observed if a few drops of a saturated solution of barium hydroxide are added to a saturated solution of barium carbonate. Explain your answer.

observation ....

explanation ....

.... [2]

(b) **(i)** Write the expression for K_w, the ionic product of water.

K_w =

[1]

(ii) The numerical value of K_w increases with increasing temperature.

Place a tick (✓) in the appropriate column in each row to show the effect of increasing the temperature of water on the pH and on the ratio $[H^+]:[OH^-]$.

effect of increasing temperature of water	decrease	stay the same	increase
pH			
ratio $[H^+]:[OH^-]$			

[2]

(c) An aqueous solution of sodium hydroxide has a pH of 13.25 at 298 K.

Calculate the concentration of this sodium hydroxide solution.

concentration = ... $mol\,dm^{-3}$ [2]

(d) Buffer solutions are used to regulate the pH of a solution to keep its pH value within a narrow range.

Write **two** equations to describe how hydrogencarbonate ions, HCO_3^-, and carbonic acid, H_2CO_3, control the pH of blood.

....

.... [2]

(e) The K_a for ethanoic acid is $1.75 \times 10^{-5}\,mol\,dm^{-3}$ at 298 K.

(i) When ethanoic acid is dissolved in water, an equilibrium mixture containing two acid-base pairs is formed.

Write an equation for this equilibrium. In the boxes label each species acidic or basic to show its behaviour in this equilibrium.

CH_3CO_2H + ... $\rightleftharpoons$ .... + ...

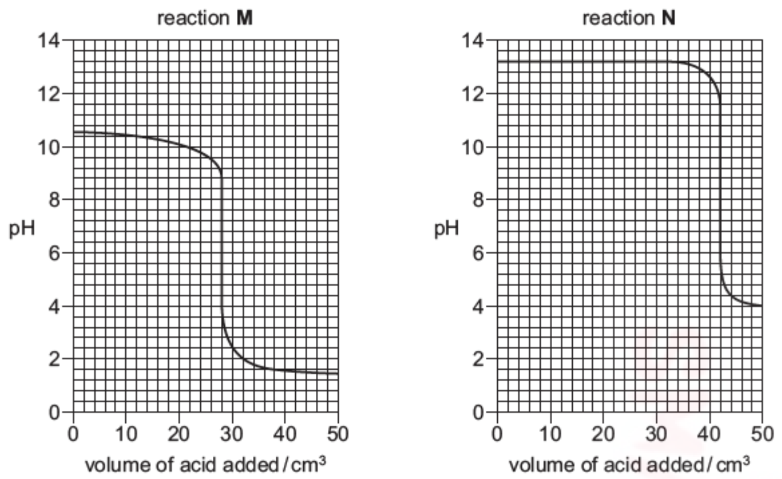
[2]

(ii) A buffer solution was prepared by adding $30.0\,cm^3$ of $0.25\,mol\,dm^{-3}$ ethanoic acid, an excess, to $20.0\,cm^3$ of $0.15\,mol\,dm^{-3}$ sodium hydroxide.

Calculate the pH of the buffer solution formed at 298 K. Give your answer to **one** decimal place.

pH = ... [4]

(f) Titration curves for two different acid-base reactions, **M** and **N**, are shown.



(i) Use the titration curve for reaction **M** to deduce the volume of acid added at the end-point for this titration.

volume of acid added at the end-point = ... cm^3 [1]

(ii) The table shows some acid-base indicators.

name of indicator	pH range of colour change
malachite green	0.2–1.8
bromocresol green	3.8–5.4
bromothymol blue	6.0–7.6
thymolphthalein	9.3–10.6

Name a suitable indicator for each of the acid-base titrations **M** and **N**. Explain your answers.

reaction **M** .... reaction **N** ....

explanation ....

....

[2]

[Total: 19]

Topic: **Chem 25 Q# 209/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

---

(d) **(i)** Explain what is meant by the term *partition coefficient*, $K_{partition}$.

....

....

....

.... [2]

(ii) The partition coefficient of organic compound **H** between dichloromethane and water is 4.75.

- 2.50 g of compound **H** was dissolved in water and made up to 100 cm^3 in a volumetric flask.
- 50 cm^3 of this aqueous solution were shaken with 10 cm^3 of dichloromethane.

Calculate the mass of compound **H** that was extracted into the dichloromethane.

mass of compound **H** extracted = ... g [2]

[Total: 14]

Topic: **Chem 25 Q# 210/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) When sodium oxide reacts with water an alkaline solution is obtained.

(i) Explain why the solution obtained is alkaline. You should use the Brønsted-Lowry theory of acids and bases in your answer.

....

....

....

.... [2]

(ii) Calculate the pH of the solution obtained when 3.10 g of sodium oxide are added to 400 cm^3 of water.

pH = ... [3]

Topic: **Chem 25 Q# 211/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** **(i)** State what is meant by the term *partition coefficient*.

....

....

.... [1]

Ammonia is soluble in both water and organic solvents.
An aqueous solution of ammonia is shaken with the immiscible organic solvent trichloromethane.
The mixture is left to reach equilibrium.

Samples are taken from each layer and titrated with dilute hydrochloric acid.

- A 25.0 cm^3 sample from the trichloromethane layer requires 13.0 cm^3 of 0.100 $mol\,dm^{-3}$ HC*l* to reach the end-point.
- A 10.0 cm^3 sample from the aqueous layer requires 12.5 cm^3 of 0.100 $mol\,dm^{-3}$ HC*l* to reach the end-point.

(ii) Calculate the partition coefficient, $K_{partition}$, of ammonia between trichloromethane and water.

$K_{partition}$ = ... [2]

(iii) Butylamine, $C_4H_9NH_2$, is also soluble in both water and organic solvents.

Suggest how the value of $K_{partition}$ of butylamine between trichloromethane and water would compare to the value of $K_{partition}$ calculated in **(ii)**. Explain your answer.

....

....

.... [2]

Topic: **Chem 25 Q# 212/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

(i) Calculate the pH of 0.10 $mol\,dm^{-3}$ HCN(aq).

pH = ... [2]

Topic: **Chem 25 Q# 213/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(b) The solubility of $Sr(OH)_2$ is 3.37 × $10^{-2}\,mol\,dm^{-3}$ at 0 °C.

(i) Write an expression for the solubility product of $Sr(OH)_2$.

K_{sp} =

[1]

(ii) Calculate the value of K_{sp} at 0 °C. Include units in your answer.

K_{sp} = ... units = ...
[2]

Topic: **Chem 25 Q# 214/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** The table lists values of solubility products, K_{sp}, of some Group 2 carbonates.

	solubility product in water at 298 K, K_{sp} / mol^2 dm^{-6}
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	5.0×10^{-9}
$SrCO_3$	1.1×10^{-10}

Use the data in the table to describe the trend in the solubility of the Group 2 carbonates down the group.

....

.... [1]

(b) **(i)** Write an equation to show the equilibrium for the solubility product for $MgCO_3$. Include state symbols.

$\rightleftharpoons$

.... [1]

(ii) With reference to your equation in **(i)**, suggest what is observed when a few cm^3 of concentrated Na_2CO_3(aq) are added to a saturated solution of $MgCO_3$. Explain your answer.

....

....

.... [2]

(c) Use the data in the table to calculate the solubility of $MgCO_3$ in water at 298 K, in g dm^{-3}.

solubility of $MgCO_3$ = ... g dm^{-3} [2]

Topic: **Chem 25 Q# 215/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(b) **(i)** Isocyanic acid is a weak acid.

$$HNCO \rightleftharpoons H^+ + NCO^- \qquad K_a = 1.2 \times 10^{-4}\ \text{mol dm}^{-3}$$

Calculate the pH of a 0.10 mol dm^{-3} solution of isocyanic acid.

pH = ... [2]

(ii) Sodium cyanate, NaNCO, is used in the production of isocyanic acid. Sodium cyanate is prepared commercially by reacting urea, $(NH_2)_2CO$, with sodium carbonate. Other products in this reaction are carbon dioxide, ammonia and steam.

Write an equation for the production of NaNCO by this method.

.... [1]

(c) Barium hydroxide, $Ba(OH)_2$, is completely ionised in aqueous solutions. During the addition of 30.0 cm^3 of 0.100 mol dm^{-3} $Ba(OH)_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid, the pH was measured.

(i) Calculate the [OH$^-$] at the end of the addition.

[OH$^-$] = ... mol dm^{-3} [2]

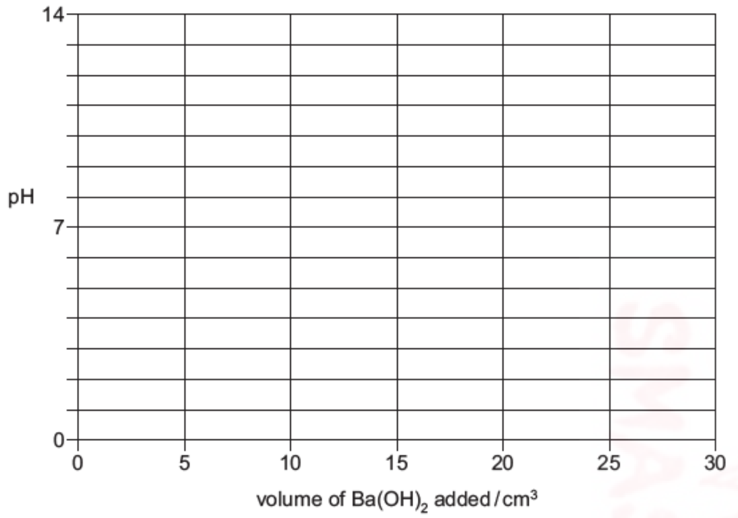
(ii) Use your value in **(i)** to calculate [H$^+$] and the pH of the solution at the end of the addition.

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

final pH = ...

[2]

(iii) On the following axes, sketch how the pH changes during the addition of a total of 30.0 cm^3 of 0.100 mol dm^{-3} $Ba(OH)_2$ to 20.0 cm^3 of 0.100 mol dm^{-3} isocyanic acid.



[3]

Topic: **Chem 25 Q# 216/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(ii) The reaction for the Haber process to produce ammonia is shown.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^\circ = -92\ kJ\ mol^{-1}$$

At 500 °C, when pressure is measured in atmospheres, the numerical value of K_p for this equilibrium is 1.45×10^{-5}.

- Write the expression for K_p for this equilibrium.

K_p =

- Calculate the partial pressure of NH_3 at equilibrium at 500 °C, when the partial pressure of N_2 is 20 atm and that of H_2 is 60 atm.

p_{NH_3} = ... atm [2]

[Total: 17]

Topic: **Chem 25 Q# 217/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Sodium chlorate(I), $NaClO$, is the active ingredient in commercial bleach. The concentration of chlorate(I) ions was determined by titration.

- 10.0 cm^3 of a bleach solution was diluted to 250 cm^3 in a volumetric flask using distilled water.
- Dilute sulfuric acid and an excess of potassium iodide solution were added to a 25.0 cm^3 portion of this solution to liberate iodine.
- The resulting solution required 20.80 cm^3 of 0.100 mol dm^{-3} aqueous sodium thiosulfate solution to react with the iodine produced.

The titration reactions are shown.

$$ClO^- + 2I^- + 2H^+ \rightarrow I_2 + Cl^- + H_2O$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate the concentration, in mol dm^{-3}, of ClO^- ions in the bleach solution.

concentration of ClO^- = ... mol dm^{-3} [3]

(b) An indicator was used in the thiosulfate-iodine titration.

(i) Name a suitable indicator for this titration.

.... [1]

(ii) State the expected colour change you would observe at the end-point in this titration.

from .... to .... [1]

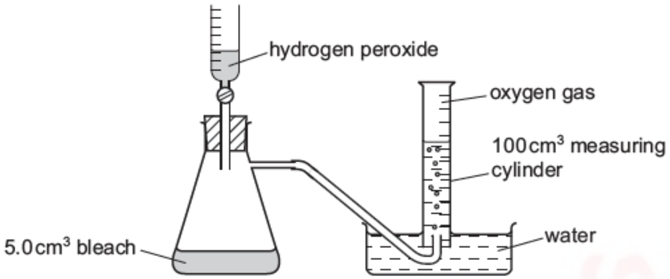
(iii) State when in the procedure you would add the indicator.

....

.... [1]

(c) The concentration of chlorate(I) ions can also be determined by adding an excess of hydrogen peroxide to the sample of bleach and measuring the volume of oxygen gas produced.

$$H_2O_2 + NaClO \rightarrow NaCl + O_2 + H_2O$$



When an excess of aqueous hydrogen peroxide was added to 5.0 cm³ of a different bleach solution, 82 cm³ of oxygen was produced at room temperature and pressure.

Calculate the concentration of ClO^- ions in this bleach solution.

concentration of ClO^- = ... mol dm^{-3} [2]

Topic: **Chem 25 Q# 218/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(d) Trichlorocyanuric acid, $C_3Cl_3N_3O_3$, acts as a chlorine buffer and disinfectant for swimming pools. It reacts with water to give chloric(I) acid, $HClO$.

$$C_3Cl_3N_3O_3 + 3H_2O \rightleftharpoons C_3H_3N_3O_3 + 3HClO$$

(i) Write the expression for K_c for this equilibrium.

K_c =

[1]

(ii) In outdoor swimming pools, the $HClO$ is decomposed by sunlight. The decomposition of $HClO$ is a redox reaction which forms a gas that relights a glowing splint.

Describe and explain the effect of the decomposition of $HClO$ on the equilibrium in **(d)**. State the effect on K_c.

....

....

effect on K_c ....

[2]

(iii) The decomposition of $HClO$ is a redox reaction.

Suggest an equation for this reaction.

.... [1]

(e) The buffer solution in blood is a mixture of carbonic acid, H_2CO_3, and hydrogencarbonate ions, HCO_3^-. Healthy blood has a pH of 7.40.

$$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_a = 7.94 \times 10^{-7}\ \text{mol dm}^{-3}$$

(i) Explain how this buffer system acts to control the blood pH. Include equations in your answer.

....

....

....

.... [2]

(ii) A patient's blood has a $[HCO_3^-]:[H_2CO_3]$ ratio of 9.5 : 1.

Calculate the pH of the patient's blood.

pH = ... [2]

[Total: 16]

Topic: **Chem 25 Q# 219/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Dicarboxylic acids dissociate in stages.

$$HO_2C(CH_2)_nCO_2H \overset{\text{stage 1}}{\rightleftharpoons} HO_2C(CH_2)_nCO_2^- + H^+ \overset{\text{stage 2}}{\rightleftharpoons} {}^-O_2C(CH_2)_nCO_2^- + 2H^+$$

(a) The pK_a values for stage 1 and stage 2 for some dicarboxylic acids are listed below.

n in $HO_2C(CH_2)_nCO_2H$	pK_a(1) for stage 1	pK_a(2) for stage 2
1	2.83	5.69
2	4.16	5.61
3	4.31	5.41

For comparison, the pK_a of ethanoic acid, CH_3CO_2H, is 4.76.

(i) State the mathematical relationship between pK_a and the acid dissociation constant K_a.

.... [1]

(ii) With reference to the table above, suggest why the pK_a(1) values

- are all smaller than the pK_a of ethanoic acid,

....

....

....

- become larger as n increases.

....

[3]

(iii) Suggest why all the pK_a(2) values in the table above are larger than the pK_a of ethanoic acid.

....

.... [1]

(b) The monosodium salts of edible dicarboxylic acids are added to some foodstuffs as buffers.

(i) Explain what is meant by the term *buffer solution*.

....

.... [2]

(ii) Write two equations to show how monosodium butanedioate, $HO_2CCH_2CH_2CO_2Na$, acts as a buffer.

....

.... [2]

Topic: **Chem 25 Q# 220/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 One method of producing hydrogen from natural gas is the reaction between hydrogen sulfide and methane.

$$2H_2S(g) + CH_4(g) \rightleftharpoons CS_2(g) + 4H_2(g)$$

(a) Write the expression for K_p for this reaction, and state its units.

K_p =

units ....

[2]

(b) The initial partial pressures of the two gases in a mixture at 1000 K are recorded.

$H_2S(g)$ 200 atm $CH_4(g)$ 100 atm

The mixture is left to reach equilibrium.

It is found that the equilibrium partial pressure of $CS_2(g)$ is 2 atm and that of the remaining $CH_4(g)$ is 98 atm.

(i) Calculate the equilibrium partial pressures of $H_2S(g)$ and $H_2(g)$.

$p(H_2S)$ = ... atm

$p(H_2)$ = ... atm

[2]

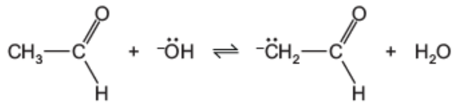
(ii) Calculate the value of K_p at this temperature.

K_p = ... [1]

Topic: **Chem 25 Q# 221/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(b) **(i)** A three-step mechanism has been proposed for the reaction in **(a)**.

step 1



(ii) Describe the chemical behaviour of CH_3CHO in step 1.

.... [1]

Topic: **Chem 25 Q# 222/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(c) **(i)** Explain what is meant by a *partition coefficient*.

....

.... [1]

(ii) The partition coefficient of a particular pesticide between hexane and water is 6.0. A solution contains 0.0042 g of the pesticide dissolved in 25 cm^3 of water. The solution is shaken with 25 cm^3 of hexane.

Calculate the mass of pesticide that will be dissolved in the hexane layer at equilibrium.

[2]

Topic: **Chem 25 Q# 223/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Silver sulfate, Ag_2SO_4, is sparingly soluble in water. The concentration of its saturated solution is 2.5×10^{-2} mol dm^{-3} at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of Ag_2SO_4, and state its units.

K_{sp} =

units: .... [1]

(ii) Calculate the value for $K_{sp}(Ag_2SO_4)$ at 298 K.

K_{sp} = ... [1]

Topic: **Chem 25 Q# 224/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) Solutions of iron(III) sulfate are acidic due to the following equilibrium.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad K_a = 8.9 \times 10^{-4}\,mol\,dm^{-3}$$

Calculate the pH of a 0.1 mol dm^{-3} solution of iron(III) sulfate, $Fe_2(SO_4)_3$.

pH = ...
[2]

[Total: 13]

Topic: **Chem 25 Q# 225/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(d) Phosphate ions in water can be removed by adding a solution containing $Ca^{2+}(aq)$ ions, which form a precipitate of calcium phosphate, $Ca_3(PO_4)_2$.

(i) Write an expression for the K_{sp} of $Ca_3(PO_4)_2$.

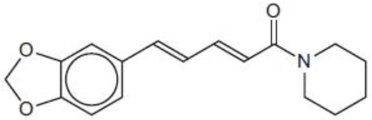
K_{sp} =

(ii) The solubility of $Ca_3(PO_4)_2$ is 2.50×10^{-6} mol dm^{-3} at 298 K.

Calculate the solubility product, K_{sp}, of $Ca_3(PO_4)_2$ at this temperature. Include the units.

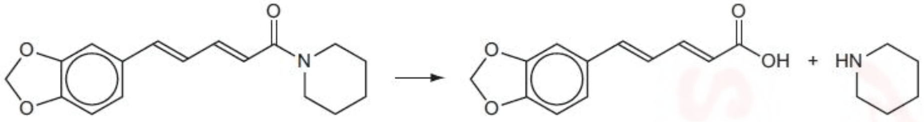
K_{sp} = ... units ....
[4]

3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:



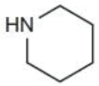
piperine piperic acid piperidine

(c) **(i)** Write the expression for K_w.

....

(ii) Use your expression and the value of K_w in the *Data Booklet* to calculate the pH of 0.150 mol dm^{-3} NaOH(aq).

(iii) The pH of a 0.150 mol dm^{-3} solution of piperidine is 11.9.



piperidine

Suggest why this answer differs from your answer in **(c)(ii)**.

....

.... [4]

(d) 20.0 cm^3 of 0.100 mol dm^{-3} HCl was slowly added to a 10.0 cm^3 sample of 0.150 mol dm^{-3} piperidine. The pH was measured throughout the addition.

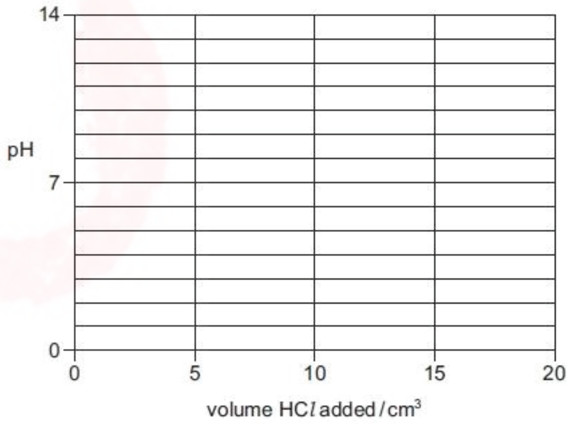
(i) Calculate the number of moles of HCl remaining at the end of the addition.

moles of HCl = ...

(ii) Hence calculate the [H$^+$] and the pH at the end of the addition.

pH = ...

(iii) On the following axes, sketch how the pH will change during the addition of a total of 20.0 cm^3 of 0.100 mol dm^{-3} HCl. Mark clearly where the end point occurs.



(iv) From the following list of indicators, put a tick in the box by the side of the indicator most suitable for this titration.

indicator	pH at which colour changes	place **one tick only** in this column
A	0 - 1	
B	3 - 4	
C	11 - 12	
D	13 - 14	

[6]

[Total: 16]

(c) A number of analytical and separation techniques rely on substances having different partition coefficients.

State what is meant by the term *partition coefficient*.

[1]

(d) The partition coefficient of **X** between ethoxyethane and water is 40.0.
A solution contains 4.00 g of **X** dissolved in 0.500 dm^3 of water.

Calculate the mass of **X** that can be extracted from this aqueous solution by shaking it with

(i) 0.050 dm^3 of ethoxyethane,

(ii) two successive portions of 0.025 dm^3 of ethoxyethane.

[4]

Using the symbol **HZ** to represent a Brønsted-Lowry acid,

(c) **(i)** Explain what is meant by a *buffer solution*.

(ii) Explain how the working of a buffer solution relies on a reversible reaction involving a Brønsted-Lowry acid such as **HZ** and a Brønsted-Lowry base such as **Z**⁻.

[4]

(d) Propanoic acid, $CH_3CH_2CO_2H$, is a weak acid with $K_a = 1.34 \times 10^{-5}$ mol dm^{-3}.

(i) Calculate the pH of a 0.500 mol dm^{-3} solution of propanoic acid.

Buffer solution **F** was prepared by adding 0.0300 mol of sodium hydroxide to 100 cm^3 of a 0.500 mol dm^{-3} solution of propanoic acid.

(ii) Write an equation for the reaction between sodium hydroxide and propanoic acid.

(iii) Calculate the concentrations of propanoic acid and sodium propanoate in buffer solution **F**.

[propanoic acid] = ... mol dm^{-3}

[sodium propanoate] = ... mol dm^{-3}

(iv) Calculate the pH of buffer solution **F**.

pH = ...

[6]

Topic: **Chem 25 Q# 229/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) The reaction between Fe^{3+} ions and I^- ions is an equilibrium reaction.

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$$

(iii) Write the expression for K_c for this reaction, and state its units.

K_c =

units .... [2]

An experiment was carried out using solutions of $Fe^{3+}(aq)$ and $I^-(aq)$ of equal concentrations. 100 cm^3 of each solution were mixed together, and allowed to reach equilibrium.

The concentrations at equilibrium of $Fe^{3+}(aq)$ and $I_2(aq)$ were as follows.

$[Fe^{3+}(aq)] = 2.0 \times 10^{-4}\,mol\,dm^{-3}$

$[I_2(aq)] = 1.0 \times 10^{-2}\,mol\,dm^{-3}$

(iv) Use these data, together with the equation given in **(c)**, to calculate the concentrations of $Fe^{2+}(aq)$ and $I^-(aq)$ at equilibrium.

$[Fe^{2+}(aq)]$ = ... $mol\,dm^{-3}$

$[I^-(aq)]$ = ... $mol\,dm^{-3}$

(v) Calculate the K_c for this reaction.

K_c = ... [4]

Topic: **Chem 25 Q# 230/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine	$H_3N^+CH_2CO_2^-$
lysine	$H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid	$H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

(b) Some organic compounds have very different solubilities in water and in organic solvents such as hexane. They may be extracted from an aqueous reaction mixture by shaking the mixture with portions of hexane and separating the two layers.
The process of distribution of a compound between two solvents is called *partition*.

(i) State what is meant by the term *partition coefficient*.

....

....

.... [1]

Topic: **Chem 25 Q# 231/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(b) Water ionises to a small extent as follows.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \qquad \Delta H = +58\,kJ\,mol^{-1}$$

(i) Write an expression for K_c for this reaction.

....

(ii) Write down the expression for K_w, the ionic product of water, and explain how this can be derived from your K_c expression in **(i)**.

....

....

(iii) State and explain how the value of K_w for hot water will differ from its value for cold water.

....

.... [3]

(c) K_w can be used to calculate the pH of solutions of strong and weak bases.

(i) Use the value of K_w in the *Data Booklet* to calculate the pH of 0.050 mol dm^{-3} NaOH.

pH = ...

Ammonia ionises slightly in water as follows.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The following expression applies to this equilibrium.

$$[H_2O] \times K_c = [NH_4^+][OH^-]/[NH_3] = 1.8 \times 10^{-5}\,mol\,dm^{-3}$$

(ii) Calculate [OH$^-$(aq)] in a 0.050 mol dm^{-3} solution of NH_3. You may assume that only a small fraction of the NH_3 ionises, so that [NH_3] at equilibrium remains at 0.050 mol dm^{-3}.

[OH$^-$(aq)] = ...

(iii) Use the value of K_w in the *Data Booklet*, and your answer in **(ii)**, to calculate [H$^+$(aq)] in 0.050 mol dm^{-3} NH_3(aq).

[H$^+$(aq)] = ...

(iv) Calculate the pH of this solution.

pH = ... [6]

[Total: 11]

Topic: **Chem 25 Q# 232/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 The most typical oxides of tin and lead are SnO, SnO_2, PbO and PbO_2.

The following two generalisations can be made about the oxides of the elements in Group IV.

- As the metallic character of the elements increases down the Group, the oxides become more basic.
- The oxides of the elements in their higher oxidation states are more acidic than the oxides of the elements in their lower oxidation states.

(c) Lead(II) chloride is slightly soluble in water.

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K_{sp} = 2.0 \times 10^{-5}$

(i) Write an expression for the solubility product, K_{sp} for lead(II) chloride and state its units.

K_{sp} = ... units ....

(ii) Calculate $[Pb^{2+}(aq)]$ in a saturated solution of $PbCl_2$.

....

....

An excess of $PbCl_2(s)$ is stirred with 0.50 mol dm^{-3} NaCl until equilibrium has been established. The excess $PbCl_2(s)$ is then filtered off.

(iii) Assuming $[Cl^-]$ remains at 0.50 mol dm^{-3} throughout, calculate the $[Pb^{2+}(aq)]$ in the remaining solution.

....

....

(iv) Suggest an explanation for the difference between this value and the value that you calculated in **(ii)**.

....
[4]

[Total: 10]

Topic: Chem 26 Q# 233/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(c) A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction 1 $\quad CH_3CHClCOOH + NH_3 \rightarrow CH_3CHClCOO^- + NH_4^+$

In an excess of NH_3, $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $\quad CH_3CHClCOO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

A student investigates the rate of reaction 2. The student mixes $CH_3CHClCOO^-$ with a large excess of NH_3. The graph in Fig. 5.3 shows the results obtained.

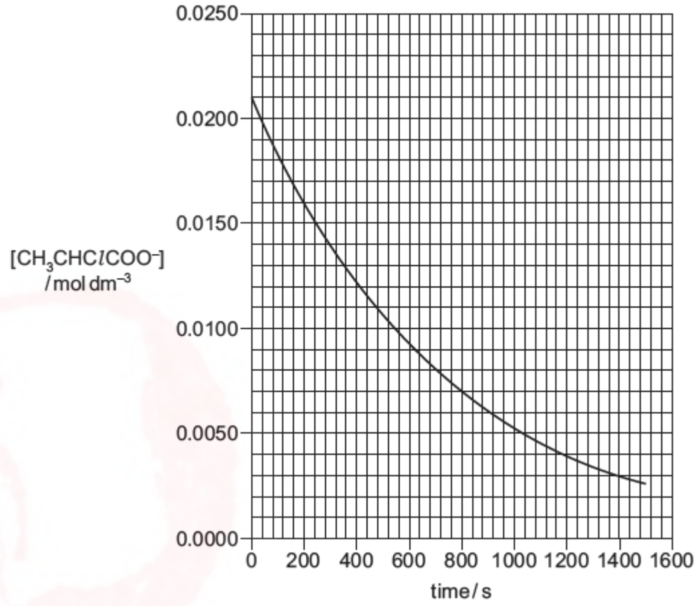


Fig. 5.3

(ii) Use the graph in Fig. 5.3 to show that reaction 2 is first order with respect to $[CH_3CHClCOO^-]$.

....

....

....

.... [2]

(iii) Explain why a **large** excess of NH_3 needs to be used in order to obtain the results in Fig. 5.3.

....

.... [1]

(iv) The student measures the effect of changing the concentration of NH_3 on the rate of reaction 2. Table 5.1 shows the results obtained.

Table 5.1

experiment	[$CH_3CHClCOO^-$] / mol dm^{-3}	[NH_3] / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
1	0.00120	0.00300	1.47×10^{-5}
2	0.00120	0.00450	2.21×10^{-5}

Use the information in Table 5.1 and in **(c)(ii)** to determine whether the nucleophilic substitution reaction proceeds via an S_N1 or an S_N2 mechanism.
Explain your answer.

....

....

....

.... [2]

(v) Describe the effect of an increase in temperature on the rate of reaction of $CH_3CHClCOO^-$ and NH_3.
Explain your answer.

....

....

....

.... [2]

Topic: **Chem 26 Q# 234/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Dinitrogen pentoxide, N_2O_5, is dissolved in an inert solvent (solv) and the rate of decomposition of N_2O_5 is investigated. This reaction produces nitrogen dioxide, which remains in solution, and oxygen gas.

$$N_2O_5(solv) \rightarrow 2NO_2(solv) + \tfrac{1}{2}O_2(g)$$

(a) Suggest what measurements could be used to follow the rate of this reaction from the given information.

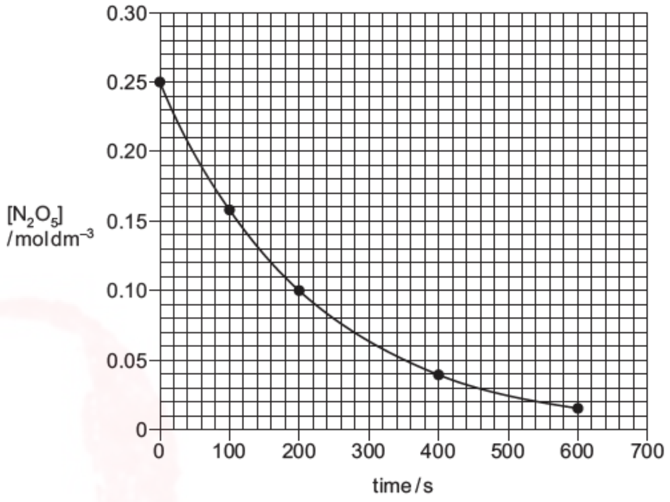
....

.... [1]

(b) In a separate experiment, the rate of the decomposition of $N_2O_5(g)$ is investigated.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

The graph shows the results obtained.



The reaction is first order with respect to N_2O_5. This can be confirmed from the graph using half-lives.

(i) Explain the term *half-life of a reaction*.

....

.... [1]

(ii) Determine the half-life of this reaction. Show your working on the graph.

half-life = ... s [1]

(iii) Suggest the effect on the half-life of this reaction if the initial concentration of N_2O_5 is halved.

.... [1]

(c) **(i)** Use the graph in **5(b)** to determine the rate of reaction at 200 s. Show your working.

rate = ...

units = ...
[2]

The rate equation for this reaction is shown.

$$\text{rate} = k[N_2O_5]$$

(ii) Use your answer to **(c)(i)** to calculate the value of the rate constant, *k*, for this reaction and state its units.

k = ... units .... [1]

(d) Nitrogen dioxide reacts with ozone, O_3, as shown.

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

The rate equation for this reaction is rate = $k[NO_2][O_3]$.

Suggest a possible two-step mechanism for this reaction.

....

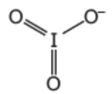
.... [2]

[Total: 9]

Topic: **Chem 26 Q# 235/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Iodates are compounds that contain the IO_3^- anion.

(a) The IO_3^- anion is shown.



(d) A student collects some data for the reaction of H_2O_2 with acidified IO_3^-, as shown in the table.

experiment	$[H_2O_2]$ / mol dm^{-3}	$[IO_3^-]$ / mol dm^{-3}	$[H^+]$ / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
1	0.0500	0.0700	0.025	1.47×10^{-5}
2	0.100	0.0700	0.050	2.94×10^{-5}
3	0.100	0.140	0.025	5.88×10^{-5}
4	0.150	0.140	0.025	8.82×10^{-5}

(i) Use the data to determine the order of reaction with respect to $[H_2O_2]$, $[IO_3^-]$ and $[H^+]$.

Show your reasoning.

order with respect to $[H_2O_2]$ = ...

....

....

....

order with respect to $[IO_3^-]$ = ...

....

....

....

order with respect to $[H^+]$ = ...

....

....

....
[3]

(ii) Use your answer to **(d)(i)** to write the rate equation for this reaction.

rate = ... [1]

(iii) Calculate the value of the rate constant, *k*, using data from experiment 4 and your answer to **(d)(ii)**.

Give the units of *k*.

k = ...

units = ...
[2]

Topic: **Chem 26 Q# 236/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide, NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

The rate equation for the forward reaction is shown.

$$\text{rate} = k[NO]^2[O_2]$$

(a) Complete the following table.

the order of reaction with respect to [NO]	
the order of reaction with respect to $[O_2]$	
the overall order of reaction	

[1]

(b) Two separate experiments are carried out at 30 °C to determine the rate of the forward reaction.

experiment	[NO] / mol dm^{-3}	$[O_2]$ / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1	0.00300	0.00200	1.51×10^{-4}
2		0.00500	6.05×10^{-5}

(i) Use the data for experiment 1 to calculate the value of the rate constant, *k*. State the units of *k*.

k = ... units = ...
[2]

(ii) Calculate the value of [NO] in experiment 2.

[NO] = ... mol dm^{-3} [1]

(c) Define the term *rate-determining step*.

.... [1]

(d) Peroxodisulfate ions, $S_2O_8^{2-}$, react with iodide ions, I^-.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

The rate equation for the reaction in the absence of any catalyst is shown.

$$\text{rate} = k[S_2O_8^{2-}][I^-]$$

(i) Suggest equations for a two-step mechanism for this reaction, stating which of the two steps is the rate-determining step.

step 1 ....

step 2 ....

rate-determining step = ...

[2]

(ii) A large excess of peroxodisulfate ions is mixed with iodide ions. Immediately after mixing, $[I^-] = 0.00780$ mol dm^{-3}. Under the conditions used, the half-life of $[I^-]$ is 48 seconds.

Calculate the iodide ion concentration 192 seconds after the peroxodisulfate and iodide ions are mixed.

iodide ion concentration = ... mol dm^{-3} [1]

[Total: 8]

Topic: **Chem 26 Q# 237/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** Manganese(IV) oxide, MnO_2, catalyses the decomposition of hydrogen peroxide, H_2O_2, as shown.

$$2H_2O_2(aq) \xrightarrow{MnO_2} 2H_2O(l) + O_2(g)$$

The mechanism involves the formation of the intermediate species, Mn^{2+}, in the first step which is subsequently used up in the second step.

(b) The equation for the decomposition of hydrogen peroxide without a catalyst is shown.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Under certain conditions this reaction is found to be first order with respect to hydrogen peroxide, with a rate constant, *k*, of 2.0×10^{-8} s^{-1} at 298 K.

Calculate the initial rate of decomposition of a 0.75 mol dm^{-3} hydrogen peroxide solution at 298 K.

initial rate = ... mol dm^{-3} s^{-1} [1]

(c) A four-step mechanism is suggested for the reaction between hydrogen peroxide and iodide ions in an acidic solution.

step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$
step 2 $H^+ + IO^- \rightarrow HIO$
step 3 $HIO + I^- \rightarrow I_2 + OH^-$
step 4 $OH^- + H^+ \rightarrow H_2O$

Step 1 is the rate-determining step.

(i) State what is meant by the term *rate-determining step*.

....

.... [1]

(ii) Use this mechanism to construct a balanced equation for this reaction.

.... [1]

(iii) Deduce the order of reaction with respect to each of the following.

H_2O_2 = ... I^- = ... H^+ = ... [1]

Topic: **Chem 26 Q# 238/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 Gold is an unreactive metal that can only be oxidised under specific conditions.

(b) Aqueous gold(III) chloride, $AuCl_3$, reacts with aqueous hydrogen peroxide, H_2O_2, under certain conditions, forming Au, O_2 and HC*l*.

A student carries out separate experiments using different initial concentrations of $AuCl_3$ and H_2O_2. The initial rate of each reaction is measured.

The table shows the results that are obtained.

experiment	$[AuCl_3]$ / mol dm^{-3}	$[H_2O_2]$ / mol dm^{-3}	rate of production of O_2(g) / dm^3 minute^{-1}
1	0.05	0.50	7.66×10^{-2}
2	0.10	0.50	1.53×10^{-1}
3	0.15	1.00	4.60×10^{-1}

(i) Write an equation for the reaction of $AuCl_3$ with H_2O_2.

.... [1]

(ii) Determine the rate equation of the reaction.

Show your reasoning, quoting data from the table.

....

....

....

....

.... [3]

(iii) Use the results of experiment 2 to calculate the value of the rate constant, *k*, for this reaction.

Include the units of *k*.

rate constant, *k* = ...

units = ... [2]

Topic: **Chem 26 Q# 239/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 When $ClNO_2$ reacts with NO an equilibrium is established.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

In each $ClNO_2$ molecule the nitrogen atom is bonded to the chlorine atom and bonded to each of the oxygen atoms separately.

(b) The reaction between $ClNO_2$ and NO is first order with respect to each reactant.

(i) Write the rate equation for this reaction.

rate = ... [1]

(ii) Deduce the units of the rate constant, *k*, when the concentrations of both gases are measured in mol dm^{-3} and the rate is measured in mol dm^{-3} s^{-1}.

.... [1]

(iii) State and explain whether or not the reaction **could** take place in a single step.

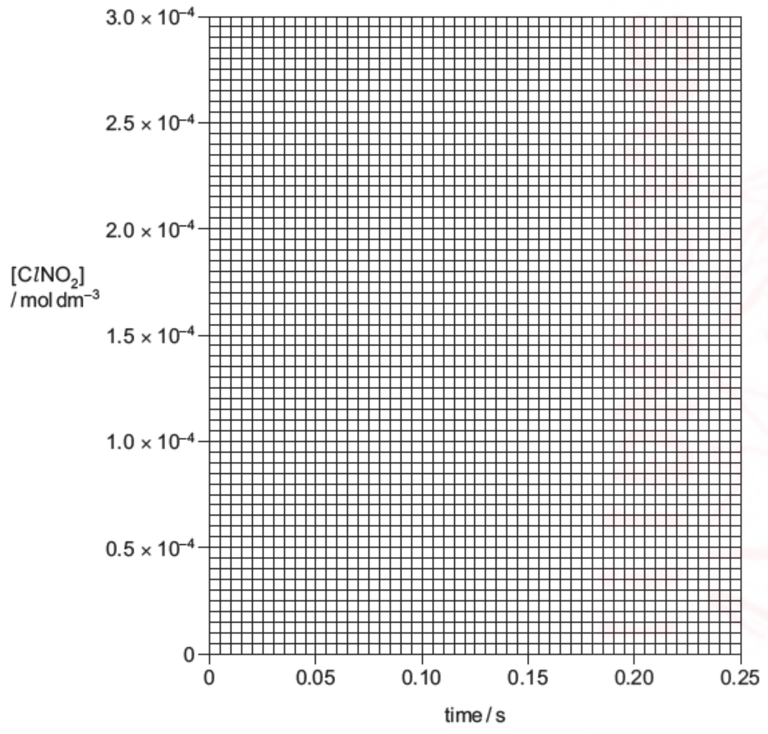
....

....

.... [1]

(c) An experiment is carried out in which the initial [ClNO$_2$] is 2.0×10^{-4} mol dm^{-3}. A large excess of NO is used. The initial rate of reaction is 1.0×10^{-4} mol dm^{-3} s^{-1}. The rate of the reaction is assumed to be constant for the first 0.20 seconds.

(i) Draw a graph on the grid to show how the concentration of ClNO$_2$ varies for the first 0.20 seconds.



[2]

(ii) Deduce the concentration of the NO$_2$ product at 0.20 seconds.

.... [1]

(iii) After 20 seconds the concentration of ClNO$_2$ remains constant.

Explain this observation.

.... [1]

Topic: **Chem 26 Q# 240/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Chlorate(I) ions undergo the following reaction under aqueous conditions.

$$2NH_3 + ClO^- \rightarrow N_2H_4 + Cl^- + H_2O$$

A series of experiments was carried out at different concentrations of ClO$^-$ and NH$_3$.

The table shows the results obtained.

experiment	[ClO$^-$] / mol dm^{-3}	[NH$_3$] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.200	0.100	0.256
2	0.400	0.200	2.05
3	0.400	0.400	8.20

(i) Use the data in the table to determine the order with respect to each reactant, ClO$^-$ and NH$_3$.

Show your reasoning.

....

....

....

....

....

.... [2]

(ii) Write the rate equation for this reaction.

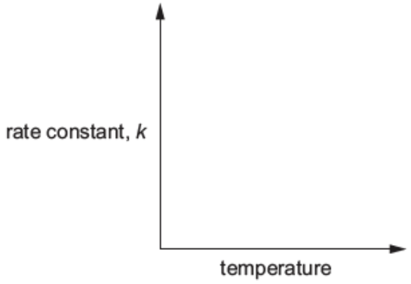
rate = ... [1]

(iii) Use the results of experiment 1 to calculate the rate constant, k, for this reaction. Include the units of k.

k = ...

units = ...
[2]

(iv) On the axes sketch a graph to show how the value of k changes as temperature is increased.



[1]

(b) In another experiment, the reaction between chlorate(I) ions and iodide ions in aqueous alkali was investigated.

A solution of iodide ions in aqueous alkali was added to a large excess of chlorate(I) ions and $[I^-]$ was measured at regular intervals.

(i) Describe how the results of this experiment can be used to confirm that the reaction is first-order with respect to $[I^-]$.

....

....

.... [2]

A three-step mechanism for this reaction is shown.

step 1 $ClO^- + H_2O \rightarrow HClO + OH^-$

step 2 $I^- + HClO \rightarrow HIO + Cl^-$

step 3 $HIO + OH^- \rightarrow H_2O + IO^-$

(ii) Use this mechanism to deduce the overall equation for this reaction.

.... [1]

---

2 Nitrogen monoxide, NO(g), reacts with hydrogen, $H_2(g)$, under certain conditions.

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

(a) Define the term *rate of reaction*.

....

.... [1]

(b) Identify a change in the reaction mixture that would enable the rate of this reaction to be studied.

.... [1]

The rate equation for this reaction is given.

$$\text{rate} = k[NO]^2[H_2]$$

The result of an experiment in which NO reacted with H_2 is shown in the table.

initial [NO] / mol dm^{-3}	initial [H_2] / mol dm^{-3}	initial rate of reaction / mol dm^{-3} s^{-1}
2.50×10^{-3}	2.50×10^{-3}	1.27×10^{-3}

(c) Use the data and the rate equation to calculate a value for the rate constant k.
Give the units of k.

k = ...

units = ...
[2]

(d) A second experiment is performed at the same temperature. The initial concentration of $H_2(g)$ is 4.60×10^{-3} mol dm^{-3}. The initial rate of the reaction is 2.31×10^{-3} mol dm^{-3} s^{-1}.

Calculate the initial concentration of NO(g).

initial concentration of NO(g) = ... mol dm^{-3} [1]

(e) State the order of the reaction with respect to NO(g) and with respect to H_2(g), and the overall order of the reaction.

[NO]	
[H_2]	
overall order	

[1]

(f) The reaction is believed to proceed in three steps.

1 $2NO \rightarrow N_2O_2$

2 $N_2O_2 + H_2 \rightarrow N_2O + H_2O$

3 $N_2O + H_2 \rightarrow N_2 + H_2O$

(i) Deduce which of the three steps is the rate-determining step.

.... [1]

(ii) Explain your answer to **(i)**.

....

....

.... [1]

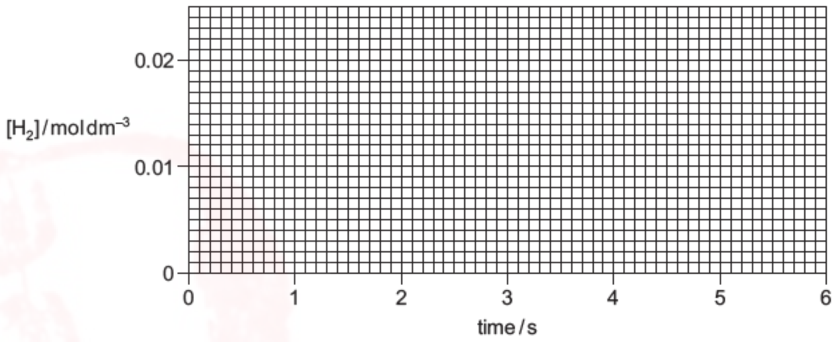
(g) A third experiment is performed under different conditions. A small amount of H_2(g) of concentration 0.0200 mol dm^{-3} is mixed with a large excess of NO(g). The concentration of H_2(g) is found to have a constant half-life of 2.00 seconds under the conditions used.

(i) Define the term *half-life*.

....

.... [1]

(ii) Use the axes below to construct a graph of the variation in the concentration of H_2(g) during the first 6 seconds under the conditions used.



[2]

(h) NO(g) acts as a catalyst in the oxidation of atmospheric sulfur dioxide.

(i) Give two equations to describe how NO(g) acts as a catalyst in this process.

equation 1 ....

equation 2 ....

[1]

(ii) Explain why NO(g) can be described as a catalyst in this reaction.

....

.... [1]

(iii) Describe, with the aid of an equation, an environmental consequence of the oxidation of atmospheric sulfur dioxide.

....

.... [1]

[Total: 14]

Topic: **Chem 26 Q# 242/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(f) Some transition metals and their compounds act as catalysts. The catalysis can be classified as heterogeneous or homogeneous.

Complete the table by placing **one** tick (✓) in each row to indicate the type of catalysis in each reaction.

	heterogeneous	homogeneous
Fe in the Haber process		
Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction		
NO_2 in the oxidation of SO_2		
V_2O_5 in the Contact process		

[2]

[Total: 14]

Topic: **Chem 26 Q# 243/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 The compound nitrosyl bromide, NOBr, can be formed by the reaction shown.

$$2NO + Br_2 \rightleftharpoons 2NOBr$$

(c) The rate of the reaction was measured at various concentrations of the two reactants, NO and Br_2, and the following results were obtained.

experiment	[NO] / mol dm^{-3}	[Br_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.03	0.02	3.4×10^{-3}
2	0.03	0.04	6.8×10^{-3}
3	0.09	0.04	6.1×10^{-2}
4	0.12	0.06	to be calculated

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[NO]^a[Br_2]^b$$

(i) What is meant by the term *order of reaction* with respect to a particular reagent?

....

.... [1]

(ii) Use the data in the table to deduce the values of *a* and *b* in the rate equation. Show your reasoning.

....

....

....

.... [2]

(iii) Use the data in the table to calculate the initial rate for experiment 4.

initial rate = ... mol dm^{-3} s^{-1} [1]

(iv) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction. Include the units of *k*.

rate constant, *k* = ... units .... [2]

(v) By considering the rate equation, explain why the rate decreases with decreasing temperature.

....

.... [1]

(d) The reaction between X and Y was studied.

$$2X + Y \rightarrow Z$$

The following sequence of steps is a proposed mechanism for the reaction.

step 1 $2X \rightarrow V$
step 2 $V + Y \rightarrow Z$

The general form of the rate equation for this reaction is as follows.

$$\text{rate} = k[X]^m[Y]^n$$

Step 1 is the slower step in the mechanism.

Deduce the values of *m* and *n* in the rate equation.

m = ... *n* = ...

[1]

Topic: **Chem 26 Q# 244/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Describe a suitable method for studying the rate of this reaction at a temperature of 40 °C, given the following.

- a solution of 0.10 mol dm^{-3} 1-chloro-1-phenylethane, labelled **A**
- a solution of 0.10 mol dm^{-3} sodium hydroxide, labelled **B**
- 0.10 mol dm^{-3} HCl
- volumetric glassware
- ice-cold solvent
- stopclock
- access to standard laboratory equipment and chemicals

[4]

(b) The rate of this reaction was measured at different initial concentrations of the two reagents. The table shows the results obtained.

experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	0.20	0.15	to be calculated

(i) Deduce the order of reaction with respect to each of $[C_6H_5CHClCH_3]$ and $[OH^-]$. Explain your reasoning.

order with respect to $[C_6H_5CHClCH_3]$ ....

order with respect to $[OH^-]$ ....

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm^{-3} s^{-1}

units of *k* = ...

[1]

(iii) Calculate the relative rate for experiment 4.

relative rate for experiment 4 = ... [1]

Topic: **Chem 26 Q# 245/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Chlorine dioxide undergoes the following reaction in aqueous solution.

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O$$

The initial rate of the reaction was measured at different initial concentrations of ClO_2 and OH^-. The table shows the results obtained.

experiment	$[ClO_2]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.25×10^{-2}	1.30×10^{-3}	2.33×10^{-4}
2	2.50×10^{-2}	1.30×10^{-3}	9.34×10^{-4}
3	2.50×10^{-2}	2.60×10^{-3}	1.87×10^{-3}

(i) Use the data in the table to determine the rate equation, showing the order with respect to each reactant. Show your reasoning.

rate equation = ...

[3]

(ii) Calculate the value of the rate constant, *k*, using the data from experiment 2. State its units.

k = ... units .... [2]

(b) **(i)** Explain the difference between heterogeneous and homogeneous catalysts.

....

....

.... [1]

(ii) Complete the table using ticks (✓) to indicate whether the catalyst used in the reaction is heterogeneous or homogeneous.

catalysed reaction	heterogeneous	homogeneous
manufacture of ammonia in the Haber process		
removal of nitrogen oxides from car exhausts		
oxidation of sulfur dioxide in the atmosphere		

[2]

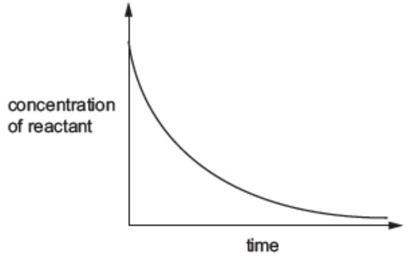
(c) Some reactions are catalysed by one of the products of the reaction. This is called autocatalysis. An example of autocatalysis is the reaction between acidified manganate(VII) ions, MnO_4^-, and ethanedioic acid, $(CO_2H)_2$. Mn^{2+} ions catalyse this reaction. The reaction is slow in the absence of a catalyst.

(i) Balance the equation for this reaction.

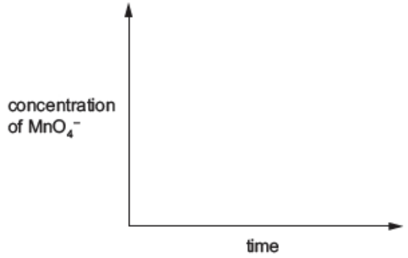
$......MnO_4^- + ...H^+ + ...(CO_2H)_2 \rightarrow ......Mn^{2+} + ...CO_2 + ...H_2O$

[2]

(ii) The graph shown is a concentration-time graph for a typical reaction.



On the axes below, sketch the curve you would expect for the autocatalysed reaction in **(i)**.



[2]

(d) **(i)** Describe, with the aid of a reaction pathway diagram, the effect of a catalyst on a reversible reaction. Suggest why catalysts are used in industrial processes.

....

....

.... [3]

Topic: **Chem 26 Q# 246/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Ethanal, CH_3CHO, dimerises in alkaline solution according to the following equation.

$$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

The initial rate of this reaction was measured, starting with different concentrations of CH_3CHO and OH^-. The following results were obtained.

$[CH_3CHO]$/mol dm^{-3}	$[OH^-]$/mol dm^{-3}	initial rate of reaction (relative values)
0.10	0.015	1
0.20	0.015	2
0.40	0.030	8

(i) Deduce the order of the reaction with respect to CH_3CHO.

.... [1]

(ii) Deduce the order of the reaction with respect to OH^-.

.... [1]

(iii) State the overall rate equation for this reaction.

rate = ... [1]

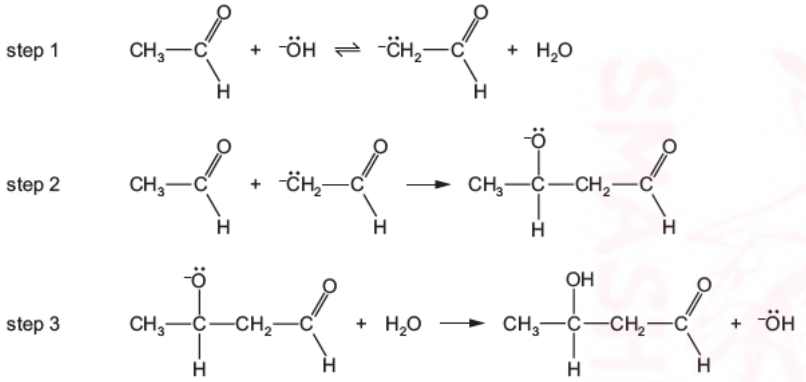
(iv) State the units for the rate constant, *k*.

.... [1]

(v) Calculate the initial rate of reaction (relative value) for a reaction where the [CH_3CHO] is $0.30\,mol\,dm^{-3}$ and [OH^-] is $0.030\,mol\,dm^{-3}$.

[1]

(b) (i) A three-step mechanism has been proposed for the reaction in **(a)**.



Using your rate equation in **(iii)**, predict which is the rate-determining step. Explain your answer.

rate-determining step ....

explanation ....

....

[2]

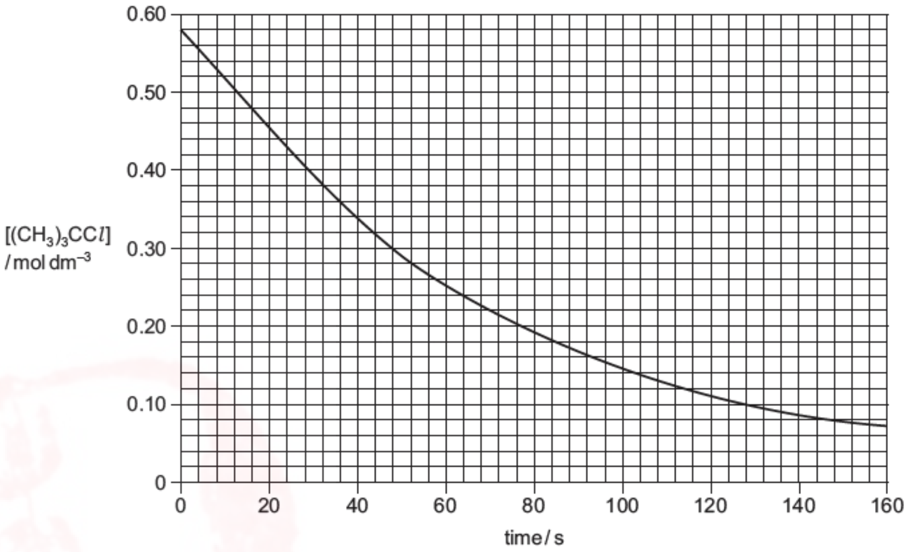
Topic: **Chem 26 Q# 247/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 In aqueous solution, 2-chloro-2-methylpropane, $(CH_3)_3CCl$, reacts with sodium hydroxide, NaOH. This is a nucleophilic substitution reaction.

$$(CH_3)_3CCl(aq) + NaOH(aq) \rightarrow (CH_3)_3COH(aq) + NaCl(aq)$$

The rate of this reaction was investigated using a **large excess** of sodium hydroxide.

(b) The graph below shows the results of the experiment.



The reaction is first order with respect to [$(CH_3)_3CCl$]. This can be confirmed from the graph using half-lives.

(i) What is meant by the *half-life* of a reaction?

....

.... [1]

(ii) Calculate the half-life for this reaction. Show all your working and show clearly any construction lines on the graph.

[1]

(iii) What would be the effect on the half-life of this reaction if the initial concentration of [$(CH_3)_3CCl$] was **doubled**?

.... [1]

(c) **(i)** Use the graph in **(b)** to determine the rate of reaction at 80 s.
Show all your working.

rate = ... units .... [2]

The rate equation for this reaction is shown.

rate = $k[(CH_3)_3CCl]$

(ii) Calculate the value of the rate constant, *k*, for this reaction and give its units.

k = ... units .... [1]

[Total: 9]

Topic: **Chem 26 Q# 248/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** The oxidation of nitrogen(II) oxide is shown in the equation.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

experiment number	[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.032	0.012	4.08×10^{-3}
2	0.032	0.024	8.15×10^{-3}
3	0.064	0.024	3.28×10^{-2}
4	0.096	0.036	

(i) Use the data in the table to determine the order with respect to each reactant. Show your reasoning.

....

....

....

....

(ii) Calculate the initial rate in experiment 4. Give your answer to **two** significant figures.

initial rate = ... mol dm^{-3} s^{-1}

(iii) Write the rate equation for this reaction.

....

(iv) Use the results of experiment 1 to calculate the rate constant, *k*, for this reaction.
Include the units of *k*.

rate constant, *k* = ... units ....
[6]

(b) **(i)** On the following axes

- draw two Boltzmann distribution curves, at two different temperatures, T_1 and T_2 ($T_2 > T_1$),
- label the curves and the axes.

(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction.

....

....

.... [5]

(c) The compound nitrosyl fluoride, NOF, can be formed by the following reaction.

$$2NO(g) + F_2(g) \rightleftharpoons 2NOF(g)$$

The rate is first order with respect to NO and F_2.
The reaction mechanism has **two** steps.

Suggest equations for the two steps of this mechanism, stating which is the rate determining slower step.

....

....

.... [2]

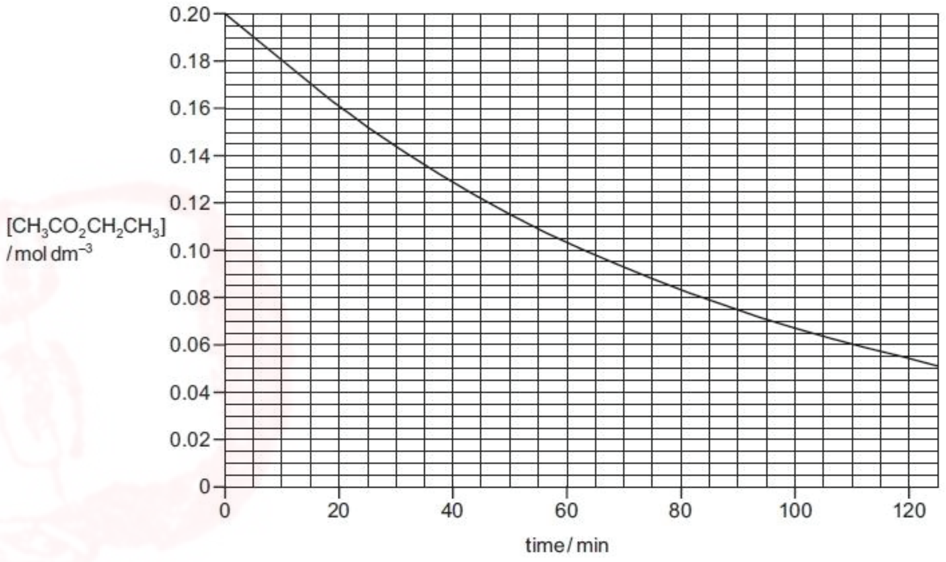
[Total: 13]

---

2 Ethyl ethanoate is hydrolysed slowly by water in the following acid-catalysed reaction.

$$CH_3CO_2CH_2CH_3 + H_2O \xrightarrow{H^+} CH_3CO_2H + CH_3CH_2OH$$

The concentration of ethyl ethanoate was determined at regular time intervals as the reaction progressed.
Two separate experiments were carried out, with different HC*l* concentrations.
The following graph shows the results of an experiment using [HC*l*] = 0.1 mol dm^{-3}.



(a) When the experiment was carried out using [HC*l*] = 0.2 mol dm^{-3}, the following results were obtained.

time / min	$[CH_3CO_2CH_2CH_3]$ / mol dm^{-3}
0	0.200
10	0.160
25	0.115
50	0.067
75	0.038
100	0.022
125	0.013

(i) Plot these data on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to show that the reaction is first order with respect to $CH_3CO_2CH_2CH_3$.

Show all your working, and show clearly any construction lines you draw on the graphs.

(iii) Use the graphs to calculate the order of reaction with respect to HC*l*.

Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant.

rate =

[7]

(b) **(i)** Why is it **not** possible to determine the order of reaction with respect to water in this experiment?

(ii) Although $[CH_3CO_2CH_2CH_3]$ decreases during each experiment, [HC*l*] remains the same as its initial value.

Why is this?

[2]

[Total: 9]

3 **(a)** Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysis.
Choose **one** example of each type, and for **each** example you should

- state what the catalyst is, and whether it is acting as a homogeneous or a heterogeneous catalyst,
- write a balanced equation for the reaction,
- outline how the catalyst you have chosen works to decrease the activation energy.

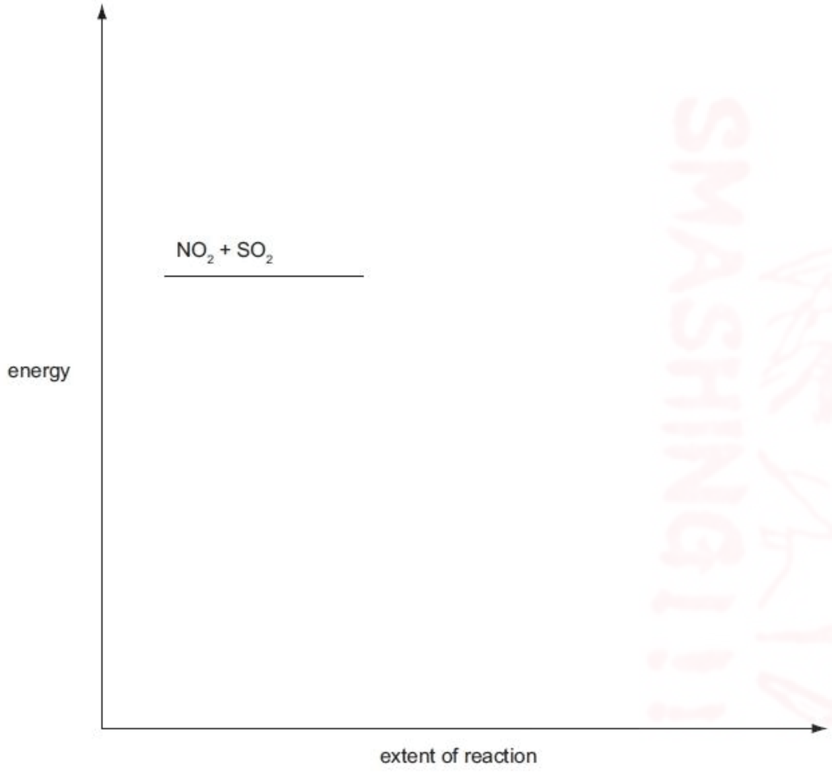
[8]

(b) The reaction between SO_2, NO_2 and O_2 occurs in two steps.

$$NO_2 + SO_2 \rightarrow NO + SO_3 \qquad \Delta H_1^\circ = -88\,kJ\,mol^{-1}$$
$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \qquad \Delta H_2^\circ = -57\,kJ\,mol^{-1}$$

The activation energy of the first reaction, E_{a_1}, is higher than that of the second reaction, E_{a_2}.

Use the axes below to construct a fully-labelled reaction pathway diagram for this reaction, labelling E_{a_1}, E_{a_2}, ΔH_1° and ΔH_2°.



[2]

[Total: 10]

Topic: **Chem 26 Q# 251/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(b) At 800 K, nitrogen monoxide reacts with hydrogen according to the following equation.

equation **I** $\qquad 2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

The following table shows how the initial rate of this reaction depends on the partial pressures of the reagents.

experiment	$p(H_2)$ / atm	p(NO) / atm	initial rate / atm s^{-1}
1	0.64	1.60	1.50×10^{-7}
2	0.64	0.80	3.75×10^{-8}
3	0.32	1.60	7.50×10^{-8}

(i) Find the order of the reaction with respect to each reactant, explaining how you arrive at your answer.

(ii) Write down the rate equation and the units of the rate constant.

The following mechanism has been put forward for this reaction.

step 1 $\quad NO + NO \rightarrow N_2O + O$
step 2 $\quad H_2 + O \rightarrow H_2O$
step 3 $\quad H_2 + N_2O \rightarrow N_2 + H_2O$

(iii) Show how the overall stoichiometric equation **I** can be derived from the three equations for the individual steps given above.

(iv) Suggest which of the three reactions in the mechanism is the rate determining step. Explain your answer.

[8]

Topic: **Chem 26 Q# 252/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Acetals are compounds formed when aldehydes are reacted with an alcohol and an acid catalyst. The reaction between ethanal and methanol was studied in the inert solvent dioxan.

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\text{methanol}}{2CH_3OH} \overset{H^+}{\rightleftharpoons} \underset{\text{acetal } \mathbf{A}}{CH_3CH(OCH_3)_2} + H_2O$$

(a) When the initial rate of this reaction was measured at various starting concentrations of the three reactants, the following results were obtained.

experiment number	$[CH_3CHO]$ /mol dm^{-3}	$[CH_3OH]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	relative rate
1	0.20	0.10	0.05	1.00
2	0.25	0.10	0.05	1.25
3	0.25	0.16	0.05	2.00
4	0.20	0.16	0.10	3.20

(i) Use the data in the table to determine the order with respect to each reactant.

order with respect to $[CH_3CHO]$ ....

order with respect to $[CH_3OH]$ ....

order with respect to $[H^+]$ ....

(ii) Use your results from part **(i)** to write the rate equation for the reaction.

....

(iii) State the units of the rate constant in the rate equation ....

(iv) Calculate the relative rate of reaction for a mixture in which the starting concentrations of all three reactants are 0.20 mol dm^{-3}.

relative rate = ...

[6]

(b) The concentration of the acetal product was measured when experiment number 1 was allowed to reach equilibrium. The result is included in the following table.

	$[CH_3CHO]$ /mol dm^{-3}	$[CH_3OH]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	[acetal **A**] /mol dm^{-3}	$[H_2O]$ /mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	$(0.20–x)$			x	
at equilibrium				0.025	

(i) Complete the second row of the table in terms of x, the concentration of acetal **A** at equilibrium. You may wish to consult the chemical equation opposite.

(ii) Using the [acetal **A**] as given, 0.025 mol dm^{-3}, calculate the equilibrium concentrations of the other reactants and products and write them in the third row of the table.

(iii) Write the expression for the equilibrium constant for this reaction, K_c, stating its units.

K_c = ... units = ...

(iv) Use your values in the third row of the table to calculate the value of K_c.

K_c = ...

[9]

[Total: 15]

Topic: **Chem 26 Q# 253/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 The combustion of fuels in motor vehicles, trains, aeroplanes and power stations produces the pollutant gas NO_2.

(d) In the atmosphere, NO_2 acts as a catalyst for the oxidation of SO_2 to SO_3.

$$SO_2(g) + ½\,O_2(g) \xrightarrow{NO_2} SO_3(g)$$

(i) What is the environmental significance of this reaction?

....

The oxidation takes place in two steps. The initial reaction is that between NO_2 and SO_2.

reaction 1 $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ $\Delta H = -168\,kJ\,mol^{-1}$

(ii) Write an equation to show how the NO_2 is regenerated in the second step of the oxidation.

....

(iii) Write an expression for the equilibrium constant, K_p for *reaction 1*, stating its units.

K_p =

units ....

(iv) If equal amounts of $NO_2(g)$ and $SO_2(g)$ are allowed to react at room temperature, it is found that 99.8% of the gases have been converted into products at equilibrium. Calculate a value for K_p.

K_p = ...

(v) The temperature of the atmosphere decreases with height. How will this affect the position of the equilibrium in *reaction 1*? Explain your answer.

....

.... [7]

[Total: 11]

Topic: Chem 27 Q# 254**/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Separate samples of 0.02 mol of calcium carbonate and 0.02 mol of barium carbonate are heated until completely decomposed to the metal oxide and carbon dioxide.

(a) State which of these two Group 2 carbonates requires the **higher** temperature before it begins to decompose. Explain your answer.

....

....

.... [2]

(b) After decomposition is complete, the 0.02 mol sample of calcium oxide is taken and added to 2.00 dm³ of water. A solution is formed with no solid present. Dilute sulfuric acid is then added dropwise until a precipitate is seen.

The same procedure is repeated with the 0.02 mol sample of barium oxide, using the same concentration solution of dilute sulfuric acid.

Identify the sample to which **most** sulfuric acid must be added to cause a precipitate to appear.

Explain your answer. You should refer to the solubilities of the precipitates and relevant energy terms in your answer.

....

....

....

.... [3]

(c) **(i)** Calculate the mass, in g, of CO_2 produced by the decomposition of 0.020 moles of calcium carbonate.

mass of CO_2 = ... g [1]

(ii) Calculate the minimum mass, in g, of propane that would, on complete combustion, produce the same mass of CO_2 calculated in **(c)(i)**.
Give your answer to three significant figures.

mass of propane = ... g [2]

[Total: 8]

Topic: **Chem 27 Q# 255/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(d) $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.

(ii) Construct an equation for the thermal decomposition of $(NH_4)_2Cr_2O_7$.

.... [1]

[Total: 15]

Topic: **Chem 27 Q# 256/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** The carbonates and hydroxides of Group 2 elements show similar trends in thermal stability.

Suggest and explain the variation in the trend in the thermal stability of the Group 2 hydroxides.

....

....

....

....

.... [3]

Topic: **Chem 27 Q# 257/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** The most common oxidation states of cobalt are +2 and +3.

Complete the electronic configurations of the following free ions.

- Co^{2+} [Ar] ....
- Co^{3+} [Ar] ....

[1]

(b) Co^{2+} and Co^{3+} both form complexes with $edta^{4-}$.

half-equation	$E^{\ominus}$/V
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$[Co(edta)]^- + e^- \rightleftharpoons [Co(edta)]^{2-}$	+0.38
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28

Use the data in the table to predict what happens, if anything, when separate aqueous solutions of Co^{3+} and $[Co(edta)]^-$ are left to stand in the air.

aqueous solution of Co^{3+}

....

....

aqueous solution of $[Co(edta)]^-$

....

....

[3]

(c) Hydrated cobalt(II) nitrate, $Co(NO_3)_2{\bullet}6H_2O$, is a red solid that behaves like hydrated magnesium nitrate, $Mg(NO_3)_2{\bullet}6H_2O$, when heated.

Describe in detail what you would expect to observe when crystals of $Co(NO_3)_2{\bullet}6H_2O$ are heated in a boiling tube, gently at first and then more strongly.

....

....

....

.... [2]

Topic: **Chem 27 Q# 258/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(d) Explain why the thermal stability of the Group 2 nitrates increases down the group.

....

....

....

.... [2]

[Total: 8]

Topic: **Chem 27 Q# 259/** ALvl Chemistry/2020/w/TZ 1/Paper 4(b)/Q# 2/www.SmashingScience.org

(ii) State and explain how the solubilities of the hydroxides of the Group 2 elements vary down the group.

....

....

....

....

....

....

.... [4]

Topic: **Chem 27 Q# 260/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** **(i)** Describe and explain the trend in the solubility of the Group 2 hydroxides down the group.

[4]

Group 2 hydroxides decompose on heating to give the corresponding metal oxide and water vapour.

(ii) Suggest which of $Mg(OH)_2$ and $Sr(OH)_2$ will decompose at a **lower** temperature.

Explain your answer.

[2]

[Total: 6]

Topic: **Chem 27 Q# 261/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Group 2 metals form stable carbonates and sulfates.

(i) State and explain the trend in the thermal stability of the Group 2 carbonates down the group.

[3]

(ii) The sulfates of Group 2 elements become less soluble down the group.

Explain this trend.

[3]

Topic: **Chem 27 Q# 262/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 The elements in Group 2 include magnesium, calcium, strontium and barium.

(b) The Group 2 metal nitrates decompose when heated.

(iii) Describe and explain the variation in thermal stability of the Group 2 metal nitrates down the group.

[3]

(c) Describe and explain the variation in the solubility of the Group 2 metal sulfates down the group.

[4]

[Total: 12]

Topic: **Chem 27 Q# 263/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Group 2 nitrates decompose when heated.

Write an equation for the decomposition of strontium nitrate.

.... [1]

(b) Describe and explain how the thermal stability of Group 2 nitrates changes with increasing atomic number.

....

....

....

....

.... [3]

(c) The variation in the thermal stability of Group 2 amides is similar to that of Group 2 nitrates.

(i) Suggest whether calcium amide, $Ca(NH_2)_2$, will decompose more or less readily than barium amide, $Ba(NH_2)_2$. Explain your answer.

....

.... [1]

(ii) $Ba(NH_2)_2$ decomposes when heated to form barium nitride, Ba_3N_2, and ammonia as the only products.

Write an equation for this reaction.

.... [1]

Topic: **Chem 27 Q# 264/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** The following table lists the solubilities of the hydroxides and carbonates of some of the Group 2 elements, **M**, at 25 °C.

element **M**	solubility / mol dm^{-3}	
	$M(OH)_2$	MCO_3
Mg	2.0×10^{-4}	1.5×10^{-3}
Ca	1.5×10^{-2}	1.3×10^{-4}
Sr	3.4×10^{-2}	7.4×10^{-5}
Ba	1.5×10^{-1}	9.1×10^{-6}

(i) Explain why the solubility of the Group 2 hydroxides, $M(OH)_2$, increases down the group.

....

....

....

....

.... [3]

(ii) Suggest a reason for the general decrease in the solubility of the Group 2 carbonates, MCO_3, down the group.

....

.... [1]

(iii) When carbon dioxide is passed through a saturated solution of calcium hydroxide (limewater), a white precipitate of calcium carbonate is formed.

Use the data in the table to deduce, for **each** of Mg, Sr and Ba, whether or not a saturated solution of its hydroxide could also be used to test for carbon dioxide.
Explain your answer. No calculations are required.

....

....

....

....

.... [2]

Topic: **Chem 27 Q# 265/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** The enthalpy change of solution, ΔH°_{sol}, of the Group 2 sulfates becomes more endothermic down the group.

State and explain the trend in the solubility of the Group 2 sulfates down the group.

....

....

....

....

.... [3]

Topic: **Chem 27 Q# 266/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) The decomposition temperatures of the Group 2 carbonates vary down the group.

State and explain the variation in the decomposition temperatures.

....

....

....

....

....

.... [3]

Topic: **Chem 27 Q# 267/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 (a) (i) State how the solubilities of the hydroxides of the Group 2 elements vary down the group.

.... [1]

(ii) Explain the factors that are responsible for this variation.

....

....

....

....

.... [3]

(c) Metal peroxides contain the $^-O–O^-$ ion.
The peroxides of the Group 2 elements, MO_2, decompose on heating to produce a single gas and the solid oxide, MO, only.

(i) Write an equation for the thermal decomposition of strontium peroxide, SrO_2.

.... [1]

(ii) Suggest how the temperature at which thermal decomposition of MO_2 occurs varies down Group 2.
Explain your answer.

....

....

....

....

.... [3]

(d) (i) The ethanedioates of the Group 2 elements, MC_2O_4, decompose on heating to produce a mixture of two different gases and the solid oxide, MO, only.

Complete the equation for the thermal decomposition of barium ethanedioate.

$BaC_2O_4 \rightarrow$ .... + ... + ...

[1]

Topic: **Chem 27 Q# 268/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) The table lists values of solubility products, K_{sp}, of some Group 2 carbonates.

	solubility product in water at 298 K, K_{sp} / $mol^2 dm^{-6}$
$MgCO_3$	1.0×10^{-5}
$CaCO_3$	5.0×10^{-9}
$SrCO_3$	1.1×10^{-10}

(d) (i) Magnesium nitrate decomposes at a **lower** temperature than barium nitrate.

Explain why.

....

....

.... [2]

(ii) A sample of barium nitrate was heated strongly until no further change occurred. A white solid was formed.

Write an equation for the action of heat on barium nitrate.

.... [1]

(iii) When water was added to the white solid produced in **(d)(ii)**, an alkaline solution was produced. Adding sulfuric acid to this solution produced a white precipitate.

Write equations to explain these observations.

....

.... [2]

[Total: 11]

Topic: **Chem 27 Q# 269/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Describe and explain the variation in the solubilities of the hydroxides of the Group 2 elements.

....

....

....

....

....

.... [4]

Topic: **Chem 27 Q# 270/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** When copper(II) carbonate is heated strongly, it decomposes in a similar way to Group 2 carbonates.

Predict what would be observed when anhydrous copper(II) carbonate is heated.

....

.... [1]

(b) Describe and explain how the thermal stability of the Group 2 carbonates varies down the group.

....

....

....

.... [3]

(ii) $CaCN_2$ decomposes readily on contact with water forming an insoluble white solid and ammonia only.

Suggest an equation for this reaction.

.... [2]

[Total: 8]

Topic: **Chem 27 Q# 271/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Limewater is a saturated solution of $Ca(OH)_2$ in water. It is used to test for the presence of CO_2 in a gaseous mixture.

(i) Write an equation for the reaction between limewater and CO_2.

.... [1]

A saturated solution of $Ba(OH)_2$ can be used instead of $Ca(OH)_2$ to test for CO_2. A saturated solution of $Mg(OH)_2$ cannot be used for this test.

(ii) Explain why a saturated solution of $Ba(OH)_2$ **can** be used to test for CO_2.

....

.... [1]

(iii) Explain why a saturated solution of $Mg(OH)_2$ **cannot** be used to test for CO_2.

....

....

.... [2]

(b) Describe and explain the trend in the thermal stabilities of the carbonates down Group 2.

....

....

....

....

.... [3]

(c) Nickel carbonate, $NiCO_3$, decomposes on heating.

Use the *Data Booklet* to explain whether $NiCO_3$ will decompose more or less readily than $CaCO_3$.

....

....

....

.... [2]

[Total: 9]

Topic: **Chem 27 Q# 272/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 Two elements, **V** and **W**, are in adjacent groups in the Periodic Table.

V reacts with oxygen to form an acidic gas, **X**. **V** forms an anion with formula VO_m^-.

W reacts with oxygen to form an acidic gas, **Y**. **W** forms an anion with formula WO_n^{2-}.

A solution of WO_n^{2-} forms a white precipitate with $Ba^{2+}(aq)$ but shows no visible reaction with $Mg^{2+}(aq)$.

(a) Complete the table below.

	identity or value
V	
X	
m	
W	
Y	
n	

[3]

(b) By referring to enthalpy changes, explain why WO_n^{2-} forms a white precipitate with $Ba^{2+}(aq)$ but shows no visible reaction with Mg^{2+}.

....

....

.... [3]

[Total: 6]

Topic: **Chem 27 Q# 273/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) **(i)** When anhydrous calcium nitrate is heated strongly, it decomposes to leave a white solid.

Identify this white solid and suggest **another** observation for this reaction.

....

.... [1]

(ii) The ease of thermal decomposition of the Group II nitrates **decreases** down the group.

Explain this trend.

....

....

.... [2]

Topic: **Chem 27 Q# 274/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) **(i)** Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements down the group.

....

....

....

....

.... [3]

When lithium nitrate, $LiNO_3$, is heated, it readily decomposes giving off a brown gas. This reaction is similar to that which occurs when magnesium nitrate is heated, but it does not occur with other Group I nitrates.

(ii) Suggest an equation for the action of heat on $LiNO_3$.

.... [1]

(iii) Suggest why the Group I nitrates other than $LiNO_3$ do **not** decompose in this way when heated.

....

.... [1]

[Total: 7]

Topic: **Chem 27 Q# 275/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Gaseous ammonia reacts with gaseous hydrogen chloride to form solid ammonium chloride.

$$NH_3 + HCl \rightarrow NH_4Cl$$

The bonding in ammonium chloride includes ionic, covalent and co-ordinate (dative covalent) bonds.

(b) When a sample of dry ammonia is needed in the laboratory, the gas is passed through a tower containing lumps of solid calcium oxide, CaO.

(i) Suggest why the usual drying agent for gases, concentrated H_2SO_4, is **not** used for ammonia.

....

(ii) Write an equation for the reaction between CaO and H_2O.

....

(iii) Suggest why CaO rather than MgO is used to dry ammonia.

....

[3]

(c) **(i)** Write an equation showing the thermal decomposition of calcium nitrate, $Ca(NO_3)_2$.

....

(ii) State and explain how the thermal stabilities of the nitrates vary down Group II.

....

....

....

.... [4]

[Total: 10]

Topic: **Chem 27 Q# 276/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(e) Describe and explain the trend in the solubilities of the sulfates of the elements in Group II.

....

....

....

....

....

....

.... [4]

[Total: 18]

Topic: Chem 28 Q# 277/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Titanium is a transition element in Period 4. It is commonly found as TiO_2 in minerals.

(a) **(i)** Define transition element.

....

....

.... [1]

(ii) Identify **two** typical properties of transition elements.

1 ....

2 ....

[1]

(b) The TiO^{2+} ion forms when TiO_2 reacts with an excess of sulfuric acid.

TiO^{2+} can be reduced by zinc metal in acidic conditions to form a purple solution containing Ti^{3+}(aq).

(i) TiO^{2+}(aq) is a colourless ion.

Suggest why.

....

....

.... [2]

(ii) Give the electronic configuration of an isolated Ti^{3+} ion.

$1s^2$ .... [1]

(iii) Write an ionic equation for the reduction of TiO^{2+} by zinc metal in acidic conditions.

.... [1]

(c) Acidified Ti^{3+}(aq) reacts with oxygen dissolved in water as shown.

$$4Ti^{3+} + O_2 + 2H_2O \rightarrow 4TiO^{2+} + 4H^+ \qquad \Delta G^{\circ} = -436.1\ kJ\ mol^{-1}$$

The standard reduction potential, E°, of $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ is +1.23 V.

(ii) When aqueous citrate ions, $C_6H_5O_7^{3-}$, are added to Ti^{3+}(aq), the $[Ti(C_6H_5O_7)_2]^{3-}$(aq) complex forms.

Explain, in terms of d-orbitals, why Ti^{3+} is able to form complex ions.

....

.... [1]

(iii) Acidified $[Ti(C_6H_5O_7)_2]^{3-}$(aq) does not react with oxygen dissolved in water, unlike acidified Ti^{3+}(aq).

Suggest what this means for the value of the standard reduction potential, E°, of the following half-cell.

$$[Ti(C_6H_5O_7)_2]^{2-}(aq) + e^- \rightleftharpoons [Ti(C_6H_5O_7)_2]^{3-}(aq)$$

Explain your answer.

....

.... [1]

(d) Some reactions of TiO_2 are shown in Fig. 3.1.

The anion, acac⁻, is a bidentate ligand.

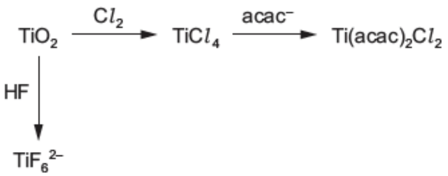


Fig. 3.1

(i) The titanium ions in TiF_6^{2-} and $Ti(acac)_2Cl_2$ have a coordination number of 6.

State what is meant by coordination number.

....

.... [1]

(ii) Write an equation for the formation of TiF_6^{2-} from TiO_2.

.... [1]

(iii) State what is meant by bidentate ligand.

....

....

.... [2]

(iv) $Ti(acac)_2Cl_2$ shows both optical and geometrical (cis/trans) isomerism.

$Ti(acac)_2Cl_2$ exists as three stereoisomers.

The structure of one stereoisomer of $Ti(acac)_2Cl_2$ is shown in Fig. 3.2.

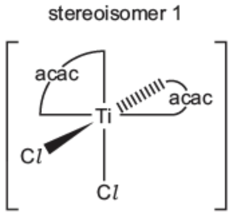
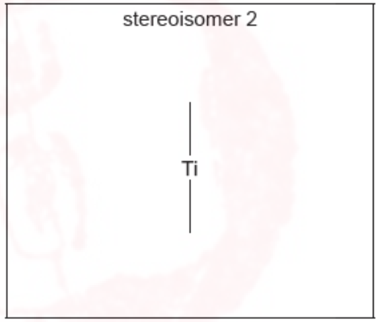
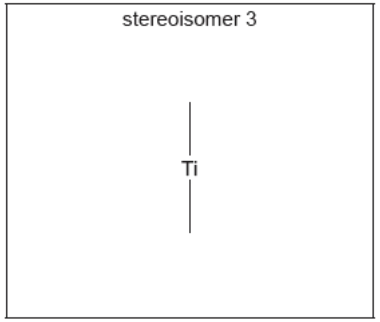


Fig. 3.2

Complete the structures of the other two stereoisomers of $Ti(acac)_2Cl_2$.





[2]

(v) The acac⁻ anion is symmetrical.

Deduce which, if any, of stereoisomers 1, 2 and 3 in **(d)(iv)** are polar.
Explain your answer.

....

....

.... [2]

[Total: 19]

Topic: **Chem 28 Q# 278/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) The concentration of $Cu^{2+}(aq)$ in a solution can be determined by the reaction of Cu^{2+} ions with I^- ions.

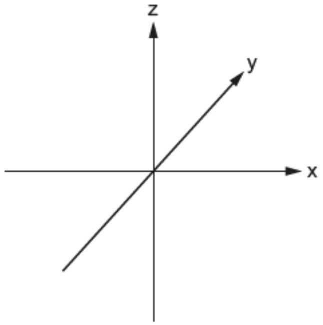
reaction 1 $2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$

The I_2 produced in reaction 1 is titrated against a solution containing thiosulfate ions, $S_2O_3^{2-}$, using a suitable indicator.

reaction 2 $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(iii) Copper(I) and copper(II) both contain electrons in all five 3d orbitals.

Sketch the shape of a $3d_{xy}$ orbital on the axes provided.



[1]

Topic: **Chem 28 Q# 279/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) The reaction of I^- ions with persulfate ions, $S_2O_8^{2-}$, can be catalysed by Fe^{3+} ions.

$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

Write equations to show how Fe^{3+} catalyses this reaction.

....

.... [2]

Topic: **Chem 28 Q# 280/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 An excess of sodium iodide is added to a solution of copper(II) sulfate. Iodine and a white precipitate of copper(I) iodide are formed.

(a) Write an equation for the reaction that occurs.

.... [1]

(b) **(i)** Explain why the copper(II) sulfate solution is coloured.

....

....

....

....

.... [4]

(ii) Suggest why the precipitate of copper(I) iodide is white.

....

.... [1]

(c) Use suitable E° values from the *Data Booklet* to predict whether iodide ions can reduce Cu^{2+} to Cu^+ under standard conditions. Explain your answer.

....

....

.... [2]

(d) An excess of sodium iodide is added to copper(II) sulfate solution. Copper(I) iodide forms as a precipitate. After precipitation, $[Cu^+]$ is much lower than $1.0\,mol\,dm^{-3}$.

Use this information and your answer to **(c)** to explain how the relevant electrode potentials change and hence why I^- ions can reduce Cu^{2+} ions.

....

....

....

....

.... [2]

[Total: 10]

5 **(a)** $[MnCl_4]^{2-}$ is a complex ion.

(i) Deduce the oxidation state of manganese in $[MnCl_4]^{2-}$.

oxidation state = ... [1]

(ii) The $[MnCl_4]^{2-}$ complex does **not** contain any 180° bond angles.

Draw a three-dimensional diagram to show the shape of the $[MnCl_4]^{2-}$ complex.

State one bond angle on your diagram.

Mn

[2]

(b) A solution of cobalt(II) sulfate contains the complex ion $[Co(H_2O)_6]^{2+}$.

A solution containing $[Co(H_2O)_6]^{2+}$ is reacted separately with an excess of each of NaOH(aq), NH_3(aq) and NaCl(aq).

Write an equation for each of these reactions. State **one** observation that can be made immediately after the reaction, include the colour and state of the cobalt-containing product.

(i) $[Co(H_2O)_6]^{2+}$ and an excess of NaOH(aq)

equation ....

observation ....

[2]

(ii) $[Co(H_2O)_6]^{2+}$ and an excess of NH_3(aq)

equation ....

observation ....

[2]

(iii) $[Co(H_2O)_6]^{2+}$ and an excess of NaCl(aq)

equation ....

observation ....

[2]

(iv) Name the type of reaction that occurs in **(b)(iii)**.

.... [1]

(c) Cobalt forms the complex ion $[Co(NH_3)_2(en)_2]^{2+}$. The abbreviation en is used for the bidentate ligand 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$. The complex ion shows both geometrical and optical isomerism.

(i) Define the term *bidentate ligand*.

....

.... [2]

(ii) Draw three-dimensional diagrams for the two **optical** isomers of $[Co(NH_3)_2(en)_2]^{2+}$.

Each en ligand can be represented using  .

Co

Co

[2]

[Total: 14]

Topic: **Chem 28 Q# 282/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Samples of $[Cu(H_2O)_6]^{2+}$ are reacted separately with an excess of aqueous sodium hydroxide or with an excess of aqueous ammonia.

Give the following information about these reactions.

(i) reaction 1: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous of sodium hydroxide

colour and state of the copper-containing species ....

ionic equation ....

type of reaction .... [3]

(ii) reaction 2: $[Cu(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

colour and state of the copper-containing species ....

ionic equation ....

type of reaction .... [3]

(b) Copper(I) oxide is added to hot dilute sulfuric acid. A blue solution, **X**, and a red-brown solid, **Y**, form.

Suggest the identities of **X** and **Y**. Name the type of reaction.

X ....

Y ....

type of reaction .... [2]

[Total: 8]

Topic: **Chem 28 Q# 283/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** **(i)** Define the term *transition element*.

....

.... [1]

(ii) State how the melting point and density of iron compare to those of calcium.

....

.... [1]

(c) The reaction between $S_2O_8^{2-}$(aq) and I^-(aq) is catalysed by adding a few drops of Fe^{3+}(aq).

(i) Use equations to show the catalytic role of Fe^{3+} in this reaction.

[2]

(ii) Fe^{3+}(aq) can oxidise I^-(aq), whereas $[Fe(CN)_6]^{3-}$(aq) cannot oxidise I^-(aq).

Use $E^\ominus$ values to explain these observations.

....

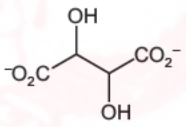
....

....

.... [2]

(d) When aqueous solutions of $S_2O_8^{2-}$ and tartrate ions are mixed the reaction proceeds very slowly. However, this reaction proceeds quickly in the presence of an Fe^{3+}(aq) catalyst. The overall equation for this reaction is shown.

tartrate ions



$$+ 3S_2O_8^{2-} + 2H_2O \rightarrow 2CO_2 + 2HCO_2^- + 6H^+ + 6SO_4^{2-}$$

(i) Suggest why this reaction is slow without the Fe^{3+} catalyst.

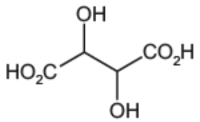
....

.... [1]

Topic: **Chem 28 Q# 284/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(e) **(i)** Complete the following table to show the structures of the organic products formed when tartaric acid reacts separately with each reagent. Identify each type of reaction.

tartaric acid



(ii) Tartaric acid reacts with the amine 1-phenylethylamine, $C_6H_5CH(NH_2)CH_3$, to form an ionic salt.

Draw the structure of the salt formed in this reaction. Include the charges on the ions.

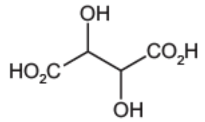
[1]

[Total: 17]

Topic: **Chem 28 Q# 285/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(e) (i) Complete the following table to show the structures of the organic products formed when tartaric acid reacts separately with each reagent. Identify each type of reaction.

tartaric acid



reagent	structure of organic product	type of reaction
an excess of $LiAlH_4$		
an excess of CH_3COCl		

[3]

Topic: **Chem 28 Q# 286/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) Explain why chromium complexes are coloured.

....

....

....

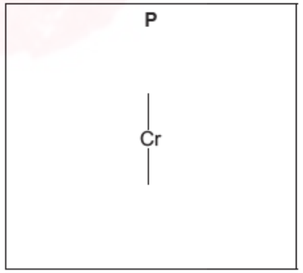
....

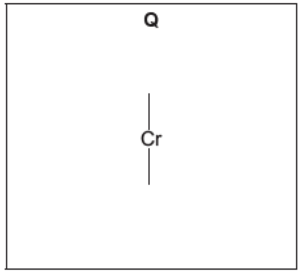
.... [4]

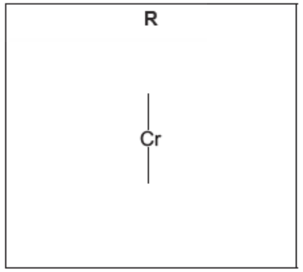
(b) Four different compounds can be obtained when anhydrous chromium(III) chloride reacts with water under various conditions. When samples of each compound are reacted separately with aqueous silver nitrate, different amounts of silver chloride are precipitated. The precipitation leaves the complex ions **P**, **Q**, **R** and **S** in solution.

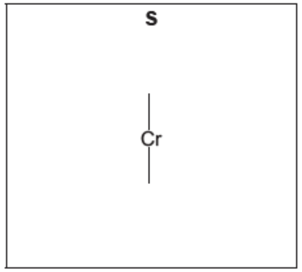
formula of compound	moles of AgC*l* precipitated per mole of complex ion	complex ion	property of complex ion
$CrCl_3(H_2O)_6$	3	**P**	non-polar
$CrCl_3(H_2O)_5$	2	**Q**	polar
$CrCl_3(H_2O)_4$	1	**R**	polar
$CrCl_3(H_2O)_4$	1	**S**	non-polar

(i) Draw three-dimensional diagrams for the structures of complex ions **P**, **Q**, **R** and **S**. Include the charges for each complex ion.









[4]

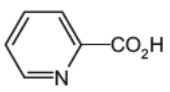
(ii) Suggest why complex ion **S** is non-polar.

....

.... [1]

(c) The structure of picolinic acid is shown.

picolinic acid



The conjugate base of picolinic acid is a bidentate ligand, **Z**.

(i) Define the term *bidentate ligand*.

....

.... [2]

(ii) Draw the structure of **Z**.

[1]

(iii) **Z** reacts with aqueous chromium(III) ions, $[Cr(H_2O)_6]^{3+}$, in a 3 : 1 ratio to form a new neutral complex.

State the coordination number and the geometry of the chromium(III) centre in the complex.

coordination number .... geometry .... [1]

(d) $(NH_4)_2Cr_2O_7$ decomposes readily on heating to form Cr_2O_3, steam and an inert colourless gas.

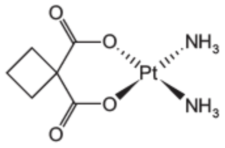
(i) Deduce the oxidation numbers of chromium in $(NH_4)_2Cr_2O_7$ and in Cr_2O_3.

$(NH_4)_2Cr_2O_7$ .... Cr_2O_3 .... [1]

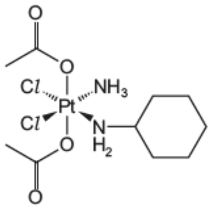
Topic: **Chem 28 Q# 287/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Carboplatin and satraplatin are used as anticancer drugs instead of cisplatin.

carboplatin



satraplatin



(ii) Suggest the geometry of the platinum centre in the carboplatin complex.

.... [1]

(iii) Suggest why carboplatin does **not** show cis-trans isomerism.

....

....

.... [1]

(iv) Satraplatin is a neutral complex, containing the ligands $CH_3CO_2^-$, $C_6H_{11}NH_2$, Cl^- and NH_3.

Deduce the oxidation state of platinum in satraplatin.

.... [1]

Topic: **Chem 28 Q# 288/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 The transition elements are able to form stable complexes with a wide range of molecules and ions.

(a) State the meaning of *transition element*.

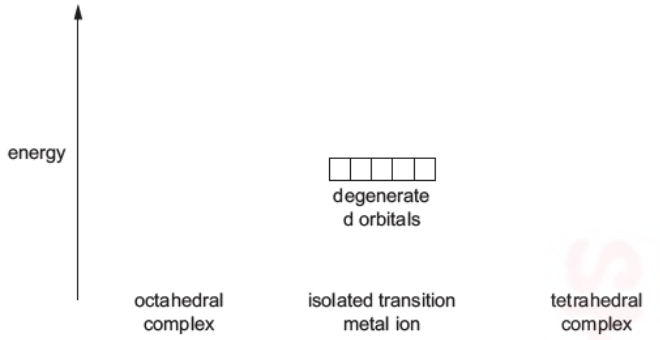
....

....

.... [1]

(b) The d orbitals in an isolated transition metal ion are degenerate. In complexes, the d orbitals occupy two energy levels.

(i) Complete the diagram to show the arrangement of d orbital energy levels in octahedral and in tetrahedral complexes.



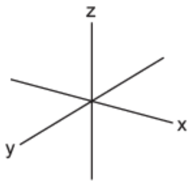
[1]

(ii) Sketch the shape of **two** d orbitals:

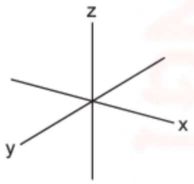
- one d orbital from the lower energy level in an octahedral complex
- one d orbital from the higher energy level in an octahedral complex.

Use the axes below.

lower energy level



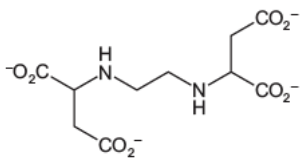
higher energy level



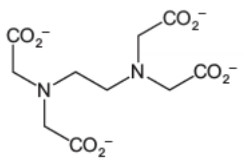
[2]

(c) Edds^{4-} and edta^{4-} are polydentate ligands that form octahedral complexes with Fe^{3+}(aq).

edds^{4-}



edta^{4-}



The formulae of the complexes are [Fe(edds)]$^-$ and [Fe(edta)]$^-$ respectively.

(i) On the diagram of edds^{4-}, circle each atom that forms a bond to the Fe^{3+} ion in [Fe(edds)]$^-$.
[1]

(ii) [Fe(edds)]$^-$ is red and [Fe(edta)]$^-$ is yellow.

Explain why the two complexes have different colours.

....

....

....

....

.... [2]

(iii) When edds^{4-}(aq) is added to Fe^{3+}(aq), the following reaction occurs.

$$[Fe(H_2O)_6]^{3+}(aq) + edds^{4-}(aq) \rightleftharpoons [Fe(edds)]^-(aq) + 6H_2O(l)$$

State the type of reaction that occurs.

.... [1]

(iv) Write an expression for the stability constant, K_{stab}, of [Fe(edds)]$^-$(aq).

K_{stab} =

[1]

(v) The table shows the values for the stability constants, K_{stab}, of both complexes.

complex	K_{stab} / mol^{-1} dm^3
[Fe(edds)]$^-$	3.98×10^{20}
[Fe(edta)]$^-$	1.26×10^{25}

Predict which of the [Fe(edds)]$^-$ and [Fe(edta)]$^-$ complexes is more stable.

Explain your answer with reference to the K_{stab} value for each complex.

....

....

.... [1]

(vi) When an excess of edta^{4-}(aq) is added to [Fe(edds)]$^-$(aq), the following equilibrium is established.

$$[Fe(edds)]^-(aq) + edta^{4-}(aq) \rightleftharpoons [Fe(edta)]^-(aq) + edds^{4-}(aq)$$

Calculate the equilibrium constant, K_c, for this equilibrium, using the K_{stab} values given in the table in **(c)(v)**.

K_c = ... [1]

[Total: 11]

Topic: **Chem 28 Q# 289/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** When 1.0 mol dm^{-3} $Na_2S_2O_3$(aq) is added to a solution containing Ag^+(aq) ions, a linear complex, **P**, is formed. $S_2O_3^{2-}$ ions are present in **P** as monodentate ligands.

(i) Define the term *monodentate ligand*.

....

.... [2]

(ii) Give the formula of **P**, including its charge.

.... [1]

(b) When 1.0 mol dm^{-3} NaCN(aq) is added to a solution of **P**, a mixture which includes a second linear complex, **Q**, is formed. In this mixture the concentration of **Q** is much greater than the concentration of **P**.

(i) Write an equation for the reaction that occurs when NaCN(aq) is added to a solution of **P**.

.... [1]

(ii) Suggest a reason why the concentration of **Q** is much greater than the concentration of **P** in the mixture.

....

....

.... [1]

(iii) Name the type of reaction in which **P** forms **Q**.

.... [1]

(c) Platinum forms a complex ion with the formula $[Pt(CN)_2Cl_2]^{2-}$. In this complex ion the carbon atom of each CN^- ligand bonds to the platinum ion. This complex shows stereoisomerism.

(i) There are only two isomers of this complex.

Draw structures of these two isomers in the boxes below.

Pt

Pt

[1]

(ii) Describe the geometry of $[Pt(CN)_2Cl_2]^{2-}$.

.... [1]

(iii) Name the type of stereoisomerism shown by $[Pt(CN)_2Cl_2]^{2-}$.

.... [1]

[Total: 9]

Topic: **Chem 28 Q# 290/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 A solution is made by dissolving $CuSO_4{\bullet}5H_2O$ in an excess of aqueous ammonia. This solution contains the copper complex $[Cu(NH_3)_4]^{2+}$.

(a) **(i)** Write an expression for the K_{stab} of $[Cu(NH_3)_4]^{2+}$.

K_{stab} =

[1]

(ii) State the colour of the solution of $[Cu(NH_3)_4]^{2+}$.

.... [1]

The solution of $[Cu(NH_3)_4]^{2+}$ is heated gently in a fume cupboard so that NH_3 is released. Some NH_3 remains in solution and some forms NH_3 gas. The colour of the solution changes; a precipitate of $Cu(OH)_2$ forms and is collected.

A sample of $Cu(OH)_2$ is added to concentrated hydrochloric acid. A reaction takes place forming a coloured copper complex, **Y**.

A sample of $Cu(OH)_2$ is added to dilute sulfuric acid. A reaction takes place forming a coloured copper complex, **Z**.

$[Cu(NH_3)_4]^{2+}$, **Y** and **Z** are different colours.

(b) Suggest an equation for the reaction of $[Cu(NH_3)_4]^{2+}$ to form $Cu(OH)_2$ as the aqueous solution of $[Cu(NH_3)_4]^{2+}$ is heated.

.... [1]

(c) Suggest an equation for the reaction of $Cu(OH)_2$ with concentrated hydrochloric acid, forming **Y**.

.... [2]

(d) Complete the table with the colour and geometry of complex **Y** and the colour, geometry and formula of complex **Z**.

	Y	Z
colour of complex		
geometry of complex		
formula of complex	▨	

[2]

(e) Explain why complexes **Y** and **Z** are coloured and why their colours are different.

....

....

....

....

....

....

....

.... [5]

[Total: 12]

Topic: **Chem 28 Q# 291/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 **(a)** The electronic configuration of transition element **Q** is $[Ar]\ 3d^2\ 4s^2$.

Predict the likely oxidation states of element **Q** in compounds.

.... [1]

(b) Suggest why transition elements often show variable oxidation states in their compounds, but typical s-block elements such as calcium do not.

....

.... [1]

Topic: **Chem 28 Q# 292/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** An aqueous solution of cobalt(II) contains the $[Co(H_2O)_6]^{2+}$ complex ion.

(i) Define the term *complex ion*.

....

.... [1]

(ii) Samples of $[Co(H_2O)_6]^{2+}$ are reacted separately with aqueous sodium hydroxide and with an excess of aqueous ammonia.

Give the following information about these reactions.

- the reaction of $[Co(H_2O)_6]^{2+}$ with aqueous sodium hydroxide

  colour and state of the cobalt-containing species ....

  ionic equation ....

  type of reaction ....

- the reaction of $[Co(H_2O)_6]^{2+}$ with an excess of aqueous ammonia

  colour and state of the cobalt-containing species ....

  ionic equation ....

  type of reaction ....

[6]

(b) When concentrated hydrochloric acid is added to a solution containing $[Co(H_2O)_6]^{2+}$, a blue solution of $[CoCl_4]^{2-}$ is formed and the following equilibrium is established.

$$[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$$

Use Le Chatelier's principle to suggest the expected observations when silver nitrate solution is added dropwise to the blue solution of $[CoCl_4]^{2-}$. Explain your answer.

....

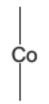
....

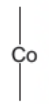
.... [2]

(c) The $[Co(NH_3)_3Cl_3]$ complex shows stereoisomerism.

Complete the three-dimensional diagrams to show the two isomers of $[Co(NH_3)_3Cl_3]$.

Suggest the type of stereoisomerism.



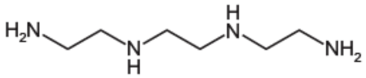


type of stereoisomerism ....

[2]

(d) Compound **X**, $C_6H_{18}N_4$, is a tetradentate ligand.

X



(i) Suggest why one molecule of **X** can form four dative bonds.

....

....

.... [1]

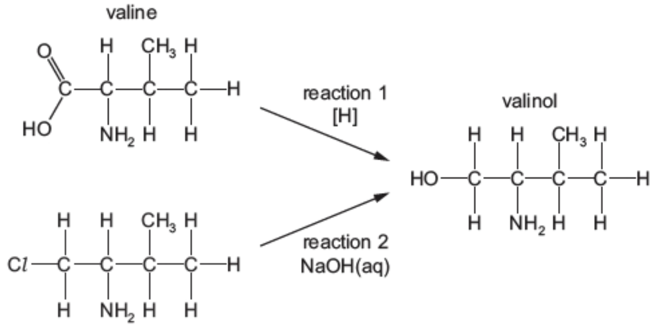
(ii) $C_6H_{18}N_4$ reacts with aqueous cobalt(II) ions, $[Co(H_2O)_6]^{2+}$, in a 1 : 1 ratio to form a new complex ion.

Construct an equation for this reaction.

.... [1]

---

6 Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(iii) Valinate, Val^-, is the anion of valine. It takes part in a ligand substitution reaction with hexaaquanickel(II) ions. Complex **Z** is formed.

$$[Ni(H_2O)_6]^{2+}(aq) + 2Val^-(aq) \rightleftharpoons \overset{\mathbf{Z}}{[Ni(H_2O)_2(Val)_2](aq)} + 4H_2O(l)$$

Write an expression for K_{stab} for this equilibrium.

K_{stab} =

[1]

(iv) At room temperature, the numerical value of K_{stab} is 2.34×10^5.

Explain what this value indicates about the equilibrium and the stability of complex **Z**.

....

....

.... [1]

(v) **Z** is an octahedral complex with formula $[Ni(H_2O)_2(Val)_2]$.

Use this information to state the type of ligand that the valinate ion is acting as in this complex.

.... [1]

[Total: 11]

Topic: **Chem 28 Q# 294/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 Iron is a transition element in the fourth period. Iron forms compounds containing the ions Fe^{2+} and Fe^{3+}.

(a) (i) Define the term *transition element*.

....

....

.... [1]

(ii) Compare the melting point and density of iron with those of calcium, an s-block element in the fourth period.

melting point ....

density ....

[1]

(iii) Complete the electronic configuration of an isolated gaseous Fe^{2+} ion.

$1s^2$ .... [1]

(iv) Aqueous Fe^{3+} ions form coloured complexes.

Explain the origin of the colour in transition element complexes.

....

....

....

....

....

.... [4]

(b) When an excess of $CN^-(aq)$ ions is added to green $[Fe(H_2O)_6]^{2+}(aq)$ ions, yellow $[Fe(CN)_6]^{4-}$ complex ions are formed.

Heating $[Fe(CN)_6]^{4-}$ with dilute nitric acid and then neutralising the product with $Na_2CO_3(aq)$ produces red crystals, containing the $[Fe(CN)_5NO]^{2-}$ complex ion.

NO is a neutral, monodentate ligand.

(i) State the shape of the $[Fe(H_2O)_6]^{2+}(aq)$ complex ion.

.... [1]

(ii) Write the equation for the reaction between $[Fe(H_2O)_6]^{2+}(aq)$ ions and an excess of $CN^-(aq)$ ions.

.... [1]

(iii) Deduce the oxidation states of iron in:

$[Fe(CN)_6]^{4-}$ .... $[Fe(CN)_5NO]^{2-}$. ....

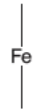
[1]

(iv) Define the term *monodentate ligand*.

....

.... [2]

(v) Complete the diagram to show the three-dimensional structure of the $[Fe(CN)_5NO]^{2-}$ complex ion.



[1]

(vi) The two complex ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5NO]^{2-}$ are different colours.

Explain why the colours of the two complex ions are different.

....

....

.... [2]

(c) **E** is a complex ion, $[Fe(C_2O_4)_2Cl_2]^{4-}$, containing Fe^{2+} with a coordination number of 6.

(i) Define the term *coordination number*.

....

.... [1]

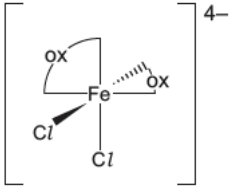
(ii) **E** shows both optical isomerism and *cis-trans* isomerism.

One isomer of **E** is shown. The $C_2O_4^{2-}$ ion is represented as ⌒ox⌒.

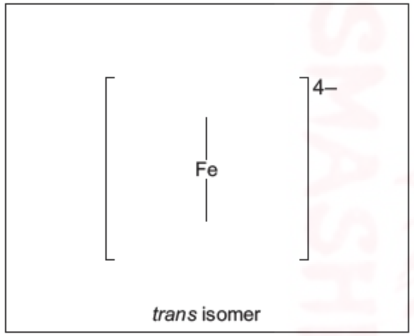
In the boxes, draw three-dimensional diagrams to show:

- the *trans* isomer of **E**
- the optical isomer of **E**.

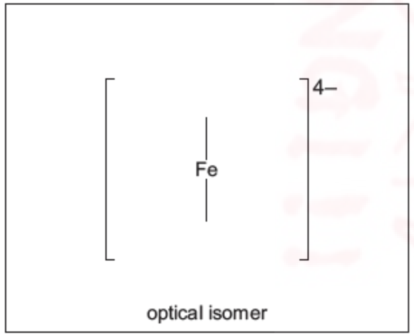
E



cis isomer



trans isomer



optical isomer

[2]

Topic: **Chem 28 Q# 295/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 Manganese, chromium and ruthenium are all transition elements.

(a) Explain what is meant by a *transition element*.

....

....

.... [1]

(b) $MnO_4^-(aq)$ and $Cr_2O_7^{2-}(aq)$ act as oxidising agents in acidic solution. Both these oxidising agents will oxidise a solution of Sn^{2+} to give a solution of Sn^{4+}. Solutions containing Sn^{2+} and solutions containing Sn^{4+} are colourless.

(i) Describe the colour change seen when an excess of $Sn^{2+}(aq)$ is added separately to

- dilute acidified $MnO_4^-(aq)$

from .... to ....

- dilute acidified $Cr_2O_7^{2-}(aq)$.

from .... to ....

[1]

(ii) Write an equation for the reaction between $Sn^{2+}(aq)$ and acidified $Cr_2O_7^{2-}(aq)$.

.... [1]

(c) Ruthenium, Ru, forms complex ions. In one such complex ion, **X**, the ruthenium ion has a co-ordination number of six. Each complex ion **X** contains one Ru^{2+} ion, one Cl^- ion, one SO_2 molecule and the remaining ligands are NH_3 molecules.

The SO_2 molecule acts as a monodentate ligand and is attached to the Ru^{2+} ion via the sulfur atom. **X** exists in two isomeric forms.

(i) State what is meant by a *co-ordination number of six*.

.... [1]

(ii) State the formula of **X**. Include its charge.

.... [1]

(iii) Draw the two isomeric forms of **X** in the boxes below. Your diagrams should show

- the three-dimensional shapes of the two isomers
- how each ligand is attached to the central ruthenium ion.

Ru

Ru

[3]

(iv) Suggest the type of isomerism shown by **X**.

.... [1]

(v) Explain the origin of colour in a transition element complex such as **X**.

....

....

....

....

....

....

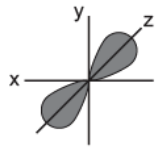
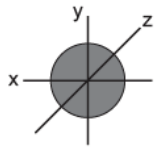
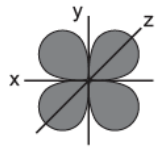
.... [3]

[Total: 12]

Topic: **Chem 28 Q# 296/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Sketches of the shapes of some atomic orbitals are shown.

Identify the type of orbital, s, p, or d.

shape of orbital			
type of orbital			

[1]

(b) Cadmium forms the two ions, Cd_2^{2+} and Cd^{2+}. The electronic configuration of cadmium in these ions is shown.

- [Kr] $4d^{10}5s^1$
- [Kr] $4d^{10}$

Use this information to explain why cadmium is **not** a transition element.

....

.... [1]

(c) Methylamine, CH_3NH_2, is a monodentate ligand.

(i) State what is meant by the term *monodentate* in this context.

....

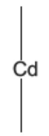
.... [1]

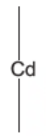
In the presence of aqueous methylamine, $[Cd(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

equilibrium **1** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O$ $\Delta H_r^{\ominus} = -57\,\text{kJ mol}^{-1}$

(ii) Complete the three-dimensional diagrams to show the isomers of $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$.

Use L to represent CH_3NH_2 in your diagrams.





[2]

(d) **(i)** State what is meant by the term *stability constant*.

....

.... [1]

(ii) Complete the table by placing **one** tick (✓) in each row to suggest how increasing temperature will affect K_{stab} and the equilibrium concentration of the cadmium complex, $[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$, for equilibrium **1**. Explain your answer.

	decreases	no change	increases
K_{stab}			
$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$			

explanation ....

....

[2]

EDTA^{4-} is a polydentate ligand. When a solution of EDTA^{4-} is added to $[Cd(H_2O)_6]^{2+}$ a new complex $[CdEDTA]^{2-}$ is formed.

The values for the stability constants for two Cd^{2+} complexes are shown.

	K_{stab}
$[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$	4.0×10^6
$[CdEDTA]^{2-}$	4.0×10^{16}

(iii) A solution containing equal numbers of moles of CH_3NH_2 and EDTA is added to $[Cd(H_2O)_6]^{2+}$.

Predict which complex is formed in the larger amount. Explain your answer.

....

.... [1]

Topic: **Chem 28 Q# 297/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** Aqueous solutions of copper(II) salts contain the blue-coloured $[Cu(H_2O)_6]^{2+}$ complex ion. Separate portions of this blue solution react with aqueous sodium hydroxide and with concentrated hydrochloric acid.

Give the following information for each of these reactions.

- reaction with aqueous sodium hydroxide

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

- reaction with concentrated hydrochloric acid

  ionic equation ....

  type of reaction ....

  colour and state of the copper-containing product ....

[6]

(b) Chloride ions can be identified using aqueous silver nitrate, $AgNO_3(aq)$.

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

0.303 g of a chloride of sulfur is completely hydrolysed with water. All the chlorine atoms present in the chloride of sulfur are converted into chloride ions. The solution is diluted to 100.0 cm^3. A 25.00 cm^3 sample of this solution is titrated with 0.0500 $mol\,dm^{-3}$ $AgNO_3(aq)$. The titration requires 22.40 cm^3 of 0.0500 $mol\,dm^{-3}$ $AgNO_3(aq)$.

Calculate the empirical formula of the chloride of sulfur. Show all your working.

empirical formula of chloride of sulfur = ... [3]

[Total: 9]

Topic: **Chem 28 Q# 298/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** **(i)** Complete the electronic configuration of a copper atom.

$1s^22s^22p^6$ .... [1]

(ii) • Explain why most copper(II) salts are coloured.

....

....

....

....

• Suggest why copper(I) salts are usually white.

....

....

[4]

(b) Brass is an alloy of copper and zinc. The following reaction can be used to determine the amount of copper in a sample of brass.

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$$

The procedure was carried out using the following steps.

- A solution of $Cu^{2+}(aq)$ was obtained by dissolving a 1.50 g sample of brass in concentrated sulfuric acid and diluting with water.
- An excess of $I^-(aq)$ was added.
- The iodine produced was titrated against a 0.500 $mol\,dm^{-3}$ solution of thiosulfate ions, $S_2O_3^{2-}(aq)$.

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

- The volume of $S_2O_3^{2-}$ solution needed to reach the end-point was 28.35 cm^3.

Calculate the percentage by mass of copper in the sample of brass.

percentage by mass of copper = ...
[3]

(d) When chloride ions are added to a solution containing $Cu^{2+}(aq)$, the complex ion $[CuCl_4]^{2-}(aq)$ is formed.

(i) State the colours of $Cu^{2+}(aq)$ and $[CuCl_4]^{2-}(aq)$.

$Cu^{2+}(aq)$ ....

$[CuCl_4]^{2-}(aq)$ ....
[1]

(ii) Name the type of reaction that occurs when $[CuCl_4]^{2-}(aq)$ is formed from $Cu^{2+}(aq)$.

.... [1]

(iii) Write an expression for the stability constant, K_{stab}, for $[CuCl_4]^{2-}(aq)$. Include the units in your answer.

K_{stab} =

units = ...
[2]

[Total: 17]

Topic: **Chem 28 Q# 299/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(c) At room temperature N_2O_3 dissociates.

$$N_2O_3(g) \rightleftharpoons NO(g) + NO_2(g)$$

(i) Write the expression for K_p for this equilibrium. Include the units in your answer.

K_p =

units = ...

[1]

A 1.00 dm³ flask at 25 °C is filled with pure $N_2O_3(g)$ at an initial pressure of 0.60 atm. At equilibrium, the partial pressure of $NO_2(g)$ is 0.48 atm.

(ii) Calculate the partial pressures of NO(g) and $N_2O_3(g)$ at equilibrium. Hence calculate the value of K_p at 25 °C.

$p(NO(g))$ = ...

$p(N_2O_3(g))$ = ...

K_p = ...

[2]

(d) NO reacts readily with oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The table shows how the initial rate of this reaction at 25 °C depends on the initial concentrations of the reactants.

initial concentration / mol dm^{-3}		initial rate / mol dm^{-3} s^{-1}
[NO(g)]	[O_2(g)]	
0.100	0.0500	3.50
0.0500	0.100	1.75
0.0500	0.0500	0.875

(i) Deduce the order of reaction with respect to each reactant. Explain your reasoning.

order with respect to [NO(g)] ....

....

order with respect to [O_2(g)] ....

....

[2]

(ii) State the rate equation for this reaction. Use the rate equation to calculate the rate constant. Include the units for the rate constant in your answer.

rate =

rate constant, k = ...

units of k = ...

[3]

(e) NO reacts with iron pentacarbonyl, $Fe(CO)_5$, as shown. NO and CO are both monodentate ligands.

$$Fe(CO)_5 + 2NO \rightarrow Fe(CO)_2(NO)_2 + 3CO$$

During this reaction the co-ordination number of the iron changes.

(i) State what is meant by the term *co-ordination number*.

....

.... [1]

(ii) Describe how the co-ordination number of the iron changes during this reaction.

from .... to ....

[1]

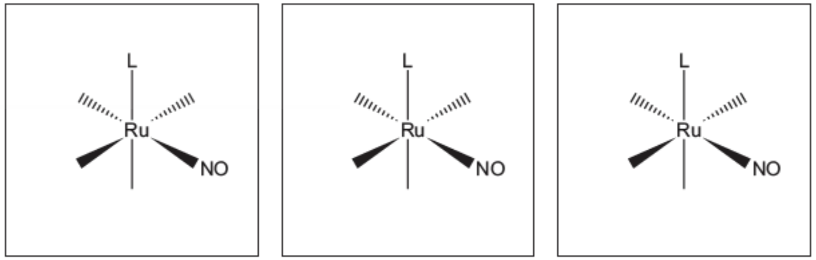
(iii) Only one stereoisomer of $Fe(CO)_2(NO)_2$ exists.

Use this information to suggest the geometry of the complex.

.... [1]

(f) The complex $Ru(NO)L_2Cl_3$ exists in three isomeric forms. L represents the monodentate ligand $C_6H_5P(CH_3)_2$.

(i) Complete the three-dimensional diagrams to show the **three** isomers of $Ru(NO)L_2Cl_3$.



[2]

(ii) Suggest the type of isomerism shown.

.... [1]

Topic: **Chem 28 Q# 300/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Complete the table to show the total number of **unpaired** electrons in the 3d and 4s orbitals of each isolated gaseous atom.

	number of **unpaired** electrons	
	3d	4s
Cr		
Mn		
Fe		

[2]

(b) Solid potassium manganate(VII), $KMnO_4$, decomposes on heating to form manganese(IV) oxide, potassium manganate(VI) and a colourless gas.

Construct an equation for this reaction.

.... [2]

(c) Explain the origin of colour in transition element complexes.

....

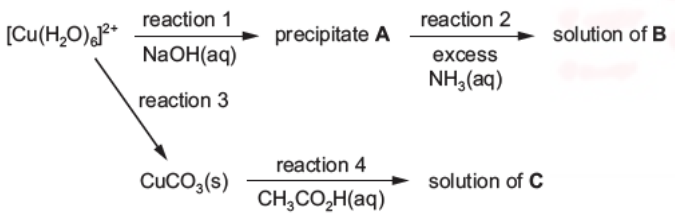
....

....

....

.... [3]

(d) The reaction scheme shows some reactions of $[Cu(H_2O)_6]^{2+}$.



(i) Write the formulae of

precipitate **A**, ...

complex ion **B**, ...

compound **C**. ....

[3]

(ii) Identify a suitable reagent for reaction 3.

.... [1]

(iii) Write an equation for reaction 4.

.... [1]

(iv) Describe **two** visual observations that would be made during reaction 4.

....

.... [1]

(e) Platin, $Pt(NH_3)_2Cl_2$, is a neutral complex of platinum(II).

Explain why $Pt(NH_3)_2Cl_2$ has no charge.

....

.... [1]

(f) **(i)** $Pt(NH_3)_2Cl_2$, displays *cis-trans* isomerism.

Draw the structure of *trans*-platin. State its shape and the $Cl–Pt–Cl$ bond angle.

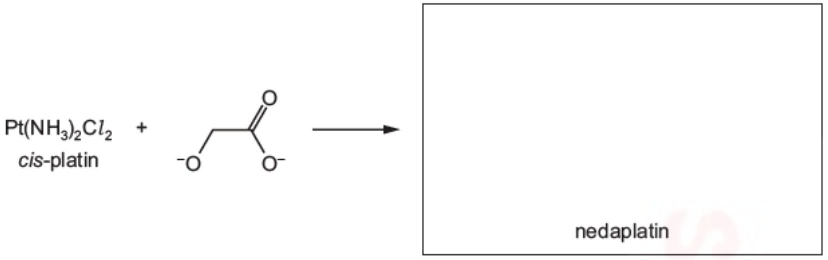
shape .... $Cl–Pt–Cl$ bond angle ....

[2]

(g) The use of *cis*-platin can cause side effects so nedaplatin has been developed.

Nedaplatin can be synthesised from *cis*-platin, $Pt(NH_3)_2Cl_2$, by replacing the two chloride ion ligands with a **single** bidentate ligand as shown.

Suggest the structure for nedaplatin.



[1]

Topic: **Chem 28 Q# 301/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Ethanedioate ions, $C_2O_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

....

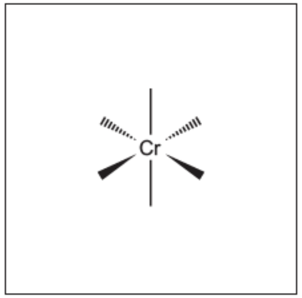
....

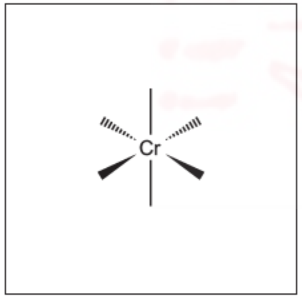
.... [1]

(b) Cr^{3+}(aq) and $C_2O_4^{2-}$(aq) ions form the complex ion $[Cr(C_2O_4)_2(H_2O)_2]^-$.

Draw **two** stereoisomers of this complex ion.

You may use  to represent $C_2O_4^{2-}$.





[2]

(c) The solubility of calcium ethanedioate, CaC_2O_4, is $6.65 \times 10^{-3}\,g\,dm^{-3}$ at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of CaC_2O_4. Include its units.

K_{sp} =

units = ...

[2]

2 **(a)** Ethanedioate ions, $C_2O_4^{2-}$, are bidentate ligands.

Explain what is meant by the term *ligand*.

....

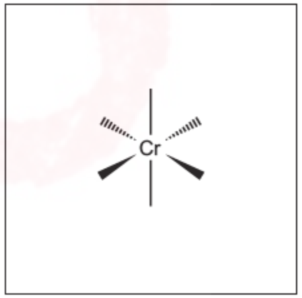
....

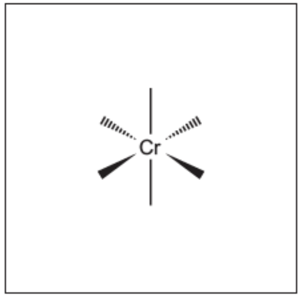
.... [1]

(b) Cr^{3+}(aq) and $C_2O_4^{2-}$(aq) ions form the complex ion $[Cr(C_2O_4)_2(H_2O)_2]^-$.

Draw **two** stereoisomers of this complex ion.

You may use  to represent $C_2O_4^{2-}$.





[2]

(c) The solubility of calcium ethanedioate, CaC_2O_4, is $6.65 \times 10^{-3}\,g\,dm^{-3}$ at 298 K.

(i) Write an expression for the solubility product, K_{sp}, of CaC_2O_4. Include its units.

K_{sp} =

units = ...

[2]

(ii) Calculate the numerical value of K_{sp} CaC_2O_4 at 298 K. Give your answer in **standard form** to **two** significant figures.

K_{sp} CaC_2O_4 = ... [2]

[Total: 7]

Topic: **Chem 28 Q# 302/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Copper is a transition element with atomic number 29.

(a) Complete the electronic configurations of a Cu atom and a Cu⁺ ion.

Cu atom $1s^22s^22p^6$ ....

Cu⁺ ion $1s^22s^22p^6$ ....

[2]

(b) Cu⁺ ions form a linear complex with Cl⁻ ions, which are monodentate ligands.

Draw the structure of this complex and include its overall charge.

[2]

(c) Cu^{2+} ions exist as $[Cu(H_2O)_6]^{2+}$ complex ions in aqueous solution.

Complete a three-dimensional diagram to show the shape of this complex.
Name its shape.
Label and state the value of one bond angle.

Cu

name of shape ....

[2]

(d) When $NH_3(aq)$ is added to $Cu^{2+}(aq)$, dropwise at first and then in excess, two chemical reactions occur as shown.

$$[Cu(H_2O)_6]^{2+} \xrightarrow[\text{reaction 1}]{\text{dropwise } NH_3(aq)} \textbf{A} \xrightarrow[\text{reaction 2}]{\text{excess } NH_3(aq)} \textbf{B}$$

For each reaction, describe what you would see and write an equation.

reaction 1

observation ....

....

equation ....

reaction 2

observation ....

....

equation ....

[4]

(e) EDTA^{4-} is a polydentate ligand. When a solution of EDTA^{4-} is added to a solution containing $[Cu(H_2O)_6]^{2+}$ a new complex is formed. The formula of this complex is $[CuEDTA]^{2-}$.

(i) Name the type of reaction occurring here.

.... [1]

(ii) Write an expression for the stability constant, K_{stab}, of $[CuEDTA]^{2-}$ in this reaction.

[1]

(iii) The numerical value of the K_{stab} of $[CuEDTA]^{2-}$ is 6.3×10^{19} at 298 K.

State what this tells us about the $[CuEDTA]^{2-}$ complex ion.

.... [1]

(f) Ethanedioate ions, $C_2O_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by the term *bidentate ligand*.

....

....

....

.... [2]

(ii) When ethanedioate ions are added to a solution of zirconium ions, Zr^{4+}, a complex ion containing four $C_2O_4^{2-}$ ions and one Zr^{4+} ion is formed. All four ethanedioate ions act as bidentate ligands in this complex.

Give the formula of this complex ion and explain why this complex is not octahedral.

....

....

....

.... [2]

[Total: 17]

---

5 **(a)** **(i)** Complete the electronic configuration of a chromium atom.

$1s^2 2s^2 2p^6 3s^2$ .... [1]

(ii) State the **two** highest oxidation states of chromium commonly seen in its compounds.

.... [1]

(b) Six different compounds or complexes, **H**, **J**, **K**, **L**, **M** and **N**, are formed when an excess of aqueous NH_3, aqueous NaOH and concentrated aqueous HC*l* are separately added to separate solutions containing $Cu^{2+}(aq)$ or $Co^{2+}(aq)$.

solution	reagent		
	an excess of $NH_3(aq)$	an excess of NaOH(aq)	an excess of concentrated HC*l*(aq)
$Cu^{2+}(aq)$	**H**	**J**	**K**
$Co^{2+}(aq)$	**L**	**M**	**N**

(i) State the colours of the following compounds or complexes.

H ....

K ....

M ....
[2]

(ii) Write the formulae of the following compounds or complexes.

L ....

N ....
[2]

(iii) State the appearance of compound **J**.

.... [1]

[Total: 7]

3 **(a)** Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

(b) Adding a measured quantity of KCN to a solution of $NiCl_2$ produces the complex $[Ni(CN)_2Cl_2]^x$.

(i) Deduce the overall charge, *x*, on this complex.

x = ... [1]

The complex can exist as two separate isomers with the same geometry (shape) around the nickel ion.

(ii) State the type of isomerism shown by these isomers.

.... [1]

(iii) If bromide ions are present in the solution, the complex $[Ni(CN)_2ClBr]^x$ can form.

Assuming that $[Ni(CN)_2ClBr]^x$ has the same geometry as $[Ni(CN)_2Cl_2]^x$, state the number of isomers of $[Ni(CN)_2ClBr]^x$ that could exist, and draw their structures in the box.

- number of isomers of $[Ni(CN)_2ClBr]^x$ ....

structures of the isomers of $[Ni(CN)_2ClBr]^x$

[3]

(c) An aqueous solution of KCN is gradually added to a solution of $NiSO_4$ until the KCN is in excess. The following series of reactions takes place.

$$NiSO_4 \xrightarrow{\text{KCN}} \underset{\text{green precipitate}}{\mathbf{C}} \xrightarrow{\text{more KCN}} \underset{\text{yellow solution}}{\mathbf{D}} \xrightarrow{\text{KCN in excess}} \underset{\text{red solution}}{\mathbf{E}}$$

- The oxidation state of nickel does **not** change during these reactions.
- None of **C**, **D** or **E** contains sulfur.
- **C** contains no potassium.
- The K : Ni ratio in **D** is 2 : 1.
- The K : Ni ratio in **E** is 3 : 1.

Use the information to suggest the formulae of **C**, **D** and **E**.

C ....

D ....

E .... [3]

[Total: 15]

7 **(a)** Complete the following electronic structures.

- the iron atom, Fe $1s^22s^22p^6$ ....
- the iron(III) ion, Fe^{3+} $1s^22s^22p^6$ ....

[1]

(b) Solutions of iron(III) salts are acidic due to the equilibrium shown.

$$[Fe(H_2O)_6]^{3+}(aq) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq) \qquad K_a = 8.9 \times 10^{-4}\,mol\,dm^{-3}$$

Calculate the pH of a $0.25\,mol\,dm^{-3}$ $FeCl_3$ solution.

pH = ... [2]

(c) The table shows numerical values of the stability constants for the following equilibrium where M can be one of the metal ions listed and L one of the ligands which replaces **one** H_2O molecule.

$$[M(H_2O)_6]^{n+}(aq) + L^-(aq) \rightleftharpoons [M(H_2O)_5L]^{(n-1)+}(aq) + H_2O(l)$$

metal ion, M	ligand, L	stability constant, K_{stab}
Fe^{3+}	F^-	1.0×10^6
Fe^{3+}	Cl^-	2.5×10^1
Fe^{3+}	SCN^-	9.0×10^2
Hg^{2+}	Cl^-	5.0×10^6

(i) What is meant by the term *stability constant*, K_{stab}?

....

.... [1]

(ii) Use the data in the table to predict the formula of the complex formed in the greatest amount when

- a solution containing equal concentrations of both F^- and SCN^- ions is added to $Fe^{3+}(aq)$,

....

- a solution containing equal concentrations of both Fe^{3+} and Hg^{2+} ions is added to $Cl^-(aq)$.

.... [1]

Ethanedioate ions, $^{-}O_2CCO_2^{-}$, are bidentate ligands. The abbreviation ed^{2-} can be used to represent ethanedioate ions.

(d) The complex $[Fe(ed)_2Cl_2]^{3-}$ can be formed according to the equation shown.

$$[Fe(H_2O)_4Cl_2]^{+}(aq) + 2ed^{2-}(aq) \rightleftharpoons [Fe(ed)_2Cl_2]^{3-}(aq) + 4H_2O(l)$$

Write the expression for the equilibrium constant, K_{stab}, and state its units.

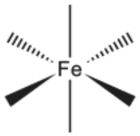
K_{stab} =

units .... [2]

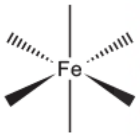
(e) $[Fe(ed)_2Cl_2]^{3-}$ shows geometrical and optical isomerism.

(i) Complete the three-dimensional diagrams to show the three stereoisomers of $[Fe(ed)_2Cl_2]^{3-}$.

You may use  to represent ed^{2-}.



isomer **A**



isomer **B**

isomer **C**

[3]

(ii) Give the letters of two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which are geometrical isomers of each other.

.... [1]

(iii) Give the letters of the two isomers of $[Fe(ed)_2Cl_2]^{3-}$ which show optical isomerism.

.... [1]

(iv) Give the letter of the isomer which has **no** dipole moment.

.... [1]

[Total: 13]

---

4 **(a)** Describe and explain how the density and melting point of cobalt compare to those of calcium.

density of cobalt ....

explanation ....

....

melting point of cobalt ....

explanation ....

.... [3]

(b) Transition metals can form complexes.

What is meant by the term *transition metal complex*?

....

.... [1]

(c) **(i)** Cobalt can form the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$.
These two compounds are structural isomers.

Define the term *structural isomer*.

....

.... [1]

(ii) Draw a three-dimensional diagram to show the structure of the ion $[Co(NH_3)_5Br]^{2+}$.
Name its shape.

$[Co(NH_3)_5Br]^{2+}$

shape .... [1]

(iii) State the type of bonding between the cobalt ion and NH_3 groups in the $[Co(NH_3)_5Br]^{2+}$ ion.

.... [1]

(iv) State the oxidation number of cobalt in

- $[Co(NH_3)_5Br]^{2+}$ oxidation number of Co = ...
- $[Co(NH_3)_5SO_4]^+$ oxidation number of Co = ... [1]

(d) Solutions of the compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ can be distinguished from each other by simple chemical tests.
Assume that any species bonded to the cobalt ion does not react in these tests.

Complete the table with two **different** tests that could be used to positively identify each compound. Give the expected observation with each compound.

test	observation with $[Co(NH_3)_5Br]SO_4(aq)$	observation with $[Co(NH_3)_5SO_4]Br(aq)$

[2]

(e) The two compounds $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ are different colours.

Explain why the colours of the two compounds are different.

....

....

.... [2]

Topic: **Chem 28 Q# 307/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Bubbling air through different aqueous mixtures of $CoCl_2$, NH_4Cl and NH_3 produces various complex ions with the general formula $[Co(NH_3)_{6-n}Cl_n]^{3-n}$.

(a) (i) Determine the oxidation state of the cobalt in these complex ions.

.... [1]

(ii) Name the **two** types of reaction undergone by the cobalt ions during the formation of these complex ions.

....

.... [2]

(iii) The complex $[Co(NH_3)_4Cl_2]^+$ shows isomerism.

Draw three-dimensional structures of the two isomers, and suggest the type of isomerism shown here.

isomer 1

isomer 2

type of isomerism .... [3]

(b) (i) What is meant by the term *co-ordination number*?

....

.... [1]

(ii) Complete the table by predicting appropriate co-ordination numbers, formulae and charges for the complexes **C**, **D**, **E** and **F**.

complex	metal ion	ligand	co-ordination number	formula of complex	charge on complex
C	Cr^{3+}	CN^-			3–
D	Ni^{2+}	$H_2NCH_2CH_2NH_2$	6		
E	Pt^{2+}	Cl^-			2–
F	Fe^{3+}	$^-O_2C–CO_2^-$		$[Fe(O_2CCO_2)_3]$	

[6]

(c) Iron(III) forms complexes in separate reactions with both SCN^- ions and Cl^- ions.

$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq)$ equilibrium 1

$Fe^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [FeCl_4]^-(aq)$ equilibrium 2

(i) Write the expressions for the stability constants, K_{stab}, for these two equilibria. Include units in your answers.

K_{stab1} =

units = ...

K_{stab2} =

units = ... [3]

(ii) An equilibrium can be set up between these two complexes as shown in equilibrium 3.

$[FeCl_4]^-(aq) + SCN^-(aq) \rightleftharpoons [FeSCN]^{2+}(aq) + 4Cl^-(aq)$ equilibrium 3

Write an expression for K_{eq3} in terms of K_{stab1} and K_{stab2}.

K_{eq3} = ... [1]

(iii) The numerical values for these stability constants are shown.

$K_{stab1} = 1.4 \times 10^2 \quad K_{stab2} = 8.0 \times 10^{-2}$

Calculate the value of K_{eq3} stating its units.

K_{eq3} = ... units = ... [2]

[Total: 19]

Topic: **Chem 28 Q# 308/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(d) The cyanate ion, NCO^-, can act as a *monodentate ligand*.

(i) State what is meant by the terms

monodentate, ...

....

ligand. ....

.... [2]

Silver ions, Ag^+, react with cyanate ions to form a linear complex.

(ii) Suggest the formula of this complex, including its charge.

.... [2]

Topic: **Chem 28 Q# 309/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** **(i)** Draw the shape of one of the d orbitals.

[1]

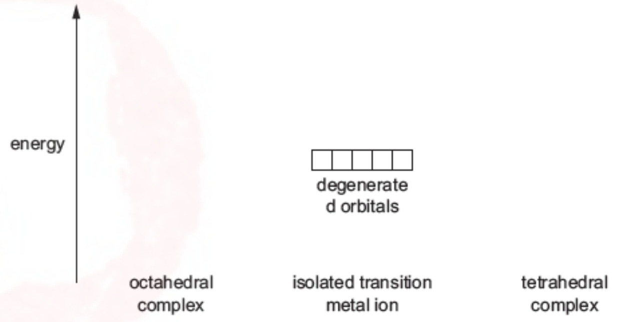
(ii) Complete the following electronic configurations.

Ni $1s^2 2s^2 2p^6 3s^2 3p^6$ ....

Ni^{3+} $1s^2 2s^2 2p^6 3s^2 3p^6$ ....

[1]

(b) **(i)** Complete the diagram to show how the presence of ligands around an isolated transition metal ion affects the **energy** of the d orbitals.



[1]

(ii) Explain why transition metal complexes are coloured.

....

....

....

.... [2]

(iii) $[Cu(H_2O)_6]^{2+}$ is pale blue but $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep purple-blue.

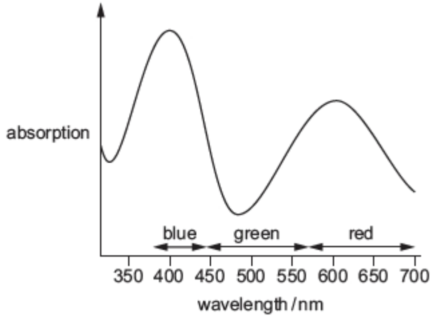
Suggest a reason for this.

....

....

.... [1]

(c) The diagram shows the visible spectrum of a solution of $[V(H_2O)_6]^{3+}$.



State and explain what colour the solution is.

colour of solution ....

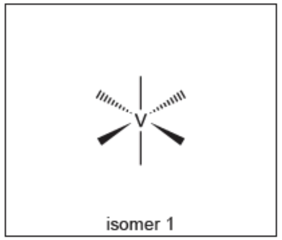
explanation ....

.... [2]

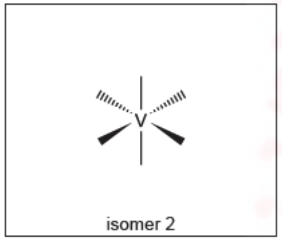
(d) (i) In the presence of chloride ions, $[V(H_2O)_6]^{3+}$ reacts to form a mixture of isomeric octahedral complexes.

$$[V(H_2O)_6]^{3+} + 2Cl^- \rightleftharpoons [V(H_2O)_4Cl_2]^+ + 2H_2O$$

Complete the three-dimensional diagrams to show the **two** isomers of $[V(H_2O)_4Cl_2]^+$.



isomer 1



isomer 2

[2]

(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

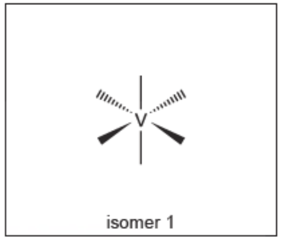
.... [1]

(e) (i) The complex $[V(H_2O)_6]^{3+}$ also reacts with ethane-1,2-diamine (*en*), $H_2NCH_2CH_2NH_2$, to form a mixture of isomeric octahedral complexes.

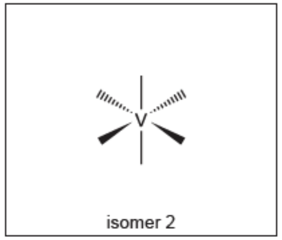
$$[V(H_2O)_6]^{3+} + 3en \rightleftharpoons [V(en)_3]^{3+} + 6H_2O$$

Complete the three-dimensional diagrams to show the **two** isomers of $[V(en)_3]^{3+}$.

You may use  to represent *en*.



isomer 1



isomer 2

[2]

(ii) State the type of isomerism shown by isomer 1 and isomer 2 in **(i)**.

.... [1]

(f) The reaction of $[Ni(H_2O)_6]^{2+}$ with aqueous ammonia produces the complex $[Ni(NH_3)_6]^{2+}$.

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

(i) Write the expression for K_{stab} for $[Ni(NH_3)_6]^{2+}$.

K_{stab} =

[1]

(ii) $[Ni(H_2O)_6]^{2+}$ also reacts with *en* to form $[Ni(en)_3]^{2+}$.
The values of the stability constants for the two complexes are shown.

K_{stab} $[Ni(NH_3)_6]^{2+} = 4.8 \times 10^7 \text{ mol}^{-6} \text{ dm}^{18}$

K_{stab} $[Ni(en)_3]^{2+} = 2.0 \times 10^{18} \text{ mol}^{-3} \text{ dm}^9$

A solution containing equal numbers of moles of ammonia and *en* is added to $[Ni(H_2O)_6]^{2+}$.

State which complex is produced in the larger amount. Explain your answer.

....

....

.... [1]

(iii) Adding a limited amount of *en* to $[Ni(H_2O)_6]^{2+}$ forms the complex $[Ni(H_2O)_2(en)_2]^{2+}$.

Suggest the number of possible stereoisomers of $[Ni(H_2O)_2(en)_2]^{2+}$. Explain your answer.
You are advised to include three-dimensional diagrams in your answer.

....

....

....

.... [2]

[Total: 18]

Topic: **Chem 28 Q# 310/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

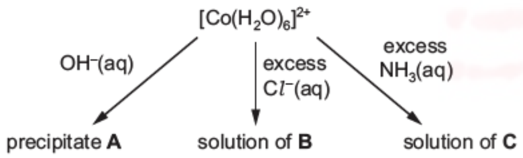
4 **(a)** Cobalt is a transition element that forms complex ions with oxidation states +2 and +3.

Explain what is meant by the term *transition element*.

....

.... [1]

(b) The following scheme shows some reactions of $[Co(H_2O)_6]^{2+}$.



(i) State the formula of each of the following.

A ....

B ....

C ....

[2]

(ii) State the colour of the following solutions.

$[Co(H_2O)_6]^{2+}$ ....

solution of **B** ....

solution of **C** ....

[2]

Topic: **Chem 28 Q# 311/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Copper is a transition element and has atomic number 29.

(a) Complete the electronic configuration for the copper atom and the copper ion in the +2 oxidation state.

- copper atom [Ar] ....
- copper ion in the +2 oxidation state [Ar] ....

[2]

(b) The following equilibrium exists between two complex ions of copper in the +2 oxidation state.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

(i) Name the *type of reaction* occurring here.

.... [1]

(ii) State the colours of these two complex ions.

$[Cu(H_2O)_6]^{2+}$ .... $[CuCl_4]^{2-}$ .... [1]

(iii) State the shape of the $[CuCl_4]^{2-}$ ion.

.... [1]

(iv) Write the expression for the stability constant, K_{stab}, for this equilibrium.

$K_{stab} =$

[1]

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 1}$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 2}$$

(i) What is meant by the term *bidentate ligand*?

....

.... [2]

(ii) The table lists the values of stability constants for these two complexes.

	stability constant, K_{stab}
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.94 × 10^7
$[Cu(en)(H_2O)_4]^{2+}$	3.98 × 10^{10}

What do these K_{stab} values tell us about the relative positions of equilibria 1 and 2?

....

.... [1]

(d) Nickel forms the complex ion $[Ni(en)_3]^{2+}$ in which it is surrounded octahedrally by six nitrogen atoms.

(i) Name the type of stereoisomerism displayed by $[Ni(en)_3]^{2+}$.

.... [1]

(ii) Draw three-dimensional diagrams to show the **two** stereoisomers of $[Ni(en)_3]^{2+}$.

[3]

Topic: **Chem 28 Q# 312/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** **(i)** Complete the following electronic configurations.

- the cobalt atom, Co $1s^22s^22p^6$ ....
- the cobalt(II) ion, Co^{2+} $1s^22s^22p^6$ ....

[1]

(ii) State the colours you would observe when concentrated HC*l*(aq) is added to an aqueous solution of cobalt(II) nitrate, $Co(NO_3)_2$.
Give the formulae and geometry of the complexes formed.

....

....

....

....

.... [5]

(b) There are two isomers with the formula $Ni(R_3P)_2I_2$, but only one structure with the formula $Co(R_3P)_2I_2$. (R = alkyl, R_3P is a monodentate ligand)

Draw diagrams showing the structure of $Co(R_3P)_2I_2$ and the two isomers of $Ni(R_3P)_2I_2$.

$Ni(R_3P)_2I_2$

$Ni(R_3P)_2I_2$

$Co(R_3P)_2I_2$

[3]

[Total: 9]

3 **(a)** Complete the electronic structures of the following species.

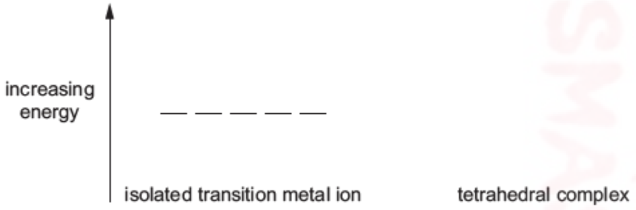
Co [Ar] ....

Co^{2+} [Ar] ....

[2]

(b) In an isolated transition metal atom the five d orbitals have the same energy. When a transition metal ion forms a tetrahedral complex the d orbitals are split into two groups of different energies.

Complete an orbital energy diagram to show this, indicating the number of orbitals in each group.



[1]

(c) Cobalt(II) forms a six co-ordinate complex containing three water molecules and three chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

.... [1]

(ii) Explain, with the aid of diagrams, how many isomers of the complex in **(i)** exist.

[2]

(d) Platinum(II) forms a four co-ordinate complex containing two ammonia molecules and two chloride ions.

(i) Write the formula of this complex showing the overall charge, if appropriate.

.... [1]

(ii) This complex exists as two isomers.

Draw the structure of these isomers and give their names.

....

[3]

(iii) One of the isomers in **(ii)** is an important anticancer drug.

State which isomer this is and explain why this isomer is effective.

isomer ....

reason ....

....

....

.... [2]

(e) Transition metal ions often exist as hexa-aqua complexes in aqueous solution. The reactions which involve ligand exchange are reversible.

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

(i) Write an expression for the stability constant, K_{stab}, for this equilibrium. Give its units.

K_{stab} =

units = ...

[2]

(ii) The numerical value for K_{stab} for this equilibrium at 298 K is 1.20×10^{13}.

Explain how this value relates to the relative stabilities of the two complexes.

....

.... [1]

[Total: 15]

Topic: **Chem 28 Q# 314/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 The transition element iron is the most abundant element in the Earth's core.

(a) What is meant by the term *transition element*?

....

.... [1]

(b) In aqueous solution, iron can form complex ions which contain ligands.

(i) Name the *type of bonding* that occurs between a ligand and a transition element.

.... [1]

(ii) Which of the following species can act as a ligand?
Complete the table by placing a tick (✓) in the appropriate column to indicate whether the species can act as a ligand or not.

species	can act as a ligand	cannot act as a ligand
NO_3^-		
BF_3		
$H_2NCH_2CH_2NH_2$		
NH_4^+		

[2]

(c) Manganese ions, Mn^{2+}(aq), show some similar chemical properties to those of copper(II) ions, Cu^{2+}(aq).

Use this information and the *Data Booklet* to suggest the formula of the manganese species formed in each of the following reactions. State the *type of reaction* taking place in each case.

	formula of manganese species formed	type of reaction
Mn^{2+}(aq) + NaOH(aq)		
Mn^{2+}(aq) + concentrated HC*l*		
Mn^{2+}(aq) + H_2O_2(aq)		

[5]

[Total: 9]

Topic: **Chem 28 Q# 315/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) **(i)** Phosphorus(III) oxide, P_4O_6, contains no P–P or O–O bonds.
In the P_4O_6 molecule, all oxygen atoms are divalent and all phosphorus atoms are trivalent.

(ii) P_4O_6 can act as a ligand.

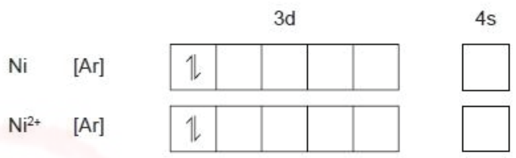
What is meant by the term *ligand*?

....

.... [1]

Topic: **Chem 28 Q# 316/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** Complete the electron configurations for Ni and Ni^{2+}.



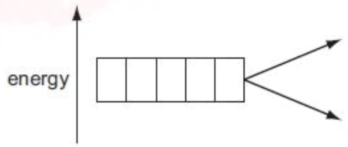
[2]

(b) The presence of electrons in d orbitals is responsible for the colours of transition element compounds.

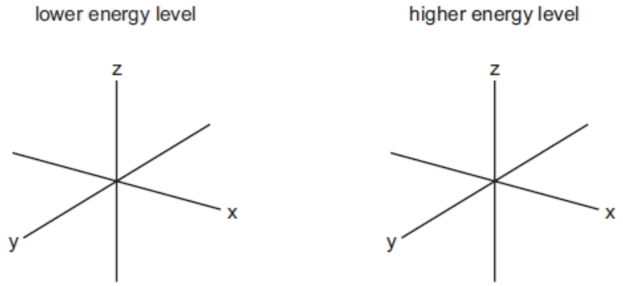
(i) The d orbitals in an isolated transition metal atom or ion are all at the same energy level.
What term is used to describe orbitals that are at the same energy level?

....

(ii) Complete the diagram to show the splitting of the d orbital energy levels in an octahedral complex ion.



(iii) On the axes below, sketch the shapes of one d orbital from the lower energy level and one d orbital from the higher energy level.



[4]

(c) The octahedral complex $[Ni(H_2O)_6]^{2+}$ is green. Explain the origin of the colour of this complex.

....

....

....

....

.... [3]

(d) When $NH_3(aq)$ is added to the green solution containing $[Ni(H_2O)_6]^{2+}$, a grey-green precipitate, **A**, is formed. This precipitate dissolves in an excess of $NH_3(aq)$ to give a blue-violet solution, **B**. Suggest formulae for **A** and **B** and write equations for the two reactions producing **A** and **B**.

....

....

....

.... [4]

Topic: **Chem 28 Q# 317/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) (i) State what is meant by the terms:

complex, ...

....

ligand. ....

....

(ii) Two of the complexes formed by copper are $[Cu(H_2O)_6]^{2+}$ and $CuCl_4^{2-}$.
Draw three-dimensional diagrams of their structures in the boxes and name their shapes.

$[Cu(H_2O)_6]^{2+}$

shape: ....

$CuCl_4^{2-}$

shape: ....

(iii) Platinum forms square-planar complexes, in which all four ligands lie in the same plane as the Pt atom.
There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$.
Suggest the structures of the two isomers, and, by comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here.

Structures of isomers:

isomer 1

isomer 2

Type of isomerism: ....

[7]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic structures of these ions.

Cu(II) [Ar] ....

Cu(I) [Ar] ....

(ii) Use these electronic structures to explain why

copper(II) salts are usually coloured,

....

....

....

....

copper(I) salts are usually white or colourless.

....

....

[5]

Topic: **Chem 28 Q# 318/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) The iron(II) complex *ferrous bisglycinate hydrochloride* is sometimes prescribed, in capsule form, to treat iron deficiency or anaemia.
A capsule containing 500 mg of this iron(II) complex was dissolved in dilute H_2SO_4 and titrated with 0.0200 mol dm^{-3} $KMnO_4$.
18.1 cm^3 of $KMnO_4$ solution were required to reach the end point.

The equation for the titration reaction is as follows.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

(i) Describe how you would recognise the end point of this titration.

....

(ii) Calculate

- the number of moles of Fe^{2+} in the capsule,

- the mass of iron in the capsule,

- the molar mass of the iron(II) complex, assuming 1 mol of the complex contains 1 mol of iron.

[4]

[Total: 16]

Topic: **Chem 28 Q# 319/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) In general, reactions of the compounds of transition elements can be classified under one or more of the following headings.

acid-base
ligand exchange
precipitation
redox

Choose the most suitable heading to describe each of the following reactions, by placing a tick (✓) in the appropriate column in the table below.
Only one tick should be placed against each reaction.

reaction	acid-base	ligand exchange	precipitation	redox
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$				
$[Cu(H_2O)_6]^{2+} + 4HCl \rightarrow [CuCl_4]^{2-} + 4H^+ + 6H_2O$				
$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$				
$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2 + 6H_2O$				
$2Fe(OH)_2 + ½O_2 + H_2O \rightarrow 2Fe(OH)_3$				
$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$				
$Cr(H_2O)_3(OH)_3 + OH^- \rightarrow [Cr(H_2O)_2(OH)_4]^- + H_2O$				
$[Cr(OH)_4]^- + 1½H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 4H_2O$				

[8]

Topic: **Chem 28 Q# 320/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 Nitrogen monoxide, NO, is formed in a reversible reaction when air is heated to the temperature of a car engine.

(c) The following information on half-reactions relates to the reaction between HNO_3 and an excess of $FeSO_4$.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^{\ominus} = +0.77\,V$$

$$3H^+ + NO_3^- + 2e^- \rightarrow HNO_2 + H_2O \qquad E^{\ominus} = +0.94\,V$$

$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad E^{\ominus} = +0.99\,V$$

(i) Suggest the formula of the nitrogen-containing final product of this reaction.

....

(ii) Write an equation for the formation of this nitrogen-containing product.

(iii) Nitrogen monoxide forms a dark brown complex with an excess of $FeSO_4(aq)$. What kind of bonding is involved in the complex formation?

....

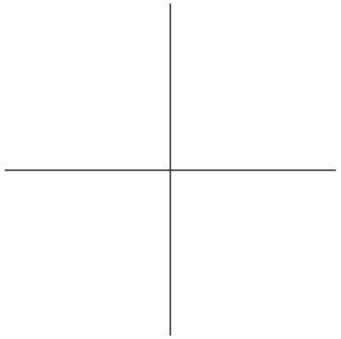
(iv) Suggest a formula for this complex.

....

[4]

[Total: 17]

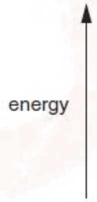
3 **(a)** On the following diagram draw a clear **labelled** sketch to describe the shape and symmetry of a typical d-orbital.



[2]

(b) Although the five d-orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups.

(i) Draw an orbital energy diagram to show this, indicating the number of orbitals in each group.



(ii) Use your diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

....

....

....

....

- The colour of a complex of a given transition element often changes when the ligands around it are changed.

....

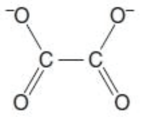
....

....

[7]

(c) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

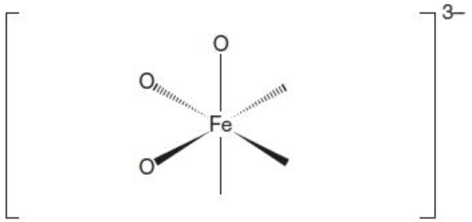
The structure of the ethanedioate ion is as follows.



[1]

(ii) Calculate the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$. ....

(iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Complete the following **displayed** formula of this ion.



[2]

Topic: **Chem 28 Q# 322/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i) What is meant by the term *ligand* in the context of transition element chemistry?

....

....

(ii) Decide which of the following species could be a ligand, and which could not be. Place a tick (✓) in the appropriate column.

species	can be a ligand	cannot be a ligand
OH^-		
NH_4^+		
CH_3OH		
CH_3NH_2		

[3]

(b) Read the following description of some reactions of copper(II) sulfate, and answer the questions that follow.

> When 0.1 mol of white anhydrous $CuSO_4$ is dissolved in liquid ammonia at –33 °C, a deep blue solution **C** results.
> When 0.2 mol of solid NaOH is added to solution **C**, and the ammonia solvent allowed to evaporate, a solid residue is obtained.
> Heating this residue to 200 °C produces a dark coloured mixture of two solids.
> When water is added to this mixture, a black solid **D** and a colourless solution **E** are formed. Neither **D** nor **E** contains nitrogen.
> Adding $BaCl_2$(aq) to solution **E** produces a white precipitate **F**.
> Solid **D** dissolves in HNO_3(aq) on warming, without evolution of gas, to give a pale blue solution containing $Cu(NO_3)_2$(aq).

(i) Suggest the formula of the compound contained in each of the following.

solution **C** ....

solid **D** ....

solution **E** ....

white precipitate **F** ....

(ii) Name the type of reaction that is occurring when **D** reacts with HNO_3(aq).

....

[5]

Topic: **Chem 28 Q# 323/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) Describe **three** characteristic chemical properties of transition elements that are not shown by Group II elements.

....

....

.... [3]

(b) When NH_3(aq) is added to a green solution containing Ni^{2+}(aq) ions, a grey-green precipitate is formed. This precipitate dissolves in an excess of NH_3(aq) to give a blue-violet solution.
Suggest an explanation for these observations, showing your reasoning and including equations for the reactions you describe.

....

....

....

....

....

.... [4]

2 **(a)** Describe **three** characteristic chemical properties of transition elements that are not shown by Group II elements.

....

....

....[3]

(b) When NH_3(aq) is added to a green solution containing Ni^{2+}(aq) ions, a grey-green precipitate is formed. This precipitate dissolves in an excess of NH_3(aq) to give a blue-violet solution.
Suggest an explanation for these observations, showing your reasoning and including equations for the reactions you describe.

....

....

....

....

....

....[4]

(c) Dimethylglyoxime, DMG, is a useful reagent for the quantitative estimation of nickel. It forms an insoluble salt with nickel ions according to the following equation.

$$Ni^{2+}(aq) + \underset{\text{DMG}}{C_4H_8N_2O_2} \longrightarrow \underset{\text{Ni-DMG}}{NiC_4H_6N_2O_2(s)} + 2H^+(aq)$$

A small coin of mass 3.40 g was dissolved in nitric acid and an excess of DMG was added. The precipitated Ni-DMG was filtered off, washed and dried. Its mass was 4.00 g.
Calculate the % of nickel in the coin.

percentage of nickel = ...% [3]

[Total: 10]

Topic: **Chem 28 Q# 324/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 One major difference between the properties of compounds of the transition elements and those of other compounds is that the compounds of the transition elements are often coloured.

(a) Explain in detail why many transition element compounds are coloured.

....

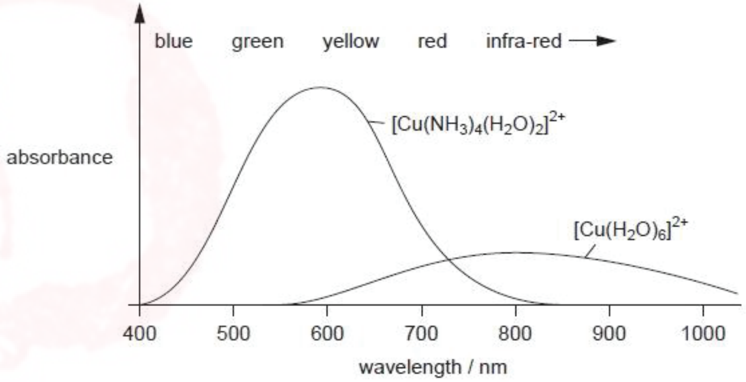
....

....

....

....[3]

(b) The following graph shows the absorption spectrum of two complexes containing copper.



(i) State the colours of the following complex ions.

$[Cu(H_2O)_6]^{2+}$ ....

$[Cu(NH_3)_4(H_2O)_2]^{2+}$ ....

(ii) Using the spectra above give **two** reasons why the colour of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion is deeper (more intense) than that of the $[Cu(H_2O)_6]^{2+}$ ion.

....

....

....

(iii) Predict the absorption spectrum of the complex $[Cu(NH_3)_2(H_2O)_4]^{2+}$, and sketch this spectrum on the above graph. [6]

(c) Copper forms a complex with chlorine according to the following equilibrium.

$$Cu^{2+}(aq) + 4Cl^{-}(aq) \rightleftharpoons [CuCl_4]^{2-}(aq)$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction, stating its units.

K_c = ... units ....

(ii) The numerical value of K_c is 4.2×10^5.
Calculate the $[[CuCl_4]^{2-}]/[Cu^{2+}]$ ratio when $[Cl^-] = 0.20\,mol\,dm^{-3}$.

....

....

[3]

[Total: 12]

Topic: Chem 29 Q# 325/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Compounds **F** and **J** are shown in Fig. 4.1.

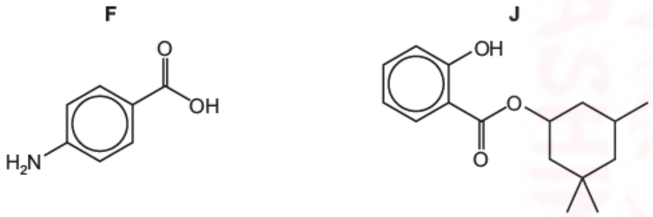


Fig. 4.1

(a) **F** and **J** both contain the arene functional group.

(i) Identify the other functional groups in **F** and **J**.

F: ....

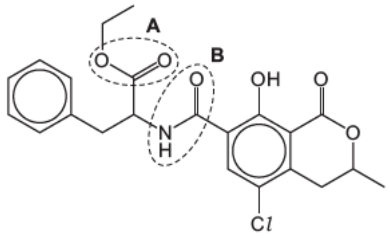
J: ....

[2]

Topic: **Chem 29 Q# 326/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 Compound **F** has been found in small quantities in some cereals and dried fruit.

F



(a) **(i)** Give the name of the functional groups labelled **A** and **B**.

A ....

B ....

[2]

(ii) State the number of chiral carbon atoms in one molecule of **F**.

.... [1]

Topic: **Chem 29 Q# 327/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Benzene can be converted into cyclohexane.

(ii) State the bond angles in benzene and cyclohexane.

bond angle in benzene .... bond angle in cyclohexane ....

Explain your answers.

....

....

....

[2]

Topic: **Chem 29 Q# 328/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

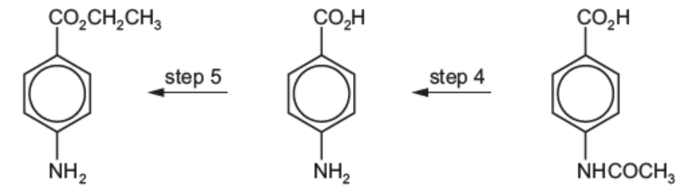
(a) Suggest **two** functional groups present in a molecule of the drug named chloramphenicol.

1 ....

2 ....

[1]

Topic: **Chem 29 Q# 329/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6(b)/www.SmashingScience.org



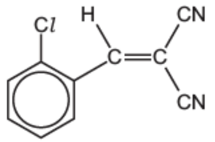
benzocaine W

(i) Give the systematic name of compound **W**.

.... [1]

Topic: **Chem 29 Q# 330/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **P** contains several functional groups.



P

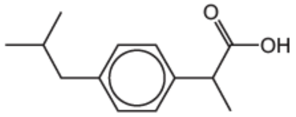
(a) Name the functional groups present in **P**.

....

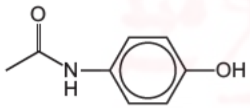
.... [2]

Topic: **Chem 29 Q# 331/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(a) Ibuprofen and paracetamol both contain the aryl (benzene) functional group.

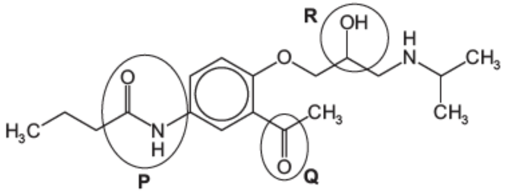
Name the **other** functional groups present in each molecule.

ibuprofen ....

paracetamol .... [2]

Topic: **Chem 29 Q# 332/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 Acebutolol is a drug that can be used to lower blood pressure.



acebutolol

(a) Give the **full name** of the circled functional groups labelled **P**, **Q** and **R** in acebutolol.

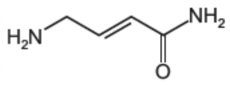
P ....

Q ....

R .... [3]

Topic: **Chem 29 Q# 333/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) Compound **W** has the following structure.

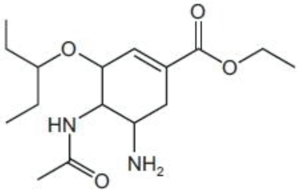


(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds .... π bonds .... [2]

Topic: **Chem 29 Q# 334/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

(b) Oseltamivir is a chiral drug. This drug is usually taken as a single optical isomer rather than as a mixture of isomers.

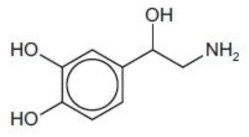
Suggest **one** benefit of taking a drug in this way.

....

.... [1]

Topic: **Chem 29 Q# 335/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Noradrenaline is a hormone and neurotransmitter, which is released during stress to stimulate the heart and increase blood pressure.



noradrenaline

(a) State the **names** of **three** functional groups in the noradrenaline molecule.

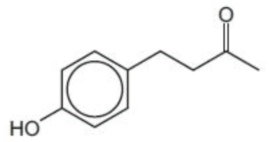
....

....

.... [3]

Topic: **Chem 29 Q# 336/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **G** is a naturally occurring aromatic compound that is present in raspberries.



compound **G**

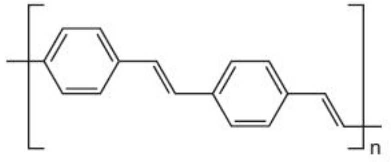
(a) Identify the functional groups present in compound **G**.

....

.... [2]

Topic: **Chem 29 Q# 337/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(d) There has been a great deal of commercial interest in the development of polymers that can conduct electricity and/or emit light. A length of one such polymer is shown.



(i) Suggest how this polymer conducts electricity.

....

(ii) Suggest the molecular geometry required for this molecule to conduct.

Explain your answer.

....

....

(iii) What is the empirical formula of this polymer?

....

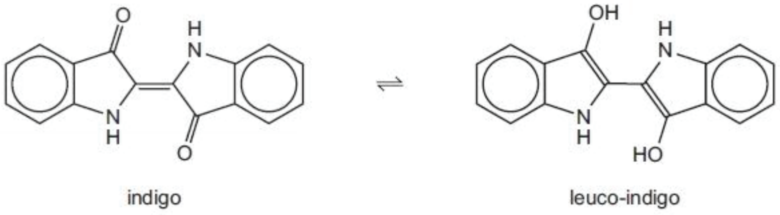
[4]

[Total: 10]

Topic: **Chem 29 Q# 338/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.

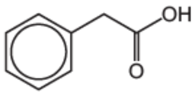


(ii) Name **three** functional groups in indigo.

.... [2]

Topic: Chem 30 Q# 339/ ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The structure of phenylethanoic acid is shown.



(c) Phenylethanoic acid can be synthesised using benzene as the starting material.

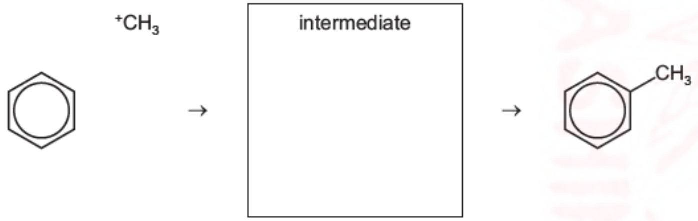
In the first stage of this synthesis, benzene reacts with chloromethane in the presence of an $AlCl_3$ catalyst to form methylbenzene.

Chloromethane reacts with $AlCl_3$ to form two ions. One of these is the carbocation $^+CH_3$.

(i) Write an equation for the reaction between chloromethane and $AlCl_3$.

.... [1]

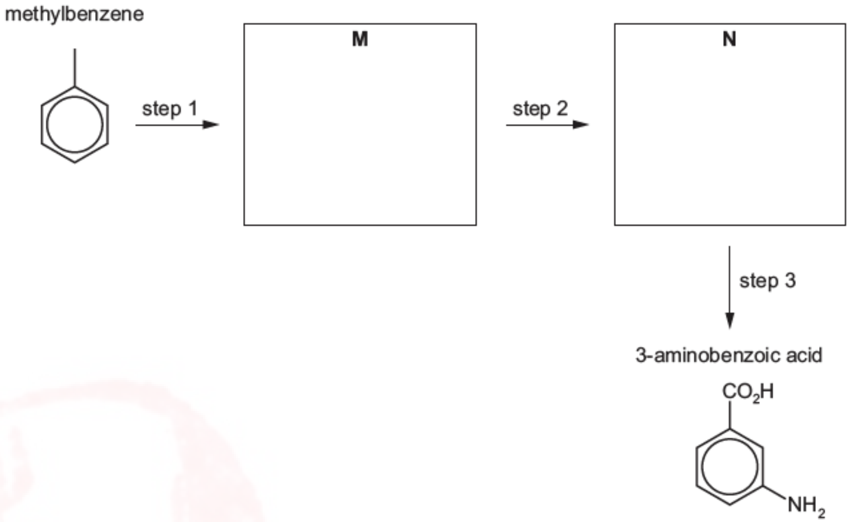
(ii) Draw the mechanism of the reaction between benzene and $^+CH_3$. Include all relevant curly arrows, charges and the structure of the intermediate.



[3]

Topic: **Chem 30 Q# 340/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** 3-aminobenzoic acid can be synthesised from methylbenzene in three steps.



(i) Draw the structures of **M** and **N** in the boxes. [2]

(ii) Suggest reagents and conditions for each step of the synthesis.

step 1 ....

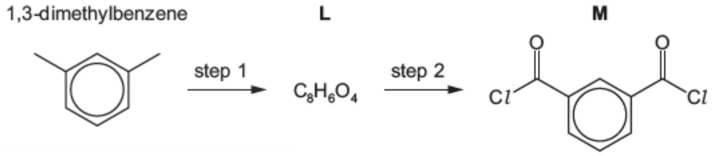
step 2 ....

step 3 ....

[3]

Topic: **Chem 30 Q# 341/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

(b) Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



(iv) A student investigates a possible synthesis of **M** directly from benzene using $COCl_2$ in the presence of an $AlCl_3$ catalyst.

Benzene initially reacts with $COCl_2$ as shown.

reaction 1 $COCl_2 + AlCl_3 \rightarrow AlCl_4^- + Cl{-}\overset{+}{C}{=}O$

reaction 2 $C_6H_6 + Cl{-}\overset{+}{C}{=}O \rightarrow C_6H_5COCl + H^+$

Reaction 2 is the electrophilic substitution of $Cl{-}\overset{+}{C}{=}O$ for H^+ in benzene.

Suggest a mechanism for reaction 2.

[3]

[Total: 12]

Topic: **Chem 30 Q# 342/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Benzene, C_6H_6, can be obtained from crude oil.

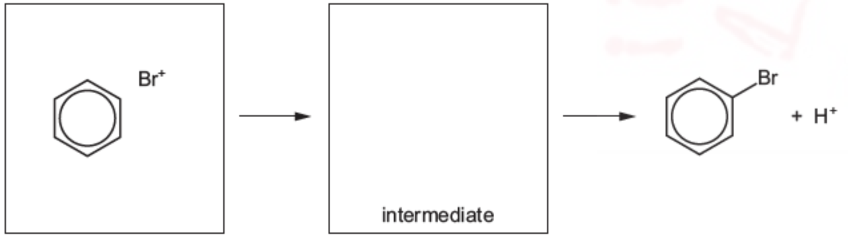
(a) Benzene reacts with bromine, in the presence of a suitable catalyst, forming bromobenzene as one product.

(i) Give the name or formula of the other product of this reaction.

.... [1]

(ii) In the presence of the catalyst, bromine can be considered to form the electrophile Br^+.

Complete the mechanism by which benzene reacts with Br^+, using curly arrows to show the movement of electron pairs.

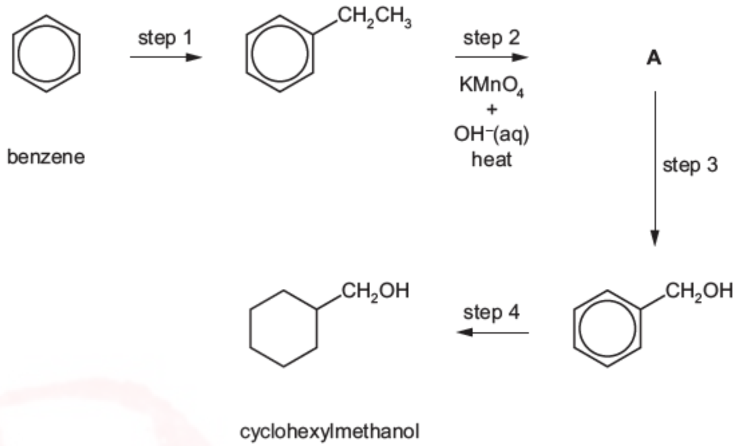


[2]

(iii) Name this mechanism.

.... [1]

(b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $C_6H_{11}CH_2OH$, as outlined below.



(i) Identify a suitable reagent and a suitable catalyst for step 1.

reagent ....

catalyst .... [2]

(ii) Draw the structure of **A**.

A

[1]

(iii) Identify suitable reagents for steps 3 and 4.

step 3 ....

step 4 .... [2]

Topic: **Chem 30 Q# 343/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, A*l*Br$_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(i) Explain why no addition reaction takes place.

....

.... [1]

A*l*Br$_3$ reacts with bromine to generate an electrophile, Br$^+$.

(ii) Draw the mechanism of the reaction between benzene and Br$^+$ ions. Include all relevant arrows and charges.

[3]

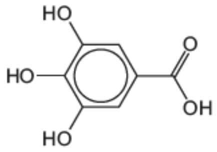
(iii) Write an equation to show how the A*l*Br$_3$ catalyst is reformed.

.... [1]

Topic: **Chem 30 Q# 344/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

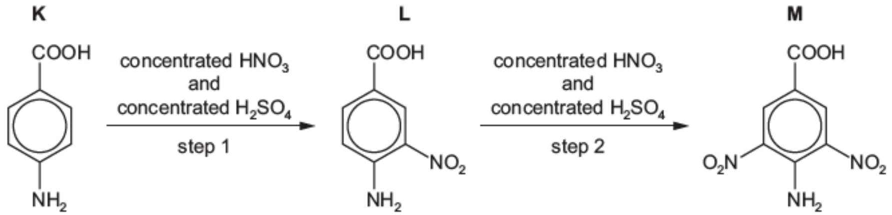
5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(c) Compound **K** is used as the starting material in a synthesis of gallic acid.

A student suggested the first two steps of the synthesis could be as shown.



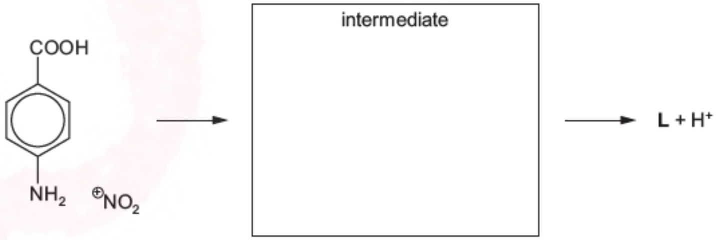
Nitronium ions, NO$_2^+$, are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of NO$_2^+$ by this method.

.... [1]

(ii) Complete the mechanism and draw the intermediate of step 1.

Include all relevant charges and curly arrows to show the movement of electron pairs.



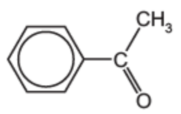
[2]

(iii) State the name of the mechanism in **(c)(ii)**.

.... [1]

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(a) Phenylethanone can be synthesised using benzene as one of the starting materials.

Identify the other reagents used and describe any essential reaction conditions.

....

.... [2]

(b) Phenylethanone is treated separately with three reagents.

Complete the table, for each reagent, to give the structural formula of one organic product formed and the name of the mechanism involved. If there is no reaction you should write 'no reaction'.

reagent	organic product	name of mechanism
chlorine gas at 10 °C in the presence of ultra-violet light		
a mixture of concentrated nitric and sulfuric acids at 50 °C		
bromine water		

[5]

---

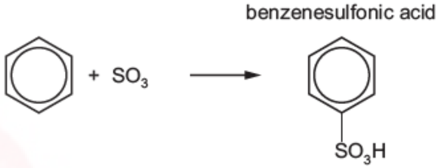
7 **(a)** Benzene can be converted into cyclohexane.

(i) For this reaction name the type of reaction and identify the reagent and conditions needed.

type of reaction ....

reagent and conditions .... [2]

(b) When benzene reacts with SO_3, benzenesulfonic acid is produced.



The mechanism of this reaction is similar to that of the nitration of benzene. Concentrated H_2SO_4 is used in an initial step to generate the SO_3H^+ electrophile as shown.

$$SO_3 + H_2SO_4 \rightarrow SO_3H^+ + HSO_4^-$$

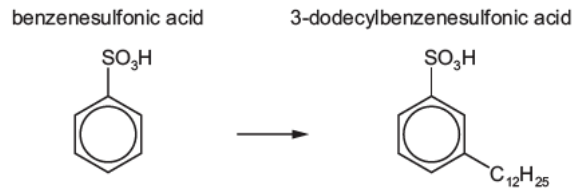
(i) Draw a mechanism for the reaction of benzene with SO_3H^+ ions. Include all necessary curly arrows and charges.

[3]

(ii) Write an equation to show how the H_2SO_4 catalyst is reformed.

.... [1]

(c) 3-dodecylbenzenesulfonic acid can be prepared from benzenesulfonic acid.



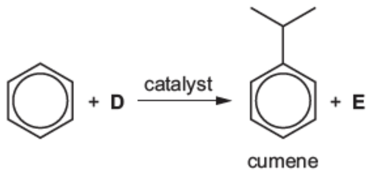
Suggest the reagents and conditions and name the mechanism for this reaction.

reagents and conditions ....

mechanism ....
[2]

Topic: **Chem 30 Q# 347/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** Benzene reacts with **D** in the presence of a suitable catalyst to give cumene and non-organic product **E**. This is an electrophilic substitution reaction.



(i) Name the reactant **D** and the non-organic product **E**.

D ....

E ....
[2]

(ii) Give the name of the type of aromatic electrophilic substitution reaction taking place.

.... [1]

(b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

(i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

.... [1]

(b) Cumene undergoes substitution reactions with chlorine to give several different isomeric products with the formula $C_9H_{11}Cl$. The substitution can occur in the aromatic ring or in the side-chain of cumene.

(i) Describe the conditions that are used to ensure substitution takes place only in the **aromatic ring**.

.... [1]

(ii) Draw the structures of the **two** major isomeric products of the reaction, formula $C_9H_{11}Cl$, when substitution takes place in the aromatic ring.

[1]

(c) Complete the following table to show the structures of the organic products formed when cumene reacts with each reagent.

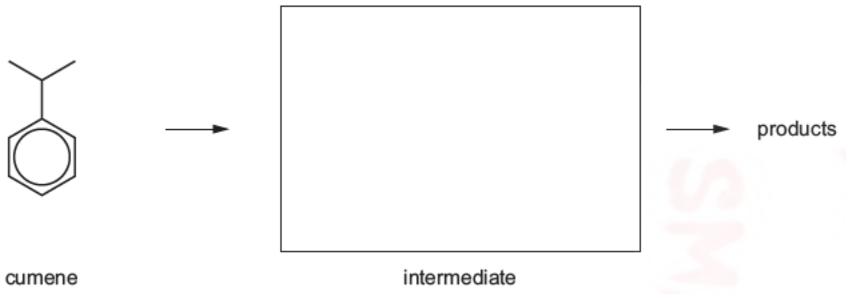
reagent	structure of organic product
hot $KMnO_4$(aq)	
H_2 + Ni, high pressure	

[2]

(d) Cumene can be nitrated using a mixture of concentrated nitric and sulfuric acids. The mechanism for this reaction is similar to the mechanism for the nitration of benzene.

Complete the mechanism for this reaction.

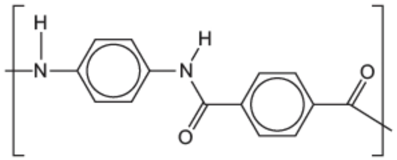
- Include all relevant charges and curly arrows showing the movement of electron pairs.
- Draw the structure of the intermediate.
- You do not need to draw the products.



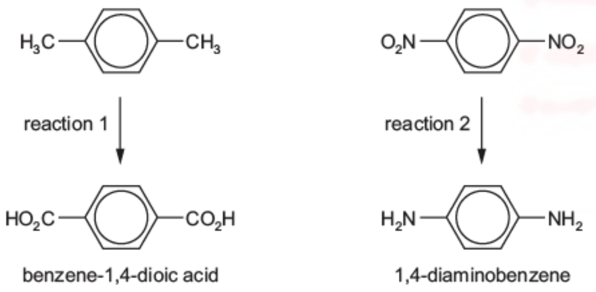
[4]

Topic: **Chem 30 Q# 348/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

The repeat unit of the polyamide *Kevlar* is shown.



(d) The monomers of *Kevlar*, benzene-1,4-dioic acid and 1,4-diaminobenzene, can be synthesised as follows.



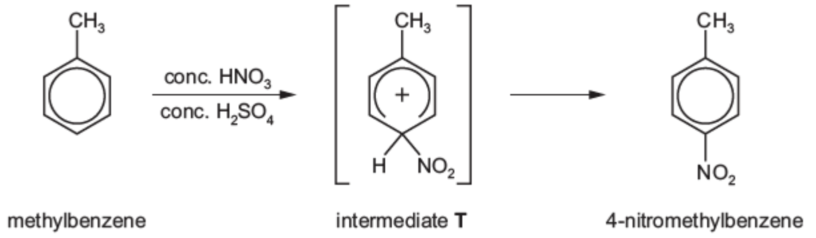
State the reagents and conditions needed for:

(i) reaction 1

.... [1]

Topic: **Chem 30 Q# 349/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** 4-nitromethylbenzene can be prepared via an electrophilic substitution reaction as shown.



(i) This reaction also forms an isomer of 4-nitromethylbenzene as a by-product.

Draw the structure of this by-product.

[1]

(ii) Write an equation for the reaction between HNO_3 and H_2SO_4 that forms the electrophile for this reaction.

.... [1]

(iii) Describe how the **structure and bonding** of the six-membered ring in intermediate **T** differs from that in methylbenzene.

....

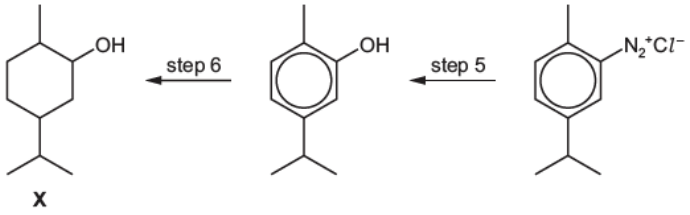
....

....

.... [3]

Topic: **Chem 30 Q# 350/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



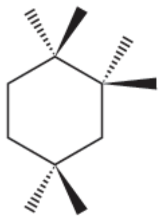
(c) During step 6, hydrogen is added to the benzene ring to produce the cyclohexane ring in **X**. The six hydrogen atoms are all added to the **same side** of the benzene ring.

(i) State the reagents and conditions needed for this reaction.

.... [1]

(ii) Complete the part structure to show the structure of the isomer of **X** that would most likely be obtained during this reaction.

X



[2]

[Total: 15]

Topic: **Chem 30 Q# 351/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d) Benzene, C_6H_6, and borazine, $B_3N_3H_6$, have planar, cyclic structures.

(i) Describe the structure of and bonding in benzene, C_6H_6.

....

....

....

....

....

....

.... [3]

(ii) In borazine, $B_3N_3H_6$, the boron and nitrogen atoms alternate around the ring. Each ring atom has a single hydrogen atom bonded to it.
All boron-nitrogen bonds in borazine are 0.144 nm in length, whereas in simple compounds B–N and B=N bond lengths are 0.154 nm and 0.136 nm respectively.

Suggest and draw the structure of borazine.

[1]

[Total: 10]

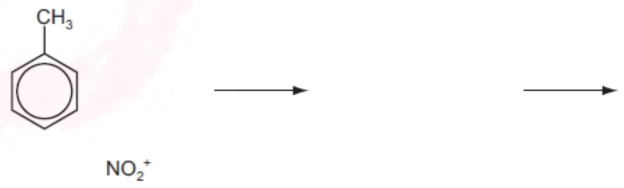
Topic: **Chem 30 Q# 352/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** Methylbenzene undergoes electrophilic substitution with nitronium ions, NO_2^+.
Nitronium ions are generated by the reaction between concentrated sulfuric acid and concentrated nitric acid.

(i) Construct an equation for the formation of nitronium ions, NO_2^+, by this method.

....

(ii) Complete the scheme to show the mechanism for this reaction. Use curly arrows to show the movement of electron pairs.

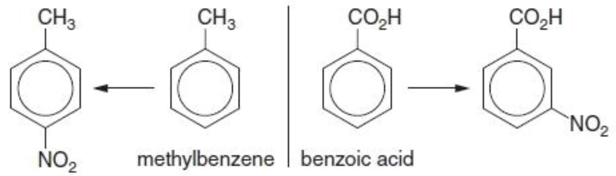


[4]

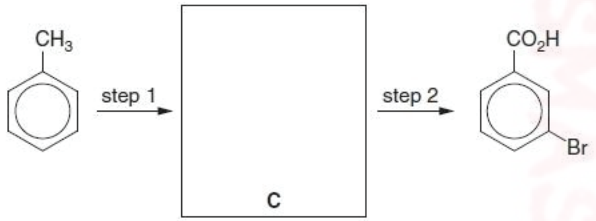
Topic: **Chem 30 Q# 353/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) **(i)** When treated with concentrated HNO_3 + H_2SO_4 at 55 °C, benzene produces nitrobenzene.
Outline the mechanism of this reaction. You should include all charges, and use curly arrows to represent the movement of electron pairs.

In aromatic substitution of monosubstituted benzenes, the orientation of an incoming group depends on the nature of the group already attached to the ring.
For example, using the same reagents and conditions as in **(i)**, methylbenzene and benzoic acid produce the following nitro compounds.



(ii) Using this information as an aid, suggest a structure for compound **C** in the following synthesis of 3-bromobenzoic acid.



(iii) Suggest reagents and conditions for steps 1 and 2.

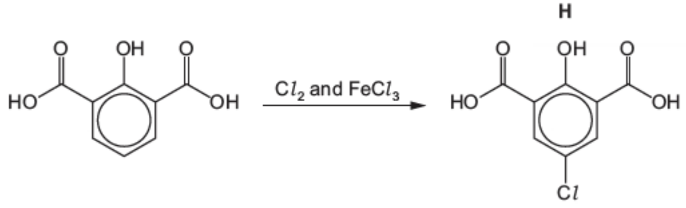
step 1	step 2

[6]

[Total: 12]

Topic: Chem 31 Q# 354/ ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(c) Compound **H** is formed in one step of a different synthesis, as shown.



(i) State the role of FeCl_3 in this step.

.... [1]

(ii) Use the *Data Booklet* to suggest **two** reasons why the chlorine atom in compound **H** substitutes into the ring at the position shown, instead of the other positions in the ring.

1 ....

....

2 ....

.... [2]

Topic: **Chem 31 Q# 355/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** Organochlorine compounds can undergo hydrolysis.

$$R{-}Cl + H_2O \rightarrow R{-}OH + HCl$$

State and explain the relative rates of hydrolysis of the following compounds.

CH_3CH_2Cl CH_3COCl C_6H_5Cl

....

....

....

....

.... [3]

Topic: Chem 32 Q# 356/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(e) Phenol and benzene both react with nitric acid, as shown in Fig. 4.5.

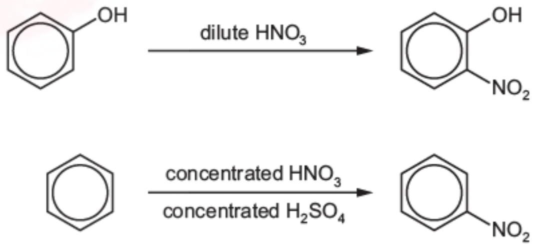


Fig. 4.5

Explain why the reagents and conditions for these two reactions are different.

....

....

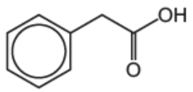
....

....

.... [3]

Topic: **Chem 32 Q# 357/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The structure of phenylethanoic acid is shown.



(b) Phenylethanoic acid, ethanol and phenol can all behave as acids.

Compare and explain the relative acidities of these three compounds.

.... > .... > ....
most acidic least acidic

....

....

....

....

.... [4]

Topic: **Chem 32 Q# 358/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 Phenol, C_6H_5OH, is a weak acid.

(a) Phenol can be made from phenylamine, $C_6H_5NH_2$.

Give the reagents and conditions for this reaction.

....

.... [2]

(b) Phenol reacts with dilute aqueous nitric acid under room conditions to give a mixture of two isomeric products with molecular formula $C_6H_5NO_3$.

Use the *Data Booklet* to draw the structural formulae of these two products in the boxes and name each product.

name ....

name ....

[2]

(c) Phenol reacts with an excess of aqueous bromine.

(i) Draw and name the organic product of this reaction in the box.

name ....

[2]

(ii) Describe **two** visual observations that can be made when phenol reacts with an excess of aqueous bromine.

observation 1 ....

observation 2 ....

[1]

(d) Write an equation for a neutralisation reaction in which phenol behaves as an acid.

.... [1]

(e) Water, phenol and ethanol can all behave as acids.

Place these three compounds in order of acidity, starting with the **most** acidic.
Explain your answer.

.... > .... > ....
most acidic least acidic

....

....

....

....

....

....

[3]

[Total: 11]

Topic: **Chem 32 Q# 359/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

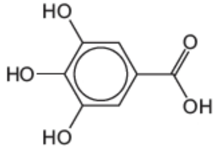
(b) Suggest why bromination of phenol occurs more readily than bromination of benzene.

[2]

Topic: **Chem 32 Q# 360/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

gallic acid



(a) Gallic acid contains the carboxylic acid and phenol functional groups.

State and explain the relative acid strength of these two functional groups.

[2]

Topic: **Chem 32 Q# 361/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = C*l* or OH).

Explain why.

[3]

(b) When phenol is reacted with bromine dissolved in an inert solvent, two isomeric bromophenols, C_6H_4BrOH, are formed.

Suggest structures for these products. Name each compound.

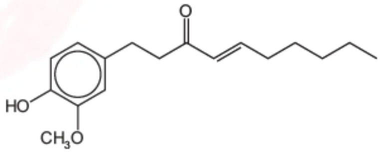
name: ....

name: ....

[2]

Topic: **Chem 32 Q# 362/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

(b) The structure of shogaol is shown.



shogaol

(c) Zingerone is formed from gingerol.

Some reactions of zingerone are shown.

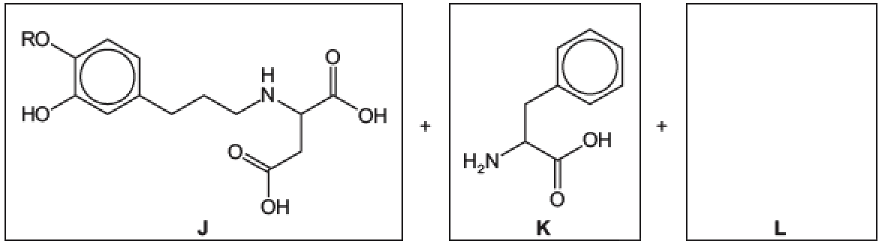
Complete the table to identify the functional groups in zingerone.

reagent and conditions	observation	functional group in zingerone indicated by the observation
benzenediazonium chloride, 5 °C, alkaline solution	red ppt.	
2,4-dinitrophenylhydrazine	orange ppt.	
warm with Tollens' reagent	no change	

[2]

Topic: **Chem 32 Q# 363/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



(c) **(i)** Aqueous bromine was added dropwise to a solution of **J** until the bromine was in excess.

State what you would observe.

....

.... [1]

(ii) **J** has the molecular formula $C_{14}H_{19}O_6N$.

Use this formula to write an equation for the reaction of excess aqueous sodium hydroxide with **one** mole of **J**.

.... [2]

Topic: **Chem 32 Q# 364/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** **(i)** State and explain the relative acidities of ethanol and phenol.

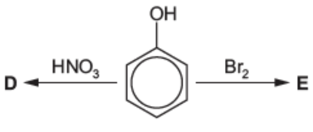
....

....

....

.... [2]

(ii) In the table below, give the reaction conditions for the formation of organic products **D** and **E** and draw their structures.



phenol

reagent	conditions	structure
HNO_3	dilute, 5°C	**D**
Br_2		**E**

[3]

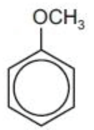
\

(iii) Name the mechanism of the reaction forming compound **E**.

.... [1]

Topic: **Chem 32 Q# 365/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Methoxybenzene reacts with Br_2(aq) in a similar manner to phenol.



methoxybenzene

(i) Draw the structural formula of the product of the reaction between methoxybenzene and an excess of bromine.

(ii) Suggest a chemical reaction you could use to distinguish between methoxybenzene and phenol. State the reagent, describe the observations you would make, and give an equation for the reaction.

reagent ....

observation ....

equation

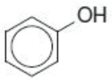
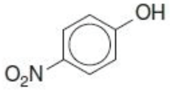
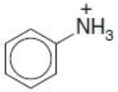
[4]

Topic: **Chem 32 Q# 366/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) **(i)** Write an equation for a reaction in which phenol, C_6H_5OH, acts as a Brønsted-Lowry acid.

....

The pK_a values for phenol, 4-nitrophenol and the phenylammonium ion are given in the table.

compound	pK_a
 	10.0
 	7.2
 	4.6

(ii) Suggest an explanation for the difference in the pK_a values of phenol and nitrophenol.

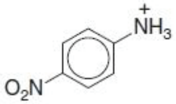
....

....

....

....

(iii) Using the information in the table opposite, predict which of the following pK_a values is the most likely for the 4-nitrophenylammonium ion.



Place a tick (✓) in the box beside the value you have chosen.

pK_a	
1.0	
4.5	
7.0	
10.0	

(iv) Explain your answer to part **(iii)**.

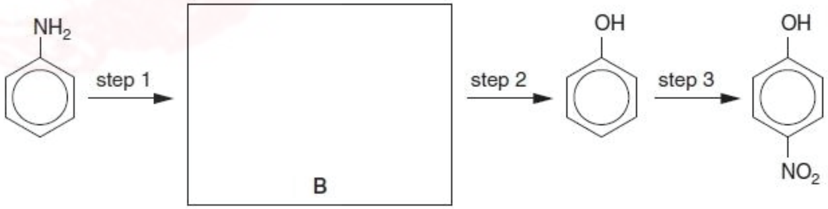
....

....

....

[5]

(c) Phenylamine can be converted to 4-nitrophenol by the following steps.



(i) Suggest the identity of intermediate **B** by drawing its structure in the box above.

(ii) Suggest reagents and conditions for the three steps in the above scheme.

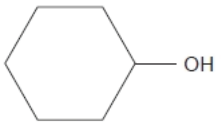
	reagent(s)	conditions
step 1		
step 2		
step 3		

[5]

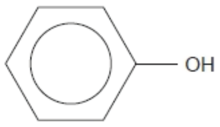
[Total: 14]

Topic: **Chem 32 Q# 367/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Cyclohexanol and phenol are both solids with low melting points that are fairly soluble in water.



cyclohexanol



phenol

(a) Explain why these compounds are more soluble in water than their parent hydrocarbons cyclohexane and benzene.

....

....

.... [2]

(b) Explain why phenol is more acidic than cyclohexanol.

....

....

.... [2]

(c) For **each** of the following reagents, draw the structural formula of the product obtained for **each** of the two compounds. If no reaction occurs write ***no reaction*** in the box.

reagent	product with cyclohexanol	product with phenol
$Na(s)$		
$NaOH(aq)$		
$Br_2(aq)$		
$I_2(aq) + OH^-(aq)$		
an excess of acidified $Cr_2O_7^{2-}(aq)$		

[7]

(d) Choose **one** of the above five reagents that could be used to distinguish between cyclohexanol and phenol. Describe the observations you would make with each compound.

reagent ....

observation with cyclohexanol ....

observation with phenol ....

[2]

[Total: 13]

6 Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

W **X** **Y**

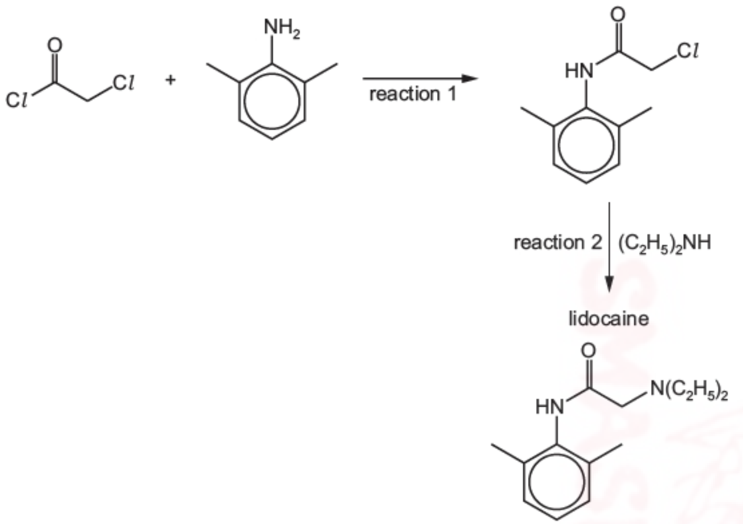


Fig. 6.1

(a) **W** can be formed by reacting $HOCH_2COOH$ with an excess of $SOCl_2$.

Write an equation for this reaction.

.... [1]

(b) After **W** and **X** have reacted together, an excess of $CH_3COONa(aq)$ is added to the reaction mixture.

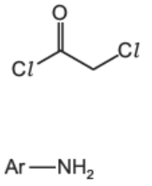
Suggest why.

....

.... [1]

(c) The reaction of **W** with **X**, reaction 1, follows an addition–elimination mechanism.

Complete the mechanism for the reaction of **W** with **X**.
Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.
Use Ar–NH_2 to represent **X**.



[4]

(d) $(C_2H_5)_2NH$ reacts with **Y** in reaction 2.

Explain why $(C_2H_5)_2NH$ can act as a nucleophile.

....

.... [1]

Topic: **Chem 33 Q# 369/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) **K** can also be synthesised from phenol, C_6H_5OH.

Fig. 4.4 shows several reactions of phenol.

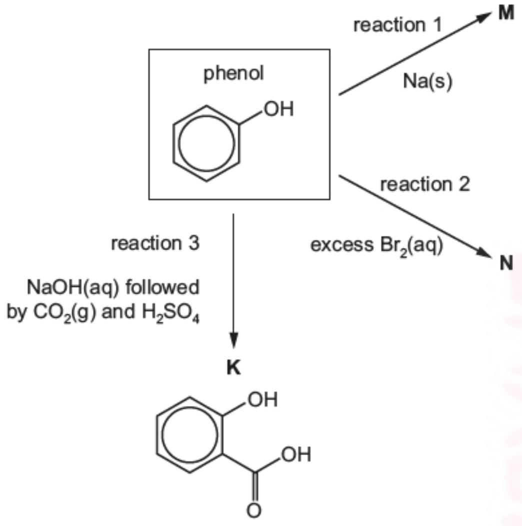


Fig. 4.4

(iii) Explain why phenol is a weaker acid than **K**.

....

....

....

.... [2]

Topic: **Chem 33 Q# 370/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** Compare and explain the relative acidities of butanoic acid, ethanol, ethanoic acid and water.

.... > .... > .... > ....

most acidic least acidic

....

....

....

....

....

.... [4]

(b) Three carboxylic acids, methanoic acid, HCO_2H, ethanedioic acid, HO_2CCO_2H, and butanedioic acid, $HO_2CCH_2CH_2CO_2H$, are compared. Two tests were carried out on separate samples of each organic acid, as shown.

The following results were obtained. ✓ = observed change ✗ = no observed reaction

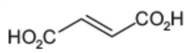
test	reagents and conditions	HCO_2H	HO_2CCO_2H	$HO_2CCH_2CH_2CO_2H$	observed change
1		✓	✗	✗	
2		✓	✓	✗	

(i) Complete the table with the reagents and conditions and the observed change for a positive test.
Assume these organic acids all have a similar acid strength. [3]

Topic: **Chem 33 Q# 371/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 Fumaric acid is a naturally occurring dicarboxylic acid.

fumaric acid

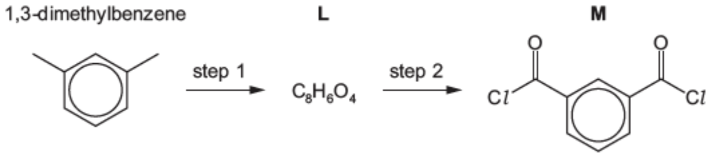


(a) Identify the products of the reaction between fumaric acid and an excess of hot, concentrated, acidified manganate(VII).

.... [1]

Topic: **Chem 33 Q# 372/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

(b) Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



(i) Draw the structure of **L**.

[1]

(ii) Suggest reactants and conditions for each step of this synthesis.

step 1 ....

step 2 ....
[2]

(iii) Write an equation for step 2.

.... [1]

Topic: **Chem 33 Q# 373/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** Compare and explain the relative acidities of 2-chloropropanoic acid, 3-chloropropanoic acid, and propanoic acid. Explain your answer.

.... > .... > ....

most acidic least acidic

explanation ....

....

....

....

....

.... [3]

(c) Three tests were carried out on separate samples of the organic acids shown in the table.
The following results were obtained.
✓ = observed change
✗ = no observed reaction

test	reagent(s) and conditions	HCO_2H	CH_3COCO_2H	HO_2CCO_2H	observed change
1		✓	✗	✗	
2		✗	✓	✗	
3		✓	✗	✓	

Complete the table with the reagent(s) and conditions and the observed change for each test.
Assume these organic acids all have a similar acid strength. [5]

Topic: **Chem 33 Q# 374/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(iii) $[Fe(C_2O_4)_2Cl_2]^{4-}$ contains ligands which are anions of ethanedioic acid, HO_2CCO_2H.

Complete the table to show any observations for the reactions of HO_2CCO_2H with the named reagents.

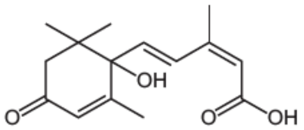
Where no change is observed, write 'none'.

reagent	observations with HO_2CCO_2H
warm acidified manganate(VII)	
2,4-dinitrophenylhydrazine	
warm Tollens' reagent	

[2]

[Total: 20]

8 Abscisic acid, $C_{15}H_{20}O_4$, is a plant hormone.



abscisic acid, $C_{15}H_{20}O_4$

(b) Abscisic acid is reacted with an excess of $NaBH_4$.

Give the molecular formula of the organic product formed.

.... [1]

(c) If abscisic acid is treated with an excess of hot, concentrated, acidified $KMnO_4$, three different carbon-containing products are formed.

(i) Draw the skeletal formula of the carbon-containing product with the **largest** molecular mass.

[1]

(ii) Identify the carbon-containing product with the **smallest** molecular mass. Explain how this product arises.

....

....

.... [2]

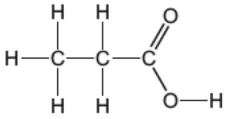
(iii) Identify the third carbon-containing product of this reaction by giving its displayed or structural formula.

[1]

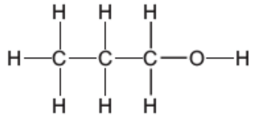
[Total: 6]

---

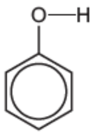
7 The three substances shown all have some acidic properties.



propanoic acid



propan-1-ol



phenol

(b) **(i)** Give the order of the relative acidities of propanoic acid, propan-1-ol and phenol, stating the most acidic first.

.... [1]

(ii) Explain your answer to **(i)**.

....

....

....

....

....

.... [2]

(c) Methanoic acid, HCO_2H, has a similar acid strength to propanoic acid.

Describe a chemical test to distinguish between these two acids. Name the acid which gives a positive result in this test and describe the observations that would be made.

....

....

....

.... [2]

(d) The ester phenyl propanoate, $C_2H_5CO_2C_6H_5$, can be made from phenol and propanoic acid in a **two-step** synthesis. The first step produces an acyl chloride.

For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

....

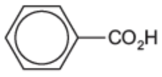
....

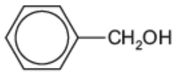
....

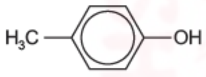
.... [3]

Topic: **Chem 33 Q# 377/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

(b) Describe and explain the relative acidities of benzoic acid, phenylmethanol and 4-methylphenol.


benzoic acid


phenylmethanol


4-methylphenol

....

....

....

....

....

.... [3]

Topic: **Chem 33 Q# 378/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(d) (i) The ethanedioates of the Group 2 elements, MC_2O_4, decompose on heating to produce a mixture of two different gases and the solid oxide, MO, only.

(ii) Describe **two** observations you would make during the reaction when ethanedioic acid, $H_2C_2O_4$, is warmed with acidified manganate(VII) ions.

....

....

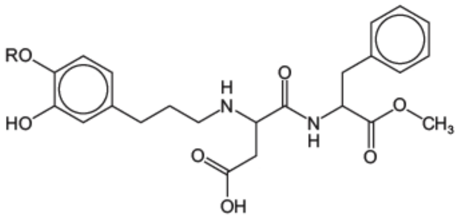
....

.... [2]

[Total: 14]

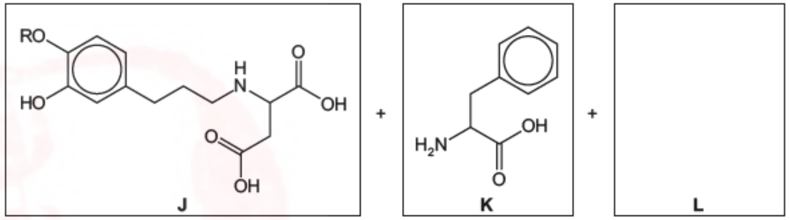
Topic: **Chem 33 Q# 379/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 The compound *Advantame* is a sweetener that tastes approximately 25 000 times sweeter than sucrose.



Advantame

(b) The decomposition of *Advantame* produces three molecules, **J**, **K** and **L**. The RO– group in *Advantame* is unreactive.



(i) Suggest possible reagents and conditions for this decomposition.

.... [1]

(ii) Name the *type of reaction* occurring.

.... [1]

(iii) Draw the structure of **L** in the box above. [1]

Topic: **Chem 33 Q# 380/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 (a) Ethanedioic acid, $C_2O_4H_2$, occurs in many vegetables. The amount that occurs in spinach can be estimated as follows.

- 40.0 g of spinach leaves are crushed and mixed with distilled water, using a mortar and pestle.
- The mixture is filtered, and the leaves are washed with a little more water.
- The combined filtrate and washings are made up to 100.0 cm^3 with water.
- A 25.0 cm^3 portion of the resulting solution is added to a conical flask, along with an excess of dilute sulfuric acid.
- The acidified solution is warmed, and then titrated with 0.0200 mol dm^{-3} $KMnO_4$.

The equation for the reaction between ethanedioic acid and acidified manganate(VII) ions is shown.

$$2MnO_4^- + 6H^+ + 5C_2O_4H_2 \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

In the titration, 15.20 cm^3 of $KMnO_4$ was required to reach the end-point.

Calculate the percentage by mass of ethanedioic acid in the spinach leaves.

percentage of ethanedioic acid = ... % [3]

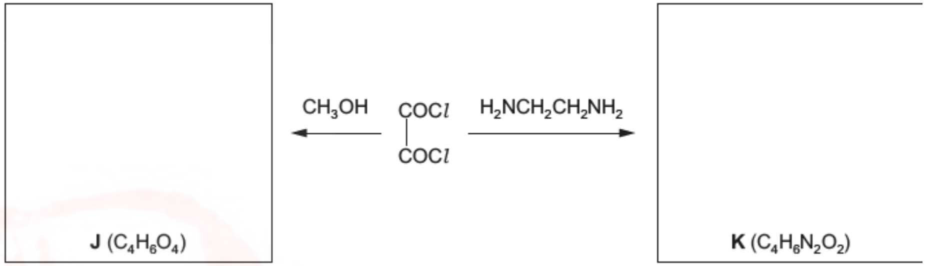
(b) Ethanedioic acid can be converted into ethanedioyl chloride:

$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(i) State a suitable reagent for this reaction.

.... [1]

(ii) For the reactions of ethanedioyl chloride below, suggest the structures of compounds **J** and **K** and draw them in the boxes.



J ($C_4H_6O_4$)

K ($C_4H_6N_2O_2$)

[2]

Topic: **Chem 33 Q# 381/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) Both chloroalkanes and acyl chlorides react with water, but only acyl chlorides fume in moist air.

(i) State which product causes the fumes in this reaction.

.... [1]

(ii) Explain why the reactivities of chloroalkanes and acyl chlorides differ.

....

....

.... [1]

Topic: **Chem 33 Q# 382/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Organohalogen compounds can undergo hydrolysis.

$$R–Cl + H_2O \rightarrow R–OH + HCl$$

State the relative rates of hydrolysis of the following compounds.

$CH_3CH_2CH_2Cl$ CH_3CH_2COCl C_6H_5Cl

Explain your answer.

[3]

Topic: **Chem 33 Q# 383/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

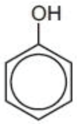
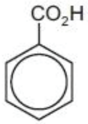
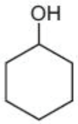
(b) **(i)** Describe and explain the relative acidities of chloroethanoic acid and ethanoic acid.

(ii) Describe and explain the relative acidities of phenol and ethanol.

[3]

Topic: **Chem 33 Q# 384/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** A series of experiments is carried out in which the reagent shown at the top of the column of the table is mixed, in turn, with each of the reagents at the side.
Complete the following table by writing in each box the formula of any gas produced.
Write **x** in the box if no gas is produced.
The first column has been completed as an illustration.

	H_2O			
Na	H_2			
KOH(aq)	x			
Na_2CO_3(aq)	x			

[5]

Topic: **Chem 33 Q# 385/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

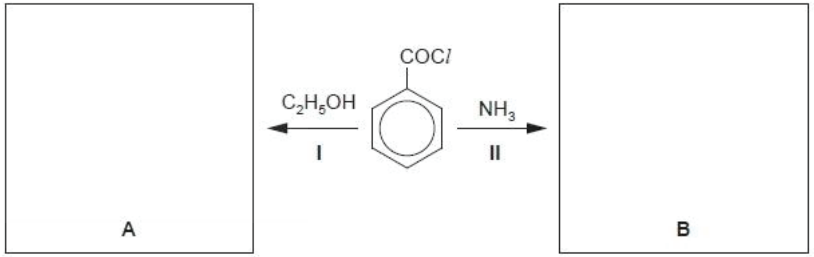
6 Acyl chlorides are useful intermediates in organic syntheses.

(a) **(i)** State a suitable reagent for converting carboxylic acids into acyl chlorides.

(ii) Construct an equation for the reaction between ethanoic acid, CH_3CO_2H, and the reagent you have stated in **(i)**.

[2]

(b) **(i)** In the boxes provided draw the structures of the compounds formed when benzoyl chloride undergoes the following reactions.



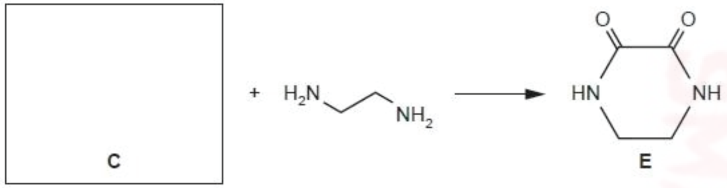
(ii) Name the functional group in

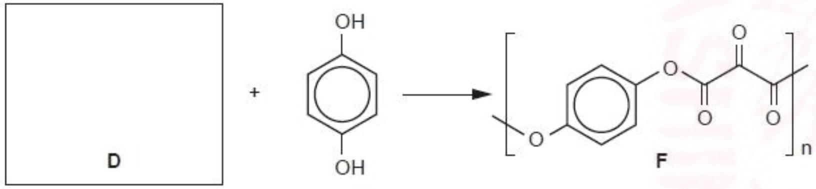
- compound **A** ....
- compound **B** ....

(iii) What *type of reaction* is reaction **II**?

.... [5]

(c) (i) Suggest suitable acyl chlorides to use in the following reaction. Draw their structures in the boxes provided.





Compound **E** dissolves in, but does not react with, cold water.

(iv) What type of polymer is compound **F**?

.... [3]

[Total: 12]

Topic: Chem 34 Q# 386/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(c) A student studies the reaction of $CH_3CHClCOOH$ with aqueous NH_3 to determine the reaction mechanism.

The student finds that when $CH_3CHClCOOH$ and NH_3 are added in a 1 : 1 stoichiometric ratio, the conjugate acid and base of the reactants are quickly formed.

reaction 1 $CH_3CHClCOOH + NH_3 \rightarrow CH_3CHClCOO^- + NH_4^+$

In an excess of NH_3, $CH_3CHClCOO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $CH_3CHClCOO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

(vi) When an excess of $CH_3CHClCOO^-$ is used, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$.

Suggest the structure of $C_6H_9NO_4^{2-}$.

[1]

[Total: 21]

Topic: **Chem 34 Q# 387/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 2-Chloropropanoic acid, $CH_3CHClCOOH$, is used in many chemical syntheses.

(b) When $CH_3CHClCOOH$ reacts with aqueous NH_3, alanine forms.

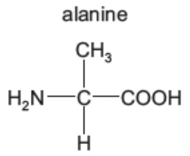


Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(i) State what is meant by isoelectric point.

....

.... [1]

(ii) Give the structural formula of alanine at pH 2.

.... [1]

Topic: **Chem 34 Q# 388/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Phenylamine, $C_6H_5NH_2$, and ethylamine, $C_2H_5NH_2$, can be distinguished by adding aqueous bromine.

(a) State what is seen when aqueous bromine is added to phenylamine.

....

.... [2]

(b) Suggest what is seen when aqueous bromine is added to ethylamine.

.... [1]

(c) Draw the structure of the organic product formed when an excess of aqueous bromine is added to phenylamine.

[1]

(d) Name the product you have drawn in **(c)**.

.... [1]

[Total: 5]

Topic: **Chem 34 Q# 389/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 Valine (Val) and lysine (Lys) are amino acids. The structures of these amino acids can be found in the *Data Booklet*.

The isoelectric point of an amino acid is the pH at which it exists as a zwitterion. The isoelectric point of valine is 6.0. The isoelectric point of lysine is 9.7.

(a) Draw the structure of valine at pH 6.0.

[1]

(b) A solution of lysine is produced with pH 9.7. Dilute sulfuric acid is added slowly until the pH of the solution is 1.0. The sulfuric acid reacts with lysine to produce different organic ions that are not present in significant concentrations at pH 9.7.

Draw the structures of three of the organic ions that form during the addition of sulfuric acid in the boxes. Draw the organic ion present at pH 1.0 in box C.

A

B

C (pH 1.0)

[3]

(c) Draw the structure of the dipeptide Val-Lys. The peptide bond should be shown fully displayed.

[2]

Topic: **Chem 34 Q# 390/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) A mixture of serine, $HOCH_2CH(NH_2)CO_2H$, and lysine, $H_2N(CH_2)_4CH(NH_2)CO_2H$, reacts to form several different products.

(i) Draw the structures of the two structural isomers with the molecular formula $C_8H_{12}N_2O_5$ that could be present in the product mixture.

The functional group formed in each case should be displayed.

[3]

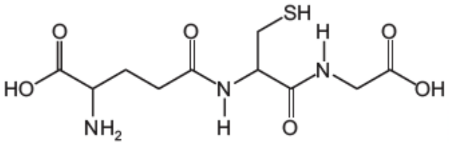
(ii) Predict the number of different structural isomers with the molecular formula $C_9H_{19}N_3O_4$ that could be present in the product mixture.

molecular formula	number of structural isomers formed
$C_9H_{19}N_3O_4$	

[1]

(c) Glutathione is a naturally occurring compound found in plants.

glutathione



(ii) Draw the structures of the three products formed after complete acid hydrolysis of glutathione. Assume the thiol group, –SH, does not react.

[2]

(iii) Glutathione is soluble in water.

By referring to the structure of glutathione, explain why glutathione is soluble in water.

....

....

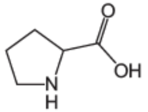
.... [1]

[Total: 13]

Topic: **Chem 34 Q# 391/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 Proline (Pro) is a naturally occurring amino acid.

proline



(a) Proline is often found bonded to glycine (Gly) in a protein.

(i) Draw the dipeptide Pro-Gly.

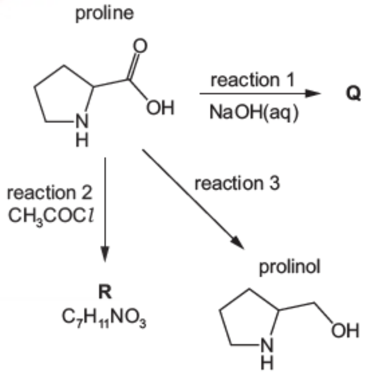
The peptide bond must be shown fully displayed.

[2]

(ii) Name the type of reaction that forms a dipeptide from two amino acids.

.... [1]

(b) The reaction scheme shows several reactions of proline.

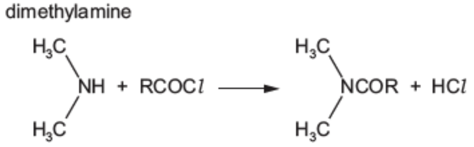


(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.

$C_4H_7NHCO_2H$ + ... [1]

(ii) Proline has a secondary amine functional group.

Secondary amines react with acyl chlorides. For example, dimethylamine reacts with RCOC*l* according to the following equation.



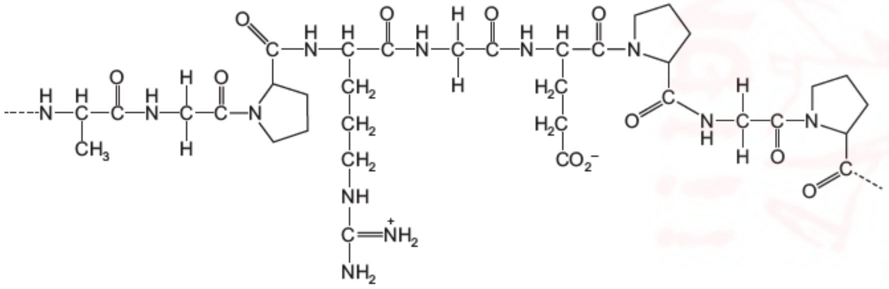
Suggest the skeletal structure of **R**, $C_7H_{11}NO_3$, the product of reaction 2.

[1]

(iii) Suggest the reagent required for reaction 3.

.... [1]

(d) Part of the structure of gelatin is shown.



Identify the number of amino acid units in the structure shown.

.... [1]

(e) (i) At pH 6.5, proline exists in aqueous solution as a zwitterion.

Draw the structure of the zwitterion of proline.

Explain how the zwitterion of proline forms.

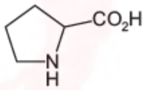
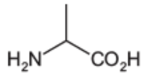
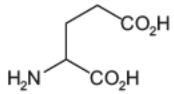
....

....

.... [2]

(ii) The isoelectric point of an amino acid is the pH at which it exists as a zwitterion.

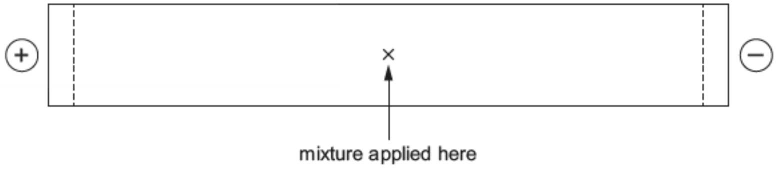
Three of the amino acids in gelatin are proline, alanine and glutamic acid. Their isoelectric points are shown.

amino acid	proline 	alanine 	glutamic acid 
isoelectric point	6.5	6.0	3.1

A mixture of these amino acids was analysed by electrophoresis using a buffer solution at pH 4.0.

Draw and label three spots on the diagram of the electropherogram to indicate the likely position of each of these three species after electrophoresis.

Explain your answer.



....

....

[4]

Topic: **Chem 34 Q# 392/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

(b) 2-aminopropanoic acid, $CH_3CH(NH_2)CO_2H$, can polymerise under suitable conditions. No other monomer is involved in this reaction.

(i) Draw a section of the polymer chain formed including **three** monomer residues. Clearly identify **one** repeat unit on your diagram.

[3]

Topic: **Chem 34 Q# 393/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) The molecular formulae of three nitrogen-containing compounds are given.

S $C_6H_5CONH_2$
T $C_6H_5NH_2$
U $C_6H_5CH_2NH_2$

Describe and explain the relative basicities of **S**, **T** and **U**.

.... > .... > ....
most basic   least basic

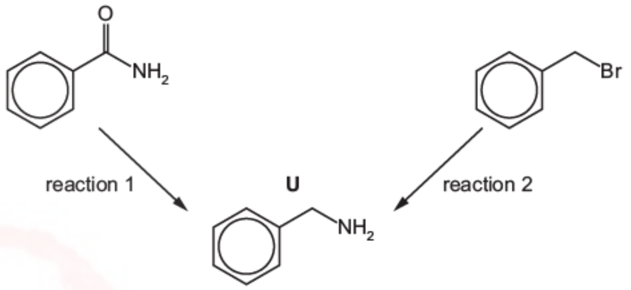
[3]

Topic: **Chem 34 Q# 394/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) The molecular formulae of three nitrogen-containing compounds are given.

S $C_6H_5CONH_2$
T $C_6H_5NH_2$
U $C_6H_5CH_2NH_2$

(b) Compound **U** can be prepared by two different methods as shown.



(i) Suggest reagents and conditions for reaction 1 and for reaction 2.

reaction 1 ....

reaction 2 ....

[2]

(ii) State the type of reaction in reaction 1 and name the mechanism in reaction 2.

type of reaction in reaction 1 ....

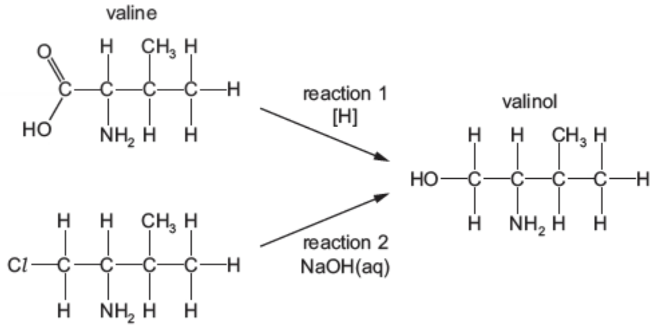
mechanism of reaction 2 ....

[2]

[Total: 7]

Topic: **Chem 34 Q# 395/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 Valinol can be synthesised by the following reactions. Reaction 1 uses valine as the starting material.



(b) Valine and glycine, H_2NCH_2COOH, form the tripeptide Gly–Val–Gly.

Draw the structure of this tripeptide. Show the peptide bonds fully displayed.

[2]

(c) **(i)** Valine exists as two stereoisomers.

Draw three-dimensional diagrams to show the two stereoisomers of valine. In your diagrams, the $–CH(CH_3)_2$ group can be represented by –R.

State the type of stereoisomerism shown.

type of stereoisomerism ....

[2]

(ii) Valine is an amino acid.

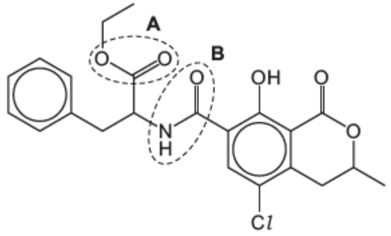
Draw the zwitterion of valine.

[1]

Topic: **Chem 34 Q# 396/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

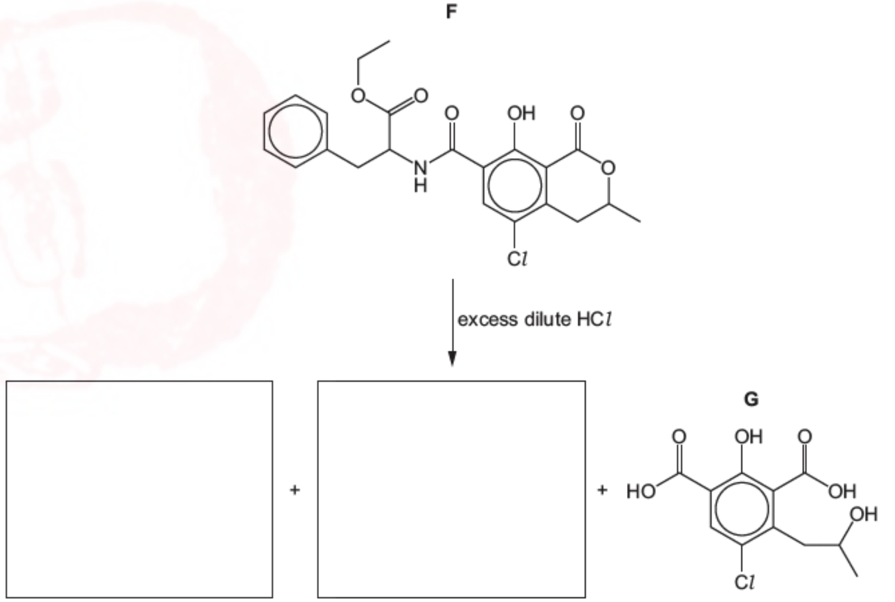
4 Compound **F** has been found in small quantities in some cereals and dried fruit.

F



(b) **F** can be hydrolysed by heating with an excess of dilute hydrochloric acid, as shown.

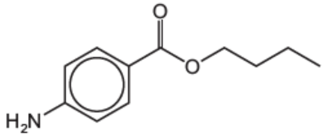
Three products are formed: **G** and two others.



Draw the structures of the other products of the reaction in the boxes provided. [3]

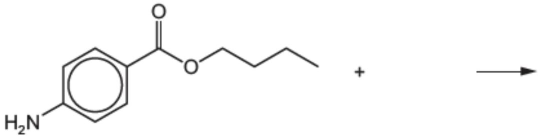
9 The structure of butamben is shown.

butamben



(a) Butamben can act as a base.

(i) Complete the equation for a reaction in which butamben acts as a base.



[1]

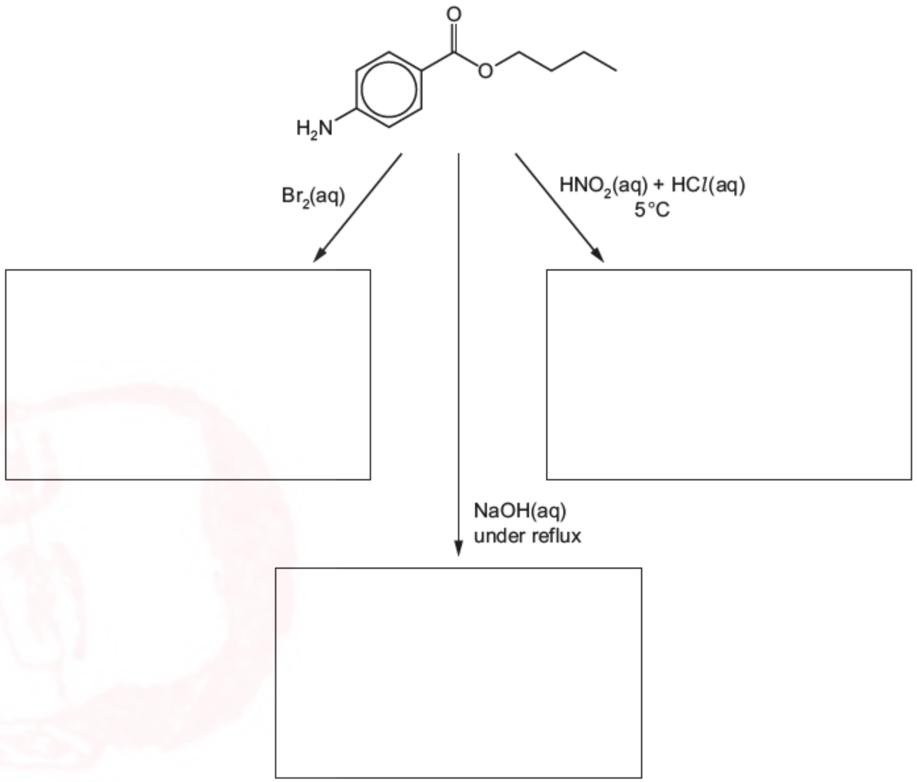
(ii) Predict whether butamben is a stronger or weaker base than ammonia. Give a reason for your answer.

....

....

.... [1]

(b) Complete the reaction scheme below to show the structural formulae of the products formed when butamben is treated separately with the stated reagent.

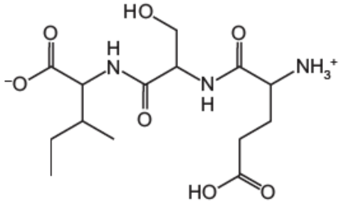


[3]

Topic: **Chem 34 Q# 398/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Proteins are natural polymers. When one particular protein is partially hydrolysed the product mixture includes tripeptide **E**.

tripeptide **E**



(a) (i) Describe the conditions that could be used to hydrolyse **E** to produce a mixture of three amino acids.

.... [1]

(ii) Draw the structures of the three amino acids produced by this hydrolysis reaction.

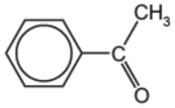
The three amino acids should be shown in the correct form for the conditions you have chosen in **(a)(i)**.

[2]

Topic: **Chem 34 Q# 399/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(c) Phenylethanone reacts with HCN in the presence of a small amount of NaCN.

(i) Name the mechanism of this reaction.

.... [1]

(ii) Draw the mechanism of this reaction below. Include all relevant charges, dipoles, lone pairs and curly arrows. Your mechanism should show the catalytic role of CN^- ions.

[4]

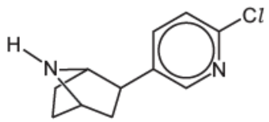
Topic: **Chem 34 Q# 400/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** Organochlorine compounds can undergo hydrolysis.

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

(b) Epibatidine is a naturally occurring organochlorine compound.

epibatidine



(i) Epibatidine is a weak base.

State what is meant by the term *weak base*.

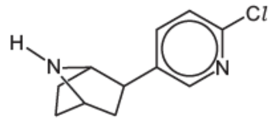
....

.... [1]

A molecule of epibatidine contains two nitrogen atoms, both of which can act as a base.

(ii) Epibatidine reacts with HC*l*(aq).

Complete the structure to suggest the product formed in this reaction.



[1]

Topic: **Chem 34 Q# 401/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c) Methylamine, CH_3NH_2, is a monodentate ligand.

In the presence of aqueous methylamine, $[Cd(H_2O)_6]^{2+}$ reacts to form a mixture of two isomeric octahedral complexes.

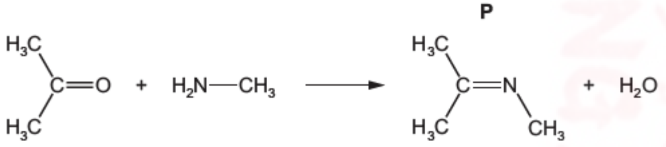
equilibrium **1** $[Cd(H_2O)_6]^{2+} + 4CH_3NH_2 \rightleftharpoons [Cd(CH_3NH_2)_4(H_2O)_2]^{2+} + 4H_2O \quad \Delta H_r^{\circ} = -57\,kJ\,mol^{-1}$

(f) Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

.... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.



Deduce the *type of reaction* shown here.

.... [1]

[Total: 13]

Topic: **Chem 34 Q# 402/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

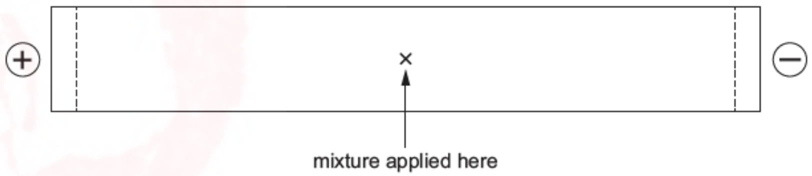
6 **(a)** Use the *Data Booklet* to draw the structure of the dipeptide val-lys. The peptide bond should be shown displayed.

[2]

(b) The isoelectric point is the pH at which an amino acid exists as a zwitterion. The isoelectric point of valine is 6.0 and of lysine is 9.8.

A mixture of the dipeptide, val-lys, and its two constituent amino acids, valine and lysine, was analysed by electrophoresis using a buffer at pH 6.0.

Draw and label **three** spots on the diagram of the electrophoresis paper to indicate the likely position of each of these three species after electrophoresis. Explain your answer.



explanation ....

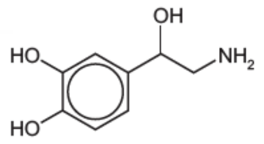
....

.... [5]

[Total: 7]

Topic: **Chem 34 Q# 403/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 Noradrenaline is a hormone found in humans.



noradrenaline

(c) HNO_2(aq) is reacted at 5 °C with separate samples of noradrenaline and phenylamine.
The reaction with phenylamine produces a stable diazonium ion.
The reaction with noradrenaline produces an unstable diazonium ion.

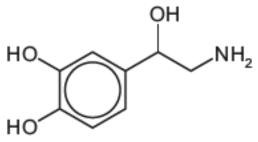
(i) Suggest why the diazonium ion produced with phenylamine is stable.

....

.... [1]

(ii) When one noradrenaline molecule reacts with one HNO_2 molecule, the products are one water molecule, one molecule of an unreactive gas, and one molecule of an organic compound made up of carbon, hydrogen and oxygen only.

Complete the chemical equation for this reaction.



+ HNO_2 → ☐ + ... + H_2O

[2]

[Total: 5]

Topic: **Chem 34 Q# 404/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(b) An amide bond forms when a carboxylic acid reacts with an amine.

(i) Complete the equation by writing the products in the box.

R–CO_2H + H_2N–R' → ☐ + ☐

[1]

(ii) Use your answer to **(i)** to work out the bonds that are broken and the bonds that are formed during the reaction between a carboxylic acid and an amine.

- bonds that are broken

....

- bonds that are formed

....

[2]

(iii) Use bond energy values from the *Data Booklet* to calculate the enthalpy change, $\Delta H^{\ominus}$, when **one** mole of amide bonds is formed in the reaction in **(i)**.

$\Delta H^{\ominus}$ = ... kJ [2]

(c) Amide bonds can also be formed by reacting acyl chlorides with amines.

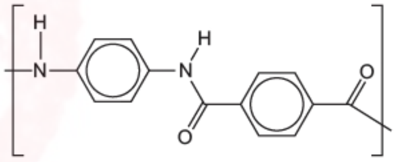
The enthalpy change for this process, $\Delta H^{\ominus}$, is $-6.00\,kJ\,mol^{-1}$.

Calculate the minimum entropy change, $\Delta S^{\ominus}$, for this reaction to be spontaneous (feasible) at 298 K.

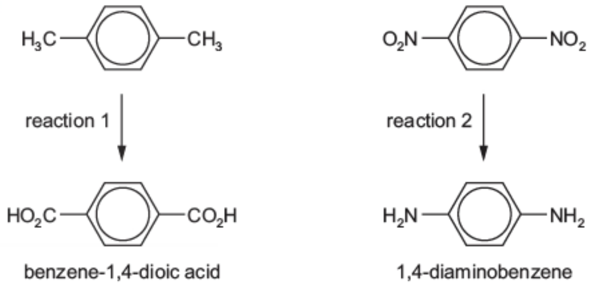
$\Delta S^{\ominus}$ = ... $JK^{-1}mol^{-1}$ [2]

Topic: **Chem 34 Q# 405/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

The repeat unit of the polyamide *Kevlar* is shown.



(d) The monomers of *Kevlar*, benzene-1,4-dioic acid and 1,4-diaminobenzene, can be synthesised as follows.



State the reagents and conditions needed for:

(ii) reaction 2

....

.... [2]

Topic: **Chem 34 Q# 406/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(b) **(i)** Explain why butylamine is basic.

....

.... [1]

(ii) Write an equation to show butylamine reacting as a base.

.... [1]

(iii) State how the basicity of butanamide, $C_3H_7CONH_2$, compares to that of butylamine.

.... [1]

(iv) State a reagent for the conversion of butanamide into butylamine.

.... [1]

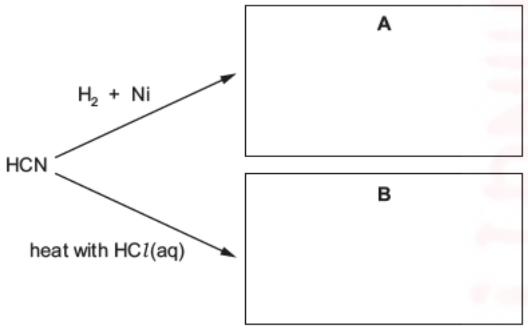
[Total: 9]

Topic: **Chem 34 Q# 407/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** Hydrogen cyanide, HCN, is a weak acid in aqueous solution.

$$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq) \qquad K_a = 6.2 \times 10^{-10}\,mol\,dm^{-3}$$

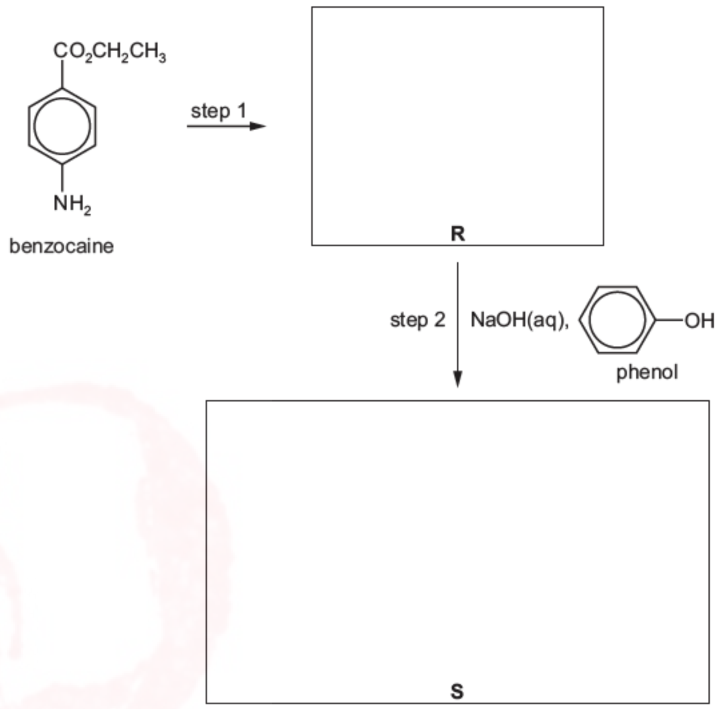
(iv) Suggest structures for the organic products **A** and **B** in the following reactions. Assume that HCN reacts in a similar way to RCN.



[2]

Topic: **Chem 34 Q# 408/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(e) Benzocaine can also be used to synthesise the dyestuff **S** by the following route.



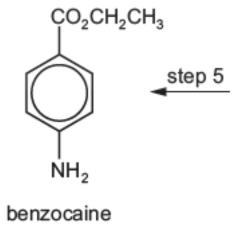
(i) Suggest the reagents used for step 1.

.... [1]

(ii) Suggest structures for compounds **R** and **S** and draw them in the boxes. [2]

[Total: 25]

Topic: **Chem 34 Q# 409/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org



(c) Suggest how the basicity of benzocaine would compare to that of ethylamine.
Explain your answer.

....

....

.... [2]

Topic: **Chem 34 Q# 410/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** One atom of each of the four elements H, C, N and O can bond together in different ways. Two examples are molecules of cyanic acid, HOCN, and isocyanic acid, HNCO. The atoms are bonded in the order they are written.

(e) When heated with HC*l*(aq), organic isocyanates, RNCO, are hydrolysed to the amine salt, RNH_3Cl, and CO_2.

$$RNCO + H_2O + HCl \rightarrow RNH_3Cl + CO_2$$

A 1.00 g sample of an organic isocyanate, RNCO, was treated in this way, and the CO_2 produced was absorbed in an excess of aqueous $Ba(OH)_2$ according to the equation shown. The solid $BaCO_3$ precipitated weighed 1.66 g.

$$Ba(OH)_2(aq) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l)$$

(i) Calculate the number of moles of $BaCO_3$ produced.

moles of $BaCO_3$ = ... [1]

(ii) Hence calculate the M_r of the organic isocyanate RNCO.

M_r of RNCO = ... [1]

The R group in RNCO and RNH_3Cl contains carbon and hydrogen only.

(iii) Use your M_r value calculated in **(ii)** to suggest the molecular formula of the organic isocyanate RNCO.

molecular formula of RNCO .... [1]

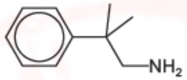
(iv) Suggest a possible structure of the amine RNH_2, which forms the amine salt, RNH_3Cl.

[1]

[Total: 23]

Topic: **Chem 34 Q# 411/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Compound **H** can be synthesised from benzene



compound **H**

(b) Write an equation to show how compound **H**, $C_{10}H_{13}NH_2$, behaves as a base.

.... [1]

(c) Compare the relative basicities of ammonia, phenylamine and compound **H**. Explain your answer.

....

....

.... [2]

[Total: 9]

Topic: **Chem 34 Q# 412/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 Copper is a transition element and has atomic number 29.

(c) Copper also forms the complex ions $[Cu(NH_3)_2(H_2O)_4]^{2+}$ and $[Cu(en)(H_2O)_4]^{2+}$ where *en* is the bidentate ligand ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 1}$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(en)(H_2O)_4]^{2+} + 2H_2O \qquad \text{equilibrium 2}$$

(e) Ethane-1,2-diamine is a useful reagent in organic chemistry.

(i) Explain how the amino groups in ethane-1,2-diamine allow the molecule to act as a Brønsted-Lowry base.

....

.... [2]

(ii) Write an equation for the reaction of ethane-1,2-diamine with an excess of hydrochloric acid.

.... [1]

(f) **(i)** Under certain conditions, ethane-1,2-diamine reacts with ethanedioic acid, HO_2CCO_2H, to form the polymer **Z**.

Draw the structure of this polymer, **Z**, showing **two** repeat units.

[2]

(ii) Name the *type of reaction* occurring during this polymerisation.

.... [1]

(iii) Polymer **Z** is an example of a biodegradable polymer.

Name a polymer that is non-biodegradable.

.... [1]

[Total: 20]

Topic: **Chem 34 Q# 413/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** **(i)** Use the *Data Booklet* to draw the structure of the tripeptide Ala-Ser-Gly showing its peptide bonds in full.

Ala-Ser-Gly

[2]

(ii) Calculate the relative molecular mass, M_r, of Ala-Ser-Gly.

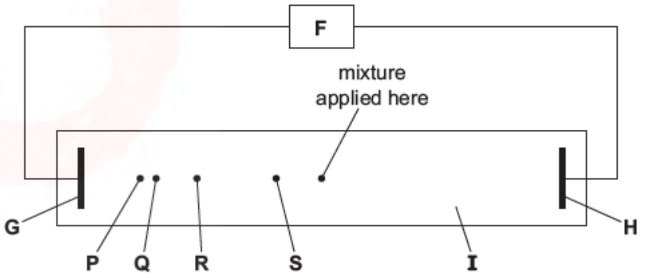
M_r = ... [1]

(b) Electrophoresis can be used to separate mixtures of amino acids and peptides.
A mixture of the tripeptide Ala-Ser-Gly and its three constituent amino acids was subjected to electrophoresis in a buffer at pH 11.

(i) Draw the structure of serine at pH 11.

[1]

At the end of the experiment the following results were seen.



(ii) Identify the components labelled **F**-**I** in the above diagram.

F ....

G ....

H ....

I ....

[4]

(c) **(i)** State the reagents and conditions needed for converting the tripeptide into its three constituent amino acids.

.... [1]

(ii) Name the *type of reaction* in **(i)**.

.... [1]

[Total: 13]

Topic: **Chem 34 Q# 414/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, in acid solution in a two step process.

(a) **(i)** Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$C_6H_5NO_2$ + ...e^- + ...H^+ → $C_6H_5NH_2$ + ...H_2O [1]

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

......$C_6H_5NO_2$ + ...HCl + ...Sn → ......$C_6H_5NH_3Cl$ + ...$SnCl_4$ + ...H_2O [2]

(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $C_6H_5NH_3Cl$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

(c) Following the reaction in **(b)**, an excess of NaOH(aq) was added to liberate phenylamine from phenylammonium chloride.

(i) Calculate the mass of phenylamine, $C_6H_5NH_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of NaOH(aq).

mass of phenylamine = ... g [1]

6 Nitrobenzene, $C_6H_5NO_2$, can be reduced to phenylamine, $C_6H_5NH_2$, in acid solution in a two step process.

(a) **(i)** Balance the half-equation for this reaction to work out how many moles of electrons are needed to reduce one mole of nitrobenzene.

$C_6H_5NO_2$ + ...e^- + ...H^+ → $C_6H_5NH_2$ + ...H_2O [1]

(ii) The reducing agent normally used is granulated tin and concentrated hydrochloric acid. In the first step, the reduction of nitrobenzene to phenylammonium chloride can be represented by the equation shown.

Use oxidation numbers or electrons transferred to balance this equation. You might find your answer to **(i)** useful.

......$C_6H_5NO_2$ + ...HCl + ...Sn → ......$C_6H_5NH_3Cl$ + ...$SnCl_4$ + ...H_2O [2]

(b) When 5.0 g of nitrobenzene was reduced in this reaction, 4.2 g of phenylammonium chloride, $C_6H_5NH_3Cl$, was produced.

Calculate the percentage yield.

percentage yield of phenylammonium chloride = ... % [2]

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(i) Calculate the mass of phenylamine, $C_6H_5NH_2$, produced when 4.20 g of phenylammonium chloride reacts with an excess of NaOH(aq).

mass of phenylamine = ... g [1]

The final volume of the alkaline solution of phenylamine in **(i)** was 25.0 cm^3. The phenylamine was extracted by addition of 50 cm^3 of dichloromethane. After the extraction, the dichloromethane layer contained 2.68 g of phenylamine.

(ii) Use the data to calculate the partition coefficient, $K_{partition}$, of phenylamine between dichloromethane and water.

$K_{partition}$ = ... [2]

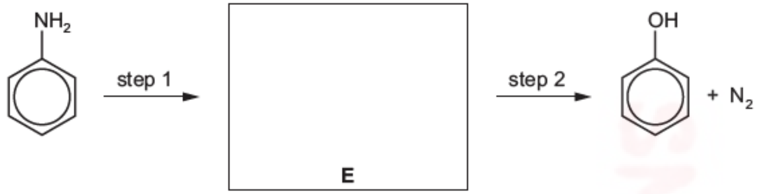
(d) How does the basicity of phenylamine compare to that of ethylamine? Explain your answer.

....

....

.... [2]

(e) Phenol can be synthesised from phenylamine in two steps.



(i) State the reagents and conditions for steps 1 and 2.

step 1 ....

step 2 ....

[2]

(ii) Draw the structure of the intermediate compound **E** in the box above. [1]

[Total: 13]

Topic: **Chem 34 Q# 415/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

(c) A section of polypeptide was hydrolysed and the following amino acids identified.

amino acid	formula
T	$CH_3CH(NH_2)CO_2H$
U	$C_6H_5CH_2CH(NH_2)CO_2H$
V	$H_2N(CH_2)_4CH(NH_2)CO_2H$

(i) Which of the amino acids **T**, **U** or **V** has the highest pH in aqueous solution? Explain why.

amino acid ....

....

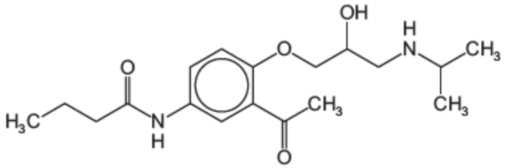
.... [1]

(ii) State how many different dipeptides could be formed from a reaction mixture consisting of amino acids **T** and **U**.

.... [1]

Topic: **Chem 34 Q# 416/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 Acebutolol is a drug that can be used to lower blood pressure.



(c) On warming with dilute hydrochloric acid, acebutolol splits to form two molecules.

(i) Draw a line through the bond broken by heating with dilute hydrochloric acid. [1]

(ii) Draw the structure of the **smaller** molecule produced by this reaction.

[1]

Topic: **Chem 34 Q# 417/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(b) **(i)** Phenylamine reacts with aqueous bromine to give compound **F**.

Describe the appearance of compound **F**.

.... [1]

(ii) Phenylamine reacts with nitrous acid to form a diazonium salt.

State the conditions for this reaction.

.... [1]

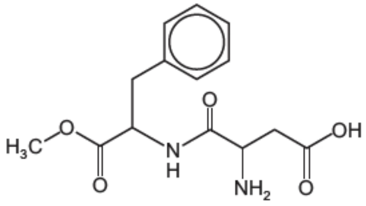
(iii) The diazonium salt in **(ii)** reacts with an alkaline solution of phenol to produce a coloured compound, **G**.

Draw the structure of **G**.

[2]

Topic: **Chem 34 Q# 418/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 **(a)** Aspartame is an artificial sweetener that has the structure shown below.



aspartame

In the stomach, aspartame is hydrolysed by acid to form three organic products.

(ii) On the diagram above, use arrows to indicate the **two** bonds that would be hydrolysed in the stomach. [2]

(iii) Draw the structures of the **three** products formed after complete acid hydrolysis of aspartame.

[3]

(b) Aspartame is soluble in water.

By referring to the structure of aspartame, explain why it is soluble in water.

....

....

.... [2]

Topic: **Chem 34 Q# 419/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

Section B

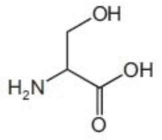
Answer **all** the questions in the spaces provided.

8 Proteins are formed by the polymerisation of amino acids.

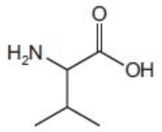
(a) **(i)** State the type of chemical reaction used to form these polymer chains.

.... [1]

(ii) The amino acids serine and valine can combine together to form a dipeptide.



serine, *ser*



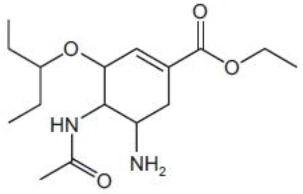
valine, *val*

Draw the skeletal structure of the dipeptide '*val-ser*'.

[2]

Topic: **Chem 34 Q# 420/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org
The human body includes organs like the stomach, which contain strong acids like HCl.

7 **(a)** Oseltamivir is an antiviral drug that slows the spread of the influenza (flu) virus.



oseltamivir

Circle **two** bonds, each in a different functional group, that could be easily hydrolysed in the body. [2]

Topic: **Chem 34 Q# 421/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

Section B

Answer **all** the questions in the spaces provided.

6 **(a)** A mixture of amino acids can be separated by electrophoresis. During an electrophoresis experiment,

- different amino acids move in different directions,
- different amino acids move at different speeds,
- some amino acids do not move at all.

Explain these observations.

....

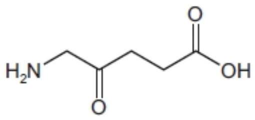
....

....

.... [3]

Topic: **Chem 34 Q# 422/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolaevulinic acid

(c) Aminolaevulinic acid reacts readily with bromoethane.

(i) Show the mechanism of the **first step** of this reaction on the diagram. Include all necessary curly arrows, lone pairs and relevant dipoles.

$H_3C—CH_2—Br$

(ii) Name the mechanism in **(c)(i)**.

....

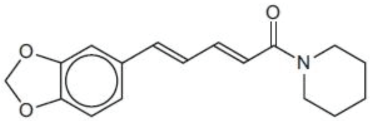
(iii) Identify the non-organic product formed in this reaction.

....

[5]

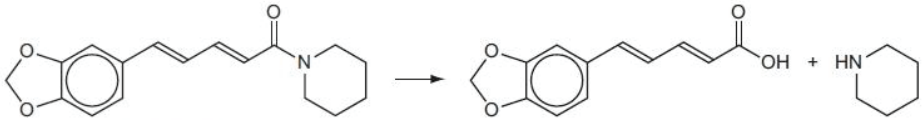
Topic: **Chem 34 Q# 423/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 Piperine is the compound responsible for the hot taste of black pepper.



piperine

Piperine is an amide and can be broken down as follows:

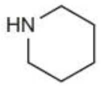


(a) Suggest reagents and conditions for this reaction.

.... [1]

Topic: **Chem 34 Q# 424/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(iii) The pH of a 0.150 mol dm^{-3} solution of piperidine is 11.9.



piperidine

(iv) How would you expect the basicity of piperidine to compare to that of ammonia? Explain your reasoning.

....

.... [1]

Topic: **Chem 34 Q# 425/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 Electrophoresis is a technique which can be used to separate amino acids or peptide fragments present in a mixture.

(a) Draw a diagram to show the apparatus used to carry out electrophoresis. You should label each of the relevant parts of the apparatus.

[4]

(b) How far an amino acid will travel during electrophoresis depends on the pH of the solution. For a given potential difference, state **two other** factors that will affect how far a given amino acid travels in a fixed time during electrophoresis.

1. ....

....

2. ....

....

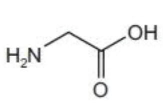
[2]

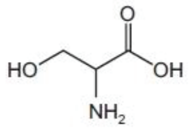
Topic: **Chem 34 Q# 426/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

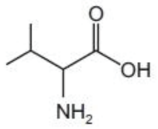
Section B

Answer **all** the questions in the spaces provided.

6 **(a)** Protein molecules are formed by the polymerisation of amino acids in the body. The structures of three amino acids are given.


glycine (*gly*)


serine (*ser*)


valine (*val*)

(i) How many different tripeptides can be made using **one** molecule of **each** of the amino acids shown?

....

(ii) Draw the tripeptide *ser-gly-val*, showing the peptide bonds in displayed form.

(iii) Within the tripeptide, which amino acid provides a hydrophobic side chain?

.... [4]

Topic: **Chem 34 Q# 427/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Because of the lack of reactivity of the nitrogen molecule, extreme conditions need to be used to synthesise ammonia from nitrogen in the Haber process.

(c) Describe and explain how the basicities of ethylamine and phenylamine compare to that of ammonia.

....

....

....

....

....

[4]

Topic: **Chem 34 Q# 428/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) Polymerisation can take place by two different methods depending on the monomers involved. The two methods are addition and condensation.
Give **two** differences between the methods.

1. ....

....

2. ....

....

[2]

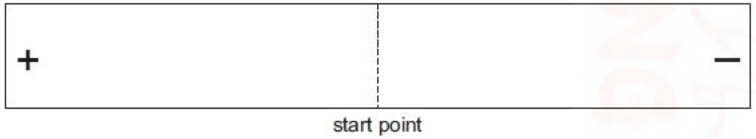
Topic: **Chem 34 Q# 429/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The analysis of a protein may be carried out by breaking it down into its amino acids. These can then be separated by a process called electrophoresis.

(a) The structures of glycine, lysine and glutamic acid at pH 7 are shown.

glycine	$H_3N^+CH_2CO_2^-$
lysine	$H_3N^+CH(CH_2CH_2CH_2CH_2NH_3^+)CO_2^-$
glutamic acid	$H_3N^+CH(CH_2CH_2CO_2^-)CO_2^-$

Draw and label three circles on the chart below to indicate the likely position of each of these amino acids after electrophoresis of a solution containing these amino acids in a buffer at pH 7.



[3]

Topic: **Chem 34 Q# 430/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

Section B

Answer **all** the questions in the spaces provided.

6 In key reactions responsible for growth and repair in the human body, amino acids react together to form polymers known as proteins.

(a) **(i)** What *type of reaction* is this polymerisation?

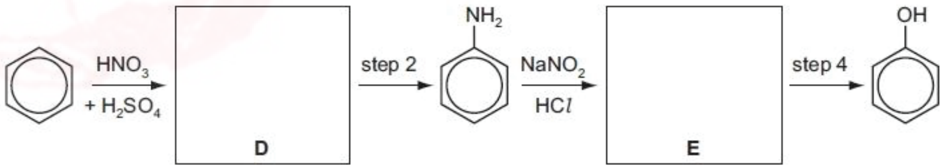
....

(ii) From stocks of glycine and alanine, it is possible to make the dipeptide gly-ala. Using the same three-letter abbreviations for the amino acids, give the structures of all other possible dipeptides that can be made from these stocks of amino acids.

[3]

Topic: **Chem 34 Q# 431/** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Phenol can be synthesised from benzene by the following route.



(i) Suggest structures for compounds **D** and **E** and draw them in the boxes above.

(ii) Suggest reagents and conditions for

step 2, ...

step 4. ....

[4]

Topic: **Chem 34 Q# 432/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 One of the key areas of investigation in understanding the structures of polypeptides and proteins is the sequence of amino acids that make up the polypeptide chains.

(a) One of the methods used to determine the amino acids present in a polypeptide chain is electrophoresis.

Sketch and label the apparatus used to carry out electrophoresis.

[4]

(b) In electrophoresis, different amino acids move in different directions and at different speeds.

(i) What factors determine the *direction of travel* of an amino acid?

....

....

....

(ii) What factors determine the *speed of movement* of an amino acid?

....

.... [3]

Topic: **Chem 34 Q# 433/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** **(i)** Write the equation for a reaction in which ethylamine, $C_2H_5NH_2$, acts as a Brønsted-Lowry base.

....

(ii) Ammonia, ethylamine and phenylamine, $C_6H_5NH_2$, are three nitrogen-containing bases.

Place these three compounds in order of basicity, with the most basic first.

most basic		least basic

(iii) Explain why you have placed the three compounds in this order.

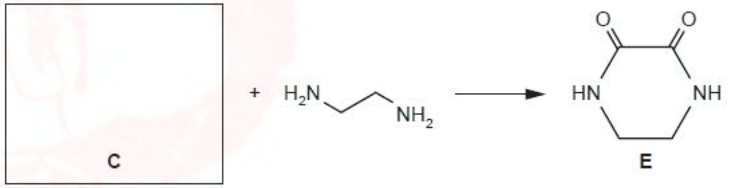
....

....

....

.... [4]

Topic: **Chem 34 Q# 434/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org



(ii) Suggest the major type of intermolecular interaction that occurs between **E** and water.

....

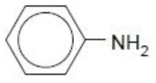
(iii) A solution of the diamine $H_2NCH_2CH_2NH_2$ in water has pH = 11 but a solution of **E** in water has pH = 7. Suggest why this is the case.

....

.... [2]

Topic: **Chem 34 Q# 435/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Ethanolamine and phenylamine are two organic bases that are industrially important. Ethanolamine is a useful solvent with basic properties, whilst phenylamine is an important starting material in the manufacture of dyes and pharmaceuticals.
The following table lists some of their properties, together with those of propylamine.

compound	formula	M_r	boiling point/°C	solubility in water
propylamine	$CH_3CH_2CH_2NH_2$	59	48	fairly soluble
ethanolamine	$HOCH_2CH_2NH_2$	61	170	very soluble
phenylamine		93	184	sparingly soluble

(a) Suggest why the boiling point of ethanolamine is much higher than that of propylamine. Draw a diagram to illustrate your answer.

....

....

[2]

(b) Describe and explain the relative basicities of propylamine and phenylamine.

....

....

....[2]

(c) Write an equation showing ethanolamine acting as a Brønsted-Lowry base.

....[1]

(e) Apart from their relative basicities, ethanolamine and phenylamine differ in many of their reactions.
For **each** of these two compounds, describe **one** test that would give a positive result with the stated compound, but a negative result with the other.

ethanolamine

test ....

observation ....

phenylamine

test ....

observation ....

[4]

[Total: 12]

Topic: **Chem 34 Q# 436/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(e) 4-aminobenzoic acid, **E**, forms a zwitterion.

(i) What is meant by the term *zwitterion*?

....

....

(ii) Draw the structural formula of the zwitterion formed from 4-aminobenzoic acid.

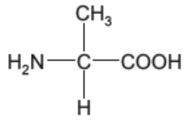
[2]

[Total: 16]

Topic: Chem 35 Q# 437/ ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) When $CH_3CHClCOOH$ reacts with aqueous NH_3, alanine forms.

alanine



$$H_2N-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large H}{|}}{C}}-COOH$$

Fig. 5.1

Alanine is an amino acid. Its isoelectric point is 6.1.

(iv) Polymer **C** forms from the reaction between alanine and 4-aminobutanoic acid, $H_2N(CH_2)_3COOH$.

Draw a repeat unit of **C**. The functional group formed should be displayed.

[2]

(v) State the type of polymerisation shown in **(b)(iv)**.

.... [1]

(vi) Scientists are investigating **C** as a replacement for poly(propene) in packaging.

Suggest an advantage of using **C** instead of poly(propene).

....

.... [1]

Topic: **Chem 35 Q# 438/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d) Polyamide **L** can be synthesised from dicarboxylic acid **J**, $HO_2C(CH_2)_2CO_2H$, and diamine **K**, $H_2N(CH_2)_6NH_2$.

Draw the repeat unit of the polymer formed in the box. Any functional groups should be shown displayed.

polyamide **L**

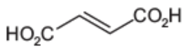
[2]

[Total: 18]

Topic: **Chem 35 Q# 439/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 Fumaric acid is a naturally occurring dicarboxylic acid.

fumaric acid



(b) Fumaric acid can form addition and condensation polymers.

(i) Draw the repeat unit of the addition polymer poly(fumaric acid).

[1]

(ii) Draw the repeat unit of the polyester formed when fumaric acid reacts with ethane-1,2-diol, $(CH_2OH)_2$.

The ester bond should be shown fully displayed.

[2]

(iii) Explain why polyesters normally biodegrade more readily than polyalkenes.

....

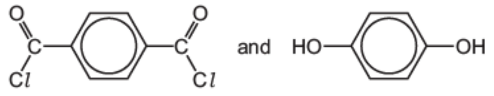
....

.... [1]

Topic: **Chem 35 Q# 440/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 **(a)** The table shows three pairs of monomers that are capable of polymerisation.

Complete the table by identifying each type of polymerisation.

pair of monomers	type of polymerisation
$HOCH_2CH_2OH$ and $HO_2CCH_2CO_2H$	
	
CH_3CHCF_2 and CH_3CHCH_2	

[1]

Topic: **Chem 35 Q# 441/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 Proteins are natural polymers.

(c) Polyesters and polyamides are two important types of condensation polymer.

(i) Draw the structure of a compound that can polymerise to produce a polyamide, without the need for a second monomer.

[1]

(ii) Draw the structures of two different compounds that can polymerise together to produce a polyester with **four** carbon atoms per repeat unit. Name the two compounds.

name ....

name ....

[4]

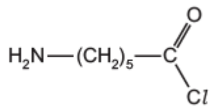
Topic: **Chem 35 Q# 442/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** Organochlorine compounds can undergo hydrolysis.

$$R\text{–}Cl + H_2O \rightarrow R\text{–}OH + HCl$$

(c) Polyamides, such as nylon-6, can be prepared from a monomer that contains both an amine and an acyl chloride functional group.

nylon-6 monomer



(i) When the nylon-6 monomer is hydrolysed, bonds are broken and formed.

By considering the two steps in the mechanism of the reaction, complete the table by placing **one** tick (✓) in each row to indicate the types of bonds broken and formed during the mechanism.

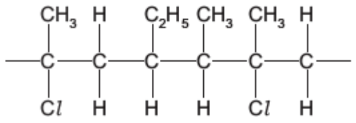
	σ bonds only	π bonds only	both σ and π bonds
bonds broken			
bonds formed			

[1]

(ii) Draw **two** repeat units of nylon-6. The amide bond should be shown fully displayed.

[2]

(d) An addition polymer made from two different alkene monomers is called a co-polymer. A section of a polyalkene co-polymer is shown.



Draw the structure of the **two** alkene monomers which produce this co-polymer.

[2]

(e) Explain why polyamides normally biodegrade more readily than polyalkenes.

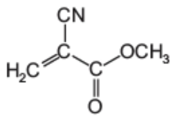
....

.... [1]

Topic: **Chem 35 Q# 443/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Methyl 2-cyanoprop-2-enoate, **W**, is the major component of *Super Glue*, a rapid-setting adhesive.
As the adhesive sets, the monomer **W** polymerises.

W



(i) Draw a section of the polymer showing **two** repeat units.

[2]

(ii) Name the type of polymerisation occurring.

.... [1]

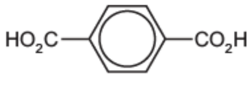
(iii) Suggest **two** types of intermolecular force that could occur between the *Super Glue* polymer and the objects glued together. For each type of intermolecular force, refer to the atoms/groups in the *Super Glue* polymer involved in the attraction.

type of intermolecular force	atoms/groups in the *Super Glue* polymer

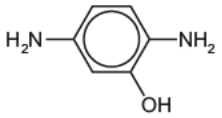
[2]

Topic: **Chem 35 Q# 444/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.



F



G

(ii) Draw the repeat unit of polyhydroxyamide. The amide bond should be shown displayed.

[2]

(b) When poly(ethene) is formed from ethene, many bonds are broken and formed.

Place **one tick** (✓) in **each row** of the table to indicate the types of bonds broken and formed in this process.

	σ-bonds only	π-bonds only	both σ- and π-bonds
bonds broken			
bonds formed			

[2]

(c) Addition polymers can be classified into two types.

- homopolymer - a polymer made up of the same monomer unit
- copolymer - a polymer made up of two or more different monomer units

The reaction of propene, $CH_3CH{=}CH_2$, with phenylethene, $C_6H_5CH{=}CH_2$, gives a copolymer.

Draw a length of the chain of this copolymer that contains one molecule of **each** monomer.

[2]

(d) **(i)** Polyalkenes biodegrade very slowly.

Explain why by referring to the structures of the polymers.

....

....

.... [1]

(ii) Some polymers will degrade in the environment.

Describe **two** processes by which this occurs.

1 ....

2 ....

[2]

Topic: **Chem 35 Q# 445/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 (a) (i) Complete the equations to show the **two** types of polymerisation. Draw **one** repeat unit for each polymer. Include any other products.

- addition polymerisation

$n\text{CH}_2\text{=CHCH}_3\text{(g)} \rightarrow$

- condensation polymerisation

$n\text{HO}_2\text{CCH}_2\text{CO}_2\text{H(s)} + n\text{HOCH}_2\text{CH}_2\text{OH(l)} \rightarrow$

[3]

(ii) Suggest the sign of the entropy changes, ΔS°, for each of the **two** types of polymerisation. Explain your answers.

- ΔS° for addition polymerisation

....

....

....

- ΔS° for condensation polymerisation

....

....

....

[2]

Topic: **Chem 35 Q# 446/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9 (a) (i) Name an example of a synthetic polyester and a synthetic polyamide.

polyester ....

polyamide ....

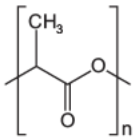
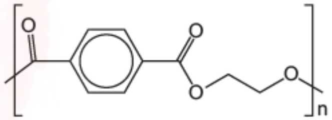
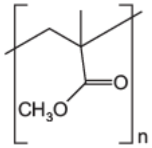
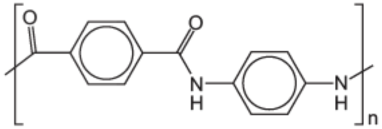
[1]

(ii) Polyesters and polyamides are formed by condensation reactions.

Name a molecule which is commonly eliminated in such reactions.

.... [1]

(b) (i) The table shows the repeat units of a number of polymers. Place a tick (✓) against the ones which are biodegradable.

polymer	repeat unit	biodegradable
A		
B		
C		
D		

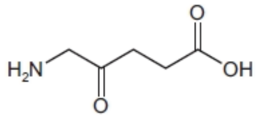
[2]

(ii) Draw the structures of two monomers used to form polymer **B**.

[2]

Topic: **Chem 35 Q# 447/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



aminolaevulinic acid

(e) Aminolaevulinic acid can undergo polymerisation.

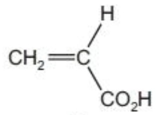
Draw the structure of the polymer showing **two** repeat units. The linkages between the monomer units should be shown fully displayed.

[2]

[Total: 15]

Topic: **Chem 35 Q# 448/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Super-absorbent polymers have the ability to absorb 200-300 times their own mass of water. They are classified as hydrogels and they are widely used in personal disposable hygiene products such as babies' nappies (diapers).
These polymers are commonly made by the polymerisation of compound **K** mixed with sodium hydroxide in the presence of an initiator.



K

(a) **(i)** Explain what is meant by the term *polymerisation*.

....

....

(ii) What type of polymerisation is involved in the formation of hydrogels?

....

(iii) Describe the changes in chemical bonding that occur during the polymerisation of **K**.

....

....

[3]

(c) **(i)** Draw the structure of at least **two** repeat units of the polymer formed by the above method from acrylic acid, **K**, when mixed with NaOH.

(ii) The C–C–C bond angle in compound **K** changes when the polymer is formed. State and explain how the C–C–C bond angle differs between a molecule of **K** and the polymer.

angle changes from .... to ....

explanation ....

....

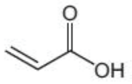
[4]

(d) **(i)** Draw a detailed diagram of a portion of the polymer you have drawn in **(c)(i)** to explain how it can absorb a large volume of water.

[3]

Topic: **Chem 35 Q# 449/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 In recent years there has been a lot of interest in polymers in the form of gels that absorb aqueous materials. One of the largest uses of these polymers is in disposable nappies (diapers). The gel which is used in this case is a polymer of propenoic acid.



propenoic acid

(a) (i) Draw a section of the polymer of propenoic acid showing **two** repeat units.

(ii) By what type of chemical reaction is this polymer formed?

....

(iii) By what type of bonding is water held on the polymer?

.... [3]

(b) For some disposable nappies (diapers), the monomer is a mixture of propenoic acid and sodium propenoate. The properties of the polymer are influenced by the proportion of sodium salt in the monomer mixture.

(i) Suggest and explain how the difference in the structure of this polymer compared to one formed only from propenoic acid might affect the water absorbing properties of the polymer.

....

....

....

(ii) Suggest a property the polymer should have in order to be used in disposable products.

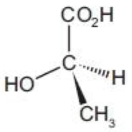
.... [3]

Topic: **Chem 35 Q# 450/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 The increasing awareness of the diminishing supply of crude oil has resulted in a number of initiatives to replace oil-based polymers with those derived from natural products. One such polymer, 'polylactide' or PLA, is produced from corn starch and has a range of applications.

(a) The raw material for the polymer, lactic acid (2-hydroxypropanoic acid), is formed by the fermentation of corn starch using enzymes from bacteria.

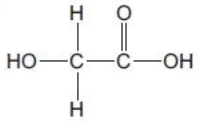
(ii) The structure of lactic acid is shown.



What type of reaction takes place in this polymerisation?

.... [1]

(d) Lactic acid can also be co-polymerised with glycolic acid.



glycolic acid

(i) Draw a section of the co-polymer showing one repeat unit.

[2]

Topic: **Chem 35 Q# 451/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 In today's world we make use of a wide range of different polymers. These polymers are often substitutes for traditional materials, but may have more useful properties.

(b) Throwing away articles made from polymers after use is a major environmental concern for **two** main reasons. Identify **each** of these reasons and suggest a strategy that has been adopted to try to overcome each of these.

reasons : ....

....

....

strategy 1 : ....

....

strategy 2 : ....

.... [3]

Topic: **Chem 35 Q# 452/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 In today's world, many traditional materials have been replaced by different sorts of polymers. This includes rigid polymers such as those used in car bodies to replace steel and flexible polymers like those used in textiles to replace cotton or wool.

(b) State **two** differences between addition and condensation polymerisation.

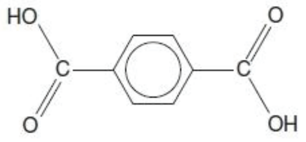
(i) ....

....

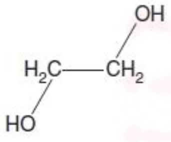
(ii) ....

....[2]

(c) The polymer formed from the co-polymerisation of the two monomers shown is known as *Terylene*.



benzene-1, 4-dicarboxylic acid



ethane-1-2-diol

(i) The two monomers react by condensation polymerisation. What other molecule is formed in this reaction?

....

(ii) Draw the structure of **one** repeat unit of *Terylene*.

(iii) What is the name given to polymers containing the same functional group as *Terylene*?

.... [4]

(d) The monomers ethene and but-1-ene can also co-polymerise to form a polyalkene, but this does not produce a regular alternating structure like *Terylene*. Explain why this is the case, drawing diagrams if you wish.

....

....

....

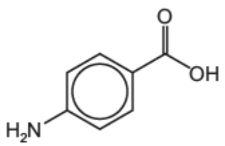
....

[2]

[Total: 10]

4 Compounds **F** and **J** are shown in Fig. 4.1.

F



J

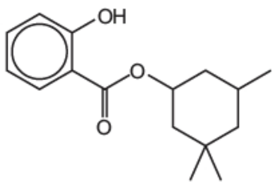
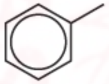
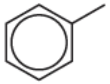
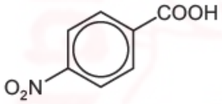
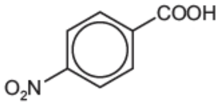
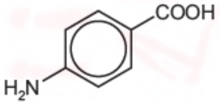


Fig. 4.1

(b) A student proposes a multi-step synthesis of **F** from benzene, as shown in Table 4.1.

(i) Complete Table 4.1 by providing relevant details of the reagents and conditions for steps 1 and 4, and the structure of product **D**.

Table 4.1

step	organic reactant	reagent(s) and conditions	organic product
1		....	
2		concentrated HNO_3 and concentrated H_2SO_4	**D**
3	**D**	hot alkaline $KMnO_4$ then dilute H_2SO_4	**E**  COOH O_2N
4	 COOH O_2N	....	**F**  COOH H_2N

[3]

(ii) In a second multi-step synthesis, the student changes the order in which the reagents and conditions are used.
The reaction scheme is shown in Fig. 4.2.
G is the major product of this synthesis.

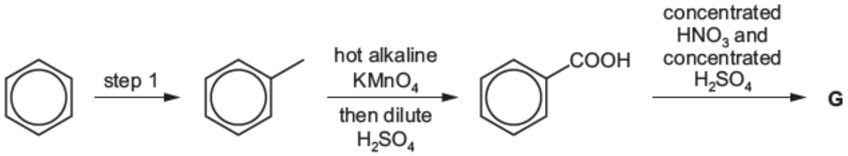


Fig. 4.2

Draw the structure of **G**.
Explain why **G** is the major product of the synthesis rather than **E**.

....

....

.... [2]

(c) **J** reacts under suitable conditions with NaOH(aq).
After acidification of the reaction mixture, compounds **K** and **L** form.

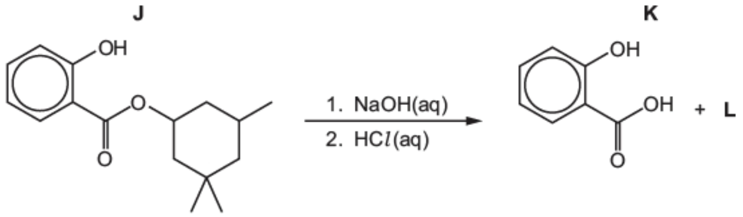


Fig. 4.3

(i) Give the molecular formula of **L**.

.... [1]

(ii) State the **two** types of reaction that occur when **J** reacts with NaOH(aq).

1 ....

2 .... [2]

(d) **K** can also be synthesised from phenol, C_6H_5OH.

Fig. 4.4 shows several reactions of phenol.

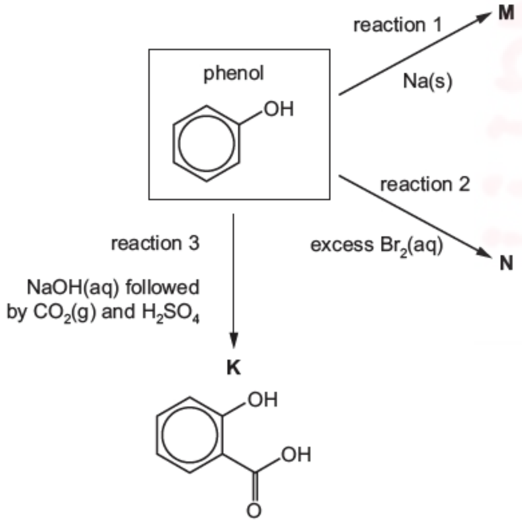


Fig. 4.4

(i) Write an equation for the formation of **M** in reaction 1.

.... [1]

(ii) Draw **N**, the product of reaction 2.

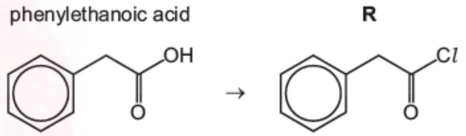
[1]

Topic: **Chem 36 Q# 454/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 Compound **T** is made by a three-stage synthesis.

(a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.

stage 1

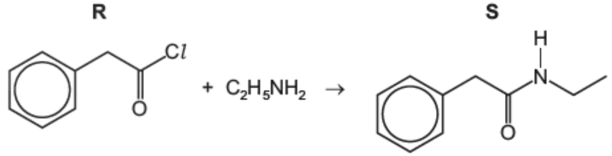


Suggest a suitable reagent for stage 1.

.... [1]

(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

stage 2



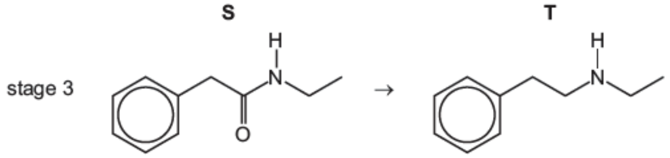
(i) Name the functional group formed in stage 2.

.... [1]

(ii) Identify the other product formed in stage 2.

.... [1]

(c) In stage 3, compound **S** reacts with a suitable reagent to form compound **T**.



(i) State the formula of a suitable reagent for stage 3.

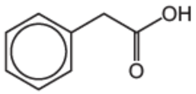
.... [1]

(ii) Name the type of reaction that occurs in stage 3.

.... [1]

Topic: **Chem 36 Q# 455/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The structure of phenylethanoic acid is shown.



(d) A three-step synthesis of phenylethanoic acid from methylbenzene is shown.

(i) State reagents and conditions for step 1.

.... [1]

(ii) Suggest the structure of compound **Q**.

[1]

(iii) State reagents and conditions for steps 2 and 3.

step 2 ....

step 3 ....

[2]

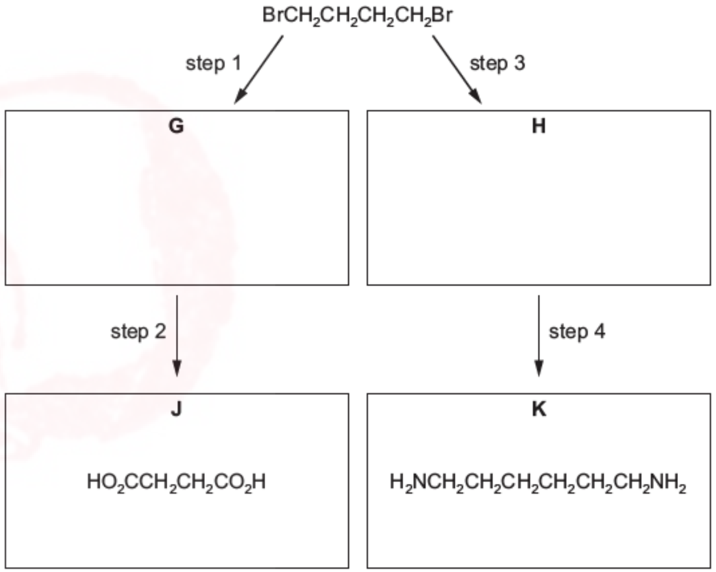
(iv) Draw the structure of an organic by-product that forms in step 1.

[1]

[Total: 14]

Topic: **Chem 36 Q# 456/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(c) 1,4-dibromobutane, Br$(CH_2)_4$Br, is used in the synthesis of the dicarboxylic acid **J** and diamine **K** as shown.



(i) Draw the structures of **G** and **H** in the boxes. [2]

(ii) Suggest reagents and conditions for each of steps 1 to 4.

step 1 ....

step 2 ....

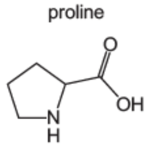
step 3 ....

step 4 ....

[4]

Topic: **Chem 36 Q# 457/** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

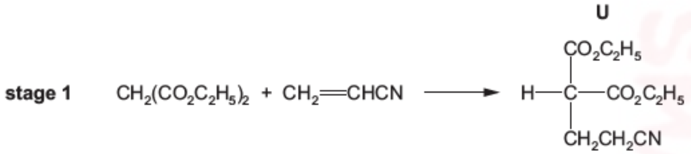
7 Proline (Pro) is a naturally occurring amino acid.



(a) Proline is often found bonded to glycine (Gly) in a protein.

(c) Proline was first synthesised in the laboratory using a multi-stage synthetic route.

In stage 1, $CH_2(CO_2C_2H_5)_2$ and $CH_2{=}CHCN$ react to form a single product **U**.



$$\text{stage 1} \quad CH_2(CO_2C_2H_5)_2 + CH_2{=}CHCN \longrightarrow H{-}\overset{\displaystyle CO_2C_2H_5}{\underset{\displaystyle CH_2CH_2CN}{C}}{-}CO_2C_2H_5$$

(i) Name **all** the functional groups present in the reactants of stage 1.

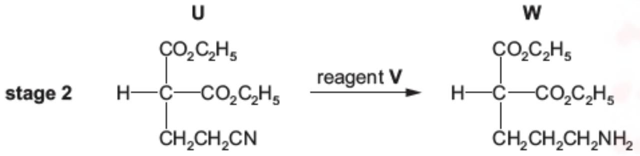
$CH_2(CO_2C_2H_5)_2$ ....

$CH_2{=}CHCN$ .... [2]

(ii) Suggest the type of reaction that occurs in stage 1.

.... [1]

In stage 2, **U** reacts with reagent **V** to form **W**.



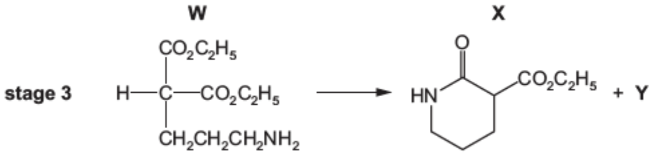
$$\text{stage 2} \quad H{-}\overset{\displaystyle CO_2C_2H_5}{\underset{\displaystyle CH_2CH_2CN}{C}}{-}CO_2C_2H_5 \xrightarrow{\text{reagent V}} H{-}\overset{\displaystyle CO_2C_2H_5}{\underset{\displaystyle CH_2CH_2CH_2NH_2}{C}}{-}CO_2C_2H_5$$

(iii) Suggest a suitable reagent **V**.

.... [1]

Stage 3 takes place in the presence of an acid catalyst.

X and **Y** are the only products of the reaction.



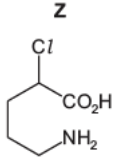
(iv) Suggest the type of reaction that occurs in stage 3.

.... [1]

(v) Deduce the identity of **Y**.

.... [1]

After several further stages, **Z** is produced.



In the final stage of the synthesis, **Z** reacts via a nucleophilic substitution mechanism to form proline.

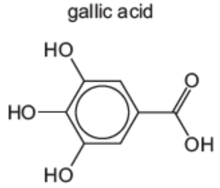
(vi) Complete the diagram to describe the reaction mechanism of the final stage. Draw curly arrows, ions and charges, partial charges and lone pairs of electrons, as appropriate.

Draw the structure of any organic intermediate ion.

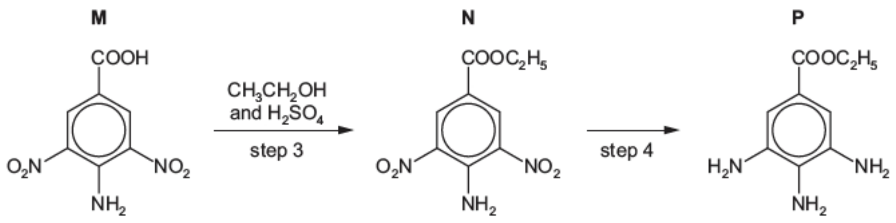
[3]

Topic: **Chem 36 Q# 458/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5c/www.SmashingScience.org

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.



Compound **M** is converted into compound **P** as shown.

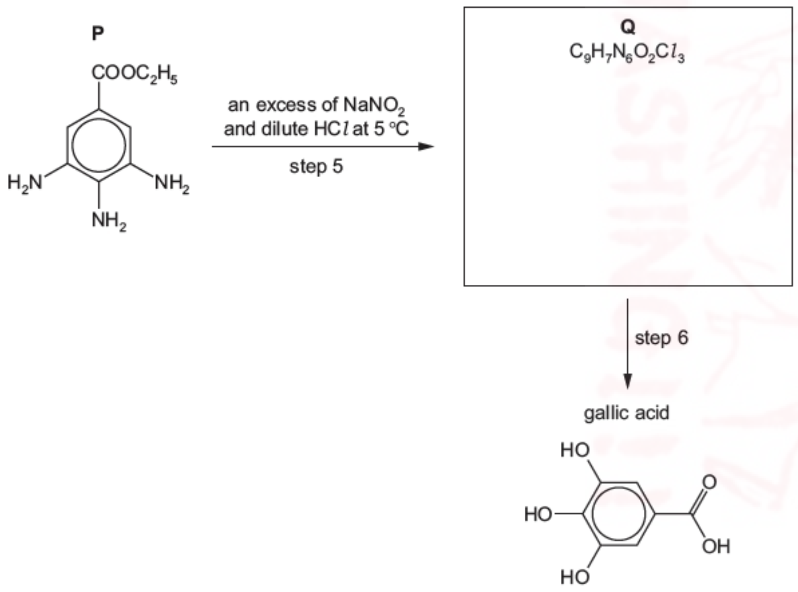


(iv) State the reagents and conditions for step 4.

.... [2]

P reacts with an excess of sodium nitrite, $NaNO_2$, and dilute HCl at 5 °C to form compound **Q**, $C_9H_7N_6O_2Cl_3$.

Compound **Q** is then converted into gallic acid.



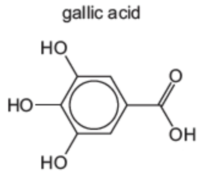
(v) Suggest the structure of compound **Q** in the box provided. [2]

(vi) State the reagents and conditions for step 6.

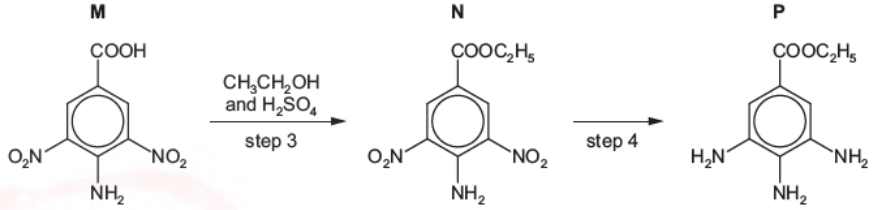
.... [1]

---

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.



Compound **M** is converted into compound **P** as shown.

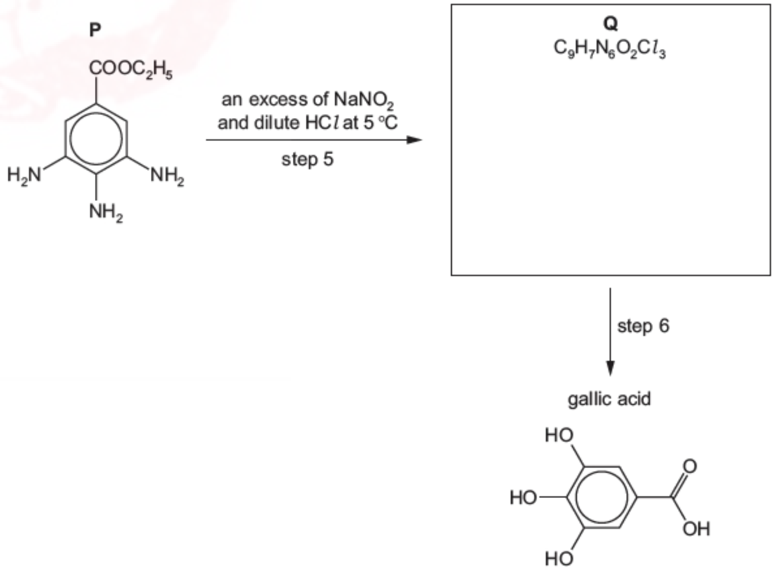


(iv) State the reagents and conditions for step 4.

.... [2]

P reacts with an excess of sodium nitrite, $NaNO_2$, and dilute HCl at 5 °C to form compound **Q**, $C_9H_7N_6O_2Cl_3$.

Compound **Q** is then converted into gallic acid.



(v) Suggest the structure of compound **Q** in the box provided. [2]

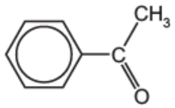
(vi) State the reagents and conditions for step 6.

.... [1]

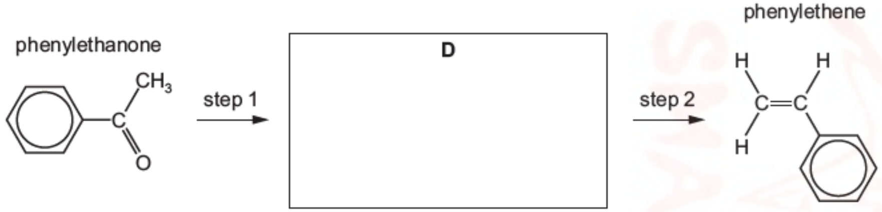
Topic: **Chem 36 Q# 460/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Phenylethanone is an important chemical with many uses.

phenylethanone



(d) Phenylethanone can be used as a starting material to make phenylethene in a two-step synthesis.



(i) Draw the structure of compound **D** in the box. [1]

(ii) Identify a suitable reagent for step 1.

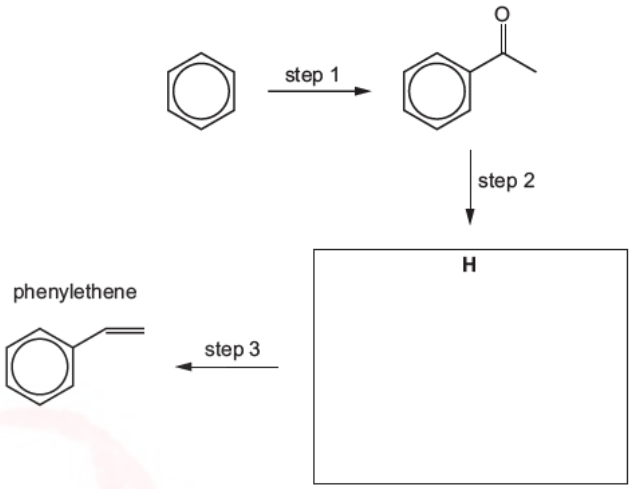
.... [1]

(iii) Identify a suitable reagent for step 2.

.... [1]

Topic: **Chem 36 Q# 461/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(f) The alkene phenylethene can be prepared from benzene in three steps.



(i) Deduce the identity of compound **H** and draw its structure in the box. [1]

(ii) Suggest reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

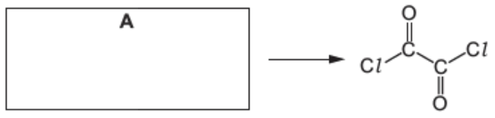
step 3 ....

[3]

[Total: 15]

Topic: **Chem 36 Q# 462/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7 Ethanedioyl dichloride, C*l*COCOC*l*, is a useful reagent in organic synthesis. It can be made from compound **A** in one step.

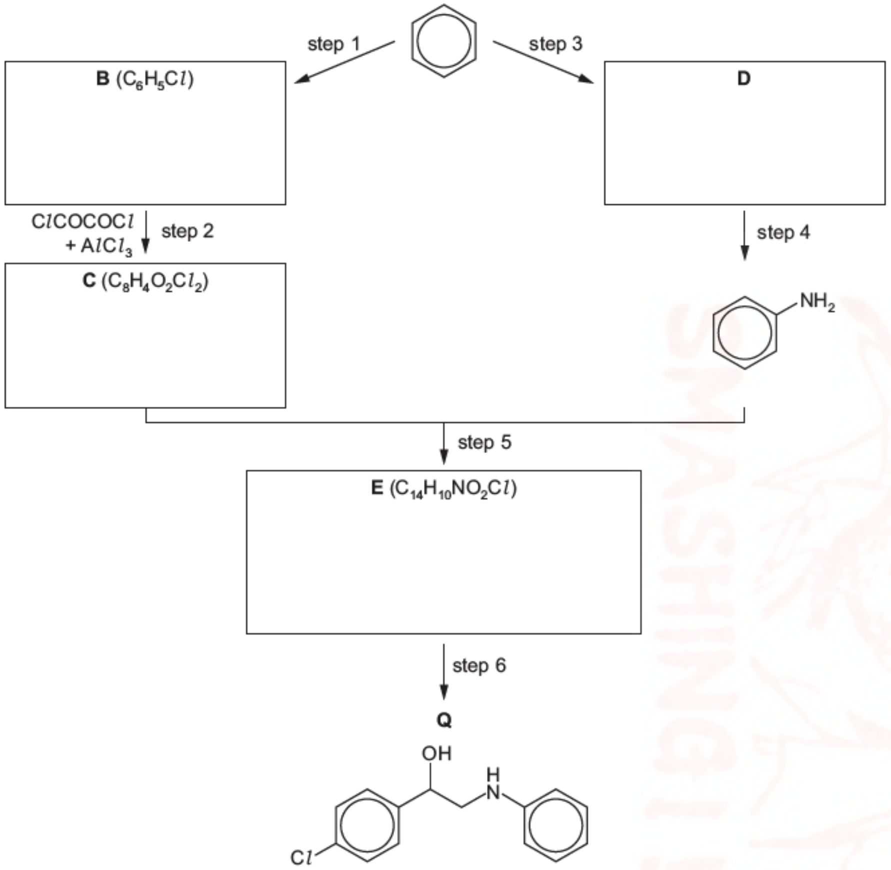


(a) **(i)** Suggest the identity of compound **A** by drawing its structure in the box. [1]

(ii) State the reagents and conditions needed to convert **A** into C*l*COCOC*l*.

.... [1]

Ethanedioyl dichloride is used in the following synthesis of compound **Q**. It is used in a 1:1 stoichiometric ratio with **B** in step 2.



(b) (i) Suggest the identities of the compounds **B**–**E** by drawing their structures in the boxes. [4]

(ii) State the reagents and conditions for the following steps.

step 1 ....

step 3 ....

step 4 ....

step 6 ....

[5]

If the amount of $ClCOCOCl$ used in step 2 is decreased, another compound is formed in step 2 with the molecular formula $C_{14}H_8O_2Cl_2$.

(iii) Suggest the structure of this compound.

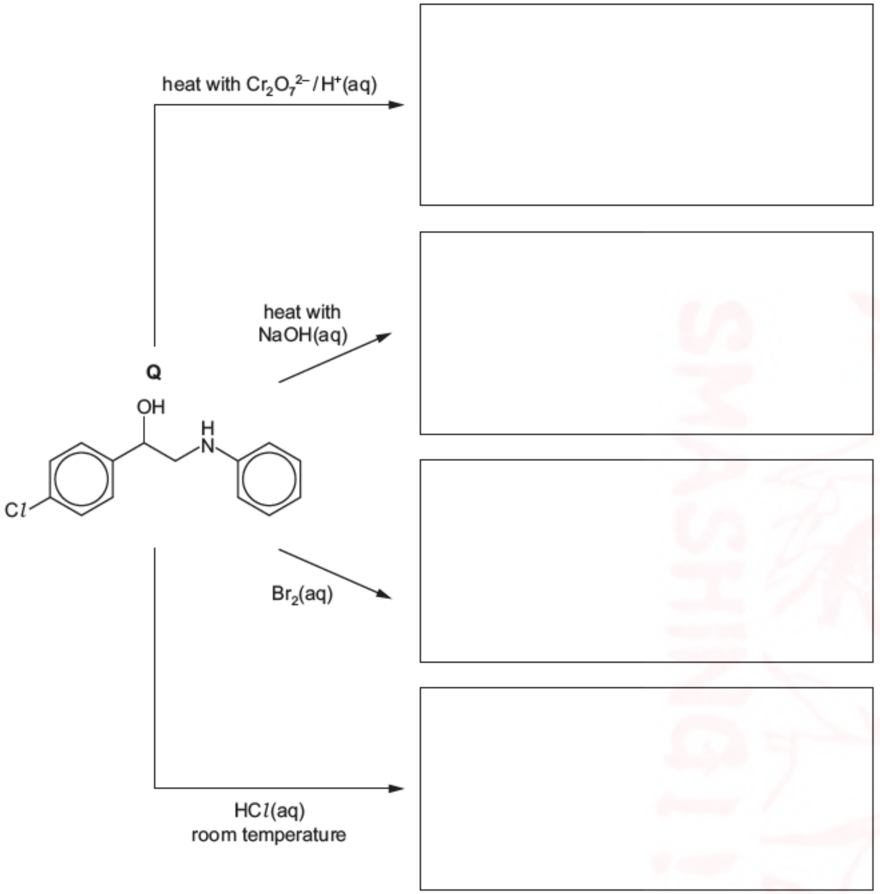
$C_{14}H_8O_2Cl_2$

[1]

(iv) Identify **all** the steps in the synthesis of **Q** from benzene that are electrophilic substitution reactions.

.... [1]

(c) Draw structures of the compounds formed when **Q** is treated with the following reagents.
If there is no reaction, write 'no reaction' in the box.

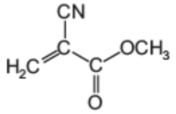


[4]

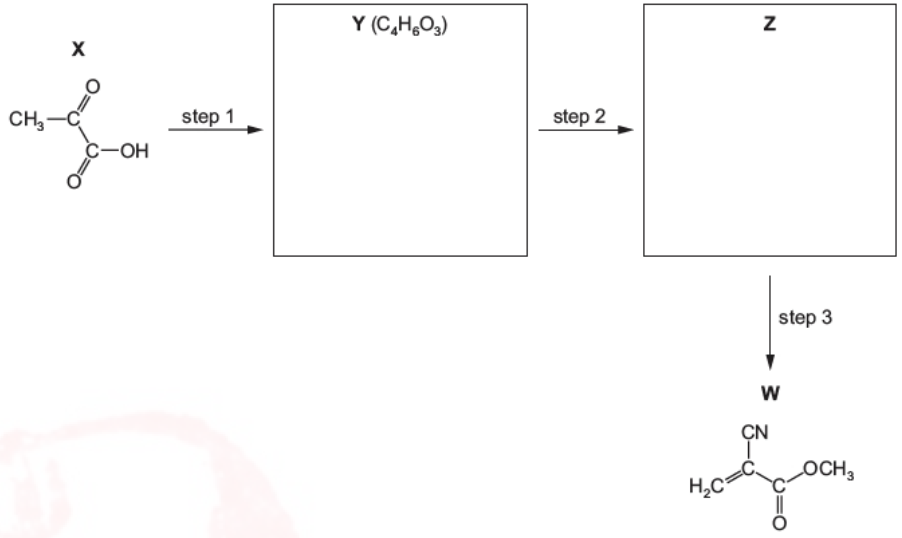
Topic: **Chem 36 Q# 463/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Methyl 2-cyanoprop-2-enoate, **W**, is the major component of *Super Glue*, a rapid-setting adhesive.
As the adhesive sets, the monomer **W** polymerises.

W



(b) **W** can be synthesised in three steps, starting from 2-oxopropanoic acid, **X**.



(i) Suggest the identities of compounds **Y** and **Z** by drawing their structures in the boxes. [2]

(ii) Suggest suitable reagents and conditions for each of the steps 1–3.

step 1 ....

step 2 ....

step 3 ....

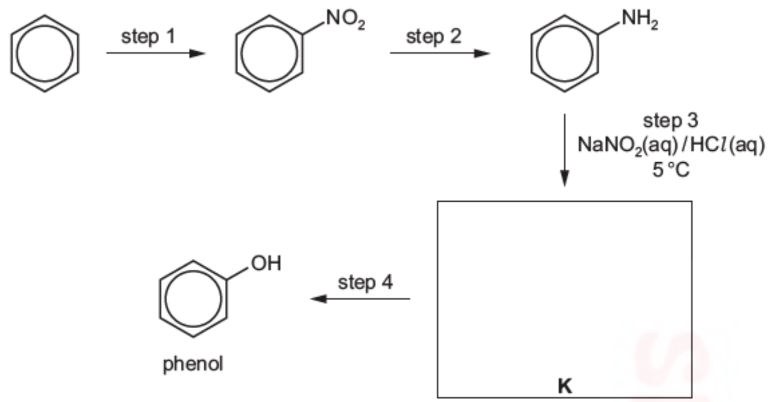
[4]

[Total: 11]

Topic: **Chem 36 Q# 464/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Chlorobenzene and phenol both show a lack of reactivity towards reactants that cause the breaking of the C–X bond (X = C*l* or OH).

(c) A student suggested that phenol can be prepared from benzene by the method shown.



(i) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

step 4 .... [3]

(ii) Deduce the structure for **K** and draw its structural formula in the box. [1]

(iii) Name the mechanism for step 1.

.... [1]

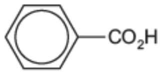
(iv) Write an equation for step 2. Use [H] for the reducing agent in this equation.

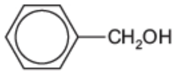
[1]

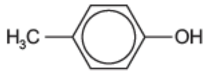
[Total: 11]

Topic: **Chem 36 Q# 465/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

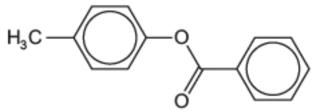
(b) Describe and explain the relative acidities of benzoic acid, phenylmethanol and 4-methylphenol.


benzoic acid


phenylmethanol


4-methylphenol

(c) The ester 4-methylphenyl benzoate is used in the manufacture of perfumes.


4-methylphenyl benzoate

Suggest a **two**-step route for the synthesis of 4-methylphenyl benzoate from 4-methylphenol and benzoic acid.
Include reagents and conditions for each step, and the structure of the intermediate compound.

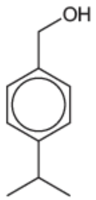
[3]

[Total: 14]

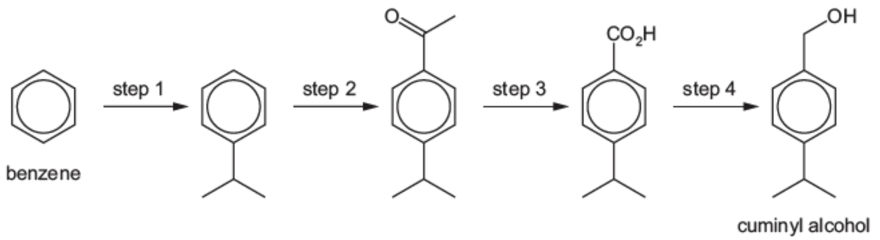
Topic: **Chem 36 Q# 466/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** Cumin is a spice used to flavour food. Two compounds responsible for its flavour are cuminaldehyde and cuminyl alcohol.


cuminaldehyde


cuminyl alcohol

(b) Cuminyl alcohol can be synthesised from benzene by the following route.



(i) Suggest reagents and conditions for steps 1–4.

step 1 ....

step 2 ....

step 3 ....

step 4 .... [4]

(ii) Name the mechanism of step 2 and state the type of reaction in step 4.

mechanism of step 2 ....

type of reaction in step 4 .... [2]

[Total: 9]

Topic: **Chem 36 Q# 467/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

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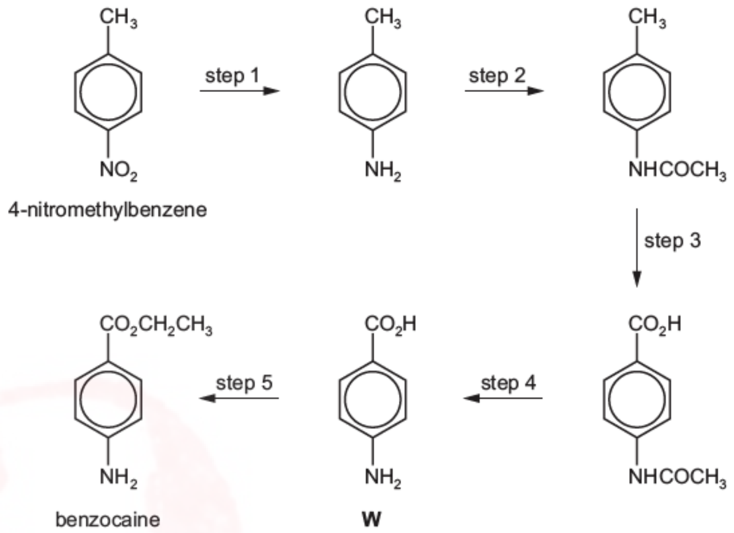
(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.



(ii) Suggest the reagents and conditions for steps 1–5.

step 1 ....

step 2 ....

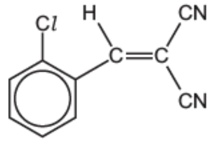
step 3 ....

step 4 ....

step 5 .... [6]

Topic: **Chem 36 Q# 468/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **P** contains several functional groups.



P

(c) Complete the following table to show the structures of the products formed and the *type of organic reaction* when **P** reacts with the four reagents.

reagent	structure(s) of product(s)		*type of organic reaction*
excess Br_2(aq)			
excess hot, concentrated, acidified MnO_4^-(aq)			
excess hot HC*l*(aq)			
excess H_2/Pt catalyst			

[8]

[Total: 12]

---

5 Compounds **J**, **K**, **L** and **M** are isomers of each other with the molecular formula $C_9H_{11}NO$.
All four isomers contain a benzene ring.
Two of the isomers contain a chiral centre.
The results of six tests carried out on **J**, **K**, **L** and **M** are shown in the table.

	test	observations with each isomer			
		J	**K**	**L**	**M**
1	add cold HC*l*(aq)	soluble	soluble	soluble	insoluble
2	add 2,4-DNPH reagent	orange ppt.	orange ppt.	orange ppt.	no reaction
3	add NaOH(aq) + I_2(aq)	pale yellow ppt.	no reaction	pale yellow ppt.	no reaction
4	warm with Fehling's solution	no reaction	red ppt.	no reaction	no reaction
5	heat with NaOH(aq)	no reaction	no reaction	no reaction	**P**(C_6H_7N) and **Q**($C_3H_5O_2Na$) produced
6	diazotization and addition of alkaline phenol	no dye produced	orange dye produced	no dye produced	no dye produced

(a) Use the experimental results in the table above to determine the group(s), in addition to the benzene ring, present in each of the four isomers **J**, **K**, **L** and **M**.

Complete the table below, identifying the group(s) present in each isomer.

group(s) in compound			
J	**K**	**L**	**M**

[5]

(b) **(i)** Name the *type of reaction* occurring in test 5 that converts **M** into **P** + **Q**.

.... [1]

(ii) Suggest structures for compounds **P** and **Q**.

P (C_6H_7N)

Q ($C_3H_5O_2Na$)

[2]

(c) Isomers **J**, **K**, **L** and **M** all have the molecular formula $C_9H_{11}NO$.

Use the information in **(a)** to suggest a structure for each of these isomers and draw these in the boxes. Draw **circles** around all chiral centres in **K** and **L**.

J

K

L

M

[5]

(d) Compound **N** is another isomer which has the same molecular formula $C_9H_{11}NO$ and also contains a benzene ring.
N contains the same functional group as **M**.
When heated with NaOH(aq), **N** produces ethylamine and a sodium salt **W**.
Suggest the structure of **W**.

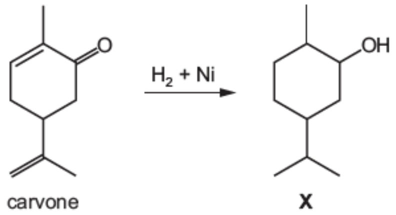
W

[1]

[Total: 14]

Topic: **Chem 36 Q# 470/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

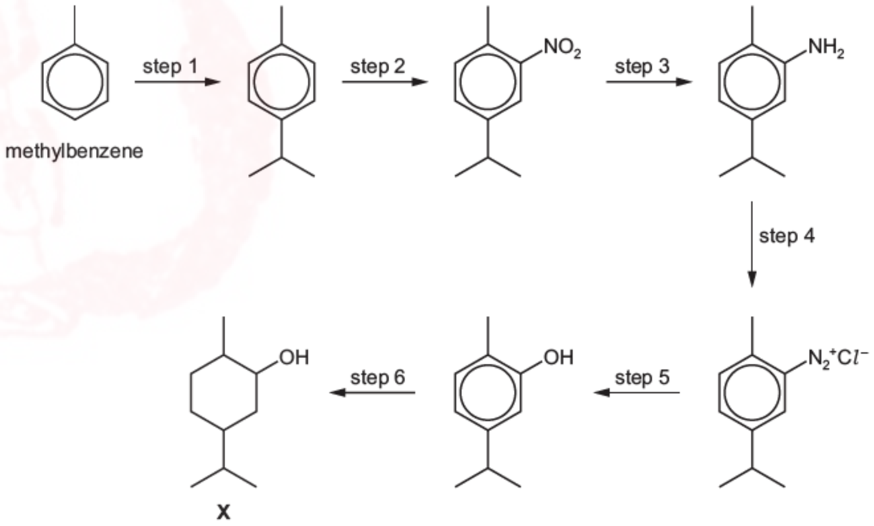
4 Carvone occurs in spearmint and a stereoisomer of carvone occurs in caraway seeds. Treating either isomer with hydrogen over a nickel catalyst produces a mixture of isomers with the structural formula **X**.



(ii) Write an equation, using molecular formulae, for this conversion of carvone to **X**.

.... [2]

X can be synthesised from methylbenzene by the following route.



(b) **(i)** Name the mechanism in step 1.

.... [1]

(ii) What type of reaction is occuring in the following steps?

step 3 ....

step 5 ....

[2]

(iii) Suggest reagents and conditions for each of the following steps.

step 1 ....

step 2 ....

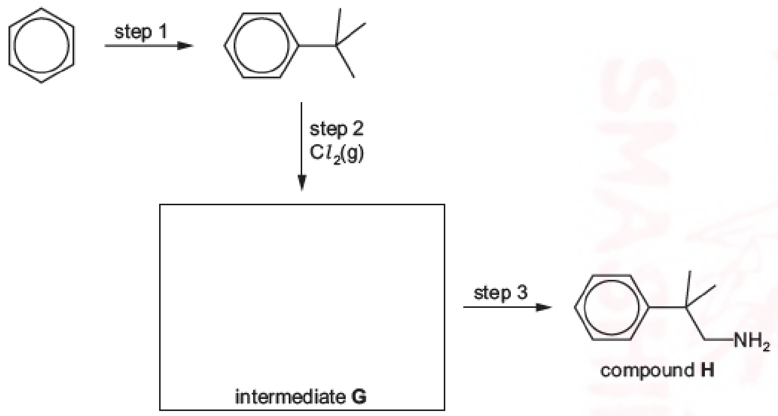
step 3 ....

step 4 ....

[6]

Topic: **Chem 36 Q# 471/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Compound **H** can be synthesised from benzene as shown.



(i) State the reagents and conditions needed for step 1.

reagents ....

conditions ....

[2]

(ii) Step 2 takes place in the presence of chlorine gas.

State the conditions for this reaction.

.... [1]

(iii) Draw the structure of intermediate G in the box. [1]

(iv) State the reagents and conditions needed for step 3.

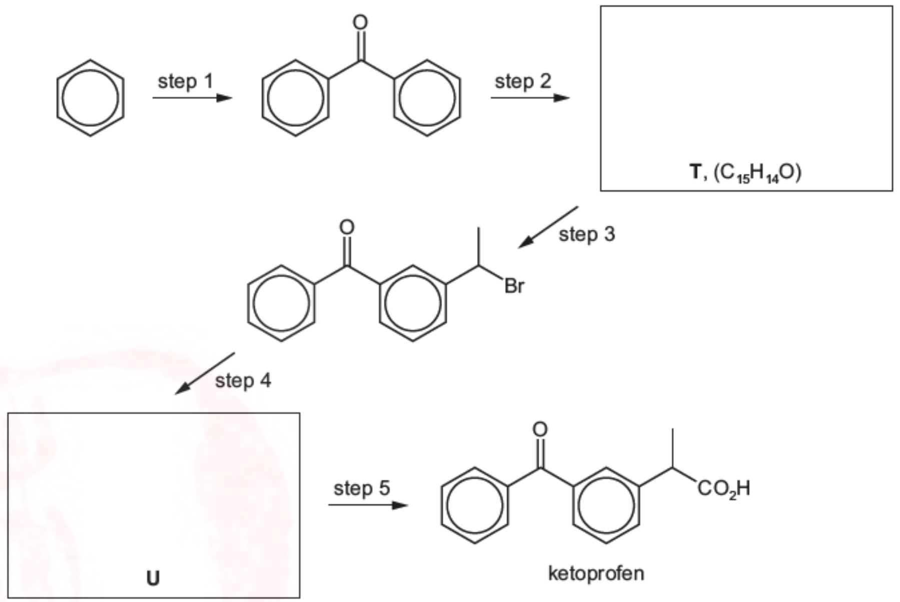
reagents ....

conditions ....

[2]

Topic: **Chem 36 Q# 472/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 The anti-inflammatory drug ketoprofen can be synthesised from benzene via the following five steps.



(a) Suggest the structures of compounds **T** and **U** and draw them in the boxes above.

[2]

(b) Suggest reagents and conditions for steps 1-5.

step 1 ....

step 2 ....

step 3 ....

step 4 ....

step 5 ....

[5]

(c) What *types of reaction* are steps 1 and 5?

step 1 ....

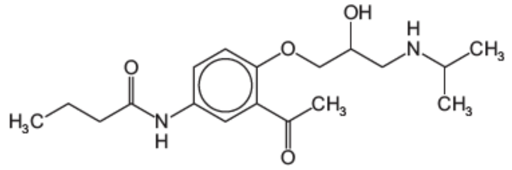
step 5 ....

[2]

[Total: 9]

Topic: **Chem 36 Q# 473/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 Acebutolol is a drug that can be used to lower blood pressure.



(d) Suggest what would be observed when acebutolol reacts with the following reagents. If no reaction would take place, write 'none' in the table below.

reagent	observation
alkaline iodine solution	
universal indicator solution	
2,4-dinitrophenylhydrazine	
Tollens' reagent	

[3]

(e) Butanoic acid can be reduced to form compound **N**. Compound **N** reacts with sodium.

(i) Suggest a suitable reducing agent for this reaction.

.... [1]

(ii) Draw the **skeletal** formula of the isomer of **N** that exists as a pair of optical isomers.

[1]

(iii) Another isomer of **N** does **not** react with acidified dichromate(VI) solution but does react with sodium.

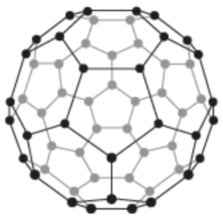
Draw the structure of this isomer.

[1]

[Total: 12]

Topic: **Chem 36 Q# 474/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(b) One of the simple molecular allotropes of carbon is buckminsterfullerene, C_{60}.



buckminsterfullerene

(i) What is the hybridisation of the carbon atoms in C_{60}?

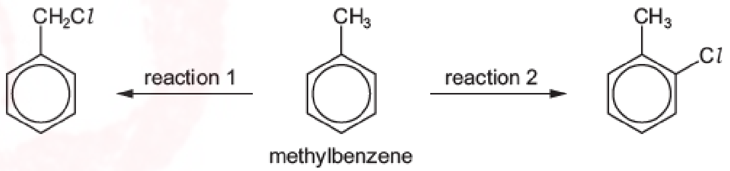
.... [1]

(ii) C_{60} reacts with an excess of hydrogen to form a single product, $C_{60}H_x$.

Using your answer to **(i)**, suggest a suitable value for *x*.

.... [1]

(c) Methylbenzene can undergo different reactions to form the products shown below.



(i) Give the reagents and conditions for these two reactions.

reaction 1 ....

reaction 2 ....

[2]

(ii) Name the mechanism of reaction 1.

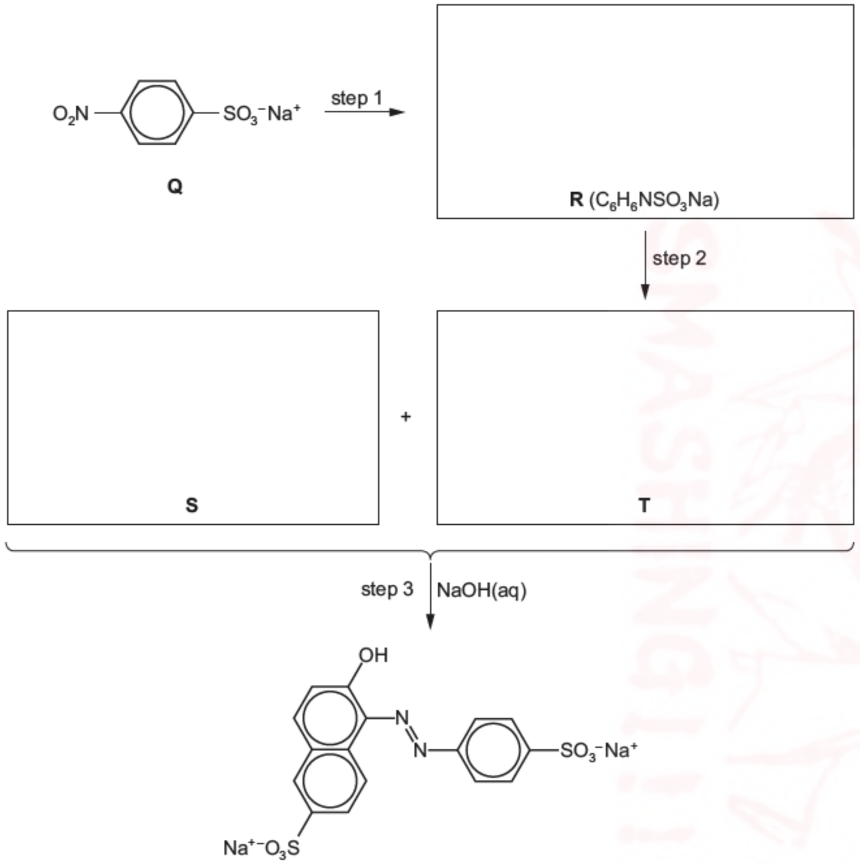
.... [1]

(iii) Draw the structure of the product obtained if reaction 1 is carried out using an excess of chlorine.

[1]

Topic: **Chem 36 Q# 475/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** *Sunset Yellow* is a yellow colouring agent used in food and drinks, which can be made by the following route.
In step 3 of this synthesis, a phenol-like compound, **S**, reacts with intermediate **T** made from amine **R**.
Assume that the $–SO_3^-Na^+$ group does not react.



Sunset Yellow

(i) Suggest structures for compounds **R**, **S** and **T** and draw them in the boxes above. [3]

(ii) Suggest reagents and conditions for

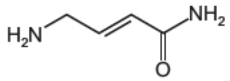
step 1, ...

step 2. ....
[3]

(iii) What type of organic salt is formed in step 2?

.... [1]

(b) Compound **W** has the following structure.



(i) How many σ and π bonds are present in a molecule of **W**?

σ bonds .... π bonds .... [2]

(ii) The products of the reactions of **W** with cold HCl and with CH_3CH_2Br are soluble in water but **not** in organic solvents.

Complete the table for these reactions of **W**.

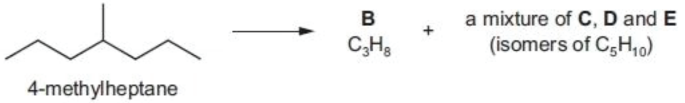
reagent	structure of product (molecular formula given)	type of reaction
HCl	($C_4H_9N_2OCl$)	
CH_3CH_2Br	($C_6H_{13}N_2BrO$)	

[3]

[Total: 12]

Topic: **Chem 36 Q# 476/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** Long chain alkanes such as 4-methylheptane can be ‘cracked’ to produce shorter chain hydrocarbons.



(iii) Compounds **C**, **D** and **E** are isomers with the molecular formula C_5H_{10}.
On heating with concentrated acidified $KMnO_4$,

- compound **C** gives CO_2 and compound **F** ($C_4H_8O_2$),
- **D** and **E** each give a 1 : 1 mixture of compounds **G** ($C_2H_4O_2$) and **H** ($C_3H_6O_2$).

Suggest structures for compounds **C** - **H**.

C	**D**	**E**
F	**G**	**H**

[3]

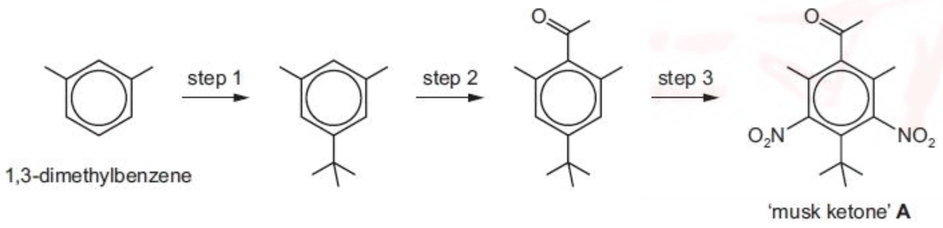
(iv) Name the type of isomerism shown between **D** and **E**.

.... [1]

Topic: **Chem 36 Q# 477/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 1,3-dimethylbenzene is a useful starting material for several commercially important compounds.

(a) The artificial 'musk ketone', **A**, is a perfume agent added to many cosmetics and detergents. It is made from 1,3-dimethylbenzene by the following route.



(i) The only by-product of step 2 is HC*l*.

Suggest the reagent that was used in this step.

.... [1]

(ii) Suggest the *type of reaction* that is occurring during both step 2 and step 3.

.... [1]

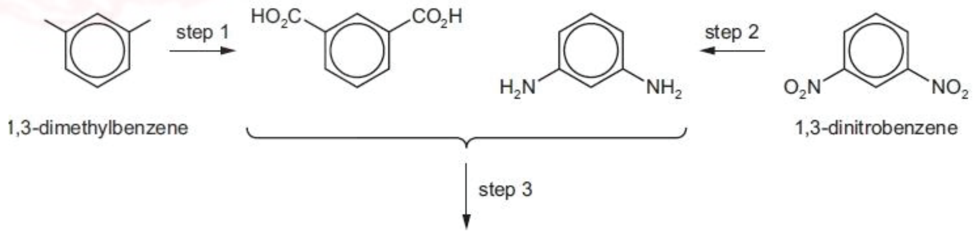
(iii) State the reagents and conditions needed for step 3.

.... [1]

(iv) Suggest the structures of the two products formed when **A** is reacted with alkaline aqueous iodine.

[2]

(b) 1,3-dimethylbenzene is also a starting material for the synthesis of the polymer *Nomex*, used in fireproof protective clothing worn by firefighters, military pilots and racing car drivers. The polymer is made from 1,3-dimethylbenzene and 1,3-dinitrobenzene by the following route.



Nomex

(i) Draw the structure of one repeat unit of *Nomex* in the box above. [1]

(ii) What *type of polymer* is *Nomex*?

.... [1]

(iii) Suggest the by-product formed during step 3.

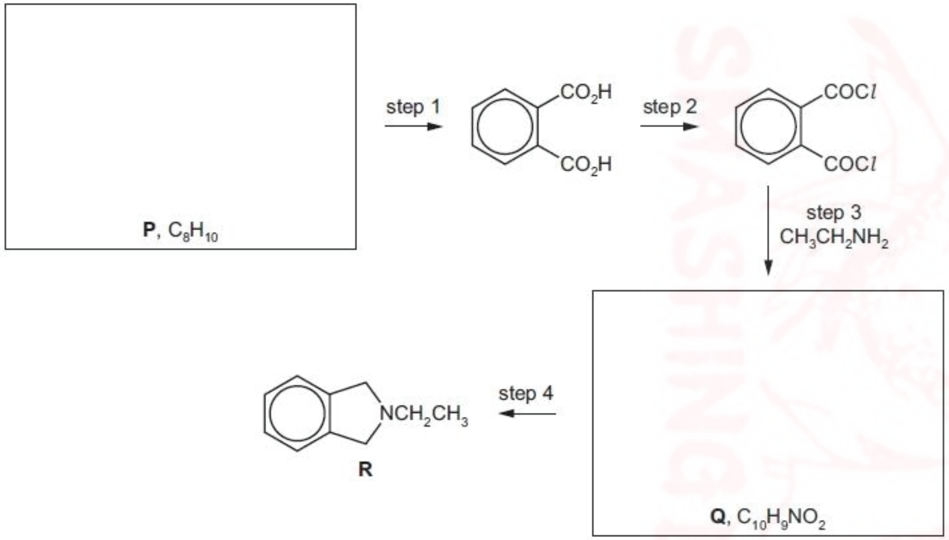
.... [1]

(iv) Suggest reagents and conditions for step 2.

.... [1]

Topic: **Chem 36 Q# 478/** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(b) Compound **R** is a useful intermediate in the synthesis of pharmaceutical compounds. It can be made from compound **P** by the following route.



(i) Suggest structures for the starting material **P** and the intermediate **Q**. [2]

(ii) Suggest reagents and conditions for the following steps in the above scheme.

step 1 ....

step 2 ....

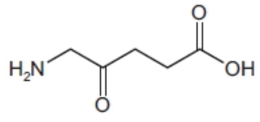
step 4 ....

[3]

[Total: 7]

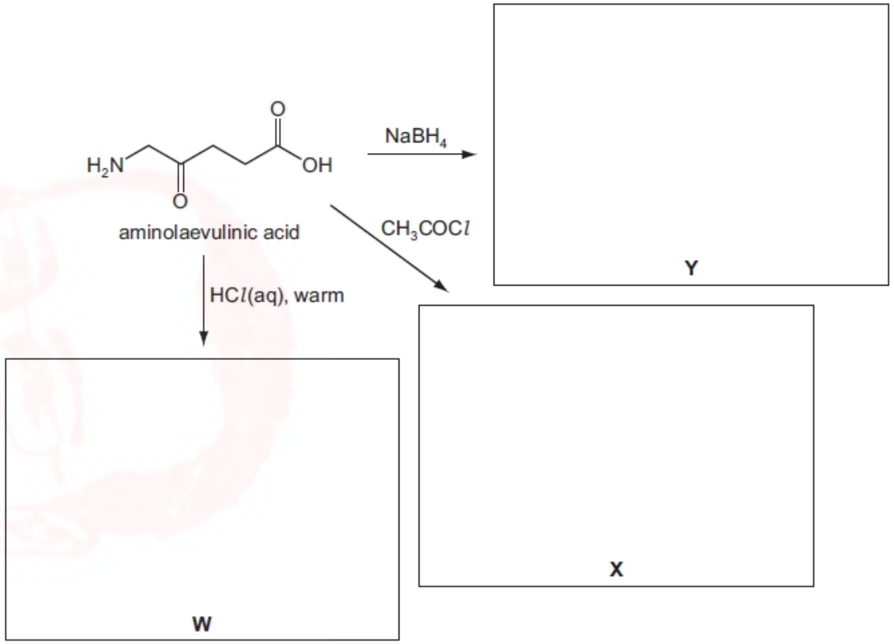
Topic: **Chem 36 Q# 479/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Aminolaevulinic acid is involved in the synthesis of haemoglobin and chlorophyll.



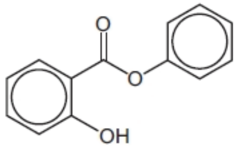
aminolaevulinic acid

(d) Three reactions of aminolaevulinic acid are shown. Draw the structures of the products **W**, **X** and **Y** in the boxes below.



[3]

(c) Phenyl 2-hydroxybenzoate is an antiseptic.



phenyl 2-hydroxybenzoate

Complete the following table about the reactions of phenyl 2-hydroxybenzoate with the three reagents.

reagent	structure of product(s)	type of reaction
Na		
excess $Br_2(aq)$		
excess hot NaOH(aq)		

[6]

[Total: 13]

---

5 The two compounds **V** and **W** are isomers with the molecular formula C_4H_8O, and show the following properties and reactions.

- Both compounds react with sodium metal, and both decolourise bromine water.
- Compound **V** forms a yellow precipitate with alkaline aqueous iodine, whereas compound **W** does not.
- When reacted with cold $KMnO_4(aq)$, both **V** and **W** produce the same neutral compound **X**, $C_4H_{10}O_3$.
- Both **V** and **W** exist as pairs of stereoisomers.

(a) Suggest which functional groups are responsible for the reactions with

(i) sodium,

....

(ii) bromine water,

....

(iii) alkaline aqueous iodine.

....

[3]

(b) Suggest structures for **V** and **W**.

V

W

[2]

(c) State the type of stereoisomerism shown by compound **V** and draw the structures of the stereoisomers.

type of stereoisomerism ....

structures of stereoisomers

isomer 1

isomer 2

[2]

(d) Suggest the structure of the neutral compound **X**.

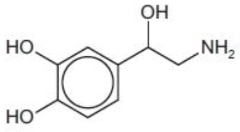
X

[1]

[Total: 8]

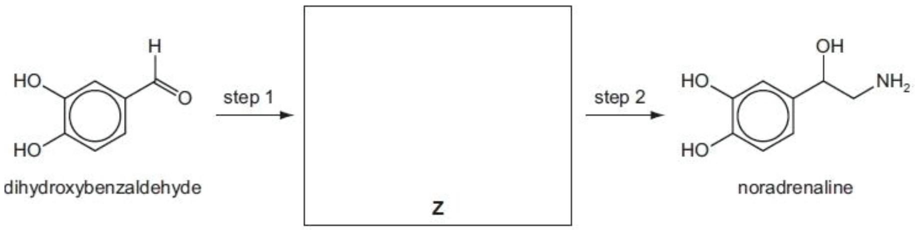
Topic: **Chem 36 Q# 482/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Noradrenaline is a hormone and neurotransmitter, which is released during stress to stimulate the heart and increase blood pressure.



noradrenaline

(b) **(i)** Consider the following two-stage synthesis of noradrenaline from dihydroxybenzaldehyde.



- Draw the structure of the intermediate **Z** in the box.
- Suggest reagents for steps 1 and 2.

step 1 ....

step 2 ....

(ii) Dihydroxybenzaldehyde reacts with Br_2(aq).

- Describe what you would see during this reaction.

....

- Draw the structure of the product.

[5]

(c) Draw the structures of the products when noradrenaline is reacted with

(i) dilute NaOH(aq),

(ii) dilute HC*l*(aq),

(iii) an excess of ethanoyl chloride, CH_3COCl.

[4]

(d) Name the **new** functional groups formed in the reaction in **(c)(iii)**.

....

.... [2]

[Total: 14]

Topic: **Chem 36 Q# 483/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

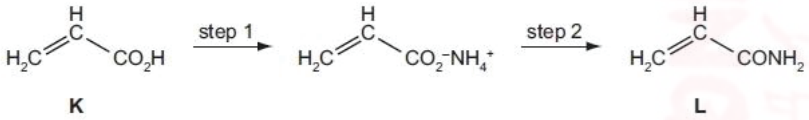
(e) Compound **L**, CH_2=CHCONH$_2$, can also be polymerised to form a super-absorbent polymer.

(i) Name the **two** functional groups in compound **L**.

....

....

Compound **K** can be converted into compound **L** by the following two-step route.



(ii) Suggest a reagent for step 1.

....

(iii) What other product is formed in step 2?

....

(iv) State the reagents and conditions necessary to re-form **K** from **L**.

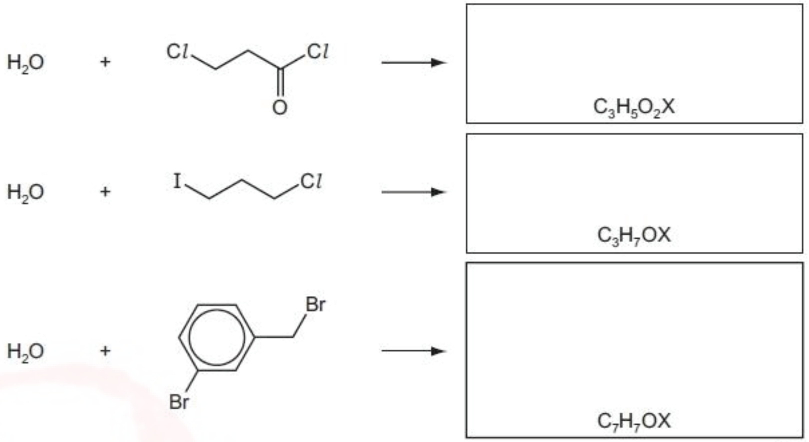
....

[5]

[Total: 17]

Topic: **Chem 36 Q# 484/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) Predict the products of the following reactions and draw their structures in the boxes below. The molecular formula of each product is given, where X = C*l*, Br or I.

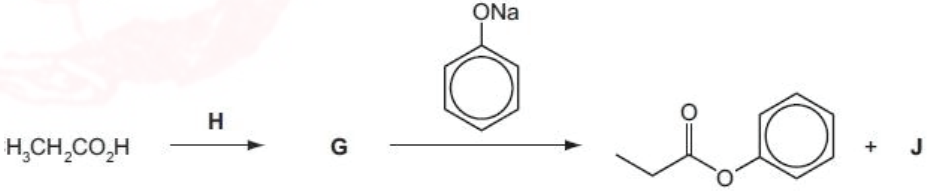


[3]

Topic: **Chem 36 Q# 485/** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(d) Propanoic acid, $CH_3CH_2CO_2H$, is a weak acid with $K_a = 1.34 \times 10^{-5}\,mol\,dm^{-3}$.

(e) Phenyl propanoate cannot be made directly from propanoic acid and phenol. Suggest the identities of the intermediate **G**, the reagent **H** and the by-product **J** in the following reaction scheme.



G is ....

H is ....

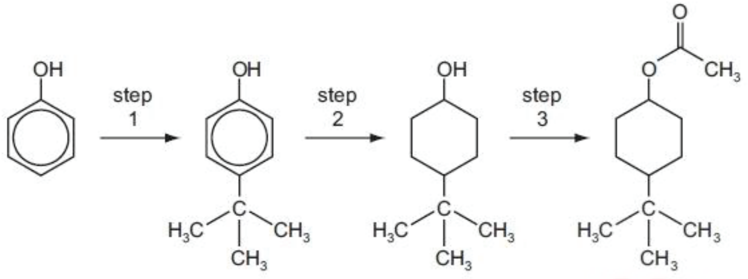
J is ....

[2]

[Total: 18]

Topic: **Chem 36 Q# 486/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) Compound **C** is responsible for the pleasant aroma of apples. It can be prepared from phenol by the following 3-step synthesis.



A **B** **C**

(i) The only by-product of step 1 is HC*l*. Suggest the reagent that was used to react with phenol to produce compound **A**.

....

(ii) What *type of reaction* is occurring in step 2?

....

(iii) What reagents and conditions are required for step 3?

....

(iv) State the reagent and conditions needed to convert **C** back to **B**, the reverse of step 3.

.... [5]

(c) **(i)** Either compound **A** or compound **B**, or both, react with the following reagents. For each reagent draw the structure of the organic product formed with **A**, and with **B**. If no reaction occurs, write 'no reaction' in the relevant box.

reagent and conditions	product with **A**	product with **B**
an excess of $Br_2(aq)$		
heat with HBr		
pass vapour over heated Al_2O_3		
heat with acidified $K_2Cr_2O_7$		

(ii) Choose **one** of the above reactions to enable you to distinguish between **A** and **B**.

State below the observations you would make with each compound.

reagent	observation with **A**	observation with **B**

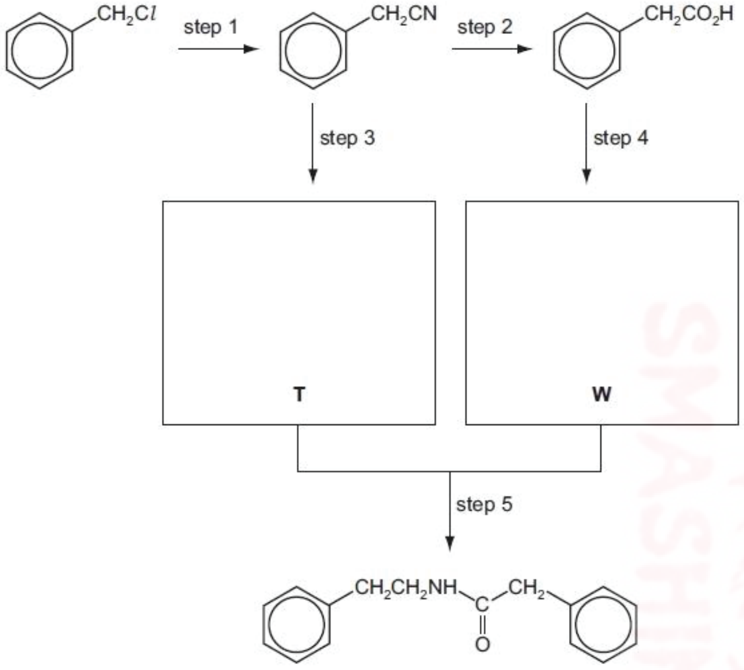
[7]

[Total: 17]

Topic: **Chem 36 Q# 487/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 Because of the lack of reactivity of the nitrogen molecule, extreme conditions need to be used to synthesise ammonia from nitrogen in the Haber process.

(d) Compound **X** is a useful intermediate in the synthesis of pharmaceuticals.
X can be synthesised from chloromethylbenzene according to the following scheme.



X

(i) What *type of reaction* is each of the following?

step 1 ....

step 2 ....

(ii) Suggest reagents and conditions for

step 1, ...

step 2. ....

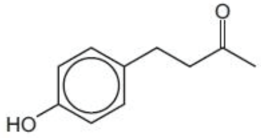
(iii) Draw the structures of the intermediates **T** and **W** in the boxes above.

[6]

[Total: 15]

---

5 Compound **G** is a naturally occurring aromatic compound that is present in raspberries.



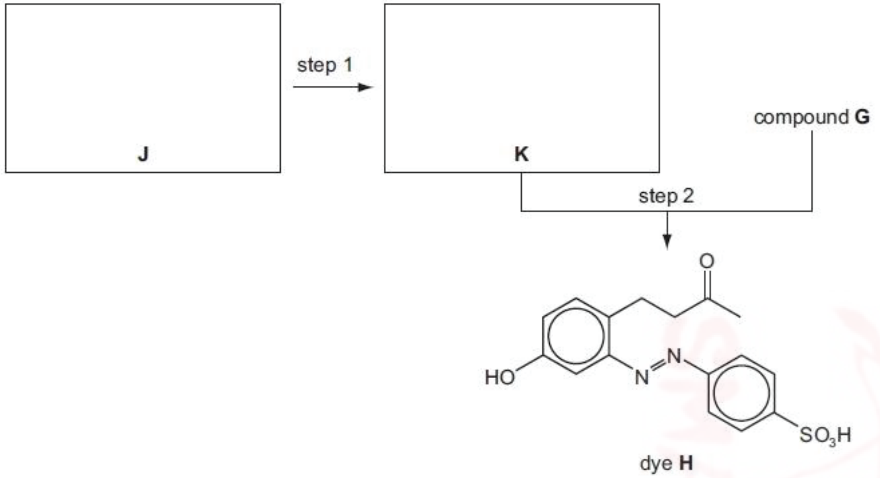
compound **G**

(b) Complete the following table with information about the reactions of the three stated reagents with compound **G**.

reagent	observation	structure of organic product	type of reaction
sodium metal			
aqueous bromine			
aqueous alkaline iodine			

[8]

(c) The dye **H** can be made from compound **G** by the route shown below.



dye **H**

(i) Draw the structures of the amine **J** and the intermediate **K** in the boxes above.

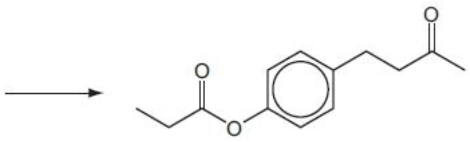
(ii) Suggest reagents and conditions for

step 1, ...

step 2. ....

[5]

(d) Suggest a reaction scheme by which compound **G** and propanoic acid could be converted into compound **L**.



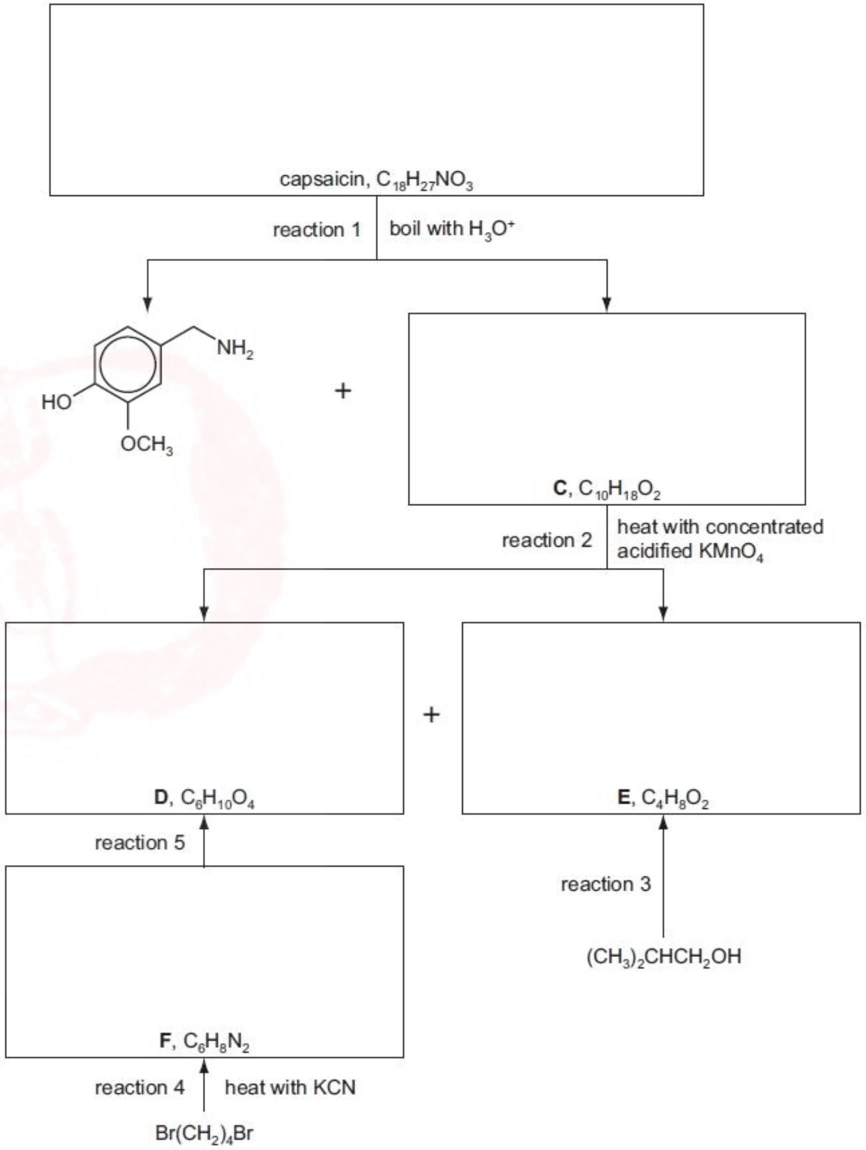
compound **L**

[3]

[Total: 18]

---

4 The compound responsible for the hot taste of chilli peppers is capsaicin. Its molecular structure can be deduced by the following reaction scheme.



Compounds **C**, **D** and **E** all react with $Na_2CO_3(aq)$.

Answer the following questions.

(a) Suggest reagents and conditions for reaction 3.

.... [1]

(b) What *type of reaction* is reaction 4?

.... [1]

(c) Suggest reagents and conditions for reaction 5.

.... [1]

(d) Name the functional group in **C** that has reacted with hot concentrated acidified $KMnO_4$.

.... [1]

(e) Suggest the name of the functional group in capsaicin that has reacted in reaction 1.

.... [1]

(f) Work out structures for compounds **C**–**F** and capsaicin, and draw their structural formulae in the boxes opposite. [5]

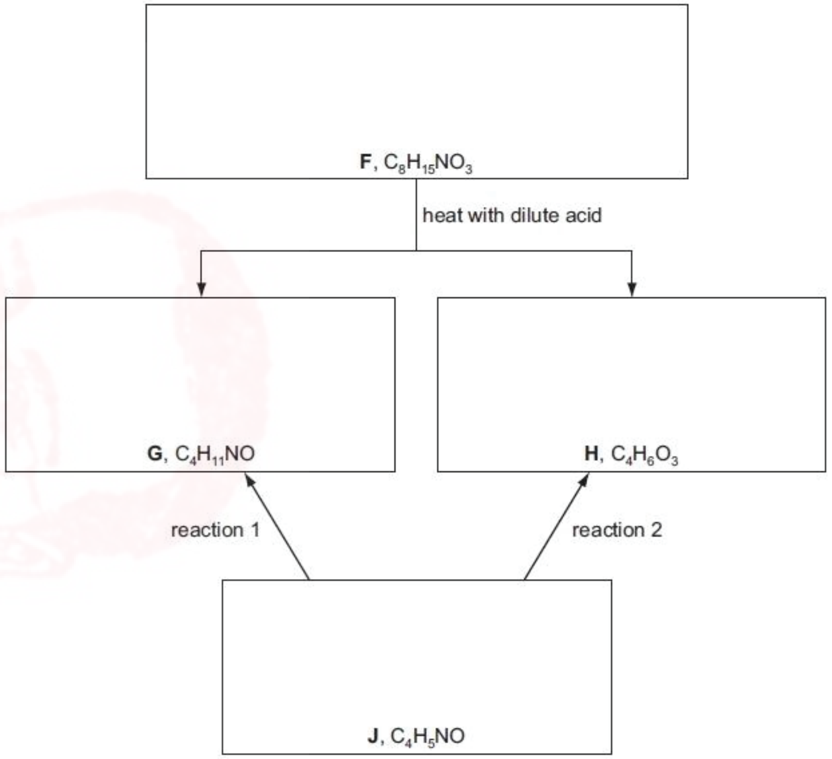
[Total: 10]

(c) The following chart shows some reactions of compound **F** which is a neutral compound.

G forms a salt with dilute H_2SO_4, whereas **H** forms a salt with NaOH(aq).

Both **G** and **H** can be obtained from compound **J** by separate one-step reactions (reaction 1 and reaction 2 below).

All four compounds **F**, **G**, **H** and **J** form a yellow precipitate with alkaline aqueous iodine.



(i) Suggest structures for **F**, **G**, **H** and **J**, and draw them in the boxes above.

(ii) Suggest reactants and conditions for

reaction 1, ...

reaction 2. ....
[6]

[Total: 14]

5 **(a)** Methoxybenzene reacts with Br_2(aq) in a similar manner to phenol.

methoxybenzene

(i) Draw the structural formula of the product of the reaction between methoxybenzene and an excess of bromine.

(ii) Suggest a chemical reaction you could use to distinguish between methoxybenzene and phenol. State the reagent, describe the observations you would make, and give an equation for the reaction.

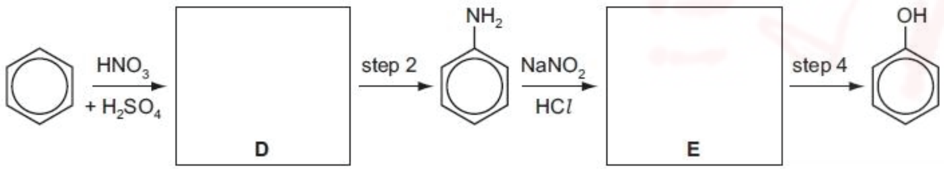
reagent ....

observation ....

equation

[4]

(b) Phenol can be synthesised from benzene by the following route.



(i) Suggest structures for compounds **D** and **E** and draw them in the boxes above.

(ii) Suggest reagents and conditions for

step 2, ...

step 4. ....

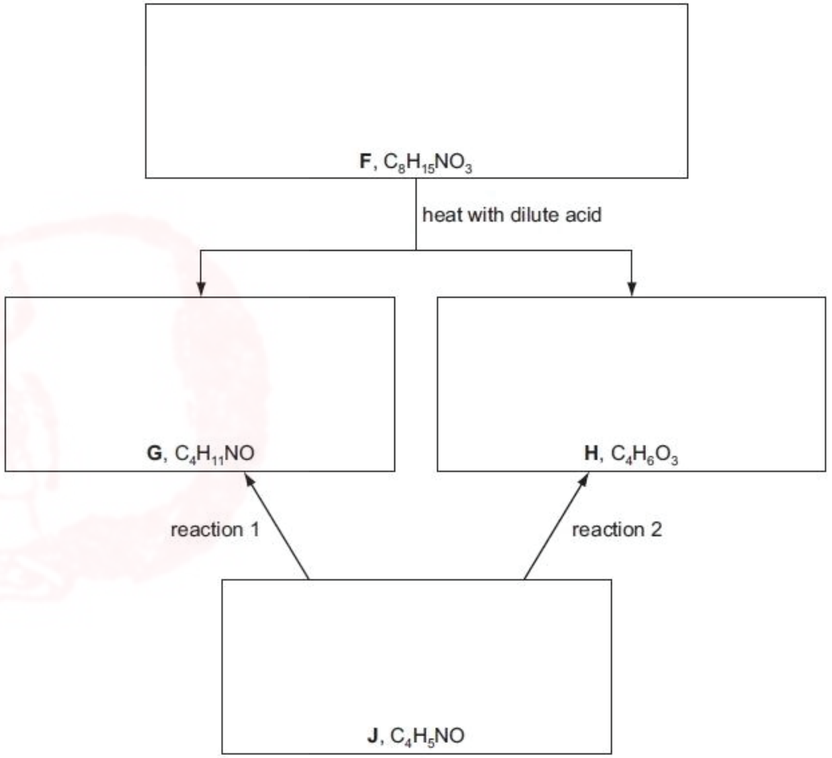
[4]

(c) The following chart shows some reactions of compound **F** which is a neutral compound.

G forms a salt with dilute H_2SO_4, whereas **H** forms a salt with NaOH(aq).

Both **G** and **H** can be obtained from compound **J** by separate one-step reactions (reaction 1 and reaction 2 below).

All four compounds **F**, **G**, **H** and **J** form a yellow precipitate with alkaline aqueous iodine.



(i) Suggest structures for **F**, **G**, **H** and **J**, and draw them in the boxes above.

(ii) Suggest reactants and conditions for

reaction 1, ...

reaction 2. ....

[6]

[Total: 14]

3 Indigo is the dye used in blue jeans. Although originally extracted from plants of the type *indigofera*, it is now almost entirely made artificially.

Indigo is insoluble in water but this disadvantage can be overcome by converting it into the water-soluble colourless leuco-indigo. If cloth soaked in a solution of leuco-indigo is left to dry in the air, the leuco-indigo is converted into the insoluble blue indigo, which is precipitated out onto the fibres of the cloth.

indigo leuco-indigo

(c) Suggest **two** chemical tests that could be used to distinguish between indigo and leuco-indigo. Write your answers in the following table.

test	reagents and conditions	observation with indigo	observation with leuco-indigo
1			
2			

[5]

(d) When indigo is heated with hydrogen and a nickel catalyst, compound **A**, $C_{16}H_{28}N_2O_2$, is formed.

(i) Suggest a structure for **A**.

(ii) Calculate the volume of hydrogen, measured at room temperature and pressure, that would have been absorbed if 2.50 g of indigo had undergone this reaction.

volume = ... dm^3 [3]

(e) Suggest the structure of the product formed when indigo reacts with an excess of Br_2(aq).

[3]

[Total: 16]

Topic: **Chem 36 Q# 493/** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **C** has the molecular formula $C_7H_{14}O$. Treating **C** with hot concentrated acidified $KMnO_4$(aq) produces two compounds, **D**, C_4H_8O, and **E**, $C_3H_4O_3$. The results of four tests carried out on these three compounds are shown in the following table.

test reagent	result of test with		
	compound **C**	compound **D**	compound **E**
Br_2(aq)	decolourises	no reaction	no reaction
Na(s)	fizzes	no reaction	fizzes
I_2(aq) + OH^-(aq)	no reaction	yellow precipitate	yellow precipitate
2,4-dinitrophenylhydrazine	no reaction	orange precipitate	orange precipitate

(a) State the functional groups which the above four reagents test for.

(i) Br_2(aq)

....

(ii) Na(s)

....

(iii) I_2(aq) + OH^-(aq)

....

(iv) 2,4-dinitrophenylhydrazine

.... [4]

(b) Based upon the results of the above tests, suggest structures for compounds **D** and **E**.

D, C_4H_8O **E**, $C_3H_4O_3$ [2]

(c) Compound **C** exists as two stereoisomers.

Draw the structural formula of **each** of the two isomers, and state the type of stereoisomerism involved.

type of stereoisomerism .... [3]

[Total: 9]

Topic: **Chem 36 Q# 494/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b) The iodoform test can be used, along with other reactions, to work out the structures of unknown compounds.
Use the information in the table below to deduce the structures of the compounds in the following scheme, and draw these structures in the boxes provided.

$$\underset{\textbf{D}}{C_7H_{12}O} \xrightarrow{\text{hot concentrated acidified KMnO}_4} \underset{\textbf{E}}{C_3H_6O} + \underset{\textbf{F}}{C_4H_6O_3}$$

Results of tests (✓ indicates a positive result; ✗ indicates a negative result)

test	results of tests with each compound		
	D	**E**	**F**
iodoform	✗	✓	✓
Fehling's solution	✓	✗	✗
2,4-dinitrophenyl-hydrazine reagent	✓	✓	✓
Na_2CO_3(aq)	✗	✗	✓

structures

D($C_7H_{12}O$)

E(C_3H_6O)

F($C_4H_6O_3$)

[3]

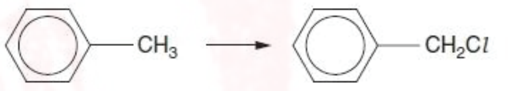
(c) Treatment of compound **F** with $NaBH_4$ gives compound **G**, $C_4H_8O_3$. Heating **G** with Al_2O_3 gives a mixture of three isomeric unsaturated carboxylic acids **H**, **J** and **K**, $C_4H_6O_2$, two of which are stereoisomers of each other.
Suggest structures for **G**, **H**, **J**, and **K**, and name the type of stereoisomerism shown.

$$\textbf{G} \xrightarrow{Al_2O_3} \textbf{H} + \textbf{J} + \textbf{K}$$

type of stereoisomerism ....[5]

Topic: **Chem 36 Q# 495/** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

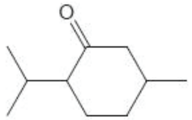
5 **(a)** There are several ways of introducing chlorine atoms into organic molecules. State the reagents and conditions necessary to carry out the following transformations.

transformation	reagents + conditions
$C_2H_4 \longrightarrow C_2H_5Cl$	
$C_2H_5OH \longrightarrow C_2H_5Cl$	
$C_2H_6 \longrightarrow C_2H_5Cl$	
$C_2H_4 \longrightarrow C_2H_4Cl_2$	
$CH_3CO_2H \longrightarrow CH_3COCl$	
	
	

[6]

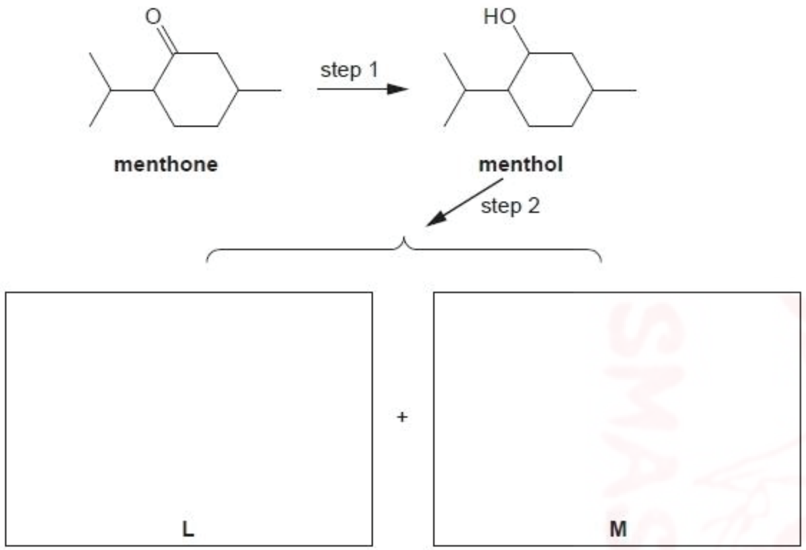
Topic: **Chem 36 Q# 496/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Menthone, $C_{10}H_{18}O$, is a cyclic ketone that occurs in oil of peppermint.



menthone

(b) Menthone can be reduced to menthol, which can be dehydrated to a mixture of two alkenes, **L** and **M**.



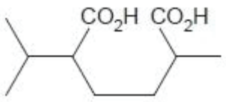
(i) Suggest reagents for

step 1, ...

step 2. ....

(ii) Suggest structures for **L** and **M** and draw them in the boxes above. [4]

(c) When heated with concentrated, acidified $KMnO_4(aq)$, one of the two alkenes **L** or **M** produces the dicarboxylic acid **N**.



N

(i) Give the letter of the alkene that produced **N** by this reaction.

....

(ii) Suggest the structure of the product, **P**, of the reaction between the other alkene you have drawn and hot concentrated acidified $KMnO_4$.

P

(iii) Suggest **one** chemical test that would enable you to distinguish between **N** and **P**.

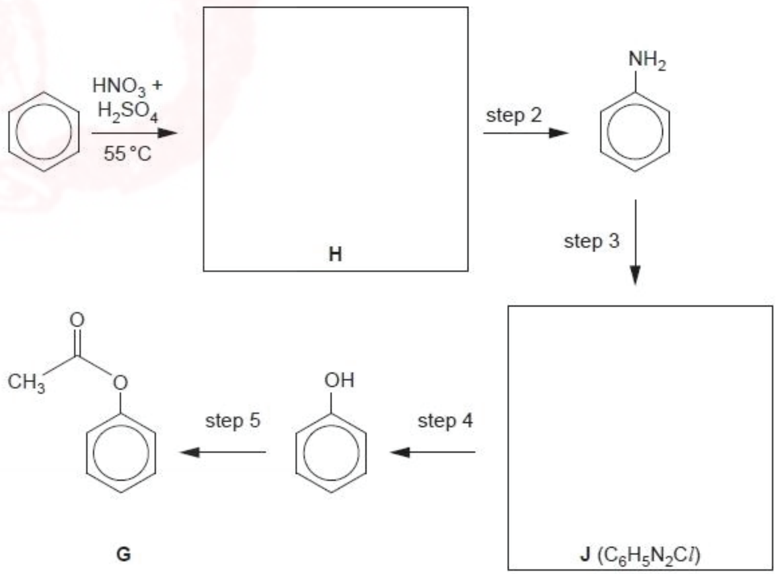
reagent(s) ....

observation ....

[3]

Topic: **Chem 36 Q# 497/** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Compound **G** can be synthesised from benzene by the route shown below.



(i) **Name** the functional group formed in step 5.

....

(ii) Draw the structures of the intermediates **H** and **J** in the boxes above.

(iii) Suggest reagents and conditions for the following.

step 2 ....

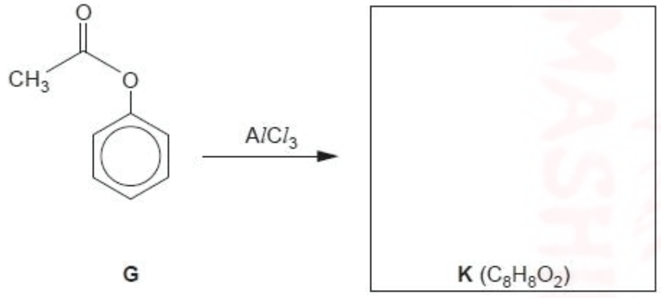
step 3 ....

step 4 ....

step 5 ....

[7]

(b) In a reaction discovered just over 100 years ago by the German chemist Karl Fries, compound **G** is converted into compound **K** when it is heated with $AlCl_3$.
Compound **K** is a structural isomer of **G**.



Compound **K** is a 1,4-disubstituted benzene derivative. It is insoluble in water, but dissolves in NaOH(aq). It gives a white precipitate with Br_2(aq), and a yellow precipitate with alkaline aqueous iodine.

(i) What is meant by the term *structural isomerism*?

....

....

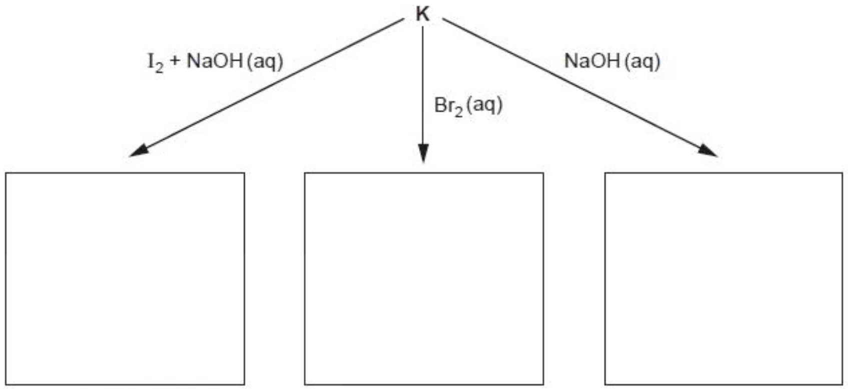
(ii) Use the information given above to **name** two functional groups in compound **K**.

....

....

(iii) Suggest the structural formula of **K**, and draw it in the box above.

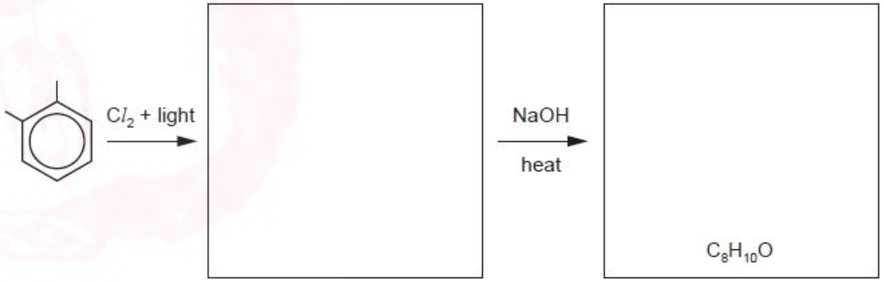
(iv) Suggest structures for the aromatic products of the following reactions.

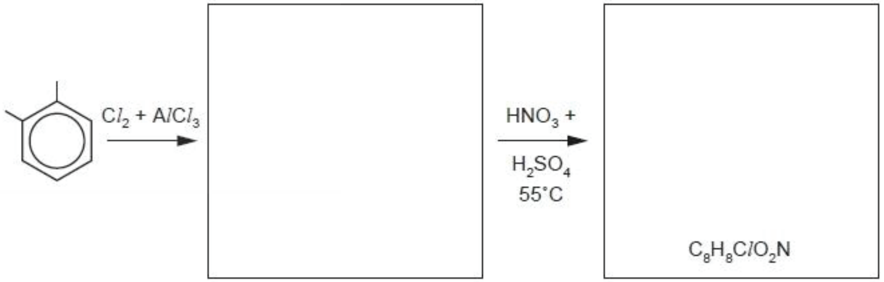


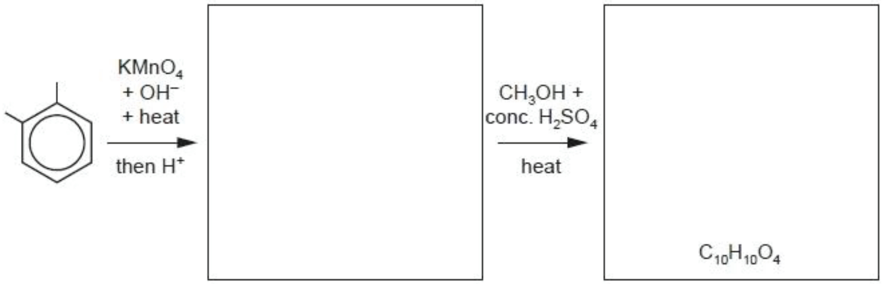
[7]

Topic: **Chem 36 Q# 498/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 Predict the products of the following reactions and draw their structures in the boxes provided. Note that the molecular formula of the final product is given in each case.



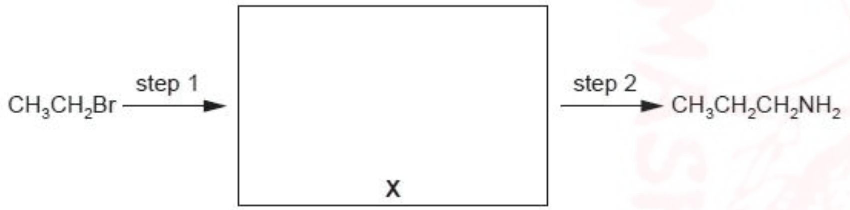




[6]

Topic: **Chem 36 Q# 499/** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) Propylamine can be synthesised from bromoethane by the following route.



(i) Draw the structure of the intermediate compound **X** in the box above.

(ii) Suggest reagents and conditions for

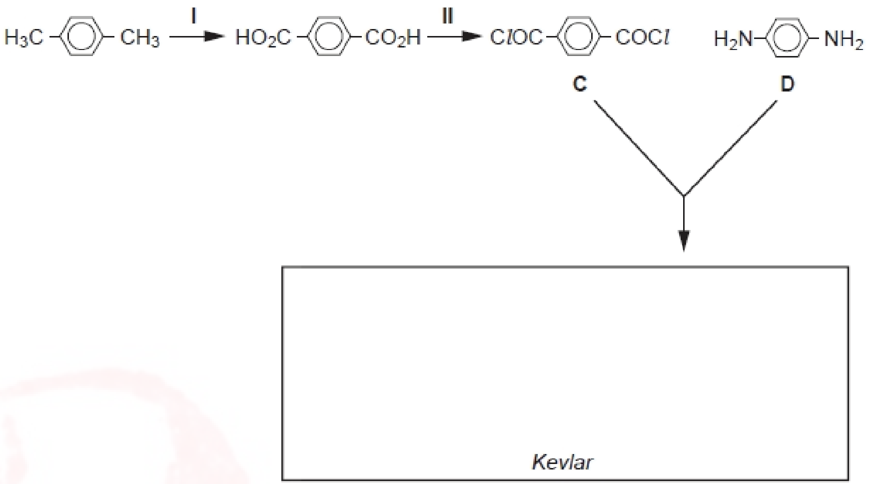
step 1 ....

step 2 ....

[3]

Topic: **Chem 36 Q# 500/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 *Kevlar* is a tough polyamide used in bullet-proof vests and high-specification bicycle tyres. It can be manufactured by the following process.



(a) **(i)** Suggest reagents and conditions for

reaction **I**, ...

reaction **II**. ....

(ii) Draw the structural formula of **one** repeat unit of *Kevlar* in the box above.

[4]

(b) The di-acid chloride **C** reacts with a variety of reagents. Suggest the structural formulae of the products of the reaction of **C** with

(i) CH_3NH_2,

(ii) $HOCH_2CH_2OH$.

[3]

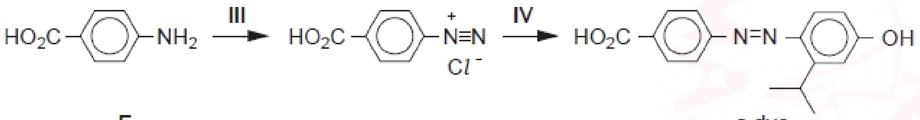
(c) The diamine **D** also reacts with a variety of reagents. Suggest the structural formulae of the products of the reaction of **D** with

(i) HC*l*(aq),

(ii) Br_2(aq).

[3]

(d) 4-aminobenzoic acid, **E**, is a useful intermediate for making dyes.



E

a dye

Suggest reagents and conditions for

reaction **III**, ...

reaction **IV**. ....

[4]

---

6 Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

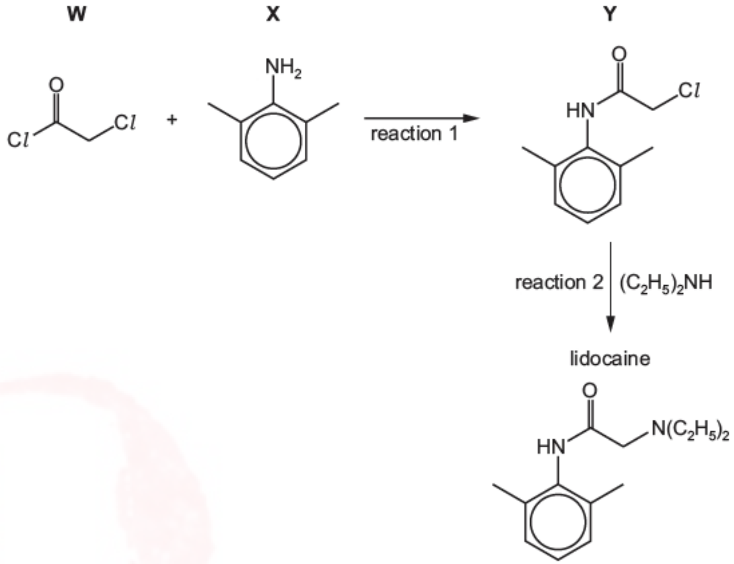


Fig. 6.1

(e) The purity of lidocaine can be checked using thin-layer chromatography. Ethyl ethanoate is used as the solvent.

The R_f values of **X** and lidocaine are given in Table 6.1.

Table 6.1

compound	R_f
X	0.49
lidocaine	0.71

(i) Identify the substances used as the mobile and stationary phases in this thin-layer chromatography experiment.

mobile phase ....

stationary phase ....

[1]

(ii) Describe how an R_f value can be calculated.

....

.... [1]

(iii) Suggest why the R_f value for **X** is less than that for lidocaine.

....

.... [1]

Topic: **Chem 37 Q# 502/** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(f) The proton (^1H) NMR spectrum of lidocaine is shown in Fig. 6.2.

lidocaine

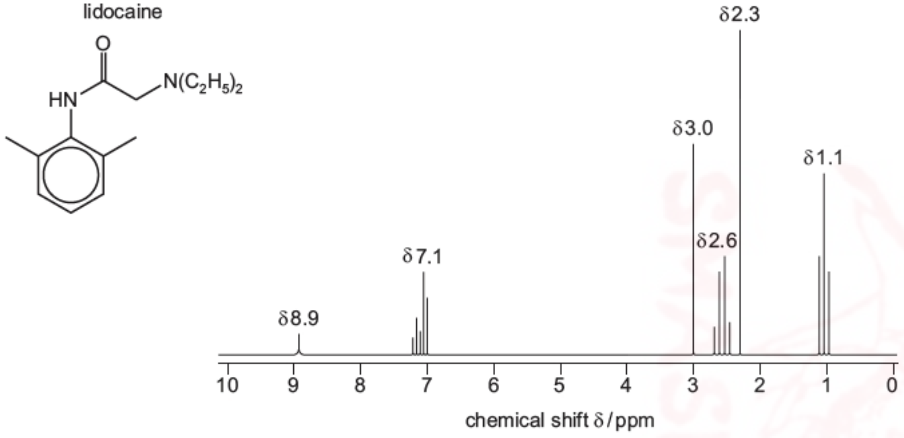


Fig. 6.2

Table 6.2

environment of proton	example	chemical shift range δ / ppm
alkane	$-CH_3$, $-CH_2-$, >CH–	0.9–1.7
alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, >CH–C=O	2.2–3.0
alkyl next to aromatic ring	CH_3–Ar, $-CH_2$–Ar, >CH–Ar	2.3–3.0
alkyl next to electronegative atom	CH_3–O, $-CH_2$–O, $-CH_2-Cl$	3.2–4.0
attached to alkene	=CHR	4.5–6.0
attached to aromatic ring	**H**–Ar	6.0–9.0
aldehyde	**H**COR	9.3–10.5
alcohol	RO**H**	0.5–6.0
phenol	Ar–O**H**	4.5–7.0
carboxylic acid	RCOO**H**	9.0–13.0
alkyl amine	R–N**H**–	1.0–5.0
aryl amine	Ar–N**H**$_2$	3.0–6.0
amide	RCON**H**R	5.0–12.0

(i) Name the splitting patterns at δ2.6 and δ1.1.

δ2.6 .... δ1.1 .... [1]

(ii) The relative peak area of the peaks at δ3.0 and δ2.3 is 1 : 3 respectively.

Identify the protons in the ^1H NMR spectrum of lidocaine that are responsible for the peaks at the following chemical shift values.

δ7.1 ....

δ3.0 ....

δ2.3 .... [2]

(iii) Predict the number of peaks in the **carbon-13** (^{13}C) NMR spectrum of lidocaine.

.... [1]

[Total: 14]

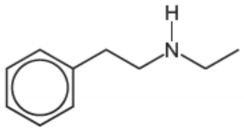
Important values, constants and standards

molar gas constant	$R = 8.31\,J\,K^{-1}\,mol^{-1}$
Faraday constant	$F = 9.65 \times 10^4\,C\,mol^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23}\,mol^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,C$
molar volume of gas	$V_m = 22.4\,dm^3\,mol^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,dm^3\,mol^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,kJ\,kg^{-1}\,K^{-1}$ ($4.18\,J\,g^{-1}\,K^{-1}$)

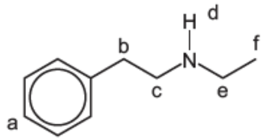
Topic: **Chem 37 Q# 503/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 Compound **T** is made by a three-stage synthesis.

T



(e) The proton (^1H) NMR spectrum of compound **T** shows hydrogen atoms in different environments. Six of these environments are shown on the structure using letters a, b, c, d, e and f.



Use the letters a, b, c, d, e and f to answer the questions that follow. The questions relate to the proton (^1H) NMR spectrum of **T**.

Proton d does not cause splitting of the peaks for protons c or e under the conditions used.

Each answer may be one, or more than one, of the letters a, b, c, d, e and f.

(i) Identify the proton or protons with a chemical shift (δ) in the range 6.0 to 9.0.

.... [1]

(ii) Identify the proton or protons whose peak will disappear if D_2O is added.

.... [1]

(iii) Identify the proton or protons whose peak is a triplet.

.... [1]

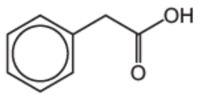
(iv) Identify the proton or protons with the lowest chemical shift (δ).

.... [1]

[Total: 12]

Topic: **Chem 37 Q# 504/** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The structure of phenylethanoic acid is shown.



(a) Give the number of different peaks in the carbon-13 (^{13}C) NMR spectrum of phenylethanoic acid.

number of peaks = ... [1]

Topic: **Chem 37 Q# 505/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 The carbon-13 (^{13}C) NMR spectrum of compound **A**, $C_8H_8O_2$, contains six peaks.

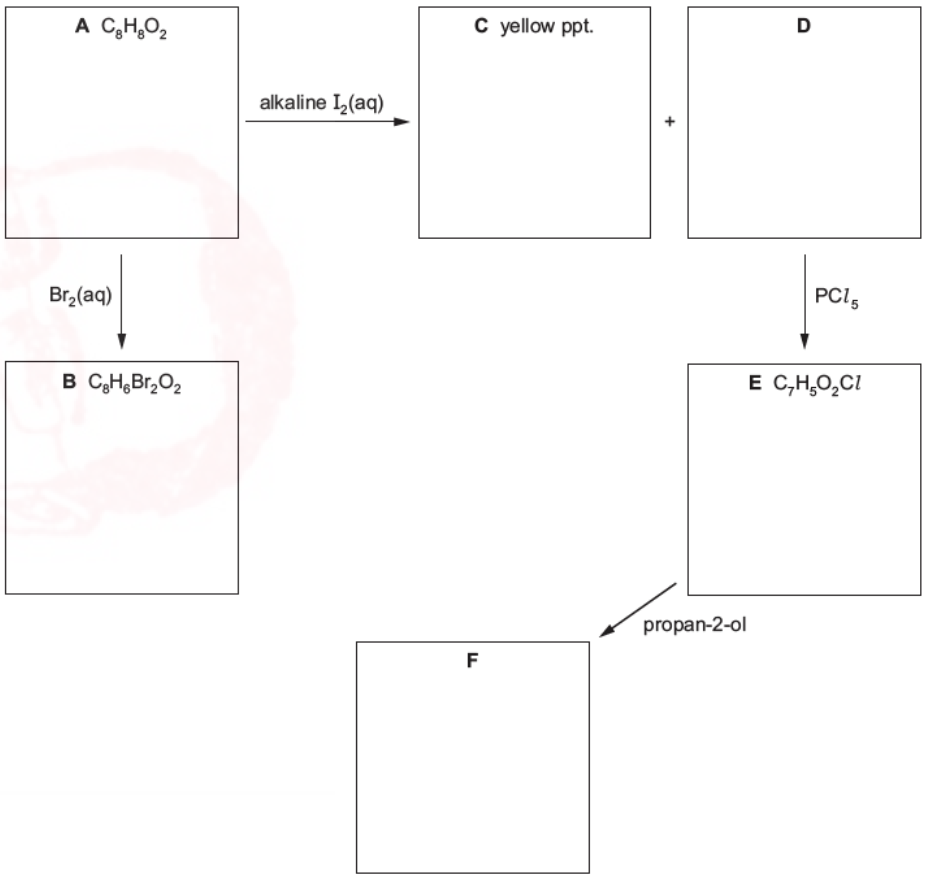
Compound **A** reacts with an excess of bromine water to give compound **B**, $C_8H_6Br_2O_2$.

Compound **A** reacts with alkaline aqueous iodine to form a yellow precipitate **C** and compound **D**.

Compound **D** reacts with PCl_5 to form compound **E**, $C_7H_5O_2Cl$.

Compound **E** reacts with propan-2-ol to form compound **F**.

Draw the structures of compounds **A**, **B**, **C**, **D**, **E** and **F** in the boxes.



[6]

Topic: **Chem 37 Q# 506/** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(ii) Each compound, HCO_2H, HO_2CCO_2H and $HO_2CCH_2CH_2CO_2H$, is dissolved seperately in $CDCl_3$. Proton (^1H) NMR and carbon-13 (^{13}C) NMR spectra are then obtained.

Complete the table.

compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR
HCO_2H		
HO_2CCO_2H		
$HO_2CCH_2CH_2CO_2H$		

[2]

(iii) The proton NMR spectrum of HCO_2H in D_2O is obtained.

Describe and explain the difference observed between this spectrum and the proton NMR spectrum of HCO_2H in **(b)(ii)**.

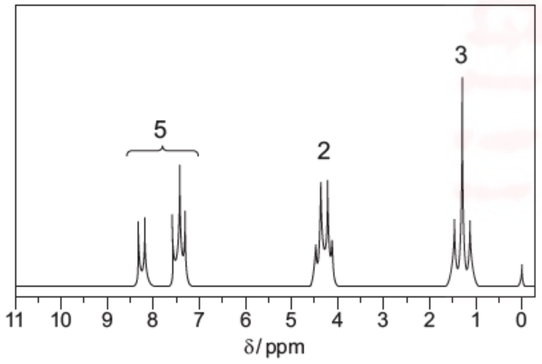
....

....

.... [1]

Topic: **Chem 37 Q# 507/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 The proton NMR spectrum of compound **E** in the solvent $CDCl_3$ is shown. The molecular formula of compound **E** is $C_9H_{10}O_2$.



(a) Explain why $CDCl_3$ is used as a solvent instead of $CHCl_3$.

.... [1]

(b) Explain why TMS is added to give the small peak at chemical shift δ = 0.

.... [1]

(c) Compound **E** is hydrolysed by hot NaOH(aq), giving two organic products only. One of these products is ethanol.

Name the functional group in compound **E** that is hydrolysed by hot NaOH(aq).

.... [1]

(d) **(i)** Describe and explain the splitting patterns of the peaks at δ = 1.4 and δ = 4.3.

splitting pattern at δ = 1.4 ....

reason for splitting pattern at δ = 1.4 ....

splitting pattern at δ = 4.3 ....

reason for splitting pattern at δ = 4.3 ....

[2]

(ii) Each molecule of compound **E** contains five protons which give rise to the peaks between δ = 7.0 and δ = 8.5.

Identify the functional group in compound **E** which contains these protons.

.... [1]

(iii) Give the structural formula of compound **E**.

[1]

(e) The mass spectrum of compound **E** includes fragment ions with *m*/*e* values of 29 and 77.

Give the formulae of these fragment ions.

fragment ion with *m*/*e* = 29 ....

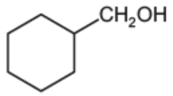
fragment ion with *m*/*e* = 77 ....

[2]

[Total: 9]

Topic: **Chem 37 Q# 508/** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b) Benzene can be used as a starting material in the synthesis of cyclohexylmethanol, $C_6H_{11}CH_2OH$,



cyclohexylmethanol

(iv) Deduce the number of peaks in the carbon-13 NMR spectrum of cyclohexylmethanol.

.... [1]

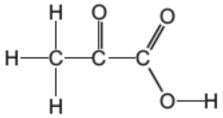
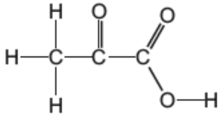
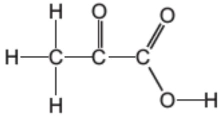
[Total: 10]

Topic: **Chem 37 Q# 509/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d) A sample of pyruvic acid, CH_3COCO_2H, is analysed by carbon-13 NMR spectroscopy. Three peaks are observed.

Complete the table by:

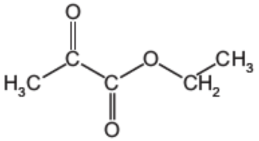
- circling the carbon atom responsible for the chemical shift
- stating the hybridisation of the circled carbon atom.

chemical shift (δ)	carbon atom responsible for chemical shift	hybridisation of the circled carbon atom
27		
163		
192		

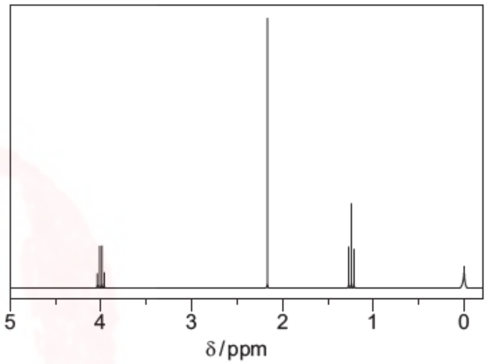
[2]

(e) An ester of pyruvic acid, **F**, is dissolved in $CDCl_3$ and analysed by proton NMR spectroscopy.

F



The proton NMR spectrum of **F** is shown.



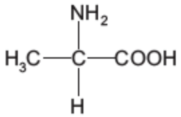
Use the proton NMR spectrum of **F** to complete the table.

chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak
1.3			
2.2			
4.0			

[3]

(f) Deuterium oxide, D_2O, where D is ^2H, can be used as a solvent in proton NMR spectroscopy.
The proton NMR spectrum of alanine in $CDCl_3$ has 4 peaks.
The proton NMR spectrum of alanine in D_2O has 2 peaks.

alanine



$$H_3C-\overset{\displaystyle NH_2}{\underset{\displaystyle H}{C}}-COOH$$

On the diagram of alanine, circle the protons that show peaks in **both** NMR spectra.
Explain your answer.

....

....

.... [2]

Topic: **Chem 37 Q# 510/** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Benzene reacts with bromine in the presence of an aluminium bromide catalyst, $AlBr_3$, to form bromobenzene. This is a substitution reaction. No addition reaction takes place.

(c) **(i)** There are four different carbocations with the same formula, $C_4H_9^+$. One structure is given in the table.

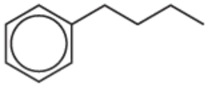
Suggest the structural formulae of the three other carbocations.

structure 1	structure 2	structure 3	structure 4
$CH_3CH_2CH_2CH_2^+$			

[3]

(ii) Benzene reacts with each of these carbocations in separate Friedel-Crafts alkylation reactions.
In each reaction an organic compound with formula $C_{10}H_{14}$ is formed. The number of peaks observed in the carbon-13 NMR spectrum of each compound is given.

Suggest the structures for the three other compounds.

 number of peaks in carbon-13 NMR = 8	number of peaks in carbon-13 NMR = 6
number of peaks in carbon-13 NMR = 7	number of peaks in carbon-13 NMR = 8

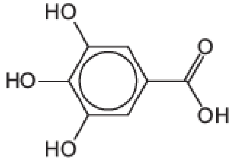
[4]

Topic: **Chem 37 Q# 511/** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 Gallic acid, $C_7H_6O_5$, is a naturally occurring aromatic molecule.

(d) **(i)** State the number of peaks that would be observed in the ^{13}C NMR spectrum of gallic acid.

gallic acid



.... [1]

(ii) The proton NMR spectrum of gallic acid dissolved in D_2O is recorded.

- Predict the number of peaks observed and any expected splitting pattern.
- State the expected chemical shift range (δ) of each peak predicted.

....

....

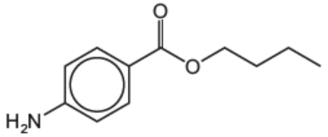
.... [2]

[Total: 21]

Topic: **Chem 37 Q# 512/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 The structure of butamben is shown.

butamben



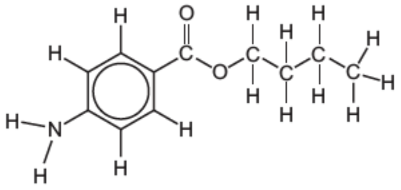
(a) Butamben can act as a base.

(c) The proton NMR spectrum of butamben in $CDCl_3$ contains one or more peaks that show a triplet splitting pattern.

(i) State the number of peaks in the spectrum that show a triplet splitting pattern.

.... [1]

(ii) On the diagram of butamben below, circle the protons responsible for the peak or peaks you identified in **(c)(i)**.



[1]

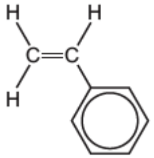
(iii) Describe and explain how the proton NMR spectrum of butamben in D_2O would differ from the proton NMR spectrum of butamben in $CDCl_3$.

....

.... [2]

Topic: **Chem 37 Q# 513/** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4(d)/www.SmashingScience.org

phenylethene



(iv) State the number of peaks in the C-13 NMR spectrum of **phenylethene**.

.... [1]

(v) Suggest C-13 chemical shift ranges expected for the different types of carbon environment in **phenylethanone**.

....

....

.... [2]

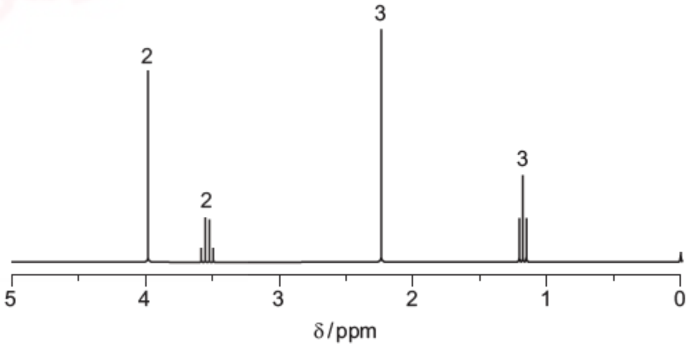
[Total: 18]

Topic: **Chem 37 Q# 514/** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b) State the use of TMS and $CDCl_3$ in NMR spectroscopy.

- TMS ....
- $CDCl_3$ .... [1]

(c) The proton NMR spectrum of compound **X**, $C_5H_{10}O_2$, is shown.



(i) By considering both the relative peak areas and their δ values, use the *Data Booklet* to

- deduce the part of the molecule that produces the peak at δ 2.2,

....

- deduce the part of the molecule that produces the peaks at δ 1.2 and δ 3.5,

....

- deduce the part of the molecule that produces the peak at δ 4.0.

....

[3]

(ii) When reacted with aqueous alkaline iodine, **X** produces a yellow precipitate.

Use this information and your answers to **(c)(i)** to suggest a structure for **X**.

[1]

(d) Compound **W** is an ester with the molecular formula $C_5H_{10}O_2$.

The proton NMR spectrum of **W** contains only **two** peaks.

The relative areas of these two peaks are in the ratio 9 : 1.

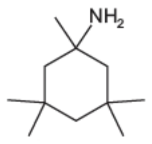
Suggest a structure for this ester, **W**.

[1]

Topic: **Chem 37 Q# 515/** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 The names of many drugs used in medicine often include parts of the names of the functional groups their molecules contain.

(c) Neramexane is another drug.



neramexane

(i) Suggest the number of peaks in the carbon-13 NMR spectrum of neramexane.

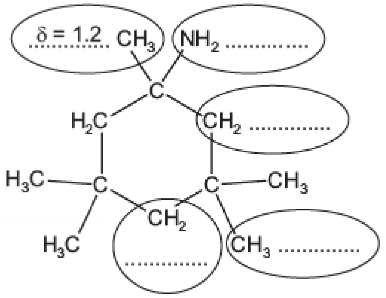
.... [1]

The proton (^{1}H) NMR spectrum of neramexane in $CDCl_3$ shows five peaks with the following chemical shifts (δ).

δ/ppm	number of protons responsible	splitting pattern (singlet, doublet, triplet, quartet or multiplet)
0.9		singlet
1.2	3	
1.4	2	
1.7	4	
2.2		broad singlet

(ii) Complete the table. [4]

(iii) Use the *Data Booklet* and the table in **(c)(ii)** to complete the assignment of the correct δ values to each of the circled hydrogen atoms on the structure of neramexane.



[2]

(iv) One of the peaks in the proton (^1H) NMR spectrum disappears when the sample is shaken with D_2O.

Identify the peak and explain why it disappears.

....

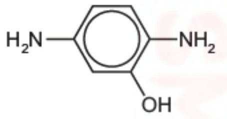
.... [1]

[Total: 15]

Topic: **Chem 37 Q# 516/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** Polyhydroxyamide is a fire-resistant polyamide which is formed from the two monomers, **F** and **G**.

F



G

(i) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **F** and **G**.

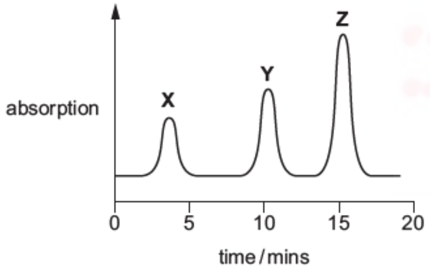
	number of peaks
F	
G	

[2]

Topic: **Chem 37 Q# 517/** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** An aldehyde, an alkane and a carboxylic acid, all of similar volatility, are mixed together. The mixture is then analysed in a gas chromatograph.

The gas chromatogram produced is shown.



The separation of the compounds depends on their relative solubilities in the stationary phase. The stationary phase is a liquid alcohol.

(i) Complete the table to suggest which compound in the mixture is responsible for each peak **X**, **Y** and **Z**. Explain your answer by reference to the intermolecular forces of the compounds.

peak	organic compound	explanation
X		
Y		
Z		

[2]

(ii) A student calculates the areas underneath the three peaks in the chromatogram.

peak	**X**	**Y**	**Z**
area / mm²	19	32	47

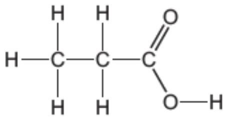
The area underneath each peak is proportional to the mass of the respective compound.

Calculate the percentage **by mass** in the original mixture of the compound responsible for peak **Z**.

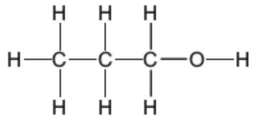
% of mixture responsible for peak **Z** = ... [1]

Topic: **Chem 37 Q# 518/** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

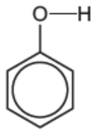
7 The three substances shown all have some acidic properties.



propanoic acid

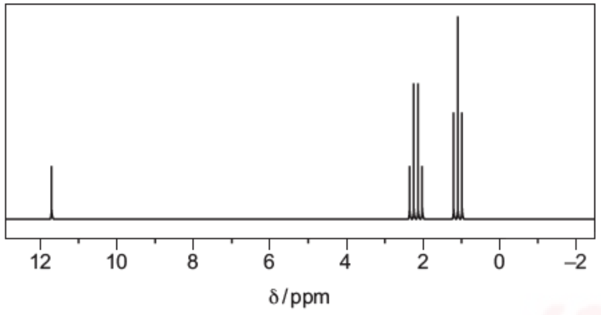


propan-1-ol



phenol

(e) An unknown compound, **Z**, is propan-1-ol, propanal or propanoic acid. The proton NMR spectrum of **Z** dissolved in $CDCl_3$ is shown.



(i) From the proton NMR spectrum, identify **Z**.

.... [1]

(ii) State one feature that would be seen, and why, in the proton NMR spectra of each of the two compounds that are not **Z**.

....

....

....

.... [2]

Topic: **Chem 37 Q# 519/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** Two molecules of compound **F** react together under suitable conditions to form compound **G**. Some information about compounds **F** and **G** is given.

- The mass spectrum of **F** has a peak due to the molecular ion at m / e = 106, and a peak at m / e = 107 with an abundance 8% of the 106 peak.
- The mass spectrum of **G** has a peak due to the molecular ion at m / e = 212, and major peaks at m / e = 91 and m / e = 105.
- Both **F** and **G** contain oxygen and are neutral compounds which are insoluble in water.
- The ^1H NMR spectrum of **F** includes a singlet peak at δ = 10.0 due to one proton.
- The ^1H NMR spectrum of **G** includes a singlet peak at δ = 5.1 due to two protons.
- When **G** is heated with dilute sulfuric acid, benzoic acid, $C_6H_5CO_2H$, and phenylmethanol, $C_6H_5CH_2OH$, are produced.

Use this information to answer **(i)** – **(vi)**.

(i) Explain how the mass spectrum of **F** shows that a molecule of **F** contains seven carbon atoms. Show your working.

[1]

(ii) Suggest the molecular formula of the fragment of **G** at m / e = 91.

.... [1]

(iii) Suggest the molecular formulae of **F** and **G**.

F ....

G .... [2]

(iv) Suggest structures for compounds **F** and **G**.

F

G

[2]

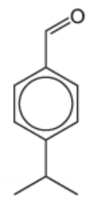
(v) On the structures you have drawn in **(iv)**, circle the protons responsible for the ^1H NMR peaks at δ = 10.0 in **F** and δ = 5.1 in **G**. [1]

(vi) State the type of reaction that **G** undergoes when heated with dilute sulfuric acid.

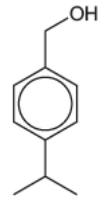
.... [1]

Topic: **Chem 37 Q# 520/** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** Cumin is a spice used to flavour food. Two compounds responsible for its flavour are cuminaldehyde and cuminyl alcohol.



cuminaldehyde



cuminyl alcohol

(i) Deduce the number of peaks that would be present in the ^{13}C NMR spectrum of cuminyl alcohol.

number of peaks .... [1]

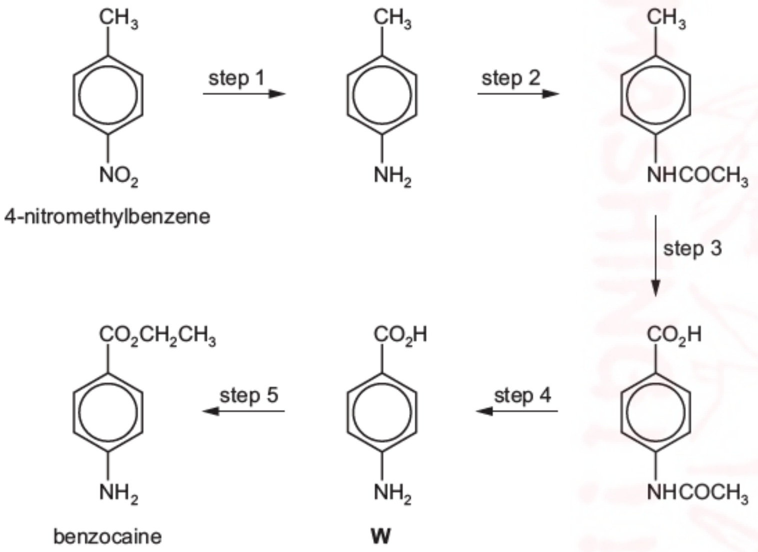
(ii) Identify **two** bonds that are responsible for the differences in the infra-red spectra of cuminaldehyde and cuminyl alcohol, and state their absorption ranges.

bond responsible for the difference	absorption range in the infra-red spectrum/cm^{-1}	
	cuminaldehyde	cuminyl alcohol
		▨
	▨	

[2]

Topic: **Chem 37 Q# 521/** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b) Benzocaine is used as a local anaesthetic. It can be synthesised from 4-nitromethylbenzene by the route shown.

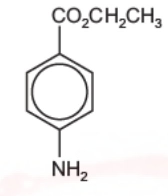


(d) A sample of benzocaine, shown below, was analysed by proton NMR and carbon-13 NMR spectroscopy.

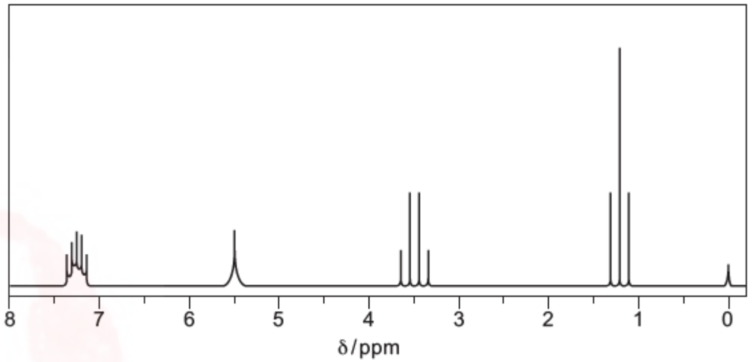
(i) Predict the number of peaks that would be seen in the carbon-13 NMR spectrum.

.... [1]

(ii) Benzocaine was dissolved in CDCl_3 and the proton NMR spectrum of this solution was recorded.



benzocaine



Suggest why CDCl_3 and not CHCl_3 is used as the solvent when obtaining a proton NMR spectrum.

....

.... [1]

(iii) Use the *Data Booklet* and the spectrum in **(d)(ii)** to complete the table for the proton NMR spectrum of benzocaine. The actual chemical shifts, δ, for the four absorptions have been added.

δ/ppm	group responsible for the peak	number of ^{1}H atoms responsible for the peak	splitting pattern
1.2			
3.5			
5.5			
7.1–7.4			multiplet

[4]

(iv) Explain the splitting pattern for the absorption at δ1.2 ppm.

....

.... [1]

(v) The proton NMR spectrum of benzocaine dissolved in D_2O was recorded.

Suggest how this spectrum would differ from the spectrum in **(d)(ii)**.
Explain your answer.

....

.... [1]

Topic: **Chem 37 Q# 522/** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 The reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol is:

$$\underset{\text{1-chloro-1-phenylethane}}{C_6H_5CHClCH_3} + OH^- \rightarrow \underset{\text{1-phenylethanol}}{C_6H_5CH(OH)CH_3} + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(d) The proton NMR spectrum of a sample of 1-phenylethanol shows four peaks: a multiplet for the C_6H_5 protons and three other peaks as shown in the table. When the sample is shaken with D_2O and the proton NMR spectrum recorded, **fewer** peaks are seen.

Complete the table for the proton NMR spectrum of 1-phenylethanol, $C_6H_5CH(OH)CH_3$.
Use of the *Data Booklet* might be helpful.

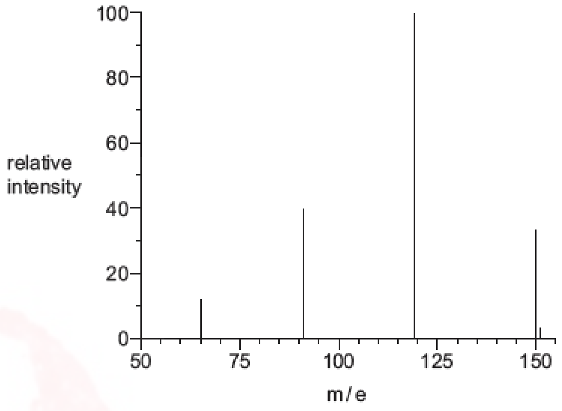
δ/ppm	number of ^1H atoms responsible for the peak	group responsible for the peak	splitting pattern	result on shaking with D_2O
1.4				
2.7				
4.0				
7.2-7.4	5	C_6H_5	multiplet	peak remains

[4]

Topic: **Chem 37 Q# 523/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9 This question is about compound **T**, $C_xH_yO_z$.

(a) Part of the mass spectrum of **T** is shown.
The peak heights of the M and M+1 peaks are 33.9 and 3.4 respectively.



(i) Calculate x, the number of carbon atoms present in **T**.

x = ... [2]

(ii) Deduce the molecular formula of **T**.

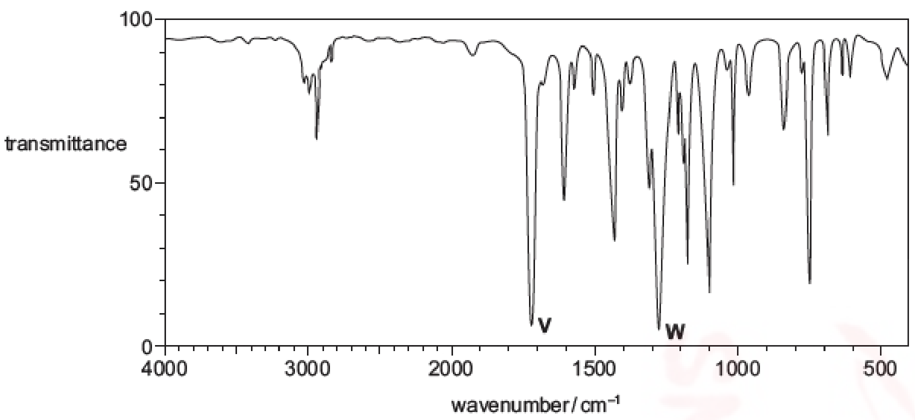
.... [1]

(iii) The mass spectrum has a peak at m/e = 119.

Identify the fragment lost from **T** to produce this peak.

.... [1]

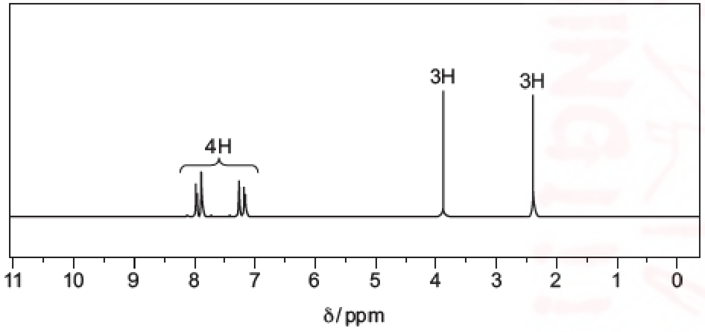
(b) The infra-red spectrum of **T** is shown.



Identify the type of bond responsible for each of the peaks **V** and **W**.
Use the *Data Booklet* to help you.

V .... **W** .... [1]

(c) The proton NMR spectrum of **T** in $CDCl_3$ is shown.



(i) Complete the table for the proton NMR spectrum of **T**.
Use the *Data Booklet* to help you.

δ / ppm	type of proton
3.9	
7.2–7.9	

[1]

(ii) The peak at δ = 2.4 ppm is due to a proton attached to a saturated carbon atom.

State the **two** possible types of proton.

1. ....

2. ....

[1]

(iii) Adding D_2O to **T** does **not** change its proton NMR spectrum.

What does this tell you about the functional groups present in **T**?

.... [1]

(d) Use the information to draw **two** possible structures of **T** which are functional group isomers of each other.

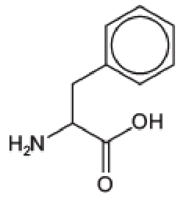
[2]

[Total: 10]

Topic: **Chem 37 Q# 524/** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(e) Use the *Data Booklet* to help you answer this question.

The carbon-13 NMR spectrum of **K** was recorded.



K

(i) State how many different carbon environments are present in **K**.

.... [1]

(ii) The chemical shifts, δ, due to two of the carbon atoms x and y present in **K** are given in the table.

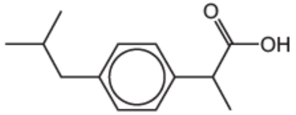
carbon atom	δ / ppm
x	130
y	170

On the structure of **K**, circle **and** label **two** carbon atoms which could correspond to x and y.
[1]

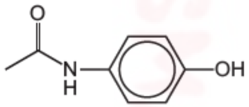
[Total: 12]

Topic: **Chem 37 Q# 525/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 Ibuprofen and paracetamol are pain-relief drugs.



ibuprofen



paracetamol

(c) Draw the structures of the organic products when ibuprofen and paracetamol react separately with $LiAlH_4$.

product with ibuprofen

product with paracetamol

[2]

(d) A student carried out some reactions with solutions of ibuprofen and paracetamol using reagents **D** and **E** and the following results were obtained.
(✓ means a reaction took place.)

reagent	ibuprofen	paracetamol
D	✓	✗
E	✗	✓

(i) Suggest a possible identity for each reagent **D** and **E**.

D ....

E ....

[2]

(ii) Give the structure of the organic product formed when reagent **D** reacted with ibuprofen.

product with ibuprofen

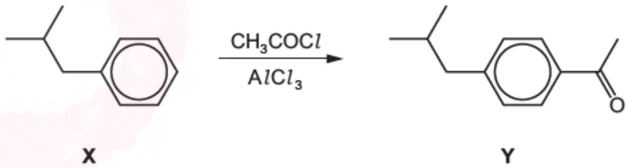
[1]

(iii) Give the structure of the organic product formed when reagent **E** reacted with paracetamol.

product with paracetamol

[1]

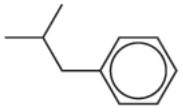
(e) One of the steps in the manufacture of ibuprofen is shown.



(i) Write an equation for the reaction between CH_3COCl and $AlCl_3$.

.... [1]

(ii) Complete the mechanism for the conversion of **X** into **Y**. Include all necessary curly arrows, any relevant dipoles and charges.



X

[3]

(iii) Name the mechanism in **(ii)**.

.... [1]

Topic: **Chem 37 Q# 526/** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 Compound **F** contains the elements carbon, hydrogen and oxygen only. All carbon-carbon bonds in **F** are single bonds. The structure of **F** was analysed by mass spectrometry and infra-red and NMR spectroscopy.

(a) The mass spectrum shows that the *m*/*e* value for the M peak is 90.

The ratio of the heights of the M and M+1 peaks is 22.1 : 0.7.

(i) Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **F**.

number of carbon atoms = ... [2]

(ii) Suggest the molecular formula of **F**.

molecular formula = C H O [1]

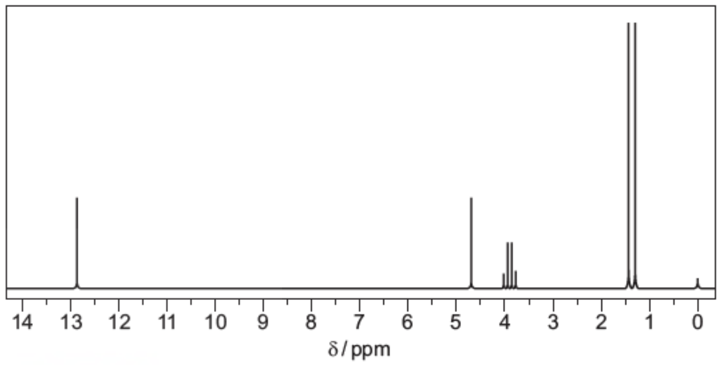
(b) The infra-red spectrum of **F** was obtained.

Use the *Data Booklet* and your knowledge of infra-red spectroscopy to identify the type of bond and the functional group responsible for these **three** absorptions.

absorption / cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong		
2680	very broad and strong		
1725	strong		

[2]

(c) **F** was dissolved in deuterated trichloromethane, $CDCl_3$, and the proton NMR spectrum of this solution obtained.



(i) Use the *Data Booklet* and your answer to **(a)(ii)** to complete Table 1 for the proton NMR spectrum of **F**.
The actual chemical shifts for the four absorptions in **F** have been added for you.

Table 1

δ / ppm	type of proton	relative peak area
1.4		
3.9		
4.7		
12.9		

[4]

(ii) Describe and explain the splitting pattern for the absorption at δ = 1.4.

....

.... [1]

(iii) **F** was dissolved in D_2O and the proton NMR spectrum of this new solution obtained. Two of the absorptions in Table 1 were not present in this spectrum.

Which absorptions were **not** present?

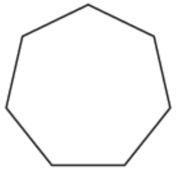
.... and .... [1]

(iv) Suggest the structure of **F**.

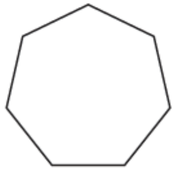
[1]

(d) Molecules of cycloheptadiene, C_7H_{10}, consist of a seven-membered ring with two carbon-carbon double bonds.

(i) Complete the skeletal formulae of two isomers of cycloheptadiene.



P



Q

[1]

The isomers **P** and **Q** were analysed using carbon-13 NMR spectroscopy.

(ii) Predict the number of peaks that will be seen in the carbon-13 NMR spectra of **P** and **Q**.

isomer	number of peaks
P	
Q	

[2]

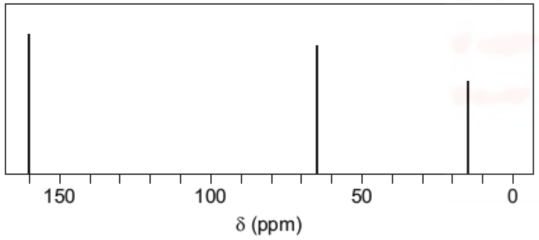
Topic: **Chem 37 Q# 527/** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

(b) Ethanedioic acid can be converted into ethanedioyl chloride:

$$HO_2CCO_2H \rightarrow ClOCCOCl$$

(c) When ethanedioyl chloride is reacted with silver ethanedioate, AgO_2CCO_2Ag, in ethoxyethane at –30 °C, an oxide of carbon, **L**, is formed. The molecule of **L** has no overall dipole and has molecular formula C_4O_6.

The carbon-13 NMR spectrum of a solution of **L** in ethoxyethane, $CH_3CH_2OCH_2CH_3$, is shown below.



(i) Use the *Data Booklet* to state in the boxes below the δ values for the peaks in the spectrum which are due to the carbon atoms in ethoxyethane.

$CH_3—CH_2—O—CH_2—CH_3$

δ values

[2]

(ii) Explain what the rest of the carbon-13 NMR spectrum indicates about the structure of **L**.

.... [1]

(d) When pure **L** is reacted with an excess of CH_3OH, a mixture of three compounds is formed.

L	and	CH_3OH	→	**M**	and	**N**	and	**O**
(C_4O_6)				($C_2H_2O_4$)		($C_3H_4O_4$)		($C_4H_6O_4$)

M is formed as one of the products when either **N** or **O** is heated with aqueous acid.

The table gives information of the peaks recorded in the carbon-13 NMR spectra of **M**, **N** and **O**.

compound	peaks recorded in carbon-13 NMR spectrum
M	δ 162
N	δ 53 δ 160 δ 162
O	δ 53 δ 160

(i) Suggest the structures of **M**, **N** and **O**.

M, ($C_2H_2O_4$)

N, ($C_3H_4O_4$)

O, ($C_4H_6O_4$)

[3]

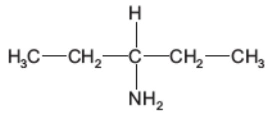
(ii) Suggest a structure for **L** that fits all the data given in **(c)** and **(d)**.

L, (C_4O_6)

[1]

Topic: **Chem 37 Q# 528/** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(c) Compound **H** is a primary amine which has three peaks in its carbon-13 NMR spectrum.



$H_3C{-}CH_2{-}CH(NH_2){-}CH_2{-}CH_3$

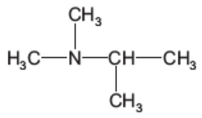
compound **H**

(i) An isomer of **H** is another primary amine **J** which also has three peaks in its carbon-13 NMR spectrum.

Use this information to suggest the structure of **J**.

[1]

(ii) Another isomer of **H** is the tertiary amine **K**. It has three peaks in its proton NMR spectrum. One of the peaks is a doublet.



$H_3C{-}N(CH_3){-}CH(CH_3){-}CH_3$

K

Circle the protons responsible for the doublet. [1]

Topic: **Chem 37 Q# 529/** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(d) The NMR spectrum of cysteine, $H_2NCH(CH_2SH)CO_2H$, shows five absorptions.

After shaking a solution of cysteine with a few drops of D_2O, the NMR spectrum shows **only two** absorptions, **E** and **F**, shown below.

(i) Identify the **two** types of protons responsible for the absorptions **E** and **F**.

E ....

F ....

[1]

(ii) State and explain the splitting patterns of the absorptions **E** and **F**.

E ....

....

F ....

.... [2]

Topic: **Chem 37 Q# 530/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

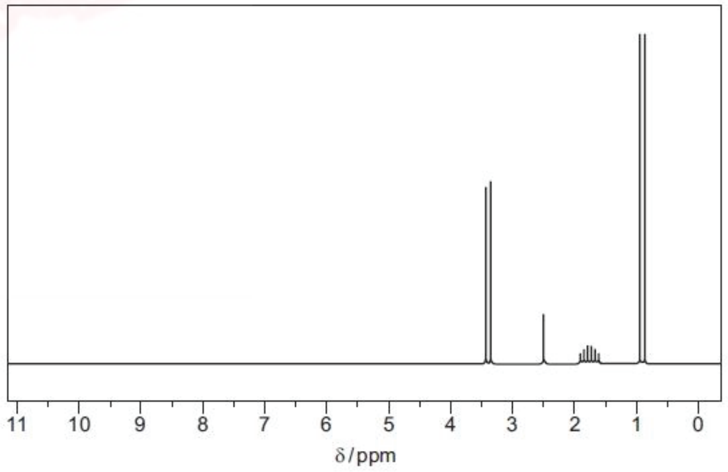
8 **T** is a saturated alcohol. It was analysed by mass spectroscopy and NMR spectroscopy.
In the mass spectrum, the molecular ion peak, M, was at an m/e value of 74 and the ratio of the heights of the M and M+1 peaks was 20.4 : 0.9.

(a) **(i)** Use the ratio of the heights of the M and M+1 peaks to calculate the number of carbon atoms in a molecule of **T**.

(ii) What is the molecular formula of **T**?

molecular formula = ...
[3]

(b) The NMR spectrum of **T** given below shows four absorptions. The absorption at 1.8 ppm is a multiplet and that at 2.5 ppm is a singlet.



(i) Use this information and your answer to **(a)(ii)** to deduce the structure of **T**.

T

(ii) Describe and explain which type of proton is responsible for each of the absorptions.

(iii) The absorption at 1.8 ppm is a multiplet and that at 2.5 is a singlet.
State and explain the splitting patterns of the other absorptions, at 0.9 and 3.4 ppm.

(iv) Describe and explain how the NMR spectrum of **T** dissolved in D_2O would differ from the one shown.

[9]

[Total: 12]

Topic: **Chem 37 Q# 531/** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b) **(i)** A mixture of amino acids can also be separated by thin-layer chromatography.
Identify the mobile and the stationary phases in this type of chromatography.

mobile phase ....

stationary phase ....

(ii) What is the process by which thin-layer chromatography can separate a mixture?

[3]

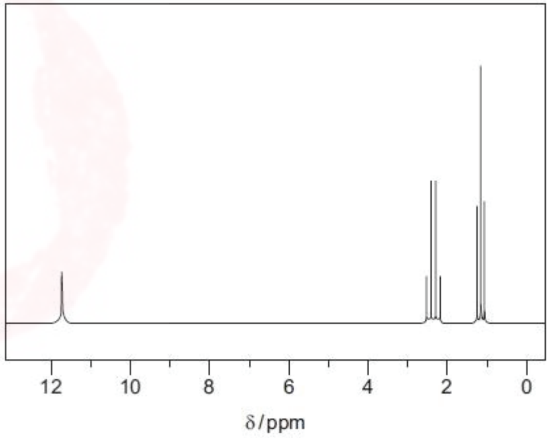
Topic: **Chem 37 Q# 532/** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 The combination of mass spectroscopy and NMR spectroscopy provides a powerful method of analysis for organic compounds.

(a) The mass spectrum of a compound **G** contains M and M+1 peaks in the ratio of their heights of 74 : 2.5.
Use these data to calculate the number of carbon atoms present in **G**. Show your working.

[2]

(b) The NMR spectrum of compound **G** is shown.



(i) Use the *Data Booklet* and your knowledge of NMR spectroscopy to identify the type of proton responsible for each of the three absorptions.

δ / ppm	type of proton
1.1	
2.2	
11.8	

(ii) The addition of D_2O causes one of these absorptions to disappear.
Explain why this happens and state which absorption is affected.

(iii) Draw the structural formula of **G**.

[6]

(c) Several structural isomers of **G** exist.

(i) Draw the structural formula of an isomer of **G** with only two absorptions in its NMR spectrum.

(ii) Use the *Data Booklet* to suggest where these absorptions would occur.

peak	δ / ppm
1	
2	

[3]

[Total: 11]

Topic: **Chem 37 Q# 533/** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 Modern methods of analysis have had far-reaching effects on a number of branches of science including medicine, forensic science, environmental monitoring and archaeology.

(c) Various forms of chromatography can be used to separate and analyse mixtures. HPLC (high performance liquid chromatography) can be used to separate each of the following mixtures. State another method of chromatography which would separate each mixture.

insecticides in a sample of water ....

dyes present in a foodstuff ....

drug residue in an athlete's urine ....

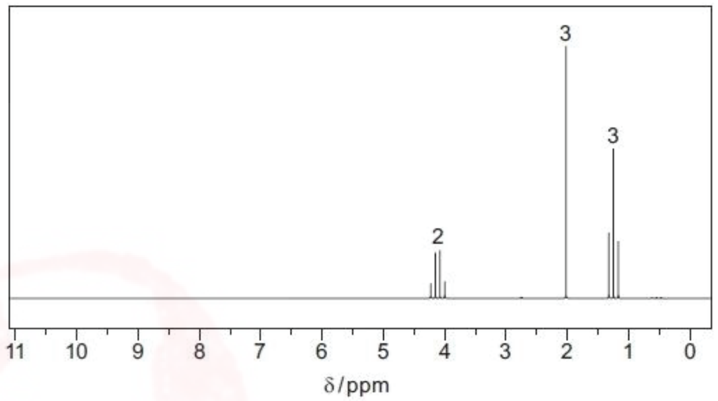
[3]

[Total: 10]

Topic: **Chem 37 Q# 534/** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) A sample of a liquid, **P**, was found at the scene of the crime and was analysed using mass spectrometry and NMR spectroscopy.

The mass spectrum has M and M+1 peaks in the ratio of 5.1 : 0.22 with the M peak at *m*/*e* = 88.
The NMR spectrum is shown



Use the data to suggest a structure for **P**, explaining your answer.

structure of **P**

[5]

[Total: 10]

8 Chromatography is an important analytical technique in chemistry. There is a number of techniques under the general heading of chromatography.

(a) Paper and gas chromatography rely on partition to separate the components in a mixture, whereas thin-layer chromatography uses adsorption.

Explain what is meant by **(i)** *partition* and **(ii)** *adsorption*, in the context of chromatography.

(i) partition ....

....

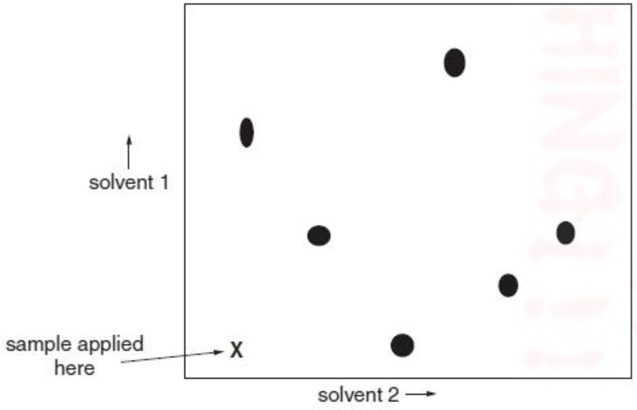
....

(ii) adsorption ....

....

....[2]

(b) In paper or thin-layer chromatography, better separation may be achieved by running the chromatogram in one solvent, then turning the paper at right angles and running it in a second solvent. The chromatogram below was produced in this way.



(i) Ring the spot which was insoluble in solvent 1.

(ii) Label as **A** and **B** the spots which were **not** resolved using solvent 1.

[2]

---

8 **(a)** NMR spectroscopy and X-ray crystallography are two techniques that use electromagnetic radiation to look at the structures of large molecules.

For each technique state the sub-atomic particle involved, and explain how this particle interacts with the radiation.

NMR..

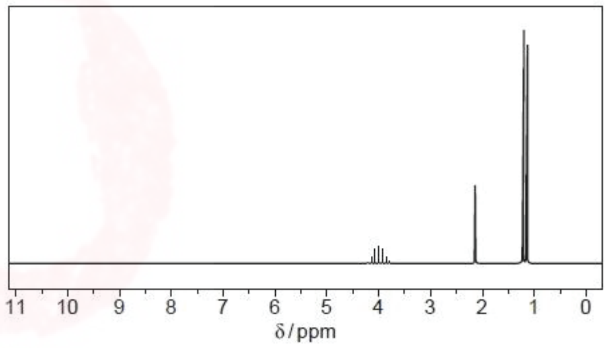
....

X-ray ....

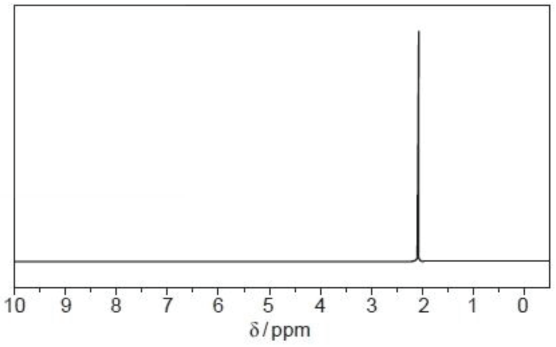
....

[4]

(b) The two NMR spectra **1** and **2** were obtained before and after an alcohol, **Y**, was oxidised to give compound **Z**. The numbers of hydrogen atoms responsible for each peak have **not** been shown. All the peaks have been shown.



1



2

(i) State which spectrum, **1** or **2**, was produced by the alcohol, giving a reason for your answer.

spectrum ....

reason ....

....

(ii) The mass spectrum of **Y** showed an M : M+1 peak ratio of 17.6:0.6.
Use this and other information in the question to suggest the identities of both **Y** and **Z**.

(iii) Draw a displayed formula for **Y** in the box provided

Y is

(iv) Explain why the NMR spectrum of **Z** only shows one peak.

....

....

[7]

[Total: 11]

9 A range of modern analytical techniques has made the identification of molecules, and atoms in compounds, much more rapid than traditional laboratory analysis.

(a) One instrumental technique is NMR spectroscopy, which uses the fact that under certain conditions protons can exist in two different energy states.
Explain how these different energy states arise.

....

....

....[2]

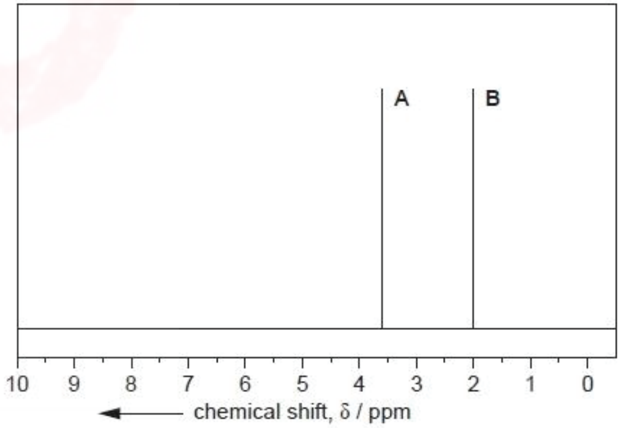
(b) When methanol, CH_3OH, is examined using NMR spectroscopy, it absorbs at two different frequencies. Explain why, and predict the relative areas of the two peaks.

....

....

....[2]

(c) The NMR spectrum below is that of one of three possible isomers of molecular formula $C_3H_6O_2$.



The compound could be propanoic acid, methyl ethanoate or ethyl methanoate.

(i) In the boxes provided, draw the structures of the three compounds.

propanoic acid	methyl ethanoate	ethyl methanoate

(ii) Explain which compound produced the spectrum shown, indicating which protons are responsible for each of the peaks **A** and **B**.

....

....

....

(iii) The NMR spectrum of another of the compounds has a peak at δ11.0.
State which compound this would be, and identify the proton(s) responsible for this peak.

compound ....

proton(s) ....

[4]

Topic: **Chem 37 Q# 538/** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 This question is about the modern techniques of analysis which may be used to determine molecular structures.

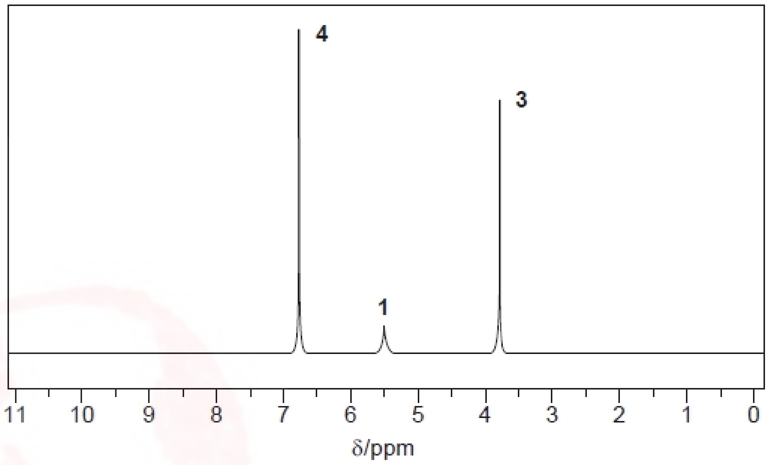
(c) NMR spectroscopy, in contrast to X-ray crystallography, is frequently used to examine protons in organic molecules.

(i) What feature of protons enables their detection by NMR spectroscopy?

.... [1]

(ii) The NMR spectrum below was obtained from a compound **X**, $C_xH_yO_z$. In the mass spectrum of the compound, the M : M+1 ratio was found to be 25:2.

Determine the values of x, y and z in the formula of **X** and deduce a possible structure for the compound, explaining how you arrive at your conclusion.



....

....

....

....

....

....

....

....

Possible structure of **X**

[5]

Mark Scheme

Q# 1/ Topic: Chem 1 ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a)	Ca $3s^23p^64s^2$ and Ca^{2+} $3s^23p^6$	1

Q# 2/ Topic: **Chem 1** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a)	oxygen: $(1s^2)\ 2s^22p^4$ fluorine: $(1s^2)\ 2s^22p^5$	1

Q# 3/ Topic: Chem 2 ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)(ii)	$20 \times [0.9(+2) + 0.1(+3)] - 2x = 0$ $\therefore x = 21$	1

Q# 4/ Topic: **Chem 2** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(b)(iii)	$3SiF_4 + 2H_2O \rightarrow 2H_2SiF_6 + SiO_2$	1

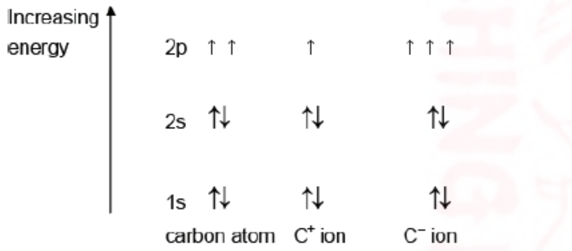
Q# 5/ Topic: **Chem 2** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$	
	balanced with all formulae correct	1
	state symbols	1

Q# 6/ Topic: **Chem 2** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(b)	giant ionic	1
	strong bond / attraction between **AND** positive and negative ions / anions and cations / Na^+ and O^{2-} / oppositely charged ions	1

Q# 7/ Topic: **Chem 2** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1 (a)		2

Q# 8/ Topic: **Chem 2** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a)	$4BF_3 + 3NaBH_4 \rightarrow 2B_2H_6 + 3NaBF_4$	1

Q# 9/ Topic: **Chem 2** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) $n(H_2) = 8/24 = 0.33$ mol [1]

from equation, this is produced from 0.22 mol of A*l* ecf (× 2/3) [1]

$A_r(Al) = 27$ thus mass of A*l* = 27 × 0.22 = 5.9 – 6 g hence 5.9–6.0% ecf (× 27) [1]
[3]

[Total: 14]

Q# 10/ Topic: **Chem 2** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) moles of oxygen = 9.3/16 = 0.581 mol
moles of lead = 90.7/207 = 0.438 mol (both 3 s.f.) (1)

so formula is Pb_3O_4 (1) **[2]**

Q# 11/ Topic: **Chem 2** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) **(i)** any **two** from:
brown fumes or vapour evolved / gas relights glowing splint / black solid formed (2)

(ii) $2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$ (1) **[3]**

[Total: 11 max 10]

Q# 12/ Topic: **Chem 2** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) **(i)** $\mathbf{2}\ Ca_3(PO_4)_2 + \mathbf{6}\ SiO_2 + \mathbf{10}\ C \longrightarrow \mathbf{1}\ P_4 + \mathbf{6}\ CaSiO_3 + \mathbf{10}\ CO$ (2)

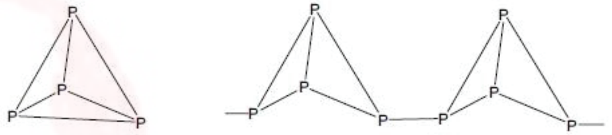
Q# 13/ Topic: **Chem 2** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(ii)

allotrope	type of structure	type of bonding
white	**simple / molecular**	**covalent**
red	**giant / polymeric**	**covalent**

(4)

(iii)



white P_4 (1) red P_n (1)

(in each case P has to be trivalent. Many alternatives allowable for the polymeric red P) (2)
(8 max 7) [7]

[Total: 11]

Q# 14/ Topic: **Chem 2** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(d) **(i)**
Ca = 28.2/40.1 = 0.703 ⇒ 1
C = 25.2/12 = 2.10 ⇒ 3
H = 1.4/1 = 1.4 ⇒ 2 (1 mark for initial step of calc'n)
O = 45.1/16 = 2.82 ⇒ 4

formula is $CaC_3H_2O_4$ (1) [2]

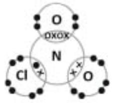
(ii) malonic acid must be $C_2H_4O_4$, i.e. $\mathbf{CH_2(CO_2H)_2}$ (must be structural) [1]
[3]

[Total: 10]

Q# 15/ Topic: Chem 3 ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)	3 bonding-pair centres and one lone pair (on iodine)	1
3(b)	$3I_2 + 6NaOH \rightarrow NaIO_3 + 5NaI + 3H_2O$	1

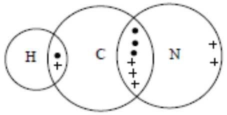
Q# 16/ Topic: **Chem 3** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	 **M1:** eight electrons around N atom [N=O, N-O, N-C*l* with N-O as dative] **M2:** all other electrons correct	2

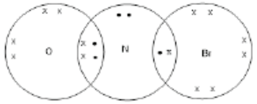
Q# 17/ Topic: **Chem 3** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(d)	**M1** bond angle 104–105° **M2** **explanation** two lone pairs and two bonding pairs **M3** lone pairs repel more	3

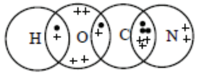
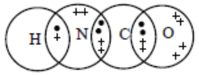
Q# 18/ Topic: **Chem 3** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(ii)		1
3(a)(iii)	C: sp **and** N: sp angle 180°	2

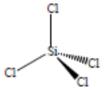
Q# 19/ Topic: **Chem 3** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	N +2 to +3 (and oxidised)	1
	Br_2/Br 0 to –1 (and reduced)	1
1(b)		
	3 bonding pairs around N (in a structure involving NOBr)	1
	rest of molecule correct	1

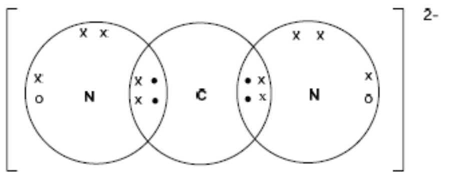
Q# 20/ Topic: **Chem 3** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	 	1 + 1
	16 electrons on each diagram	1
2(a)(ii)	HNC = 115–125° AND NCO = 180°	1
2(a)(iii)	cyanic acid, because it's a stronger / higher bond enthalpy / triple / C≡N / more electrons involved bond	1

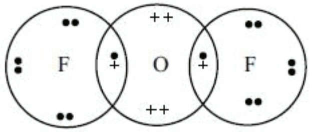
Q# 21/ Topic: **Chem 3** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)(iii)	 diagram	1
	bond angle = 109.5	1
1(a)(iv)	SiO_2	1
	SiO_2 is giant covalent / molecular but $SiCl_4$ is simple molecular / covalent	1

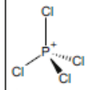
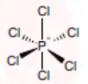
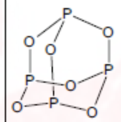
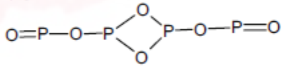
Q# 22/ Topic: **Chem 3** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(c)(i)		2

Q# 23/ Topic: **Chem 3** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

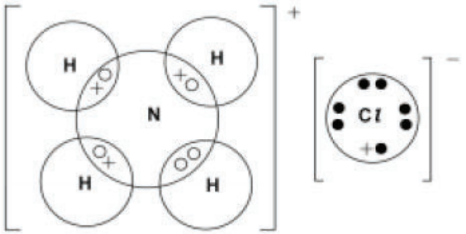
(b) (i)	F_2O / OF_2	1
(ii)		1
(iii)	bent ***or*** non-linear	1

Q# 24/ Topic: **Chem 3** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) (i)	PCl_5 5 bonding pairs around P	1	
(ii)	 	1 1	[3]
(c) (i)	 P_4O_6 structure where each P has three P-O bonds and each O has two P-O bonds e.g. 	1	

Q# 25/ Topic: **Chem 3** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)**



8 e⁻ around chlorine [1]
1 H–electron (+) on the C*l*⁻ ion [1]
3 covalent (ox) and one dative (oo) around N [1]

[3]

Q# 26/ Topic: **Chem 3** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

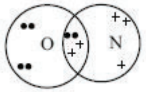
4 (a) (i) volatilities decrease down the group [1]

due to greater van der Waals (VDW) forces (*intermolecular is not sufficient*) [1]

due to larger no of electrons [1]

Q# 27/ Topic: **Chem 3** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2. (a) (i)



[1]

Q# 28/ Topic: **Chem 3** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) N≡N triple bond is (very) strong
or the N_2 molecule has no polarity [1]

Q# 29/ Topic: **Chem 3** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) (i) $\underset{+}{Cl}:\overset{\cdot\cdot}{\underset{-}{C}}:Cl$ *or* $Cl{=}\overset{\cdot\cdot}{C}{-}Cl$ (1)

bent *or* non-linear *or* angle = 100–140° (1)

(ii) $CCl_2 + H_2O \longrightarrow CO + 2HCl$ (1) [3]

[Total: 8]

Q# 30/ Topic: **Chem 3** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) CO_2 is a gas (at room temperature); SiO_2 is a high melting solid [1]
CO_2: simple / discrete molecular / covalent [1]
SiO_2: giant covalent *or* macromolecular / giant molecular [1]
[3]

Q# 31/ Topic: Chem 5 ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (the energy change) when 1 mol of bonds [1]
is broken in the gas phase [1]

Q# 32/ Topic: **Chem 5** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(iii) ΔH = E(C-H) – E(H-Cl) = 410 – 431 = **–21** kJ mol^{-1} [1]

(iv) ΔH = E(C-H) – E(H-I) = 410 – 299 = **+111** kJ mol^{-1} ecf [1]

(v) The reaction with iodine is endothermic *or* ΔH is positive *or* requires energy [1]

Q# 33/ Topic: **Chem 5** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) bonds broken are Si-Si and Cl-Cl = 222 + 244 = 466 kJ mol^{-1}
bonds formed are 2 × Si-Cl = 2 × 359 = 718 kJ mol^{-1}
ΔH = $\underline{-252}$ kJ mol^{-1} [2]

[2]

Q# 34/ Topic: **Chem 5** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(ii) –180 kJ mol^{-1} [1]

(iv) –180 = 2 E(NO) – 994 – 496 [1]
E(NO) = **+655 kJ mol^{-1}** [1]

Q# 35/ Topic: **Chem 5** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(iii) H-H = 436 Cl-Cl = 244 H-Cl = 431

ΔH = 436 + 244 – 2(431) = –182 kJ mol^{-1} [2]

H-H = 436 Br-Br = 193 H-Br = 366

ΔH = 436 + 193 – 2(366) = –103 kJ mol^{-1} [2]

(iv) H-Br bond is weaker than the H-Cl bond – allow converse. [1]
[8]

(b) (i) light [1]

(ii) bonds broken = C-H & I-I = 410 + 151 = 561
bonds made = C-I & H-I = 240 + 299 = 539
ΔH = 551 – 539 = +22 kJ mol^{-1} [2]

(iii) The overall reaction is endothermic *or* no strong bonds/only weak bonds are formed *or* high E_{act} [1]
[4]

Q# 36/ Topic: **Chem 5** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) bond energies:
S-S = 264 kJ mol^{-1}
Cl-Cl = 244 kJ mol^{-1}
S-Cl = 250 kJ mol^{-1}

ΔH = 8 × 264 + 8 × 244 – 16 × 250 = +64 kJ mol^{-1} (2) **[2]**

Q# 37/ Topic: Chem 6 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i)	oxidising agent [1] $H_2O_2 + 2H^+ + 2I^- \rightarrow 2H_2O + I_2$ [1]	**2**

Q# 38/ Topic: **Chem 6** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(c)(i)	M1: moles of thiosulfate = 0.02230 × 0.150 = 3.345 × 10^{-3} M2: [Cu^{2+}] = 2 × ½ × 3.345 × 10^{-3} ÷ 0.0250 = **0.134** (mol dm^{-3}) ecf	**2**
1(c)(ii)	starch	**1**

Q# 39/ Topic: **Chem 6** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(b)(iii)	step 2 and Cl is reduced / oxid no. decreases / oxid no. +1 → –1 *or* step 2 and I is oxidised / oxid no. increases / oxid no. –1 → +1	**1**

Q# 40/ Topic: **Chem 6** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	N +2 to +3 (and oxidised)	**1**
	Br_2/Br 0 to –1 (and reduced)	**1**

Q# 41/ Topic: Chem 7 ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(e)	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	**1**

Q# 42/ Topic: **Chem 7** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(b)(i)	ketamine is acting as a base	**1**
6(b)(ii)	carbonyl group	**1**

Q# 43/ Topic: **Chem 7** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b)	$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$ **or** $CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$	**1**

Q# 44/ Topic: **Chem 7** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) **(i)** $\Delta H^{\circ} = +2 \times 33.2 - 157.3 + 302.9 = (+)\,212\,\text{kJ mol}^{-1}$ ecf [2]

(ii) $\Delta H^{\circ} = -168.6 + 2 \times 157.3 = (+)146\,\text{kJ mol}^{-1}$ **allow** ecf from **(c)(i)** [1]
high T/temperature since ΔH is positive/endothermic [1]

[Total: 16]

Q# 45/ Topic: **Chem 7** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** **(i)** (nitrates are) soluble [1]

(ii) $Ba^{(2+)}$ and $Pb^{(2+)}$ [1]

$SO_4^{(2-)}$ [1]

$BaCO_3/PbCO_3/CaSO_4$ are insoluble [1]

[4]

(b) **(i)** fertilisers/animal manure [1]

(ii) washing powder/detergents/fertilisers/animal manure [1]

(iii) growth/production of algae/weeds/plants
or eutrophication [1]

[3]

Q# 46/ Topic: **Chem 7** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** **(i)** $NH_3 + HZ \longrightarrow NH_4^+ + Z^-$ [1]
$CH_3OH + HZ \longrightarrow CH_3OH_2^+ + Z^-$ [1]

(ii) $NH_3 + B^- \longrightarrow NH_2^- + BH$ [1]
$CH_3OH + B^- \longrightarrow CH_3O^- + BH$ [1]

[4]

(b) **(i)** a reaction that can go in either direction [1]

(ii) **rate** of forward = **rate** of backward reaction
or forward/back reactions occurring but concentrations of all species do not change [1]

[2]

Q# 47/ Topic: **Chem 7** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** **(i)** One that can go in either direction. [1]

(ii) both forward & reverse reactions are going on at the same time, but the concentrations of all species do not change (owtte)
or rate of forward = rate of backward reaction [1]

Q# 48/ Topic: Chem 9 ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)(ii)	$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl$	1

Q# 49/ Topic: **Chem 9** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2	**(a)**	Na	Mg	Al	Si	P	S	Cl	Ar	3
		1	0	1	2	3	2	1	0	
	(b) (i)	$SiCl_4$ white solid/ppt **or** misty/white/steamy fumes pH 0–3 PCl_5 misty/white/steamy fumes pH 0–3								3
	(ii)	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$								1
										7

Q# 50/ Topic: **Chem 9** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** $SiCl_4$: **white** solid *or* **white/steamy** fumes [1]

$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$ [1]

PCl_5: fizzes *or* white/steamy fumes [1]
$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$ [1]
[4]

Q# 51/ Topic: **Chem 9** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) $Na_2O(s) + H_2O(aq/l) \longrightarrow 2NaOH(aq)$ [1]
$MgO(s) + H_2O(aq/l) \longrightarrow Mg(OH)_2(s)$ *or* $Mg(OH)_2(aq)$ [1]
pH 12.5-14 [NaOH] **AND** 8-10.5 $[Mg(OH)_2]$ respectively [1]
[3]

[Total: 12]

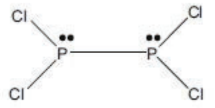
Q# 52/ Topic: **Chem 9** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** (+)1; (+)2; (+)3; (+)4 [1]
O.N. corresponds to the no. of electrons in outer/valence shell/lost [1]

(b) PCl_5 fizzes or white/misty fumes or heat evolved [1]
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ *or* $PCl_5 + 3H_2O \rightarrow HPO_3 + 5HCl$
(allow partial hydrolysis: $PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$) [1]

(c) **(i)** P = 30.4/31 = 0.98 Cl = 69.6/35.5 = 1.96 [1]
Thus E.F = **PCl_2** [1]
$M_r(PCl_2) = 102$, so $2 \times PCl_2 = 204 \approx 200$, so M.F. = **$P_2Cl_4$** [1]

(ii)



(ignore lone pairs on Cl) [1]

(iii) O.N. = (+)2 [1]

(iv) $(HO)_2P\text{-}P(OH)_2$ *or* $H(HO)P(=O)\text{-}P(=O)(OH)H$ ecf from structure in **(ii)** [1]
Allow HO-P-OH or HO-P=O (with H below P)

[Total: 10]

Q# 53/ Topic: **Chem 9** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** $PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$ (1)

$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$ (or giving H_2SiO_3, $Si(OH)_4$ etc.) (1) **[2]**

Q# 54/ Topic: **Chem 9** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) P: burns with white / yellow flame *or* copious white smoke / fumes produced (1)

$4P$ (or P_4) $+ 5O_2 \longrightarrow P_4O_{10}$ (1)

S: burns with blue flame / choking / pungent gas produced (1)

$S + O_2 \longrightarrow SO_2$ (1) [4]

Q# 55/ Topic: **Chem 9** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) (i) amphoteric [1]

(ii) $2NaOH + PbO \longrightarrow Na_2PbO_2 + H_2O$ [1]
(*or* $NaOH + PbO + H_2O \longrightarrow NaPb(OH)_3$ etc.)

[2]

Q# 56/ Topic: Chem 10 ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(b)(i)	$BaO(s) + H_2O(l) \rightarrow Ba(OH)_2(aq)$ [1]	1

Q# 57/ Topic: **Chem 10** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)	$Mg(g) \rightarrow Mg^+(g) + e^-$	1
6(a)(ii)	$Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$	1
6(a)(iii)	more reactive **and** easier to ionise down the group OR more reactive **and** ionisation energies decrease down the group	1
6(b)(i)	brown gas and white solid	1
6(b)(ii)	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$	1

Q# 58/ Topic: **Chem 10** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	calcium – red flame	1
	barium – green flame	1
4(c)	the gas is colourless / looks like air / cannot be seen	1
	appearance of solid doesn't change / white solid becomes white solid	1

Q# 59/ Topic: **Chem 10** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	$2A(NO_3)_2 \rightarrow 2AO + 4NO_2 + O_2$ correct formula balanced equation	 1 1	2
1(b)(ii)	giant ionic		1

Q# 60/ Topic: Chem 11 ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(b)	$3I_2 + 6NaOH \rightarrow NaIO_3 + 5NaI + 3H_2O$	1

Q# 61/ Topic: **Chem 11** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(d) $AgCl$ white [1]
$AgBr$ cream [1]
AgI yellow [1]

Solubility decreases down the group [1]

[4]

Q# 62/ Topic: **Chem 11** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) (i) *either* burn *or* shine light/uv on mixture of $H_2 + Cl_2$ *but* NOT heat [1]

(ii) red/orange/brown colour of bromine decolourises/disappears
steamy/misty/white fumes produced
container gets warm/hot [2]

Q# 63/ Topic: Chem 12 ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) (i) *any one of:*

$2SO_2 + O_2 \longrightarrow 2SO_3$ **and** $SO_3 + H_2O \longrightarrow H_2SO_4$

or $SO_2 + NO_2 \longrightarrow SO_3 + NO$ **and** $SO_3 + H_2O \longrightarrow H_2SO_4$

or $SO_2 + \frac{1}{2}O_2 + H_2O \longrightarrow H_2SO_4$ [1]

(ii) roasting sulfide ores/extraction of metals from sulfide ores [1]

[2]

[Total: 9]

Q# 64/ Topic: **Chem 12** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (due to the) strong N≡N bond [1]
[1]

(b) (i) Any balanced equation forming a stable nitrogen oxide
e.g. $N_2 + O_2 \longrightarrow 2NO$
or
$N_2 + 2O_2 \longrightarrow 2NO_2$ [1]

(ii) in lightning [1]

in an engine/combustion of fuels (or a specific example) [1]

(iii) (NO_x produces) acid rain *or* forms (photochemical) smog [1]
[4]

Q# 65/ Topic: **Chem 12** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(iii) (formation of NO is endothermic) so high T **and** equilibrium pushed over to NO side.
or high T **and** needed to break N-N bond in N_2 [1]

Q# 66/ Topic: **Chem 12** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) $N_2 + 2O_2 \rightarrow 2NO_2$ (*or* via NO) *or* $2NO + O_2 \rightarrow 2NO_2$ [1]

(b) (i) catalytic converter **and** passing the exhaust gases over a catalyst/Pt/Rh [1]

(ii) $NO_2 + 2CO \rightarrow \frac{1}{2}N_2 + 2CO_2$ ***or*** similar [1]
Allow $2NO_2 + CH_4 \rightarrow CO_2 + N_2 + 2H_2O$

Q# 67/ Topic: **Chem 12** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 **(a)** N≡N triple bond is (very) strong
or the N_2 molecule has no polarity [1]

(b) $3Mg(s) \rightarrow 3Mg^{2+}(g)$ $\Delta H_1 = 3 \times 148 + 3 \times 2186 = 7002$
$N_2(g) \rightarrow 2N^{3-}(g)$ $\Delta H_2 = 994 + 2 \times 2148 = 5290$

LE = $-\Delta H_1 - \Delta H_2 - 461$ = **−12,753** (kJ mol^{-1}) (−[1] for each error) [3]

(c) **(i)** $Li_3N + 3H_2O \rightarrow NH_3 + 3LiOH$ (balanced equation) [1]

(ii) advantage: no high pressure/temperature/catalyst needed/standard conditions used [1]

disadvantage: Li is expensive
or Li would need to be recycled/removed
or LiOH by-product is corrosive/strongly basic
or this would be a batch, rather than continuous process [1]

(d) **(i)** Li_3N: 100 × 14/35 = 40% N [1]
urea: 100 × 28/60 = 47% N [1]

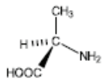
(ii) amide [1]

(iii) $NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$
or $\rightarrow NH_2CO_2H + NH_3$
or $NH_2CONH_2 + 2H_2O \rightarrow 2NH_3 + H_2CO_3$ [1]

(iv) The LiOH would be strongly alkaline
or would increase the pH of the soil
or would 'burn' the crops/reduce plant growth/stunt plants
or would contaminate the environment [1]

[Total: 12]

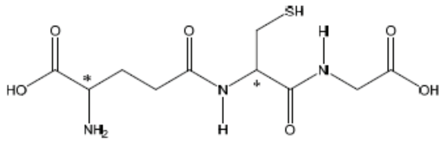
Q# 68/ Topic: Chem 13 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(b)(iii)		1

Q# 69/ Topic: **Chem 13** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)(ii)	0 (zero) in F **AND** 2 (two) in J	1

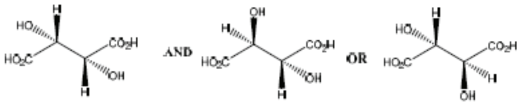
Q# 70/ Topic: **Chem 13** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(c)(i)		1

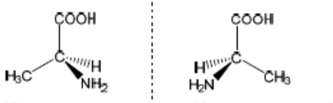
Q# 71/ Topic: **Chem 13** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(c)(vii)	Asterisk on $^*CHCO_2H$	1

Q# 72/ Topic: **Chem 13** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(c)		2

Q# 73/ Topic: **Chem 13** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10(b)(ii)	 3D, tetrahedral, both isomers of 2-aminopropanoic acid [1] optical [1]	2

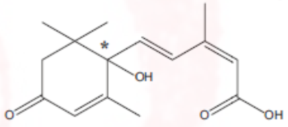
Q# 74/ Topic: **Chem 13** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(e)(i)	this is a (carbon) atom which has four different atoms or groups attached to it	1
8(e)(ii)	$CH_3CH_2CH(CH_3)COOH$	1

Q# 75/ Topic: **Chem 13** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(a)	$C_8H_{11}O_3N$	1
9(b)	yes, as it has a chiral C atom	1

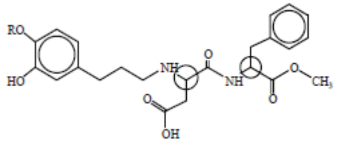
Q# 76/ Topic: **Chem 13** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)	correct chiral centre labelled **only**  $C_{15}H_{22}O_4$	1

Q# 77/ Topic: **Chem 13** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

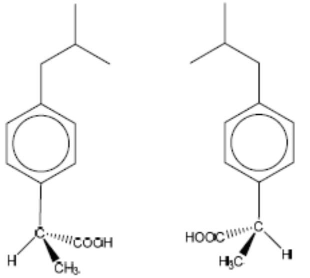
4(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 **different** groups	1

Q# 78/ Topic: **Chem 13** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

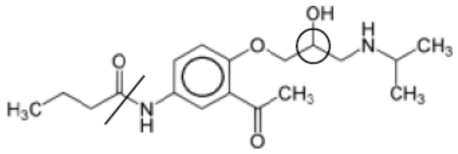
7(a)		1

Q# 79/ Topic: **Chem 13** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

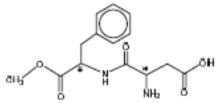
6(b)(i)	(chiral centre is a) carbon OR atom that has four different groups / atoms / species attached to it	1

6(b)(ii)	 one correct isomer second diagram shows second isomer	1 1	2

Q# 80/ Topic: **Chem 13** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

(b)		1

Q# 81/ Topic: **Chem 13** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 (a) (i)		1

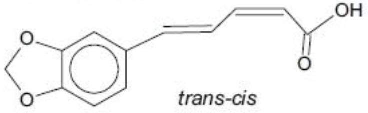
Q# 82/ Topic: **Chem 13** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b)	ketone, amine, carboxylic acid two correct 1 mark, all three 2	2	[2]

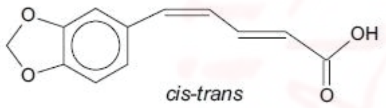
Q# 83/ Topic: **Chem 13** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) **(i)** four isomers [1]

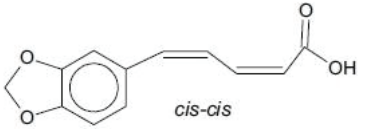
(ii) **must be skeletal**



trans-cis



cis-trans



cis-cis

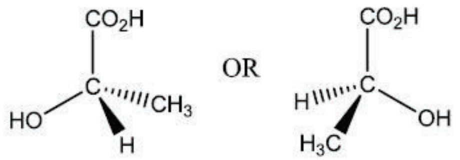
[1]

Q# 84/ Topic: **Chem 13** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) propenoic acid [1]

Q# 85/ Topic: **Chem 13** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b)



or correct diagram of the S isomer

Q# 86/ Topic: **Chem 13** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3. **(a)** **(i)** $C_{16}H_{10}N_2O_2$ [1]

Q# 87/ Topic: **Chem 13** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) **(i)** light [1]

(c) **(i)** homolytic fission is the breaking of a bond to form (two) radicals/neutral species/odd-electron species [1]

(ii) $\bullet CH_2Cl$ [1]
the C-Br bond is the weakest or needs least energy to break/breaks most easily [1]
[3]

(d)

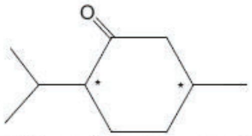
4 structures: [2]
2 or 3 structures: [1]

Correct chiral atom identified [1]
[3]

[Total: 18]

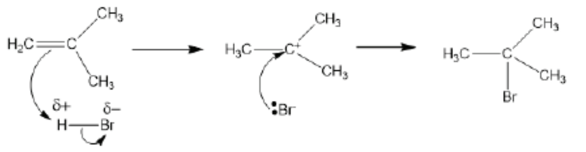
Q# 88/ Topic: **Chem 13** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)**



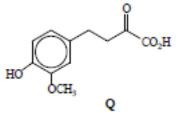
(1) for each centre – more than 2 centres shown deduct 1 mark **[2]**

Q# 89/ Topic: Chem 14 ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

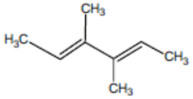
1(c)(i)	 **M1** correct dipole on HBr **AND** any correct curly arrow [1] **M2** two other correct curly arrows **AND** lone pair required on Br⁻ [1] **M3** intermediate [1]	3

1(c)(ii)	(major product is) formed via the most stable tertiary carbocation / intermediate OR tertiary halogenoalkane formed via more stable carbocation / intermediate	1

Q# 90/ Topic: **Chem 14** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8(b)(i)	dehydration / elimination	1
8(b)(ii)	heat with Al_2O_3 **OR** heat with H_3PO_4/H_2SO_4	1
8(b)(iii)	 **Q**  **R**	2

Q# 91/ Topic: **Chem 14** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

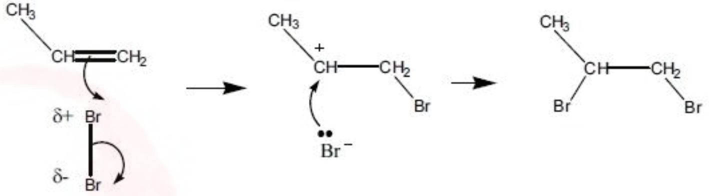
(c) (i)	(electrophilic) addition	1
(ii)		1
(d) (i)	*any four of* M1: σ-bonds between C–C **or** C–H M2: π-bonds formed from overlap of p-orbitals M3: (π-bonds/electrons) above and below the ring M4:bonds/electrons are delocalised M5: bond angle 120° M6: intermediate C–C bond length / all C–C same length / strength M7: carbons are sp^2 hybridised	3

Q# 92/ Topic: **Chem 14** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

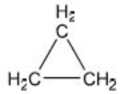
7	(a)	(i)	heat with catalyst ***or*** heat with Al_2O_3/SiO_2	1
		(ii)	B is $CH_3CH_2CH_3$	1

Q# 93/ Topic: **Chem 14** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7	(a)	(i)	heat with catalyst ***or*** heat with Al_2O_3/SiO_2	1
		(ii)	B is $CH_3CH_2CH_3$	1

	(iii)	**C** is CH_2=$CHCH_2CH_2CH_3$ **D** and **E** are CH_3CH=$CHCH_2CH_3$ (one shown as cis, the other as trans) **F** is $CH_3CH_2CH_2CO_2H$ **G** is CH_3CO_2H **H** is $CH_3CH_2CO_2H$	1 1 1 1
	(iv)	geometrical *or* cis-trans *or* *E–Z*	1
(b)	**(i)**	No particular conditions ***or*** in the dark	1
	(ii)	electrophilic addition	1
	(iii)		1 1
			[Total: 10]

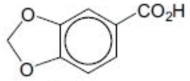
Q# 94/ Topic: **Chem 14** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10	**(a)**	**(i)**	any **three** of the following structures $CH_3CH_2CH_3$ CH_3CH=CH_2 $CH_3C{\equiv}CH$ CH_2=C=CH_2 	**2**
		(ii)	**K** since it has the greatest % of hydrocarbons / carbon-containing compounds ***or*** 99.6 % of it is burnt for energy	**1**
		(iii)	any **two** from • reacted with lime / CaO / soda lime / $Ca(OH)_2$ / KOH / NaOH / • liquefied under pressure / ≥5 atm • dissolved in water under pressure / ≥5 atm	**2**
	(b)	**(i)**	have a shorter carbon / hydrocarbon chain ***or*** shorter hydrocarbon ***or*** fewer carbon atoms in its chain ***or*** have high H / C ratio	**1**
		(ii)	Coal	**1**

	produces the largest amount of SO_2 ***or*** largest combined amount of SO_2 and NO_2	
(iii)	they burn at higher temperatures ***or*** release more heat on burning	**1**
(iv)	CO – the gas is toxic/poisonous ***or*** references to Hb **and** ability to carry oxygen	**1**
	CO_2 – the gas contributes to global warming	**1**
		[Total: 10]

Q# 95/ Topic: **Chem 14** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(iii)



+ CO_2 *or* HO_2C-CO_2H

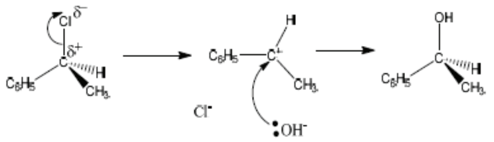
[1] [1]

Q# 96/ Topic: **Chem 14** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

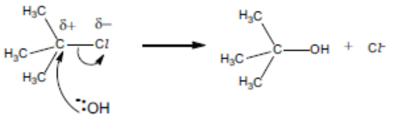
(c) No, it wouldn't be reduced. Because the reaction in **(a)** does not presuppose a particular fuel (owtte) [1]

Allow formed from N_2 and O_2 in air during combustion

Q# 97/ Topic: Chem 15 ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(c)(i)	 C-C*l* dipole and first curly arrow	1
	intermediate cation	1
	OH^- with lone pair and curly arrow	1
6(c)(ii)	Beginning with candidate's mechanism in (c)(i): **If S_N1:** racemate / mixture of / two optical isomers will be formed, because: the intermediate is planar / has a plane of symmetry / OH^- can approach from top or bottom or from any direction **If S_N2:** one optical isomer because attack always from fixed direction / from same side / the "configuration" always inverts / there is an asymmetric transition state	1

Q# 98/ Topic: **Chem 15** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a)	M1: dipole on C–C*l* bond M2: curly arrow breaking C–C*l* bond M3: curly arrow from the oxygen on ^-OH (lone pair needs to be shown) to carbon in C–C*l* bond **and** Cl^- (ion) formed in the mechanism 	3

Q# 99/ Topic: **Chem 15** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) (i) (C-X bond energy) decreases/becomes weaker (from F to I) [1]

due to bond becoming longer/not such efficient orbital overlap [1]

(ii) (as the bond energy of C-X decreases) the halogenalkanes become more reactive (answer must imply that it is from F to I) [1]

[3]

(e) (i) light/UV/hν *or* 300°C [1]

(ii) (free) radical substitution [1]

(vi) $Cl_2 \longrightarrow 2Cl^\bullet$ [1]

$CH_3CH_2^\bullet + Cl_2 \longrightarrow CH_3CH_2Cl + Cl^\bullet$ [1]

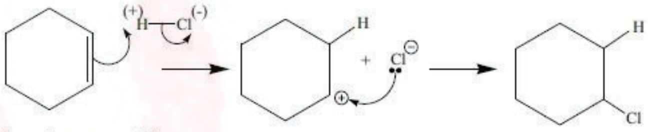
$CH_3CH_2^\bullet + Cl^\bullet \longrightarrow CH_3CH_2Cl$ [1]

[8]

[Total: 19]

Q# 100/ Topic: **Chem 15** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d)



2 curly arrows (1)
carbocation intermediate + Cl^- (1)
lone pair on Cl^- and last curly arrow (1) [3]

Q# 101/ Topic: Chem 16 ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)	$(CH_3)_2CHCHNH_2COOH + 4[H] \rightarrow (CH_3)_2CHCHNH_2CH_2OH + H_2O$ **OR** $C_5H_{11}NO_2 + 4[H] \rightarrow C_5H_{13}NO + H_2O$	**1**
6(a)(ii)	lithium aluminium hydride / $LiAlH_4$ (in dry ether)	**1**
6(a)(iii)	nucleophilic substitution	**1**

Q# 102/ Topic: **Chem 16** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	$2C_3H_7OH + 2Na \rightarrow 2C_3H_7ONa + H_2$	1

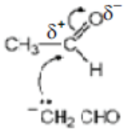
Q# 103/ Topic: **Chem 16** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8(a)	oxidation of –OH / alcohol to C=O / ketone / carbonyl	1

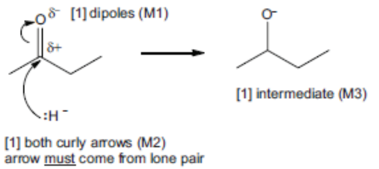
Q# 104/ Topic: Chem 17 ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(b)(ii)	carbonyl group	1

Q# 105/ Topic: **Chem 17** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

(c)	nucleophilic addition	**1**
(d)	**M1**: both curly arrows **M2**: dipole correctly shown 	**1** **1**

Q# 106/ Topic: **Chem 17** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b)	 [1] both curly arrows (M2) arrow *must* come from lone pair	3

Q# 107/ Topic: **Chem 17** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) (i) reduction *or* redox [1]

(ii) $NaBH_4$ or $LiAlH_4$ (**NOT** H_2 + Ni) [1]

[2]

Q# 108/ Topic: **Chem 17** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a) (i) aqueous alkaline iodine *or* $I_2 + OH^-(aq)$ allow NaC*l*O + KI [1]

(ii) CH_3CO- *or* $CH_3CH(OH)$- [1]

(iii) Pale yellow ppt. *or* antiseptic smell [1]

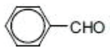
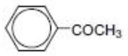
Q# 109/ Topic: **Chem 17** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a) (i) aqueous alkaline iodine *or* $I_2 + OH^-(aq)$ allow NaC*l*O + KI [1]

(ii) CH_3CO- *or* $CH_3CH(OH)$- [1]

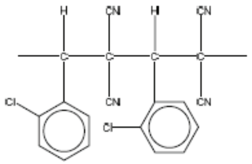
(iii) Pale yellow ppt. *or* antiseptic smell [1]

(iv)

compound	result
CH_3OH	×
CH_3CH_2OH	✓
CH_3CHO	✓
CH_3CO_2H	×
	×
	✓

•✓•✓•✓ [3]

Q# 110/ Topic: Chem 20 ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(b)		1
	addition (polymerisation)	1

Q# 111/ Topic: **Chem 20** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) PVC [1]
Combustion would produce HC*l* / dioxins as a pollutant [1]
or
nylon/acrylic [1]
Combustion would produce HCN [1]
[2]

Q# 112/ Topic: **Chem 20** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 (a) (i) One [1]

(ii) Any alkene (*or* allow a cyclic amide, as in caprolactam) [1]

Q# 113/ Topic: Chem 22 ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(d)(i)	relative abundance = 2 carbons × 1.1 × 0.62 = **1.36 / 1.4** [1] min 2sf	1
9(d)(ii)	$CH_3CH_2^+$ / $C_2H_5^+$ [1]	2

Q# 114/ Topic: **Chem 22** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org
[Cannot see where mark 2 in 4(d)(i) should be given; but it is 2 marks in the question paper]

4(d)(i)	*x* = 14.4 / 100 × 100 / 1.1 = 13.1 <u>13</u> carbon atoms (some working required)	1
4(d)(ii)	(250 – 205 = 45, so) CO_2H / C_2H_5O	1

Q# 115/ Topic: **Chem 22** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(d)	$C_6H_4NH_2^+$ **and** $CH_3CH_2CH_2CH_2^+$ [1]	1

Q# 116/ Topic: **Chem 22** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)(i)	no. of carbons = 100 × 1.25 / (22.65 × 1.1) (= **5.02**)	1
8(a)(ii)	M1: C_2H_5O M2: $C_3H_5O^+$ (positive sign required for m / e = 57 fragment)	2

Q# 117/ Topic: **Chem 22** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(b)(iii)	n = (100 / 1.1) x (14.3 / 100) = 13.0 OR n = (14.3 / 1.1) = 13.0	1
6(b)(iv)	the ratio of the (M:M+2) peaks is 3:1 **AND** halogen is chlorine / C*l*	1
6(b)(v)	relative abundance = 14.3 / 3 = 4.77 (4.8) OR RA = 14.3 × 33.3 / 100 = 4.76 (4.8)	1
6(b)(vi)	$C_{13}H_{16}NOCl$	1

Q# 118/ Topic: **Chem 22** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	^{37}Cl and ^{81}Br	1
1(b)(ii)	M peak $CH_2{}^{35}Cl^{79}Br$ M+2 peak $CH_2{}^{37}Cl^{79}Br$ OR $CH_2{}^{35}Cl^{81}Br$ M+4 peak $CH_2{}^{37}Cl^{81}Br$ two correct scores 1 mark all 3 correct scores 2 marks	2

Q# 119/ Topic: **Chem 22** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i)	(28 × 0.922) + (29 × 0.047) + (30 × 0.031) = 28.11	1

Q# 120/ Topic: **Chem 22** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a) (i)

isotope	relative abundance
^{24}Mg	**78–79**
^{25}Mg	**10**
^{26}Mg	**12–11**

(total must add up to 100 %) 1

(ii) e.g. 0.78x24 + 0.10x25 + 0.12x26 = **24.34** 1

Q# 121/ Topic: **Chem 22** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a) (i)	$101 = P^{35}Cl^{35}Cl$ $103 = P^{35}Cl^{37}Cl$ $105 = P^{37}Cl^{37}Cl$	1 1 1	
(ii)	9:6:1	1	[4]

Q# 122/ Topic: **Chem 22** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) (i) $156 = C_3H_6{}^{35}Cl^{79}Br^+$ [1]
$158 = C_3H_6{}^{37}Cl^{79}Br^+$ [1]
$158 = C_3H_6{}^{35}Cl^{81}Br^+$ [1]
$160 = C_3H_6{}^{37}Cl^{81}Br^+$ [1]

(ii) *m/e* = 15 Species = CH_3^+ [1]

[5 max 4]

[Total: 10]

Q# 123/ Topic: **Chem 22** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c) (i) **X** is bromine – M and (M+2) peaks almost same height [1]

(ii) $\frac{M}{M+1} = \frac{100}{1.1} \times \frac{9}{n} = \frac{100}{0.3}$ 1.1 × n

Hence $n = \frac{100 \times 0.3}{1.1 \times 9} = 3.03$ $p = 3$

(answer + working) [1]

(If the mass peak is at 122 and the compound contains Br and 3 C atoms then Q = (122 – 79 – 36)) thus **Q = 7** ecf from (ii) [1]

(The compound is C_3H_7Br)

(iii) *(R is at m/e 43)*, hence **$C_3H_7^+$** [1]

(d) Any **two** from H_2, H_2O, CO, C_2H_4, C_2H_2, CH_4 2 × [1]

[Total: 10]

Q# 124/ Topic: Chem 23 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	1 mol liquid and 2 mol gas formed from 3 mol solid OR two solid compounds converted to a liquid and a gas	1
2(a)(ii)	M1: (as *T* increases) *T*Δ*S* becomes greater (than Δ*H*) OR (as *T* increases) *T*Δ*S* becomes more positive M2: (as *T* increases) feasibility will increase as Δ*G* becomes more negative	2
2(b)(i)	M1: = 314 + 131 – (19 + 3 × 187) use of values and correct stoichiometry M2: = **–135** (J K⁻¹ mol⁻¹)	2
2(b)(ii)	M1: Δ*G* = 0 ∴ *T* = Δ*H* / Δ*S* = +219.3 × 10³ ÷ –(b)(i) M2: = **1624**(.4) (K)	2

Q# 125/ Topic: **Chem 23** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	enthalpy change when one mole of a solute **AND** dissolves **in water** to form a solution of infinite dilution	1
1(b)(ii)	–(–629) + (–322) + (–293) = (+)**14** (kJ mol⁻¹)	1
1(b)(iii)	(cationic) charge density decreases Li⁺ to K⁺ [1] so lattice energies become less negative / less exothermic **AND** because less **attraction** between ions [1]	2

Q# 126/ Topic: **Chem 23** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)	• enthalpy/energy change • one mole of electrons gained • by one mole of atoms • gaseous (atoms)	2
3(b)	$Ca^+(g) \rightarrow Ca^{2+}(g) + e^-$ [1]	1
3(c)	M1: selecting correct data 951, 844, 142 only M2: evaluation to give 249 (ΔH_{atom}) OR 2(951) = BE – 2(142) + 2(844) M3: evaluation to 498 (2 × 249) ecf M2 951 = ΔH_{atom} –142 + 844 ΔH_{atom} = 249 BE = **498** (kJ mol⁻¹) [3]	3
3(d)(i)	**attraction** between nucleus / protons / nuclear charge and electron [1]	1
3(d)(ii)	**repulsion** between 1– ion / electrons of O^- and electron [1]	1
3(e)	M1: selecting correct data 951, 1933, 3517 only (ignore signs) M2: evaluation to give –633 (ΔH_f) ecf ΔH_f = 951 + 1933 – 3517 = –633 (kJ mol⁻¹) [2]	2
3(f)	ionic charge / charge density (of the ions) [1] greater (attractive) force between the ions [1]	2

Q# 127/ Topic: **Chem 23** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

2(b)	M1 [H⁺] = 10⁻⁵ OR 1 × 10⁻⁵ K_a = [H⁺][A⁻] / [HA] OR pH = p*K*a + log [A⁻] / [HA] • ✓ [1] M2 moles of A⁻ = (1.35 × 10⁻⁵)(5 / 74) / (1 × 10⁻⁵) moles of A⁻ = 0.0912 [1] ecf M3 mass of sodium propanoate = 0.0912 × 96 = 8.76 [1] min 2sf ecf	3
2(c)	all of the (sodium) **propanoate** (ion) has been protonated / converted to (propanoic) acid / neutralised [1] **H⁺** is in excess / **H⁺** is 0.1 mol dm⁻³ (from the H_2SO_4) [1]	2

Q# 128/ Topic: **Chem 23** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

2(a)(i	$K_a = \frac{[H^+][Cl(CH_2)_3CO_2^-]}{[Cl(CH_2)_3CO_2H]}$ [1]	1
2(a)(ii)	pK_a = – logK_a OR $K_a = 10^{-pKa}$ [1]	1
2(a)(iii)	$[H^+] = 10^{-4.0}$ = **1×10^{-4}** [1]	1

2(a)(iv)	• $[HCl] = 1 \times 10^{-4}$ ecf 2(a)(iii) • $K_a = 10^{-4.52} = 3.02 \times 10^{-5}$ • $[Cl(CH_2)_3CO_2H] = (1 \times 10^{-4})^2 / 3.02 \times 10^{-5} = 3.3 \times 10^{-4}$ ecf • $\frac{[HCl]}{[Cl(CH_2)_3CO_2H]} = \frac{1\times10^{-4}}{3.3\times10^{-4}} = \mathbf{0.302}$ min 2sf ecf	2

Q# 129/ Topic: **Chem 23** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(f)(i)	**M1**: ΔS = ½(192) + ½(205) + ½(261) + 2(70) – 42 **M2**: (+)427 (J K^{-1} mol^{-1}) ecf	2
3(f)(ii)	ΔG (always) negative because • $\Delta H < 0$ / negative OR exothermic <u>AND</u> • $\Delta S > 0$ / positive OR $-T\Delta S < 0$ for all T	1

Q# 130/ Topic: **Chem 23** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	**M1** the only number extracted: 762, 1560, 496 **M2** correct multiplier, other four numbers used and calculation to the answer –272 = +416 + ½(496) + 762 + 1560 –141 + 798 + $\Delta H_{lattice}$ ∴ $\Delta H_{lattice}$ = **–3915** (kJ mol^{-1}) ecf	2
2(a)(iii)	• FeO more exothermic/more negative • Fe^{2+} has smaller radius/higher charge density (also same charge) • greater attraction/ stronger ionic bonds (between Fe^{2+} and O^{2-}) **All three for two marks**	2

Q# 131/ Topic: **Chem 23** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	**M1** energy released when 1 mole of an ionic compound is formed [1] **M2** from gaseous ions (under standard conditions) [1]	2
2(a)(ii)	Ca^{2+} & O^{2-} have a higher charge / charge density (than Li^+ and F^-) [1]	1
2(a)(iii)	MgO –3600 or more negative AND BaO –3200 or less negative BOTH [1]	1
2(c)	**M1:** Use of 2 × –348 (EA F) and +158 (bond energy of F_2) [1] **M2:** Use of +147 (at Mg) and +736 and +1450 (IEs of Mg) [1] **M3:** evaluation and calculation of their answer (–1102 – (147 + 158 + 736 + 1450 – 696)) = **–2897** (kJ mol^{-1}) [1] ecf	3
2(d)(i)	• (energy change) when an / one electron is added to • each atom / ion in one mole of • gaseous atoms / ions mark as • ✓ ✓ [2]	2
2(d)(ii)	F has greater nuclear charge / more protons AND greater attraction between F atom / nucleus and the electrons • ✓ BOTH [1]	1

Q# 132/ Topic: **Chem 23** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(b)(i)	ΔS° = 72.7 + 56.5 -96.2 = **+33.0 J K^{-1} mol^{-1}**	1
7(b)(ii)	**M1** $\Delta G = \Delta H^\circ - T\Delta S^\circ$ **M2** ΔG = (65.5)- (298x0.033) = **+55.7 kJ mol^{-1}** min 3sf **M3** ΔG = positive so not feasible/spontaneous	3

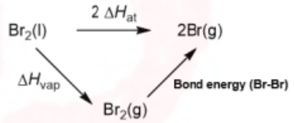
Q# 133/ Topic: **Chem 23** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(c)(i)	ΔH_4 = (3 ×) electron affinity of fluorine / F ΔH_5 = (enthalpy change of) formation of AlF_3	2
3(c)(ii)	**M1** +326 + 1½ × 158 + 5137 + 3 × –328 + ΔH_{latt} = –1504 **M2** ΔH_{latt} = –6220 (kJ mol^{-1})	2
3(c)(iii)	**M1** lattice energy of ScF_3 should be less exothermic ora **M2** Sc ion / Sc^{3+} larger than Al ion / Al^{3+} **AND** lesser attraction between the ions / ionic bonds are weaker	2

Q# 134/ Topic: **Chem 23** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

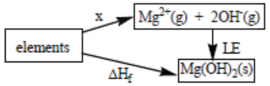
3(a)	**a measure / degree of disorder / randomness of a system**	1
3(b)	**M1:** negative – molecules have less energy in the system **M2:** positive – solid being converted into an aqueous solution **M3:** negative – gaseous ions being converted into a solid	3
3(c)(i)	(standard) Gibbs free energy <u>change</u>	1
3(c)(ii)	**M1:** $(\Delta)G = \Delta H - T\Delta S$ **M2:** description of calculating the minimum value of T for which ΔG is zero / becomes negative OR T = ΔH / ΔS [1]	2

Q# 135/ Topic: **Chem 23** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

<table>
<tr><td>6(a)</td><td>
<table>
<tr><th>energy change</th><th>always positive</th><th>always negative</th><th>either negative or positive</th></tr>
<tr><td>bond energy</td><td>✓</td><td></td><td></td></tr>
<tr><td>enthalpy of formation</td><td></td><td></td><td>✓</td></tr>
</table>
both ticks correct</td><td>1</td></tr>
<tr><td>6(b)</td><td>(energy change) when 1 mole of gaseous atoms are formed (from an element in its standard state)</td><td>1</td></tr>
<tr><td>6(c)</td><td>

M1: correct cycle: formulae and state symbols
M2: use of 1 × 193 and 2 × (112)
M3: for the correct sum and answer ecf from M2
ΔH°_{vap} (= (2 × 112) – (193)) = +31 kJ mol^{-1} [scores M2 and M3]</td><td>3</td></tr>
<tr><td>6(d)</td><td>more endothermic and greater Van der Waals / London / induced dipole-dipole forces both</td><td>1</td></tr>
<tr><td>6(e)(i)</td><td>(energy change) when 1 mole of gaseous ions is dissolved in (an excess of) water</td><td>1</td></tr>
<tr><td>6(e)(ii)</td><td>M1: Br^- has a smaller ionic radii
M2: stronger (ion-dipole) attractions with water molecules</td><td>2</td></tr>
</table>

Q# 136/ Topic: **Chem 23** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

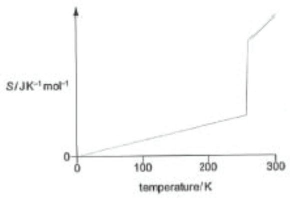
<table>
<tr><td>2(c)</td><td>

–2993 + 148 + 736 + 1450 + 2ΔH_f(OH^-(g)) = –925
2ΔH_f(OH^-(g)) = –266
ΔH_f(OH^-(g)) = –133 (kJ mol^{-1})</td><td>3</td></tr>
</table>

Q# 137/ Topic: **Chem 23** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)	natural: lightning, bacterial decomposition, volcanic emissions man-made: exhaust fumes, power stations, jet / car/ vehicle engines	1
1(b)(i)	$4NO \longrightarrow N_2O + N_2O_3$	1
1(b)(ii)	+2 to +1 **AND** +2 to +3	1
1(b)(iii)	$\Delta S = (\Delta H - \Delta G) / T$ $= (-195.2+102.8) / 298$ $= -0.310\ kJ\ mol^{-1}\ K^{-1}$ **M1** numerical answer **M2** units	2
1(b)(iv)	yes as there is a decrease in no. of moles of gas OR yes as moles of (gaseous) reactants is greater than moles of (gaseous) products	1

Q# 138/ Topic: **Chem 23** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)	 **M1** continuous increase in *S* from 0–300 K (excluding m.p.) [1] **M2** steep vertical increase in *S* **ONLY** at the m.p. **AND** continuous increase in *S* after m.p. [1]	2
8(b)	[1] for each correct tick	1

	negative $\Delta S^⦵$	positive $\Delta S^⦵$
solid dissolving in water		✓
water boiling to steam		✓

8(c)	$\Delta H^⦵ = (2 \times C{=}O) + (3 \times H\text{-}H) - (3 \times C\text{-}H) - (C\text{-}O) - (3xO\text{-}H)$ $\Delta H^⦵ = (2 \times 805) + (3 \times 436) - (3 \times 410) - (1 \times 360) - (3 \times 460)$ [1] $\Delta H^⦵ = 1610 + 1308 - 1230 - 360 - 1380 = -$ **52** (kJ mol⁻¹) [1] ecf correct answer scores [2]	2
8(d)(i)	$\Delta S^⦵ = 127 + 70 - (214 + 3 \times 131)$ [1] $= -410\ (J\ K^{-1}\ mol^{-1})$ [1] ecf correct answer scores [2]	2
8(d)(ii)	$\Delta G^⦵ = \Delta H^⦵ - T\Delta S^⦵$ [1] $\Delta G^⦵ = -131 - (298 \times -0.41) = -$ **8.8(2)** (kJ mol⁻¹) [1] correct answer scores [2]	2

8(d)(iii)	(as temperature increases) feasibility decreases	1

Q# 139/ Topic: **Chem 23** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(d)	use of (2 × 109) or 218 and (2 × 494) or 988	1
	use of (0.5 × 496) or 248	1
	use of 416, 142, 844	1
	evaluation of expression correctly $\Delta H_{lat} = -416 - (2 \times 109) - (0.5 \times 496) - (2 \times 494) - (-142 + 844) = -2572$	1
1(e)	the lattice energy of Na_2S is less exothermic	1
	the sulfide ion is larger than the oxide ion / S^{2-} larger than O^{2} / ionic radii quoted 0.184 nm and 0.140 nm AND less attraction (between the ions)/bonds are weaker	1

Q# 140/ Topic: **Chem 23** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	$\Delta H_{r1} - (538 + 2x230 + 394) = -(1216 + 286)$ $\Delta H_{r1} - 1392 = -1502$	1
	$\Delta H_{r1} =$ **–110**	1
1(b)(ii)	let $\Delta H_f(HCO_3^-(aq)) = y$ $2y - 538 = -1216 - 394 - 286 - 26$	1
	y = **–692**	1
1(b)(iii)	$\Delta H_{r3} -538 - 2(230 + 394) = -538 - 2(692)$ $\Delta H_{r3} =$ **–136**	1
1(b)(iv)	ΔH_{r3} will be identical to ΔH_{r4}, / unchanged	1
	as the reaction is the same, or: $2OH^-(aq) + 2CO_2(g) \longrightarrow 2HCO_3^-(aq)$ or metal ions stay in solution/metal ions are unchanged / are spectators	1

1(c)	**more gaseous moles** are being consumed (in reaction 3) or more **CO₂ moles** are being consumed (in reaction 3)	1
	ΔS is therefore expected to be **more negative/less positive** for reaction 3.	1
	Total:	**13**

Q# 141/ Topic: **Chem 23** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)		2

enthalpy change	positive	negative	either positive or negative
electron affinity			✓
enthalpy change of atomisation	✓		
enthalpy change of ionisation	✓		
lattice enthalpy		✓	

2(b)(i)	the second electron is removed from a (more) positively charged ion	1
2(b)(ii)	ΔH_6 is lattice (energy / enthalpy) **AND** ΔH_7 is (energy / enthalpy of) formation	1
2(c)	the electron affinity becomes less exothermic / negative down the Group 17	1
	electron affinity depends (mainly) on the electron-nucleus distance which increases down Group 17	1
2(d)	**M1** correct use of $\Delta G = \Delta H - T\Delta S$	1
	M2 $\Delta S = 26.9 - (32.7 + 102.5) = -108.3\ J\ K^{-1} mol^{-1}$ **OR** $-0.1083\ kJ\ K^{-1} mol^{-1}$	1
	M3 $\Delta G = -602 - (298 \times (-0.1083)) = -570$	1
	M4 units: kJ mol⁻¹	1

Q# 142/ Topic: **Chem 23** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(d)	hydration enthalpy and lattice energy **both** more endothermic / more positive / less exothermic / less negative (down the group) ΔH_{hyd} decreases more / faster **and** ΔH_{sol} becomes (more) endothermic / (more) positive / less exothermic / less negative	1 1 **2**
	Total:	**11**

Q# 143/ Topic: **Chem 23** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	(entropy) increases / is positive **and** H_2 / gas is formed	1	1
3(a)(ii)	(entropy) increases / is positive **and** (KC*l* (aq)) solution has (free) moving / mobile ions / aqueous ions	1	1
3(a)(iii)	(entropy) decreases / is negative **and** decrease in gas	1	1
3(b)(i)	$\Delta S^\circ = 26.9 + 214 - 65.7 = (+)175.2\ (\text{J K}^{-1}\ \text{mol}^{-1})$ $\Delta G^\circ = 117 - (298 \times 175.2 / 1000)$ OR $\Delta G^\circ = 117\,000 - (298 \times 175.2)$ $\Delta G^\circ = +64.8\ (\text{kJ mol}^{-1})$	1 1 1	3
3(b)(ii)	$T\Delta S$ is more positive than ΔH / $T\Delta S$ increases / $-T\Delta S$ more negative **and** ΔG is negative / decrease / less positive	1	1
3(c)	use of $\Delta G = 0$ or $\frac{\underline{T\Delta S}}{\Delta H} = 1$ $T = 130 / (316 / 1000) =$ **410 / 411 / 412 / 411.4** (K)	1 1	2

Q# 144/ Topic: **Chem 23** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 (a)	$\Delta H = [2(-580) + 3(-286) + 3(-1438)] - [-2061 + 4(-437) + 3(-814)]$ $= -81\ \text{kJ mol}^{-1}$	[2]

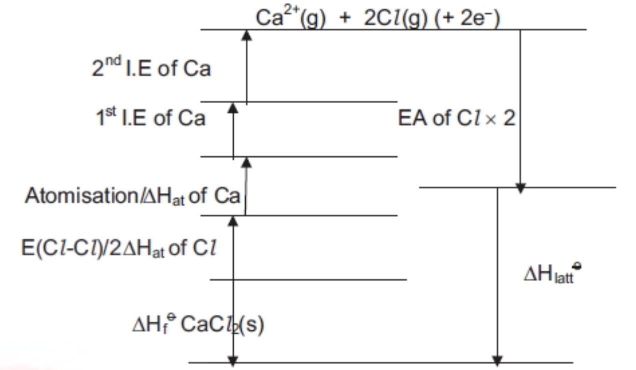
Q# 145/ Topic: **Chem 23** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b) (i)	*cis–trans* OR geometrical	[1]
(ii)	in a complex the d–orbitals are split into 2 energy levels colour is due to absorption of light (in visible region) electron promotion to higher orbital absorbs a photon the d–d energy gap is different for the two complexes, hence different colours	[1] [1] [1] [1]
		[Total: 7]

Q# 146/ Topic: **Chem 23** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a)	$K_p = \{p(CS_2) \times (p(H_2))^4\} / \{(p(H_2S))^2 \times p(CH_4)\}$ units: atm^2 OR Pa^2	[1] [1]
(b) (i)	$p(H_2S) = 196\ \text{atm}$ $p(H_2) = 8\ \text{atm}$	[1] [1]
(ii)	$K_p = (2 \times 8^4)/(196^2 \times 98) = 2.176 \times 10^{-3}$	[1]
(c) (i)	ΔS° will be positive, because more gas moles on the RHS / products	[1]
(ii)	$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T = (241 - 51)/1000 = 0.19$ OR 190 $\text{kJ mol}^{-1}\text{K}^{-1}$ OR $\text{J mol}^{-1}\text{K}^{-1}$	[1] [1]
(d)	ΔG° will become less positive/more negative as T increases, …because ΔS° is positive (*or* $-T\Delta S^\circ$ is more negative) …therefore the reaction becomes more feasible / spontaneous as T increases	[2]
		[Total: 10]

Q# 147/ Topic: **Chem 23** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i)	$Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$ (state symbols required)	1
(ii)		2
(iii)	$\Delta H_{latt}^\circ = -796 - 242 - 178 - 590 - 1150 + (2 \times 349) = -2258\ \text{kJ mol}^{-1}$	3
(b)	(higher temperature means that) particles have more energy; entropy (of the gas / system) increases because of an increase in the amount of disorder / randomness;	2
(c) (i)	see table below	2
(ii)	there is a reduction in the overall number of <u>gaseous</u> molecules	1
(d)	$\Delta S_f^\circ = 386 - (192 + (3 \times 131))$ $= -199\ (\text{J K}^{-1}\ \text{mol}^{-1})$	2
(e) (i)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $= 117 - ((298 \times 175) / 1000)$ $= (+)\ 64.85\ (\text{kJ mol}^{-1})$	2
(ii)	<u>ΔG° is positive</u> and so the reaction is <u>not spontaneous</u> (at 298 K)	1

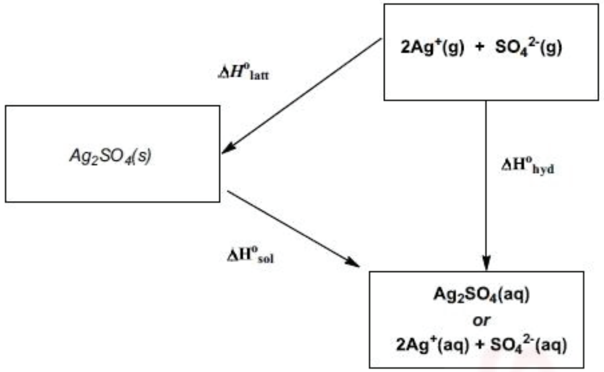
(c) (i)

reaction	sign of ΔS°
$CO(g) + O_2(g) \rightarrow CO_2(g)$	negative
$Mg(s) + ½O_2(g) \rightarrow MgO(s)$	negative
$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$	negative
$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + CO_2(g) + H_2O(l)$	positive

Q# 148/ Topic: **Chem 23** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) (i)	(energy change when) 1 mole of ions **gaseous** (ions) dissolve in **water** (to form an infinitely dilute solution) *or* **gaseous** (ions) form an **aqueous** solution	2
(ii)	$\Delta H^\circ_{latt}Ca(NO_3)_2 + \Delta H^\circ_{sol}Ca(NO_3)_2 = \Delta H^\circ_{hyd}\ Ca^{2+} + 2\Delta H^\circ_{hyd}\ NO_3^-$ $\Delta H^\circ_{latt} - 19 = -1650 + (2x -314)$ $-2259\ \text{kJ mol}^{-1}$	3
1	$Ca^{(2+)}$ is a smaller (ion) ***or*** $Ca^{(2+)}$ has a larger charge density $Ca^{(2+)}$ has a stronger attraction / bond to H_2O	2
		<u>12</u>

Q# 149/ Topic: **Chem 23** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b)		1 1 1 1

Q# 150/ Topic: **Chem 23** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(e) (i)	(enthalpy change) when **1 mole** of an **ionic compound** is **formed** from its **gaseous ions**	1 1	
(ii)	Mg^{2+} has a smaller (ionic) radii than Ca^{2+} **OR** Mg^{2+} is smaller than Ca^{2+}	1	[3]
Total			[16]

Q# 151/ Topic: **Chem 23** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) (i) the enthalpy change/released when **1 mole is formed** [1]

of ionic lattice **from** the **gas** phase **ions** [1]

(ii) $Mg^{2+} + O^{2-} \longrightarrow MgO$ [1]
[3]

(b) measurements needed:
volume/mass/weight of water (in calorimeter) [1]
initial + final temperature/temperature change/temperature rise (of the water) [1]
mass of Mg (used)/mass MgO [1]
Not *volume/moles/mass of oxygen used*
[3]

(c) ΔH = 148 + 736 + 1450 + 496/2 - 141 + 798 – 3791
= –<u>552</u> kJ mol^{-1} [3]
[3]

(d) $Na_2O(s) + H_2O(aq/l) \longrightarrow 2NaOH(aq)$ [1]
$MgO(s) + H_2O(aq/l) \longrightarrow Mg(OH)_2(s)$ *or* $Mg(OH)_2(aq)$ [1]
pH 12.5-14 [NaOH] **AND** 8-10.5 [Mg(OH)$_2$] respectively [1]
[3]

[Total: 12]

Q# 152/ Topic: **Chem 23** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) $3Mg(s) \rightarrow 3Mg^{2+}(g)$ $\Delta H_1 = 3 \times 148 + 3 \times 2186 = 7002$
$N_2(g) \rightarrow 2N^{3-}(g)$ $\Delta H_2 = 994 + 2 \times 2148 = 5290$

$LE = -\Delta H_1 - \Delta H_2 - 461 = $ **–12,753** (kJ mol^{-1}) (–[1] for each error) [3]

Q# 153/ Topic: **Chem 23** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** $Ca^{2+}(g) + 2Cl^{-}(g) \longrightarrow CaCl_2(s)$ [1]
[1]

(b) CaF_2 **and** CaS **both** have larger lattice energies (than $CaCl_2$) [1]

(i) F^- is smaller than Cl^- [1]

(ii) S^{2-} is more highly charged than Cl^- [1]
[3]

(c) $LE = -[178 + 590 + 1150] - [244 - 2 \times 349] - 796$
✓ ✓ signs✓
= **–2260** (kJ mol^{-1}) [3]
[3]

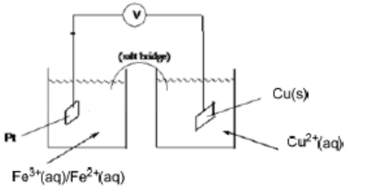
Q# 154/ Topic: Chem 24 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(c)(i)	M1: $\Delta G = -nE^{\ominus}_{cell}F$ AND n = 4 M2: ∴ $E^{\ominus}_{cell} = -436100 / -4(96500) = 1.13$ V ecf M3: $E^{\ominus}_{cell} = E^{\ominus}(O_2,4H^+\|H_2O) - E^{\ominus}(TiO^{2+}\|Ti^{3+}) = 1.23 - E^{\ominus}(TiO^{2+}\|Ti^{3+})$ ∴ $E^{\ominus}(TiO^{2+}\|Ti^{3+}) = (+)$**0.1** (V) ecf	3

Q# 155/ Topic: **Chem 24** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(c)	M1: 1.00 g Si is 1/28.1 = 0.0356 mol ∴ moles of e⁻ needed = 4 × mol Si = 0.142 faraday (3 sf) M2: $Q = It$ ∴ t = M1 × 96500 ÷ 6 = 2289 (s) ecf	2

Q# 156/ Topic: **Chem 24** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(b)(i)	**M1:** emf / potential difference / difference in electrode potential between two half-cells / two electrodes (in a cell) **M2:** (all solutions being) 1 mol dm^{-3} AND either 1 atm OR 298 K	2
3(b)(ii)	salt bridge, voltmeter, Cu(s), Cu^{2+}(aq), Pt(s), Fe^{2+} and Fe^{3+}(aq) two for one mark, four for two marks, six for three marks 	3
3(d)(ii)	$C_4H_4O_6^{2-} + 2H_2O \rightleftharpoons 2CO_2 + 2HCO_2^- + 6H^+ + 6e^-$	1

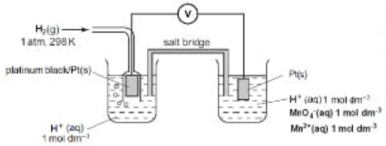
Q# 157/ Topic: **Chem 24** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(c)(i)	**M1:** $E^{\ominus}_{cell}$ for $IO_3^- / H_2O_2 = -0.68 + 1.19 = +0.51$ (∴ feasible) **M2:** $E^{\ominus}_{cell}$ for $H_2O_2 / I_2 = +1.77 - 1.19 = +0.58$ (∴ feasible) **M3:** $5H_2O_2 + I_2 \rightarrow 4H_2O + 2IO_3^- + 2H^+$	3
3(c)(ii)	$2H_2O_2 \rightarrow 2H_2O + O_2$	1

Q# 158/ Topic: **Chem 24** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(b)(i)	• Fe^{2+} *reduced* to Fe **OR** oxid no. Fe +2 → 0 • Fe^{2+} *oxidised* to Fe^{3+} (in Fe_3O_4) **OR** oxid no. Fe +2 → +3 **BOTH bullets required**	1
2(b)(ii)	$2O^{2-} \rightarrow O_2 + 4e^-$	1
2(b)(iii)	**M1**: coulombs and correct use of ÷ 96500 **M2**: correct use of 3 and 8 **M3**: correct use of 55.8 and answer **M1**: $Q = It = 50 \times 6 \times 60^2$ **OR** 1.08×10^6 C **AND** no. of faraday = $1.08 \times 10^6 \div 96500$ **OR** 11.2 / 11.19 mol e^- **M2**: $Fe^{2+} + 2Fe^{3+} + 8e^- \rightarrow 3Fe$ ∴ moles of Fe = 3 / 8 × M1 = 4.20 mol Fe ecf **M3**: mass of Fe = 55.8 × M2 = 234.2 g ecf 3sf min	3
2(c)(i)	Any one of: small size / compact, low mass, high voltage **OWTTE**	1
2(c)(ii)	Li from +1 to +1 Fe from +3 to +2	1
2(c)(iii)	$LiC_6 + FePO_4 \rightarrow LiFePO_4 + 6C$	1

Q# 159/ Topic: **Chem 24** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)	(anode =) oxygen / O_2 **AND** (cathode =) hydrogen/H_2 **BOTH [1]**	1
3(b)	**M1**: Q = 1.5 × 60 × 60 × 4.5 = 24300 (C) [1] **M2**: no. of F / moles of e^- = 24300 / 96500 = 0.25(1813) [1] ecf **M3**: volume of Cl_2 = 24 × 0.252 / 2 = **3.02** dm^3 [1] ecf min 2sf **M4**: mass of Na = 0.252 × 23 = **5.79** (5.7917) g Na [1] ecf min 2sf	4
3(c)(i)	 • MnO_4^-, H^+, Mn^{2+} in same beaker **AND** H^+ in other beaker • both electrodes Pt(s) (**ALLOW** graphite) • one solute clearly identified as 1M / 1 mol dm^{-3} • 298 K OR 1 atm • voltmeter / potentiometer labelled (or circled V) • salt bridge labelled (must touch the solution) • a good delivery system for H_2(g) • H_2(g) mark as two correct points = 1 mark [4]	4
3(c)(ii)	F_2 OR $S_2O_8^{2-}$ OR H_2O_2 OR HOC*l* OR Co^{3+} OR Pb^{4+} [1] $2Mn^{2+} + 8H_2O + 5F_2 \rightarrow 2MnO_4^- + 16H^+ + 10F^-$[1] OR $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 16H^+ + 10SO_4^{2-}$ OR $Mn^{2+} + 4H_2O + 5Co^{3+} \rightarrow MnO_4^- + 8H^+ + 5Co^{2+}$ OR $2Mn^{2+} + 8H_2O + 5Pb^{4+} \rightarrow 2MnO_4^- + 16H^+ + 5Pb^{2+}$ OR $2Mn^{2+} + 5H_2O_2 \rightarrow 2MnO_4^- + 6H^+ + 2H_2O$ OR $2Mn^{2+} + 10HOCl \rightarrow 2MnO_4^- + 6H^+ + 5Cl_2 + 2H_2O$	2

Q# 160/ Topic: **Chem 24** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

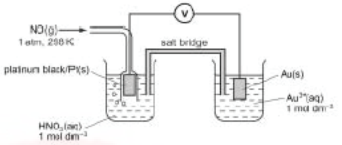
9(a)	**M1** data seen H_2O_2/H_2O +1.77V and MnO_2/Mn^{2+} +1.23 V and O_2/H_2O_2 +0.68 V OR E_{cell}= 0.55 V (first step) and 0.54 V (second step) **M2** $MnO_2 + H_2O_2 + 2H^+ \rightarrow Mn^{2+} + O_2 + 2H_2O$ **M3** $Mn^{2+} + H_2O_2 \rightarrow MnO_2 + 2H^+$	3

Q# 161/ Topic: **Chem 24** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	$6CO_2 + 24H^+ + 24e^- \rightarrow C_6H_{12}O_6 + 6H_2O$ **ALLOW** $6CO_2 + 12H^+ + 12e^- \rightarrow C_6H_{12}O_6 + 3O_2$ for both marks **ALLOW** one mark for an unbalanced equation showing the correct species of either equation	2

3(a)(ii)	salt bridge (indicated) voltmeter / V labelled O_2 good delivery system H_2 good delivery system Pt electrode H^+ / HCl / H_2SO_4 solution labelled (at least once) 1 atm 1 mol dm^{-3} quoted Every two correct responses = 1 mark	4
3(a)(iii)	E°_{cell} = (+) 1.23 V **AND** positive electrode = O_2 half-cell identified	1

Q# 162/ Topic: **Chem 24** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	Mark as • ✓✓ • voltage of an electrode / half-cell • compared / connected to (S)HE / hydrogen half-cell / electrode • under standard conditions / 1 mol dm^{-3}, 1 atm, 298 K	2
3(a)(ii)	 Mark as • ✓ • ✓ • ✓ • ✓ • HNO_3(aq) and Au^{3+}(aq) • Au(s) and Pt(s) electrode • voltmeter (or circled V) • salt bridge labelled • NO (g) • a good delivery system for NO • 1M / 1 mol dm^{-3} • 298 K **AND** 1 atm	4
3(a)(iii)	$Au^{3+} + NO + 2H_2O \rightarrow Au + NO_3^- + 4H^+$	1
3(a)(iv)	+1.50 – 0.96 = + 0.54 (V)	1
3(a)(v)	**M1 M2** any two [1] all four [2] • adding conc HNO_3 shifts equilibrium 3 to the right • *E* for (half-equation 3) increases / more positive • adding conc HC*l* shift equilibrium 2 to the left • *E* for (half-equation 2) decreases / less positive **M3** *E*(3) becomes greater than *E*(2)	3

Q# 163/ Topic: **Chem 24** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(b)(i)	$2Al^{3+} + 3O^{2-} + 3C \rightarrow 2Al + 3CO$	1
2(b)(ii)	**M1** $Q = It$ = $3.5 \times 10^5 \times 3 \times 60^2 = 3.78 \times 10^9$ C **M2** no. of mol e^- = $3.78 \times 10^9 / 96500 = 3.92 \times 10^4$ **M3** mass A*l* = $27 \times 3.92 \times 10^4 / 3 = 3.5(3) \times 10^5$ g	3

Q# 164/ Topic: **Chem 24** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	Platinum / Pt　　Aluminium / Al　　**BOTH**	**1**
1(b)(i)	**M1:** use of or quoting a valid Nernst equation $E = E^{\circ} + 0.0590 / z \log [ox] / [red]$ *OR* $E = 0.15 + (0.0590 / 2)\log 2$ **M2:** E = (+)**0.16** (0.159) V minimum 2 sig. fig. correct answer scores 2 marks	**2**
1(b)(ii)	$E_{cell} = 0.16 - (-1.66) =$ **+1.82 V**　　minimum 3 sig. fig.	**1**
1(b)(iii)	$2Al + 3Sn^{4+} \rightarrow 2Al^{3+} + 3Sn^{2+}$ **M1:** species **M2:** balancing	**2**
1(c)	**M1:** number of C (= 300 000 × 60 × 60 × 24) = 2.59×10^{10} (C) **M2:** number of F(= $2.592 \times 10^{10} / 9.65 \times 10^{4}$) = 2.69×10^{5} (moles of electrons) **M3:** moles of Al(= $2.69 \times 10^{5} / 3$) = 8.95×10^{4} **M4:** mass of Al(= $8.95 \times 10^{4} \times 27$) = **2420 kg** correct answer scores 4 marks	**4**
1(d)	**M1:** ($Cr^{2+} + 2e^- \rightleftharpoons Cr$) $E^{\circ} = -0.91$ **and** ($2H^+ + 2e^- \rightleftharpoons H_2$) $E^{\circ} = 0.00$ seen **M2:** hydrogen formed instead / hydrogen (ions) easier to reduce / hydrogen has more positive E°	**2**

Q# 165/ Topic: **Chem 24** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)	$2ClO_3^- + SO_2 \rightarrow 2ClO_2 + SO_4^{2-}$	**1**
3(b)(i)	Cl in ClO_2 gets both oxidised and reduced or Cl goes from +4 → +5 and +4 → +3	**1**
3(b)(ii)	**M1**　$ClO_2 + 2OH^- \rightarrow ClO_3^- + H_2O + e^-$ **M2**　$ClO_2 + e^- \rightarrow ClO_2^-$	**2**
3(c)(i)	**M1**　$Li \rightarrow Li^+ + e^-$ **and** $I_2 + 2e^- \rightarrow 2I^-$ **M2**　$2Li + I_2 \rightarrow 2Li^+ + 2I^-$	**2**
3(c)(ii)	$E^{\circ}_{cell} = 0.54 - (-3.04) =$ **+3.58 V** [1]	**1**
3(c)(iii)	**M1**　amount of Li = 0.10 / 6.9 = 1.45×10^{-2} mol [1] **M2**　Q needed = 96500 × 1.45×10^{-2} = **1399** (1398.55) C [1] ecf **M3**　t = 1399 / (2.5×10^{-5}) = **5.6×10^{7}** s [1] ecf 2sf min	**3**

Q# 166/ Topic: **Chem 24** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(e)(i)	$2CH_3OH + 3O_2 \rightleftharpoons 2CO_2 + 4H_2O$ OR $2CH_3OH + 3O_2 \rightleftharpoons 2CO_2 + 4H^+ + 4OH^-$	**1**
8(e)(ii)	E°_{cell} = 1.23 – 0.02 = **1.21** V	**1**

Q# 167/ Topic: **Chem 24** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

<table>
<tr><td>3(a)</td><td><table><tr><td></td><td>anode</td><td>cathode</td></tr><tr><td>AgNO₃ (aq)</td><td>oxygen / O₂</td><td>silver / Ag</td></tr><tr><td>saturated NaCl (aq)</td><td>chlorine / Cl₂</td><td>hydrogen / H₂</td></tr><tr><td>CuSO₄ (aq)</td><td>oxygen / O₂</td><td>copper / Cu</td></tr></table></td><td>3</td></tr>
<tr><td>3(b)(i)</td><td>$2I^- \rightarrow I_2 + 2e^-$</td><td>1</td></tr>
<tr><td></td><td>$Ca^{2+} + 2e^- \rightarrow Ca$</td><td>1</td></tr>
<tr><td>3(b)(ii)</td><td>• Ca / Calcium reduced and I / iodine oxidised
• Oxidation number of calcium decreases from 2 to 0
• Oxidation number of iodine increases from –1 to 0
2 points = 1 mark
3 points = 2 marks</td><td>2</td></tr>
<tr><td>3(b)(iii)</td><td>• metal / grey / silvery
• purple AND vapour / gas / fumes
• amount of melt decreases
any 2 points for 1 mark</td><td>1</td></tr>
<tr><td>3(c)</td><td>2 × 60 × 60 × 0.8 = 5760 C
AND
5760 / 96500 = 0.060 (0.0597) F</td><td>1</td></tr>
<tr><td></td><td>1.11 / 55.8 = 0.020 (0.0199) mol of Fe</td><td>1</td></tr>
<tr><td></td><td>0.06 / 0.02 = 3 ∴ Fe^{3+} or +3 or 3</td><td>1</td></tr>
</table>

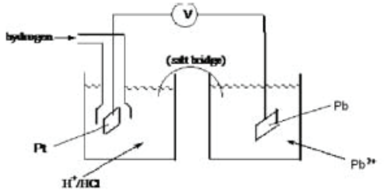
Q# 168/ Topic: **Chem 24** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)	**X** is an ammeter	**1**
6(a)(ii)	**Y** is $AgNO_3$ *or* AgF *or* $AgClO_4$	**1**
6(b)	n(Ag) = 0.500 / 107.9 = 4.6(34) × 10^{-3} n(C) = 0.200 × 40 × 60 = 480 C n(e^-) = 480/1.60 × 10^{-19} = 3(.00) × 10^{21} n(e^-)/n(Ag) = 3.00 × 10^{21} / 4.634 × 10^{-3} = 6.474 × 10^{23} (**6.5 × 10^{23}**)	**3**

Q# 169/ Topic: **Chem 24** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)	the E° for X_2 / X^- becomes less positive / decrease down the group so the halogens are less reactive (as oxidants) down the group	**2**
2(b)(i)	$Cl_2 + H_2O \longrightarrow HCl + HClO$	**1**
2(b)(ii)	Cl_2/Cl^- = +1.36 V **and** $ClO^- / (Cl^- + OH^-)$ = +0.89 V so E°_{cell} = 1.36 – 0.89 = (+) 0.47 V	**2**
2(b)(iii)	box three ticked Le Chatelier argument, more OH^- / increase reactant concentration so equilibrium shifts right *or* an argument based on the half cell with OH^-	**2**
2(c)(i)	$Br^- + 3ClO^- \longrightarrow BrO_3^- + 3Cl^-$	**1**
2(c)(ii)	E°_{cell} = 0.89 – 0.58 = + 0.31 V	**1**
2(c)(iii)	$4HBrO_3 \longrightarrow 2Br_2 + 5O_2 + 2H_2O$	**1**

Q# 170/ Topic: **Chem 24** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)	the potential **difference** between two half-cells / two electrodes (in a cell)	1
	under standard conditions of 1 atm., 298 K, (all) solutions being 1 mol dm^{-3}	1
3(b)(i)	 8 marking points, any 2 points for each mark H$_2$ / hydrogen correct delivery system for H$_2$ Pb^{2+} (aq) Pb electrode Pt electrode H$^+$(aq) solution salt bridge voltmeter / V labelled	4
3(b)(ii)	more negative	1
	shifts Pb^{2+} (+ 2e$^-$) ⇋ Pb equilibrium / reaction to the left	1
3(c)(i)	Q = 0.4 × 80 × 60 = **1920** C and use of 96500 / 193000 Moles of Pb = 1920 / 193000 = 9.95 × 10^{-3} Mass of Pb = 207.2 × 9.95 × 10^{-3} = **2.1 g** OR Q = 0.4 × 80 × 60 = **1920** C and use of 1.6 × 10^{-19} / 1.2 × 10^{22} atoms Pb = 6 × 10^{21}; moles of Pb =6 × 10^{21}/6 × 10^{23} = 0.01 Mass of Pb = 207.2 × 0.01 = **2.1 g**	2
3(c)(ii)	PbO$_2$(s) + SO$_4^{2-}$(aq) + **4H$^+$** + **2e$^-$** → PbSO$_4$(s) + **2H$_2$O**	1
3(d)	reagents / PbO$_2$ / H$_2$SO$_4$ **and** used up / concentration decreases	1
	as fuel / hydrogen is being continuously supplied / fuel has not run out	1

Q# 171/ Topic: **Chem 24** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	**A** – H$_2$, 1 atm **B** – platinum **C** – 1 mol dm^{-3} H$^+$ / HC*l* etc. **D** – salt bridge / KNO$_3$ etc. **E** – platinum **F** – 1 mol dm^{-3} Fe^{2+} **AND** 1 mol dm^{-3} Fe^{3+}	3
3(a)(ii)	positive electrode is (Pt) on RHS **AND** electrons flow clockwise	1
3(b)	cell potential is 0.77 – 0.34 =(+) 0.43 (V)	1
3(c)(i)	electrode potential would become more negative as equilibrium shifts to left / explanation in terms of the Nernst equation	1
3(c)(ii)	*E* = –0.41 + (0.059/1)log[Cr^{3+}]/[Cr^{2+}] = –0.41 + 0.059 log 4.0	1
	= –0.37 (V)	1

Q# 172/ Topic: **Chem 24** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(c)	(emf / potential / *E*) of an **electrode OR a half-cell** compared to / connected to **(S)HE** which can be called a "hydrogen half-cell" at **concentration** of 1 mol dm^{-3} **and pressure** of 1 atm (or in Pa) OR 298 K	1 1	2
4(d)(i)	half-cell: electrode Co^{2+} / Co: Co / cobalt Fe^{3+} / Fe^{2+}: Pt / carbon / graphite	1	1
4(d)(ii)	Co + 2Fe^{3+} → Co^{2+} + 2Fe^{2+}	1	1
4(d)(iii)	E°_{cell} = 0.77 – (–0.28) = (+ or –)1.05 (V)	1	1
4(e)(i)	$E_{electrode}$ = – 0.28 + (0.059 / 2) log [0.05] = **–0.32 / –0.318** (V)	1	1
4(e)(ii)	more positive	1	1
4(f)	4Fe^{3+} + V + H$_2$O → VO^{2+} + 4Fe^{2+} + 2H$^+$ VO^{2+} correct equation	1 1	
			2
		Total:	14

Q# 173/ Topic: **Chem 24** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (i)	SCP is the EMF / potential of a cell composed of two electrodes (OR half cells) under standard conditions (OR at 289K OR 1 moldm^{-3})	[1]
(ii)	voltmeter and salt bridge	[1]
(iii)	**A** is Ag **B** is Ag$^+$(aq) or AgNO$_3$(aq) **C** is Pt **D** is Fe^{2+}(aq) and Fe^{3+}(aq) (combination of **A** and **B** can be reversed with combination of **C** and **D**)	[3]
(b) (i)	Ag$^+$ + Fe^{2+} $\longrightarrow$ Ag + Fe^{3+}	[1]
(ii)	*E* = *E*° + 0.059log [Ag$^+$] = 0.80 – 0.03 = 0.77 V so E_{cell} = 0.77 – 0.77 = 0.0 V	[1] [1]
		[Total: 8]

Q# 174/ Topic: **Chem 24** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i)	any metal with an $E^\ominus$ value more negative than –0.41 V, e.g. Fe, Mn, Zn, Mg, Cr, A*l* **R:** Li/Na/K/Ca/Ba	1
(ii)	**M1**: value of E_{cell} correctly calculated (with correct sign) for metal named in **(i)** **M2**: $E^\ominus_{cell}$ is positive **and** so reaction is feasible	1 1
(b)	**M1**: $(Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O)$ $E^\ominus = +1.33$ V $(H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O)$ $E^\ominus = +1.77$ V $E^\ominus_{cell} = 0.44$ (V) **M2**: $E^\ominus_{cell}$ (0.44 V) is positive (so the reaction is feasible) / $E^\ominus(Cr_2O_7^{2-}/Cr^{3+})$ is less positive than $E^\ominus(H_2O_2/H_2O)$	1 1
(c)	**M1**: $Cr_2O_7^{2-}$: ox.no Cr = +6 because –2 = 2 × ox.no(Cr) + (7 × –2) CrO_4^{2-}: ox.no Cr = +6 because –2 = ox.no(Cr) + (4 × –2) **M2**: no change in oxidation number, so reaction is not redox	1 1
(d)	**M1**: no. moles Cr deposited = 0.0312/52 = 6.0×10^{-4} moles **M2**: deduction that 6 moles of e^- needed per mole of Cr/ reaction is $Cr_2O_7^{2-} + 14H^+ + 12e^- \rightarrow 2Cr + 7H_2O$ **M3**: no. moles of $e^- = 6 \times 6.0 \times 10^{-4} = (0.125 \times t)/96\,500$ so $t = (6 \times 6.0 \times 10^{-4} \times 96\,500)/(0.125 \times 60)$ = 46.3 min/0.772 h/2780 s	1 1 1

Q# 175/ Topic: **Chem 24** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i)	M1: salt bridge **and** voltmeter/ M2: method of H_2 gas delivery M3: X **and** Pt electrode labelled M4: solution H^+/HC*l*(aq)/H_2SO_4 **and** X^{2+} labelled	4
(ii)	25°C/298 K **and** 1 atm/101 kPa pressure **and** 1 mol dm^{-3} (solution)	1
(iii)	solution – ions ***or*** H^+ and X^{2+} **and** wires – electrons/e^-	1
(b) (i)	$X + 2Ag^+ \rightarrow 2Ag + X^{2+}$	1
(ii)	moles Ag = 1.30/107.9 = 0.0120 1 moles of X react with 2 moles Ag^+ moles of X lost = 0.012 × 0.5 = 0.00602 A_r of X = 0.67/0.006 = 111–112 **and** X = Cd	4
		<u>11</u>

Q# 176/ Topic: **Chem 24** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(e) (i)	F = Le	1
(ii)	moles of $O_2(g) = 130/24000 = 5.417 \times 10^{-3}$ mol moles of electrons needed = $4 \times 5.417 \times 10^{-3}$ ***or*** 2.17×10^{-2} mol no. of coulombs passed = 1.2 x 30 x 60 ***or*** 2160 C no. of electrons passed = $2160/1.6 \times 10^{-19}$ ***or*** 1.35×10^{22} no. of electrons per mole = $1.35 \times 10^{22}/2.17 \times 10^{-2}$ = $\mathbf{6.2 \times 10^{23}}$ (mol^{-1})	1 1 1 1

Q# 177/ Topic: **Chem 24** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c) (i)	$E^\ominus_{cell}$ (= 0.80 – 0.77 =) (+)**0.03V and** Ag^+/Ag ***or*** Ag/silver ***or*** right	1
(ii)	E_{cell} would be less positive/more negative because the [Ag^+(aq)] (in the Ag electrode) is less than 1.0 mol dm^{-3}	1
(iii)	• no change	1
	• more negative/less positive	1
(iv)	the [Ag^+(aq)] will decrease $E_{electrode}$ becomes less positive ***or*** due to the common ion effect	 1

Q# 178/ Topic: **Chem 24** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) (i)	$E^\ominus$ values: F_2/F^- = 2.87 V **and** Cl_2/Cl^- = 1.36 V fluorine (has the more positive $E^\ominus$ so) is more oxidising	1 1
(ii)	redox	1
(iii)	$ClF + 2KBr \longrightarrow KCl + KF + Br_2$	1
		[Total: 8]

Q# 179/ Topic: **Chem 24** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) (i) components to be added: voltmeter *or* **V** [1]
salt bridge <u>must be</u> labelled] [1]

(ii) M1: **A** and **B** copper (metal) or Cu **and** iron (metal) or Fe [1]
M2: either **C** or **D** as 1 mol dm^{-3}/1 M [1]
M3 **C** and **D** Cu^{2+} or $CuSO_4$ or $CuCl_2$ or Cu $(NO_3)_2$ etc. **and** Fe^{2+} or $FeSO_4$ etc. [1]

(iii) $E^\ominus_{cell}$ = 0.34 + 0.44 = **0.78** (V) [1]

(iv) if **C** is Fe^{2+}; (as [**C**] increases), the *E* of the Fe^{2+}/Fe increases/becomes more positive/less negative [1]

so the overall cell potential/E_{cell} would **decrease/become less positive/more negative** [1]

or

if **C** is Cu^{2+}; (as [**C**] increases), the E of the Cu^{2+}/Cu increases/becomes more positive/less negative [1]

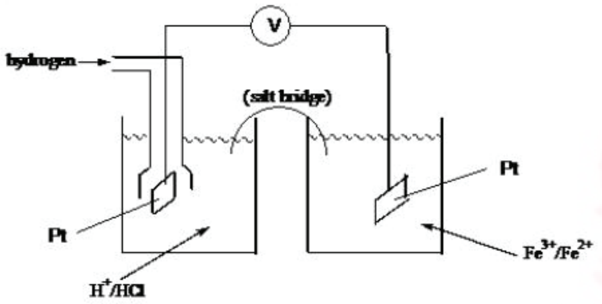
so the overall cell potential/E_{cell} would **increase/become more positive/less negative** [1]

Q# 180/ Topic: **Chem 24** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) The potential of an **electrode** compared to that of a standard hydrogen electrode (SHE)
or
the EMF of a **cell** composed of the test electrode and the SHE [1]

all measurement concentrations of 1 mol dm^{-3} **and** 298 K / 1 atm pressure [1]
[2]

(b)



H$_2$ and good delivery system [1]
Fe^{2+}/Fe^{3+} solution labelled [1]
platinum electrodes (both) [1]
salt bridge and voltmeter [1]
H$^+$ *or* HC*l* *or* H$_2$SO$_4$ [1]
(acid is not sufficient)
[5]

(c) (i) $E^\ominus = 0.77 - 0.54 = 0.23$ (V) [1]

(ii) Since $E^\ominus$ is positive/ $E^\ominus > 0$

So more products / the equilibrium will be over to the right / forward reaction is favoured
ecf from **(c)(i)** [1]

Q# 181/ Topic: **Chem 24** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i) **A** = CuSO$_4$ [1]
B = silver [1]

(ii) salt bridge [1]
voltmeter [1]

[4]

(b) (i) $0.80 - 0.34 =$ **(+) 0.46 V** [1]

(ii) If $E_{cell} = 0.17$, this is 0.29 V less than the standard $E^\ominus$,
so $E_{\text{Ag electrode}}$ must $= 0.80 - 0.29 =$ **0.51 V** [1]

(iii) $0.51 = 0.80 + 0.06\log[Ag^+]$, so $[Ag^+] = 10^{(-0.29/0.06)} =$ **<u>1.47 x 10^{-5}</u>** mol dm^{-3} ecf from **(ii)** [1]

[3]

(c) (i) $K_{sp} = [Ag^+]^2[SO_4^{2-}]$ [1]
units = mol^3 dm^{-9} ecf on K_{sp} [1]

(ii) $[SO_4^{2-}] = [Ag^+]/2$ $K_{sp} = (1.6 \times 10^{-2})^2 \times 0.8 \times 10^{-2} =$ **<u>2.05 × 10^{-6}</u>** (mol^3 dm^{-9}) [1]

[3]

Q# 182/ Topic: **Chem 24** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) (i) $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$ [1]

(ii) 5 : 1

(iii) $n(MnO_4^-) = 0.02 \times 15/1000 = 3 \times 10^{-4}$ (mol) [1]

(iv) $n(Fe^{2+}) = 5 \times 3 \times 10^{-4} = 1.5 \times 10^{-3}$ (mol) ecf from **(i)** or **(ii)** [1]

(v) $[Fe^{2+}] = 1.5 \times 10^{-3} \times 1000/2.5 =$ **0.6** (mol dm^{-3}) ecf from **(iv)** [1]

(vi) In the original solution, there was 0.15 mol of Fe^{3+} in 100 cm^3.
In the partially-used solution, there is 0.06 mol of Fe^{2+} in 100 cm^3.

So remaining Fe^{3+} = 0.15 – 0.06 = 0.09 mol. ecf from **(v)** [1]

This can react with 0.045 mol of Cu, which = 0.045 × 63.5 = **2.86 g** of copper. ecf [1]

[6]

(d) (i) $Ca_2Si + 6H_2O \longrightarrow 2Ca(OH)_2 + SiO_2 + 4H_2$ [1]

(ii) silcon has been oxidised **<u>AND</u>** hydrogen has been reduced [1]

[2]

[Total: 14]

Q# 183/ Topic: **Chem 24** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) (i) O.N.(carbon) = +3 (4 × (–2) + 2x = –2, thus 2x = +6) [1]

(iv) $\underline{2}\ K_3Fe(C_2O_4)_3 \rightarrow \underline{3}\ K_2C_2O_4 + \underline{2}\ FeC_2O_4 + \underline{2}\ CO_2$ [2]
Or $K_3Fe(C_2O_4)_3 \rightarrow \underline{3/2}\ K_2C_2O_4 + FeC_2O_4 + CO_2$

[max 5]

[Total: 14]

Q# 184/ Topic: **Chem 24** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a) (i) $Cu(s) - 2e^- \rightarrow Cu^{2+}(aq)$ allow electrons on RHS (1)

(ii) $E^\ominus$ for Ag^+/Ag is +0.80V which is more positive than +0.34V for Cu^{2+}/Cu, (1)
so it's less easily oxidised (owtte) (1)

(iii) $E^\ominus$ for Ni^{2+} is –0.25V, (1)
Ni is readily oxidised and goes into solution as $Ni^{2+}(aq)$ (1) [Mark **(ii)** and **(iii)** to max 3]

(iv) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ (1)

(v) $E^\ominus$ for Zn^{2+}/Zn is negative / = –0.76V, so Zn^{2+} is not easily reduced. (1)

(vi) The blue colour fades because $Cu^{2+}(aq)$ is being replaced by $Zn^{2+}(aq)$ *or* $Ni^{2+}(aq)$ *or* $[Cu^{2+}]$ decreases (1) **[7]**

(b) amount of copper = 225/63.5 = **3.54**(3) mol (1)
amount of electrons needed = 2 × 3.54 = **7.08/9** (7.087) mol (1)

no. of coulombs = 20 × 10 × 60 × 60 = 7.2×10^5 C
no. of moles of electrons = $7.2 \times 10^5/9.65 \times 10^4$ = **7.46** mol (1)

percentage "wasted" = 100 × (7.461 – 7.087)/7.461 = 5.01 (**5.0**)% (accept 4.98–5.10) (1) **[4]**

(c) $E^\ominus$ data: Ni^{2+}/Ni = –0.25V
Fe^{2+}/Fe = –0.44V (1)

Because the Fe potential is more negative than the Ni potential, the iron will dissolve (1) **[2]**

[Total: 13]

Q# 185/ Topic: **Chem 24** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) (i) +2 (1)

(ii) (half) the sulfur goes up by +2, (1)
(the other half) goes down by –2 (1)

(iii) HC*l* (can be read into **(iv)**) (1)

(iv) $2SCl_2 + 2H_2O \rightarrow S + SO_2 + 4HCl$ (1)

(v) (+ $AgNO_3$) white ppt. (1)
(+ $K_2Cr_2O_7$) solution turns green (1) **[7]**

[Total: 11]

Q# 186/ Topic: **Chem 24** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i) $E^\circ = 0.40 - (-0.83) = 1.23V$ (1)

(ii) $2H_2 + O_2 \longrightarrow 2H_2O$ (1)

(iii) LH electrode will become more negative (1)
RH electrode will also become more negative / less positive (1)

(iv) no change ecf from **(iii)** (1)

(v) increased conductance *or* lower cell resistance *or* increased rate of reaction (1) [6]

(b) (i) $E^\circ = 1.47 - (-0.13) = 1.60V$ (1)
(ii) $PbO_2 + Pb + 4H^+ \longrightarrow 2Pb^{2+} + 2H_2O$ (1)

(iii) $PbO_2 + Pb + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4(s) + 2H_2O$ (1)

(iv) E°_{cell} will increase (1)

as $[Pb^{2+}]$ decreases, $E_{electrode}(PbO_2)$ will become more positive, but $E_{electrode}(Pb)$ will become more negative (1) [5]

[Total: 11]

Q# 187/ Topic: **Chem 24** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(d) (i) $Zn + Sn^{4+} \longrightarrow Zn^{2+} + Sn^{2+}$ [1]

(ii) E^θ = 0.15 – (–0.76) = **0.91** V [1]
E^θ = 1.52 – 0.15 = **1.37** V [1]

(iii) $n(Sn^{2+})$ = 0.02 × 13.5/1000 × 5/2 = **6.75 × 10⁻⁴** mol use of the 5/2 ratio [1]
correct rest of working [1]
$n(Sn^{2+})$ = 0.02 × 20.3/1000 × 5/2 = **1.02 × 10⁻³** mol [1]

(iv) $n(Sn^{4+}) = 1.02 \times 10^{-3} - 6.75 \times 10^{-4} = 3.45 \times 10^{-4}$ mol [1]
∴ ratio = 6.75/3.45 = 1.96:1 ≈ **2:1**
∴ formula is $2SnO + SnO_2 \Rightarrow$ **Sn_3O_4** *(cond^l on calculation, but allow ecf)* [1]
[8]

(e) (i) volume = $1 \times 1 \times 1 \times 10^{-5} = 1 \times 10^{-5}\ m^3$ *or* **10** cm^3 [1]

(ii) mass = vol × density = 10 × 7.3 = **73** g ecf [1]
moles = mass/A_r = 73/119 = **0.61** mol ecf [1]

(iii) Q = nFz = 0.61 × 9.65 × 10⁴ × 2 = **1.18 (1.2) × 10⁵** coulombs ecf [1]
[4]

[Total: 19]

Q# 188/ Topic: Chem 25 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(c)(i)	pair I = $CH_3CHClCOOH$ (acid) and $CH_3CHClCOO^-$ (c.base) pair II = NH_3 (base) and NH_4^+ (c.acid)	1

Q# 189/ Topic: **Chem 25** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	$CH_3CHClCOOH + H_2O \rightleftharpoons CH_3CHClCOO^- + H_3O^+$ OR $CH_3CHClCOOH \rightleftharpoons CH_3CHClCOO^- + H^+$	1
5(a)(ii)	M1: $[H^+] = 10^{-1.51} = 0.0309$ (mol dm^{-3}) M2: $K_a = 0.0309^2/0.60 = 1.592 \times 10^{-3}$ ecf $pK_a = -\log 1.592 \times 10^{-3} =$ **2.80** ecf	2
5(a)(iii)	$CH_3CHClCOOH$ is a stronger acid (than propanoic acid, owing to higher $[H^+]$ [1] because electron-withdrawing effect of Cl (substituent) **AND** weakens O—H / carboxylate anion stabilised [1]	2

Q# 190/ Topic: **Chem 25** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(e)	M1: $([Hg^{2+}]) = 1.00 \times 10^{-7} \div 454.4 = 2.20 \times 10^{-10}$ (mol dm^{-3}) M2: $K_{sp} = [Hg^{2+}][I^-]^2 = 4[Hg^{2+}]^3$ = **4.26×10^{-29}** ecf M3: units = $mol^3\ dm^{-9}$ ecf	3

Q# 191/ Topic: **Chem 25** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)(ii)	M1: K_{pc} (93.8) = $[I_2(\text{cyclohexane})] \div [I_2(aq)]$ 93.8 = (0.390 / 15) ÷ (x / 20) M2: mass of $I_2(aq)$, x = **5.54×10^{-3}** (g) ecf	2
1(a)(iii)	• K_{pc} would be lower • hexan-2-one is **more** polar (than cyclohexane) OR hexan-2-one is polar **AND** cyclohexane is non-polar • I_2 is (therefore) less soluble in hexan-2-one *All three correct for two marks*	2

Q# 192/ Topic: **Chem 25** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i	$K_a = \frac{[H^+][Cl(CH_2)_3CO_2^-]}{[Cl(CH_2)_3CO_2H]}$ [1]	1
2(a)(ii)	$pK_a = -\log K_a$ OR $K_a = 10^{-pKa}$ [1]	1
2(a)(iii)	$[H^+] = 10^{-4.0}$ = **1×10^{-4}** [1]	1

2(a)(iv)	• $[HCl] = 1 \times 10^{-4}$ ecf 2(a)(iii) • $K_a = 10^{-4.52} = 3.02 \times 10^{-5}$ • $[Cl(CH_2)_3CO_2H] = (1 \times 10^{-4})^2 / 3.02 \times 10^{-5}$ $= 3.3 \times 10^{-4}$ ecf • $\frac{[HCl]}{[Cl(CH_2)_3CO_2H]} = \frac{1\times10^{-4}}{3.3\times10^{-4}} =$ **0.302** min 2sf ecf	2
2(b)	M1 $[H^+] = 10^{-5}$ OR 1×10^{-5} $K_a = [H^+][A^-] / [HA]$ OR pH = p*K*a + log $[A^-] / [HA]$ • ✓ [1] M2 moles of $A^- = (1.35 \times 10^{-5})(5 / 74) / (1 \times 10^{-5})$ moles of A^- = 0.0912 [1] ecf M3 mass of sodium propanoate = 0.0912 × 96 = **8.76** [1] min 2sf ecf	3
2(c)	all of the (sodium) **propanoate** (ion) has been protonated / converted to (propanoic) acid / neutralised [1] **H^+** is in excess / **H^+** is 0.1 mol dm^{-3} (from the H_2SO_4) [1]	2

Q# 193/ Topic: **Chem 25** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)(i)	**M1:** CH_3CO_2H and $CH_3CO_2^-$ **M2:** due to buffering action / acting as a buffer solution **M3:** CH_3CO_2H reacts with NaOH / OH^- (forming $CH_3CO_2^-$ and water) OR OH^- reacts with H^+ <u>and</u> equilibrium $CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$ shifts to the right	3
8(a)(ii)	identifying $CH_3CO_2^-$ is present (with water) at the equivalence point OR $CH_3CO_2^-$ react with water forming OH^- OR titrating a weak acid with a strong base	1

Q# 194/ Topic: **Chem 25** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(b)	**M1:** moles $MnO_4^- = 0.025 \times 0.0201 = 5.025 \times 10^{-4}$ moles $V^{2+} = 5.025 \times 10^{-4} \times 5 / 3 = 8.375 \times 10^{-4}$ **M2:** moles $VO_3^- = 8.375 \times 10^{-4}$ mass of $NH_4VO_3 = 116.9 \times 8.375 \times 10^{-4} = 0.0979$ g **M3:** % Purity of NH_4VO_3 = 100 × 0.0979 / 0.15 = 65.3 must be 3 sf	3

Q# 195/ Topic: **Chem 25** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$	1
1(b)(ii)	**M1:** $K_{sp} = [Ca^{2+}][OH^-]^2$ OR $K_{sp} = 4x^3$ **M2:** $x = \sqrt[3]{5.02 \times 10^{-6} / 4} = 0.0108 / 0.011 / 1.08 \times 10^{-2} / 1.1 \times 10^{-2}$ (mol dm^{-3}) min 2 sf	2
1(b)(iii)	less soluble / decreases due to the common ion effect OR decreases as equilibrium in (b)(i) has shifted to the left OR decreases as $[OH^-]$ increases causing $[Ca^{2+}][OH^-]^{(2)}$ to exceed its K_{sp}	1

Q# 196/ Topic: **Chem 25** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(f)	**M1:** initial amount of $C_4H_9N_2O_4SNa$ = 3.50 / 204.1 **OR** 0.0171(48) mol **AND** amount of HCl added = 0.200 × 50.0 / 1000 **OR** 0.0100 mol **M2:** equilibrium amount of $C_4H_9N_2O_4SNa$ = 0.0171(48) – 0.0100 **OR** 0.0071(48) mol **AND** equilibrium amount of ACES = 0.0100 mol ecf **M3:** $K_a = 10^{-6.88} = 1.32 \times 10^{-7}$ (mol dm^{-3}) $[H^+] = (1.32 \times 10^{-7})0.01 / 0.0071(48) = 1.86 \times 10^{-7}$ **OR** 1.8465×10^{-7} ecf **M4:** pH = $-\log(1.86 \times 10^{-7})$ = 6.73 3sf min ecf	4

Q# 197/ Topic: **Chem 25** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(e)(i)	$K_{sp} = [Pb^{2+}][IO_3^-]^2$	1
3(e)(ii)	**M1:** $3.69 \times 10^{-13} = x(2x)^2$ **OR** $x = \sqrt[3]{(3.69 \times 10^{-13} \div 4)}$ **M2:** = $4.5(2) \times 10^{-5}$ (mol dm^{-3}) min 2sf ecf	2

Q# 198/ Topic: **Chem 25** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	(pH =) $-\log[H^+]$ OR $-\lg[H^+]$ [1] (K_w =) $[H^+][OH^-]$ [1]	2
4(a)(ii)	$[H^+] = 1 \times 10^{-14} / 0.027 = 3.7037 \times 10^{-13}$ pH = $-\log(3.7037 \times 10^{-13})$= **12.4** [1] min 3sf	1
4(b)	$[H^+] = \sqrt{3.72 \times 10^{-8} \times 0.010} = 1.9287 \times 10^{-5}$ pH = $-\log(1.9287 \times 10^{-5})$= **4.7** [1] min 2sf	1
4(c)(i)	K_{pc} = (0.935 / 50) / (0.065 / 50) K_{pc} = **14.4** (14.38) [1] min 3sf	1
4(c)(ii)	**M1:** 14.4 = ((0.935 – x) / 50) / (x / 100) [1] ecf from **4(c)(i)** **M2:** x = **0.114** g [1] min 2sf ecf from M1	2

Q# 199/ Topic: **Chem 25** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)	**M1** a solution that resists changes in pH **M2** when small amounts of acid and alkali are added to it	2
8(b)(i)	$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$	1
8(b)(ii)	**M1** $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$ **M2** $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	2

8(b)(iii)	**M1** moles NH_3(initial) = 0.25 x 0.80 = 0.200 **AND** moles HC*l* = 0.20 x 0.20 = 0.040 (= moles $NH_4^+{}_{eqm}$) **M2** moles $NH_{3(eqm)}$ = 0.20 – 0.04 = 0.160 $[H^+]$ = (5.6 x10^{-10} x 0.04)/(0.16) = 1.4 x 10^{-10} (mol dm^{-3}) ecf on M1 **M3** pH = -log(1.4 x 10^{-10}) = 9.85 ecf on M2 min 2sf	3

Q# 200/ Topic: **Chem 25** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)(i)	**M1** $K_{sp} = [Ag^+]^2[CO_3^{2-}]$ **M2** units = $mol^3\ dm^{-9}$	2
7(a)(ii)	x = $^3\sqrt{}$6.3 x 10^{-12}/4 = 1.16 x 10^{-4} (mol dm^{-3}) $[Ag^+]$ = 1.16 x 10^{-4} x 2 = **2.33 x 10^{-4}** (mol dm^{-3}) min 2sf	1
7(a)(iii)	6.3 x 10^{-12} = $[0.05]^2[CO_3^{2-}]$ $[CO_3^{2-}]$ = **2.52 x 10^{-9}** (mol dm^{-3}) min 2sf	1
7(a)(iv)	**M1** $E=E^{\ominus}$ + 0.059log$[Ag^+]$ **M2** E=0.80 + 0.059log(1.2 x 10^{-4}) = **0.57** V ecf from **(a)(ii)** min 2sf	2

Q# 201/ Topic: **Chem 25** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(b)(i)	K_{eq} = 4.07x10^{-3}/1.78x10^{-4} = **22.9**	1
6(b)(ii)	3rd box ticked [to the right] **AND** as the K_{eq} is greater than one ecf on K_{eq}	1
6(b)(iii)	pK_a 1.23 $HO_2CCO_2H + H_2O \rightleftharpoons HO_2CCO_2^- + H_3O^+$ OR $HO_2CCO_2H \rightleftharpoons HO_2CCO_2^- + H^+$ pK_a 4.19 $HO_2CCO_2^- + H_2O \rightleftharpoons {}^-O_2CCO_2^- + H_3O^+$ OR $HO_2CCO_2^- \rightleftharpoons {}^-O_2CCO_2^- + H^+$	2
6(b)(iv)	pK_a = – logK_a	1

6(g)(i)	K_w = $[D^+][DO^-]$	1
6(g)(ii)	**M1** $[D^+]$ = √1.35 x 10^{-15} = 3.67 x10^{-8} **M2** pH = -log $[D^+]$ = **7.4**(3) min 2sf	2

Q# 202/ Topic: **Chem 25** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(a)	**M1** COOH is more acidic than phenol **AND** because the O-H bond in acid is weaker **OR** carboxylate ion is more stable **M2** O-H bond weakened / loses proton more easily **AND** by negative inductive effect of C=O / due to electronegative C=O **OR** carboxylate ion / anion is more stable **AND** due to delocalisation of minus charge by C=O / 2O	2
5(b)(i)	**M1** a solution which resists changes in pH / controls pH / keeps pH within a small range **M2** when small amounts of H^+ or OH^- are added	2
5(b)(ii)	**M1** no. of mol of gallic acid = 2.04 ÷ 170.0 **OR** 0.012(0) mol **M2** $[H^+] = K_a[HA]/[A^-]$ = 3.89 × 10^{-5} × 0.012/0.250 ÷ 0.0600 = 3.89 × 10^{-5} × (0.048 ÷ 0.0600) = 3.112 × 10^{-5} **M3** pH = –$\log_{10}$ (3.112 × 10^{-5}) = 4.5(1) min 2sf	3
5(b)(iii)	**M1** $C_7H_6O_5 + OH^- \rightarrow C_7H_5O_5^- + H_2O$ **OR** $H^+ + OH^- \rightarrow H_2O$ **AND** $C_7H_6O_5 \rightarrow C_7H_5O_5^- + H^+$ **M2** $C_7H_5O_5^- + H^+ \rightarrow C_7H_6O_5$	2

Q# 203/ Topic: **Chem 25** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(d)(i)	$K_{sp} = [Al^{3+}][F^-]^3$	1
3(d)(ii)	K_{sp} = 6.5 × 10^{-2} × (3 × 6.5 × 10^{-2})^3 = 4.8 × 10^{-4}	1

Q# 204/ Topic: **Chem 25** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	$K_{sp} = [Ag^+]^2[S^{2-}]$	1
5(a)(ii)	• $[S^{2-}]$ = 1.16 × 10^{-17} • $[Ag^+]$ = 2.32 × 10^{-17} • K_{sp} = **6.2(4) × 10^{-51}** minimum 2 sig. fig. correct answer scores 2 marks Award 1 mark for two points, award 2 marks for three points	2
5(a)(iii)	**M1**: moles Ag_2S = 1 / 247.9 = 0.00403 moles [1] 2sf min **M2**: 1.16 × 10^{-17} = 0.0040 / V so V = **3.5 × 10^{14}** (dm^3) [1] 2sf min ecf on M1 correct answer scores 2 marks	2
5(b)(i)	**M1:** $[H^+] = \sqrt{2.0\times10^{-9}\times0.20}$ $[H^+]$ = 2.0 × 10^{-5} (1.9976 × 10^{-5}) **M2:** pH = **4.7** (4.699) minimum 2 sig. fig. min correct answer scores 2 marks	2

5(b)(ii)	**M1: Both equilibria correctly stated** moles KOH = 0.005 × 0.2 = 1 × 10^{-3} moles HOBr(initial) = 0.020 × 0.2 = 4 × 10^{-3} moles HOBr(eqm) = 4 × 10^{-3} – 1 × 10^{-3} = **3 × 10^{-3}** moles BrO^-(eqm) = **1 × 10^{-3}** **M2:** ratio $[OBr^-]/[HOBr]$ = 1/3 $[H^+]$ = 3 × 2.0 × 10^{-9} = 6 × 10^{-9} pH = **8.2(2)** correct answer scores 2 marks	2

Q# 205/ Topic: **Chem 25** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(d)(i)	$K_{a2} = \dfrac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$	1
7(d)(ii)	K_a of H_2SO_4 is larger than K_{a2}	1

7(e)	**M1**: $[H^+]$ = $10^{-2.90}$ = 1.26 × 10^{-3} **M2**: K_a = $[1.26 \times 10^{-3}]^2$ / 0.025 = **6.3 × 10^{-5}** (mol dm^{-3})	2

Q# 206/ Topic: **Chem 25** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	**M1** pH = –log$[H^+]$ **M2** $K_a = [H^+][A^-]/[HA]$	2
3(a)(ii)	**M1** $A^- + H^+ \rightarrow HA$ **OR** $NaA + H^+ \rightarrow HA + Na^+$ **M2** $HA + OH^- \rightarrow H_2O + A^-$	2
3(b)	remaining n(HC*l*O) = 0.17 – 0.03 = 0.14 mol (dm^{-3}) $[H^+]$ = 1.35 × 10^{-7} mol dm^{-3} OR calculate pK_a (7.54) from K_a pH = –log(1.35 × 10^{-7}) = 6.87/ 6.9 OR pH = 7.54 + log(0.03/0.14) = 6.87	3

Q# 207/ Topic: **Chem 25** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(b)(i)	K_{sp} = $[Mg^{2+}(aq)][OH^-(aq)]^2$ OR K_{sp} = (2.0 × 10^{-4})(4.0 × 10^{-4})^2 = 3.2 × 10^{-11}	2
2(b)(ii)	**M1** (white) ppt. / solid (of $BaCO_3$) will appear **M2** due to the common ion effect OR the $BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$ equilibrium shifts to the left	2

Q# 208/ Topic: **Chem 25** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(b)(i)	(K_w =) $[H^+][OH^-]$	1

4(b)(ii)	[1] or each correct tick	2

effect of increasing temperature	decreases	stay the same	increase
pH	✓		
ratio of $[H^+]:[OH^-]$		✓	

4(c)	$[H^+] = 10^{-13.25} = 5.62 \times 10^{-14}$ [1] $[OH^-] = K_w/[H^+] = 1.0 \times 10^{-14}/5.62 \times 10^{-14}$ $[OH^-]$ = **0.18** (0.178) (mol dm^{-3}) [1] ecf correct answer scores [2]	2
4(d)	$HCO_3^- + H^+ \rightarrow H_2CO_3$ OR $HCO_3^- + H^+ \rightarrow CO_2 + H_2O$ [1] $H_2CO_3 + OH^- \rightarrow HCO_3^- + H_2O$ [1]	2
4(e)(i)	$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ [1] acid + base ⇌ base + acid [1]	2
4(e)(ii)	**M1** moles NaOH = 0.15 × 20/1000 = **0.0030** **AND** initial moles CH_3COOH = 0.25 × 30/1000 **OR 0.0075** [1] **M2** equilibrium moles CH_3COOH = **0.0045 AND** equilibrium moles CH_3COONa = **0.0030** [1] **M3** $[CH_3COOH]$ = 0.0045/0.05 = **0.090** AND $[CH_3COONa]$ = 0.003/0.05 = **0.060** $[H^+] = K_a \times [CH_3COOH]/[CH_3COONa] = 2.625 \times 10^{-5}$ [1] **M4** pH = –log$[H^+]$ = **4.6** [1] correct answer scores [4]	4
4(f)(i)	end point = 28 cm^3	1
4(f)(ii)	**M1** reaction **M** bromothymol (blue) / bromocresol (green) **AND** reaction **N** bromothymol (blue) / thymolphthalein [1] **M2** (both indicators have) a pH range / colour change **within** / **in** end-point / vertical region / sharp fall of the graph [1]	2

Q# 209/ Topic: **Chem 25** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(d)(i)	**M1 ratio of the concentrations of solute in two (immiscible) solvents [1]** **M2 at equilibrium [1]**	2
1(d)(ii)	$K_{partition}$ = (x/10)/(1.25-x/50) [1] 4.75(1.25-x) = 5x x = 5.9375/9.75 = **0.61 g** [1] correct answer scores [2]	2

Q# 210/ Topic: **Chem 25** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(c)(i)	the reaction produces sodium hydroxide / hydroxide ions / OH^- ions	1
	the hydroxide ions can receive / accept H^+ ions / protons	1
1(c)(ii)	Calculation of Na_2O moles 3.10 g / 62 OR 0.05	1
	Calculation of $[OH^-]$ 0.05 × (2 / 0.400) = 0.25 mol dm^{-3}	1
	Calculation of pH –log 0.25 = 0.60 14 – 0.60 = 13.40	1

Q# 211/ Topic: **Chem 25** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	(ratio of the) concentrations of a solute in two solvents / liquids at <u>equilibrium</u>	1
4(a)(ii)	$[NH_3]_{aq}$ = 0.1 × 12.5 / 10 = 0.125 mol dm^{-3} $[NH_3]_{CHCl3}$ = 0.1 × 13 / 25 = 0.052 mol dm^{-3} ratio = $K_{partition}$ = 0.052 / 0.125 = 0.416	2
4(a)(iii)	$K_{partition}$ will be larger for butylamine than for ammonia butylamine contains a hydrophobic / non-polar (C_4) group	2

Q# 212/ Topic: **Chem 25** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	$[H^+] = \sqrt{(K_a . c)} = \sqrt{(6.2 \times 10^{-10} \times 0.1)}$ $[H^+] = 7.9 \times 10^{-6}$ pH = –log$[H^+]$ = 5.1(0)	2

Q# 213/ Topic: **Chem 25** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(b)(i)	$K_{sp} = [Sr^{2+}][OH^-]^2$	1
1(b)(ii)	$K_{sp} = (3.37 \times 10^{-2}) \times (6.74 \times 10^{-2})^2 = 1.5 \times 10^{-4}$ units: $mol^3\ dm^{-9}$	2

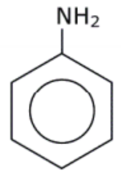
Q# 214/ Topic: **Chem 25** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	it / solubility decreases down the group and K_{sp} decreases	1
2(b)(i)	$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$	1
2(b)(ii)	(white) solid appears / precipitation (of $MgCO_3$)	1
	as $[CO_3^{2-}]$ increases shifting equilibrium to the LHS (precipitating out $MgCO_3$)	1
2(c)	solubility = $\sqrt{1.0 \times 10^{-5}} = 3.16 \times 10^{-3}$ mol dm^{-3}	1
	solubility= $3.2 \times 10^{-3} \times 84.3$ = **0.27** g dm^{-3}	1

Q# 215/ Topic: **Chem 25** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)		1 + 1
	16 electrons on each diagram	1
2(a)(ii)	HNC = 115–125° AND NCO = 180°	1
2(a)(iii)	cyanic acid, because it's a stronger / higher bond enthalpy / triple / C≡N / more electrons involved bond	1
2(b)(i)	$[H^+] = \sqrt{([HNCO]K_a)} = \sqrt{(0.1 \times 1.2 \times 10^{-4})}$ or 3.46×10^{-3}	1
	pH = log $[H^+]$ = **2.5** (2.46)	1
2(b)(ii)	$Na_2CO_3 + 2(NH_2)_2CO \longrightarrow 2NaNCO + CO_2 + 2NH_3 + H_2O$	1
2(c)(i)	($n(OH^-)$ at start = (2 × 0.1 × 30) / 1000 = 6×10^{-3} mol) ($n(OH^-)$ reacted = (0.1 × 20) / 1000 = 2×10^{-3} mol) $n(OH^-)$ remaining = (6–2) × 10^{-3} = 4×10^{-3} mol, (in 50 cm^3)	1
	so $[OH^-]_{end} = (4 \times 10^{-3} \times 1000) / 50$ = **0.08 mol dm^{-3}**	1

2(c)(ii)	$[H^+] = K_w / [OH^-] = (1 \times 10^{-14}) / 0.08 = 1.25 \times 10^{-13}$ mol dm^{-3}	1
	so pH = –log(1.25×10^{-13}) = **12.9**	1
2(c)(iii)	curve starts at 2.46 / 2.5	1
	vertical portion (end point) at vol added = 10.0 cm^3	1
	finishes at pH = 12.9	1
2(d)(i)	*monodentate*: (a species that) forms one dative / coordinate bond	1
	ligand: a species that uses a lone pair of electrons to form a dative / coordinate bond to **a metal atom / metal ion**	1
2(d)(ii)	$[Ag(NCO)_2]^-$ or $[Ag(OCN)_2]^-$ correct formula	1
	correct charge	1
2(e)(i)	$n(BaCO_3)$ =1.66 / 197.3 = 8.4(1) × 10^{-3} mol	1
2(e)(ii)	n(RNCO) = 8.41×10^{-3} mol, so M_r = 1 / (8.41×10^{-3}) = **119**	1
2(e)(iii)	molecular formula = C_7H_5NO	1

2(e)(iv)		1

Q# 216/ Topic: **Chem 25** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(d)(ii)	$K_p = (pNH_3)^2/(pN_2)(pH_2)^3$ $1.45 \times 10^{-5} = (pNH_3)^2 / 20 \times 60 \times 60 \times 60$	1
	$pNH_3 = 7.91$	1

Q# 217/ Topic: **Chem 25** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	moles of thiosulfate = $0.1 \times 20.8/1000 = \mathbf{2.08 \times 10^{-3}}$	1	
	moles of ClO^- in 25 cm³ portion = $2.08 \times 10^{-3}/2 = \mathbf{1.04 \times 10^{-3}}$	1	
	(moles of ClO^- in 250 cm³ $= 1.04 \times 10^{-2}$)		
	concentration of $ClO^- = 1.04 \times 10^{-2}/(10/1000) = \mathbf{1.04}$ (mol dm^{-3})	1	3
7(b)(i)	starch	1	1
7(b)(ii)	blue OR black to colourless	1	1
7(b)(iii)	towards / close to the end-point of the titration / when the solution goes yellow	1	1
7(c)	moles of $O_2 = 82/24\,000 = 3.42 \times 10^{-3}$ = moles ClO^- ions	1	
	concentration of $ClO^- = 3.42 \times 10^{-3}/(5/1000) = \mathbf{0.68/0.683/0.684}$ (mol dm^{-3})	1	2

Q# 218/ Topic: **Chem 25** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(d)(i)	$K_c = \dfrac{[C_3H_3N_3O_3][HClO_3]^3}{[C_3Cl_3N_3O_3][H_20]^3}$	1	1
7(d)(ii)	(position of eqm) moves to the right / forward reaction predominates / more HClO made (as [HClO] decreases)	1	
	no effect on K_c	1	2
7(d)(iii)	$2HClO \rightarrow 2HCl + O_2$ OR $2HClO \rightarrow H_2 + Cl_2 + O_2$	1	1
7(e)(i)	addition of acid: $H^+ + HCO_3^- \rightarrow H_2CO_3$ OR $H^+ + HCO_3^- \rightarrow H_2O + CO_2$	1	
	addition of base: $OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O$ OR $H^+ + OH^- \rightarrow H_2O$ and position of eqm moves to the right OR $OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$	1	2
7(e)(ii)	$K_a = ([H^+][HCO_3^-]/[H_2CO_3])$		
	$[H^+] = (7.94 \times 10^{-7}) \times 1/9.5 = 8.36 \times 10^{-8}$	1	
	$pH = -\log[H^+] = 7.08$	1	2
	Total:		16

Q# 219/ Topic: **Chem 25** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i)	$pK_a = -\log K_a$	[1]
(ii)	diacids are more acidic than CH_3CO_2H	[1]
	HO_2C- group is electron-withdrawing, stabilising the monoanion OR HO_2C- group is electron-withdrawing, weakening the O–H bond OR monoanion is stabilised by H-bonding	[1]
	as n increases, the electron–withdrawing group is further away from the ionising CO_2H group OR the (intervening) alkyl groups destabilise the anion	[1]
(iii)	removing H^+ from an anion is not electrostatically favourable	[1]
(b) (i)	a solution which *resists* changes in pH when *small* amounts of H^+ or OH^- are added	[1] [1]
(ii)	$HO_2CCH_2CH_2CO_2Na + H^+ \rightarrow HO_2CCH_2CH_2CO_2H + Na^+$ $HO_2CCH_2CH_2CO_2Na + NaOH \rightarrow NaO_2CCH_2CH_2CO_2Na + H_2O$	[1] [1]
		[Total: 9]

Q# 220/ Topic: **Chem 25** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a)	$K_p = \{p(CS_2) \times (p(H_2))^4\}/\{(p(H_2S))^2 \times p(CH_4)\}$ units: atm² OR Pa²	[1] [1]
(b) (i)	$p(H_2S)$ = 196 atm $p(H_2)$ = 8 atm	[1] [1]
(ii)	$K_p = (2 \times 8^4)/(196^2 \times 98) = 2.176 \times 10^{-3}$	[1]

Q# 221/ Topic: **Chem 25** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmasehingScience.org

(ii)	acid / proton donor / acidic behaviour	1

Q# 222/ Topic: **Chem 25** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(c) (i)	equilibrium constant (for the solution) of a solute between two (immiscible) solvents ***or*** ratio of the concentration of the solute in (each of the) two solvents ***or*** ratio of the solubility of the solute in (each of the) two solvents	1
(ii)	$\dfrac{x/(25/1000)}{(0.0042-x)/(25/1000)}$ $x = 0.0252 - 6x$	1
	$x = \mathbf{0.0036g}$	1
		[Total: 10]

Q# 223/ Topic: **Chem 25** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (i)	$K_{sp} = [Ag^+(aq)]^2[SO_4^{2-}(aq)]$ **and** units: mol³dm^{-9}	1
(ii)	$K_{sp} = (2 \times 0.025)^2 \times (0.025) = \mathbf{6.25 \times 10^{-5}}$	1

Q# 224/ Topic: **Chem 25** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d)	$[Fe^{3+}(aq)] = 0.2$ mol dm^{-3}	1
	$[H^+] = \sqrt{(c.K_a)} = \sqrt{(0.2 \times 8.9 \times 10^{-4})}$ or 1.33×10^{-2} (mol dm^{-3}) $pH = -\log([H^+]) = \mathbf{1.9}$ *(or 1.87–1.89)*	1
		[Total: 13]

Q# 225/ Topic: **Chem 25** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(d) (i)	$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$	1	

(ii)	$[Ca^{2+}]$ = 3 × 2.50 × 10^{-6} = 7.50 × 10^{-6} mol dm^{-3} $[PO_4^{3-}]$ = 2 × 2.50 × 10^{-6} = 5.00 × 10^{-6} mol dm^{-3}	1	
	= $(7.50 \times 10^{-6})^3(5.00 \times 10^{-6})^2$ = **1.05(1.1) × 10^{-26}**	1	
	$mol^5 dm^{-15}$	1	[4]

Q# 226/ Topic: **Chem 25** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) **(i)** $K_w = [H^+][OH^-]$ [1]

(ii) In 0.15 mol dm^{-3} NaOH, $[OH^-]$ = 0.15 mol dm^{-3}
$[H^+] = K_w/[OH^-]$, so $[H^+]$ = 1 × 10^{-14}/0.15 = 6.67 × 10^{-14} mol dm^{-3} [1]
pH = $-\log_{10}[H^+]$ = **13.18 (13.2)** ecf from $[H^+]$ [1]

(iii) piperidine is a poorer proton acceptor
or piperidine is partially ionised [1]

(d) **(i)** n(HC*l*) at start = 0.1 × 20/1000 = 2.0 × 10^{-3} mol
n(HC*l*) at finish = 2 × 10^{-3} – 1.5 × 10^{-3} = **0.0005/5 × 10^{-4}** mol [1]

(ii) this is in 30 cm^3 of solution, so [HC*l*] at finish = 0.5 × 10^{-3}/0.030 = 1.67 × 10^{-2} mol dm^{-3}
pH = $-\log_{10}(1.67 \times 10^{-2})$ = **1.78** ecf from **(d)(i)** [1]

(iii) pH / vol curve: start at pH 11.9 [1]
vertical portion at V = 15 cm^3 [1]
levels off at pH 1.8 [1]

(iv) indicator is **B** [1]

Q# 227/ Topic: **Chem 25** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) Ratio of the <u>concentration</u> of a solute in each of two (immiscible) solvents
or equilibrium constant representing the distribution of a solute between two solvents
or PC = $[X]_a/[X]_b$ (at a constant temperature) [1]

[1]

(d) **(i)** K_{pc} = [Z in ether]/[Z in H_2O] – allow reverse ratio
40 = (x/0.05)/((4–x)/0.5) [1]

= **3.2 g** ecf [1]

(ii) First extraction
40 = (x/0.025)/((4–x)/0.5)
x = **2.67 g** ecf [1]

(iii) Second extraction: 1.33g remain in solution
Second extraction
40 = (y/0.025)/((1.33–y)/0.5)
y = **0.887 g**

mass extracted = 2.67 + 0.89 = **3.56/3.6 g** ecf [1]

[4]

Q# 228/ Topic: **Chem 25** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(c) **(i)** a solution that resists changes in pH [1]

when small quantities of acid or base/alkali are added [1]

(ii) in the equilibrium system HZ + H_2O ⇌ Z^- + H_3O^+ [1]

addition of acid: reaction moves to the left
or H^+ combines with Z^- <u>**and**</u> forms HZ [1]

addition of base: the reaction moves to the right
or H^+ combines with OH^- <u>**and**</u> more Z^- formed [1]

[5 max 4]

(d) **(i)** $[H^+] = \sqrt{(0.5 \times 1.34 \times 10^{-5})} = 2.59 \times 10^{-3}$ (mol dm^{-3}) [1]

pH = **2.59/2.6** (min 1 d.p) ecf [1]

(ii) $CH_3CH_2CO_2H + NaOH \longrightarrow CH_3CH_2CO_2Na + H_2O$ [1]

(iii) n(acid) in 100 cm^3 = 0.5 × 100/1000 = 0.05 mol
n(acid) remaining = 0.05 – 0.03 = 0.02 mol
[acid remaining] = **0.2** (mol dm^{-3}) [1]

likewise, n(salt) = 0.03 mol
[salt] + **0.3** (mol dm^{-3}) [1]

(iv) pH = 4.87 + log(0.3/0.2) = **5.04–5.05** ecf [1]

[6]

Q# 229/ Topic: **Chem 25** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(iii) $K_c = [Fe^{2+}]^2[I_2]/[Fe^{3+}]^2[I^-]^2$ [1]

units are **mol^{-1} dm^3** ecf on expression [1]

(iv) ($[Fe^{2+}]$ must always be twice $[I_2]$, so) $[Fe^{2+}]$ = 0.02 (mol dm^{-3}) [1]

($[I^-]$ must always be equal to $[Fe^{3+}]$, so) $[I^-]$ = 2 × 10^{-4} (mol dm^{-3}) [1]

(v) $K_c = \{(0.02)^2 \times 0.01\} / \{(2 \times 10^{-4})^2 \times (2 \times 10^{-4})^2\}$ correct expression [1]
(allow ecf from incorrect expression in **(c)(iii)**)
(allow ecf from **(c)(iv)**)
= $(4 \times 10^{-6}) / (1.6 \times 10^{-1.5}) = 2.5 \times 10^9$ (mol^{-1} dm^3) [1]
[8]

Q# 230/ Topic: **Chem 25** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) **(i)** Ratio of the <u>concentration</u> of a solute in each of two solvents
or equilibrium constant representing the distribution of a solute between two solvents. [1]

(ii) illustration of some method of getting into our body via the food chain [1]

They dissolve preferentially in fats/oils [1]
[3]

Q# 231/ Topic: **Chem 25** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i) One that can go in either direction. [1]

(ii) both forward & reverse reactions are going on at the same time, but the concentrations of all species do not change (owtte)
or rate of forward = rate of backward reaction [1]

(b) (i) $K_c = [H^+][OH^-]/[H_2O]$ [1]

(ii) $K_w = [H^+][OH^-]$ [1]
rearrangement of equation in **(i)** gives $K_c[H_2O] = [H^+][OH^-]$ & $K_w = K_c[H_2O]$ (owtte) [1]
or the $[H_2O]$ is contained within K_w [1]

(iii) K_w will be higher in hot water **because** reaction is endothermic [1]

(c) (i) $[OH^-] = 5 \times 10^{-2}$; $[H^+] = (1 \times 10^{-14})/ 5 \times 10^{-2} = \mathbf{2 \times 10^{-13}}$ [1]
pH $= -\log_{10}[H^+] =$ **12.7** (correct ans = [2]) ecf [1]

(ii) $[NH_4^+] = [OH^-]$ (= x) [1]
$x^2 = 1.8 \times 10^{-5} \times 0.05 \Rightarrow x (= [OH^-]) = \mathbf{9.49 \times 10^{-4}}$ (mol dm^{-3}) (correct ans = [2]) [1]

(iii) $[H^+] = K_w/[OH^-] = (1 \times 10^{-14})/ 9.49 \times 10^{-4} = \mathbf{1.05 \times 10^{-11}}$ (mol dm^{-3}) ecf [1]

(iv) pH = **11.0** ecf [1]

[Total: 12 max 11]

Q# 232/ Topic: **Chem 25** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c) (i) $K_{sp} = [Pb^{2+}][Cl^-]^2$ (1) units = mol^3 dm^{-9} (1)

(ii) if $[Pb^{2+}] = x$, $K_{sp} = 4x^3$, so $x = \sqrt[3]{K_{sp}/4}$
$[Pb^{2+}] = \sqrt[3]{2 \times 10^{-5}/4} = \mathbf{1.71 \times 10^{-2}}$ mol dm^{-3} (1)

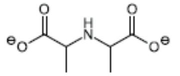
(iii) $[Pb^{2+}] = 2 \times 10^{-5}/(0.5)^2 = \mathbf{8.0 \times 10^{-5}}$ mol dm^{-3} (1)

(iv) common ion effect, or increased $[Cl^-]$ forces solubility equilibrium over to the left (1)

[Max 4]

[Total: 10]

Q# 233/ Topic: **Chem 26** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(c)(ii)	evidence on graph / paper of one half-life (use of data) / $t_{1/2}$ = 500 s [1] **constant half-life** (= first order) [1]	2
5(c)(iii)	so that $[NH_3]$ is (effectively) constant **AND** doesn't affect the rate / zero order	1
5(c)(iv)	M1: when $[NH_3]$ increases ×1.5, rate increase ×1.5 **AND** first order (w.r.t. $[NH_3]$) / rate is proportional to $[NH_3]$ M2: S_N2 **DEP on M1** (because rate is first order w.r.t. to [2-chloropropanoate] and $[NH_3]$)	2
5(c)(v)	greater proportion of particles have $E \geqslant E_A$ [1] frequency of (effective) collisions increases **AND** rate increases OR rate of collisions increases AND rate increases [1]	2
5(c)(vi)		1

Q# 234/ Topic: **Chem 26** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)	measure volume / amount of oxygen formed / mass lost / and time / against time / per unit time OR measure absorbance / transmission against time / per unit time	1
5(b)(i)	time taken for the concentration / mass / amount of a reactant to fall to half (its original value) / to halve	1
5(b)(ii)	$t_{1/2}$ = 150 s **AND** evidence on graph / paper of one half-life	1
5(b)(iii)	no change	1
5(c)(i)	**M1:** evidence on graph of tangent **AND** 4 to 5 × 10^{-4} **M2:** mol dm^{-3} s^{-1}	2
5(c)(ii)	**(c)(i) / 0.10 AND s^{-1}**	1
5(d)	**M1:** $NO_2 + O_3 \rightarrow NO_3 + O_2$ **M2:** $NO_2 + NO_3 \rightarrow N_2O_5$	2

Q# 235/ Topic: **Chem 26** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(d)(i)	**M1**: first order w.r.t. H_2O_2 **AND** change in conc. × 1.5 gives increase rate × 1.5 (expts 3 / 4) **M2**: first order w.r.t. IO_3^- **AND** change in conc. × 2 gives increase rate × 2 (as reaction first order w.r.t. H_2O_2) (expts 1 / 3) **M3**: zeroth order w.r.t. H^+ **AND** change in conc. has no effect on rate (expts 1 / 3 / 4 and 2)	3
3(d)(ii)	rate = $k[H_2O_2][IO_3^-]$ ecf	1
3(d)(iii)	**M1**: $k = 8.82 \times 10^{-5} \div (0.150 \times 0.140) = 4.20 \times 10^{-3}$ min 2sf ecf **M2**: mol^{-1} dm^3 s^{-1} ecf	2

Q# 236/ Topic: **Chem 26** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	the order of reaction with respect to [NO]: 2 the order of reaction with respect to [O2]: 1 the overall order of reaction: 3 ALL CORRECT [1]	1
1(b)(i)	$k = (1.51 \times 10^{-4}) / (0.003^2 \times 0.00200)$ k = 8389 [1] min 2sf mol^{-2} dm^6 s^{-1} [1]	2
1(b)(ii)	$8400 = (6.05 \times 10^{-5}) / (x^2 \times 0.005)$ $x = \sqrt{(6.05 \times 10^{-5}) / (8400 \times 0.005)}$ x = **0.00120 / 1.20** × **10^{-3}** [1] min 2sf ecf from Q1bi	1
1(c)	slow(est) [1]	1
1(d)(i)	**correct RDS identified** as step 1 with <u>only</u> **one $S_2O_8^{2-}$ and one I^-** [1] overall mechanism adds up to chemical equation and no cancellable species on LHS / RHS in each of the equations [1] **M2 DEP** on one $S_2O_8^{2-}$ and one I^- in step 1 e.g. step 1 $S_2O_8^{2-} + I^- \rightarrow SO_4^{2-} + SO_4I^-$ RDS = step 1 step 2 $SO_4I^- + I^- \rightarrow SO_4^{2-} + I_2$	2
1(d)(ii)	no. of $t_{1/2}$ = 192 / 48 = 4 $[I^-] = 0.0078 / 16 = \mathbf{4.9 \times 10^{-4}}$ [1] min 2sf	1

Q# 237/ Topic: **Chem 26** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(b)	rate = $2.0 \times 10^{-6} \times 0.75 = \mathbf{1.5 \times 10^{-6}}$	1
9(c)(i)	slowest step in overall reaction	1
9(c)(ii)	$H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ OR $H_2O_2 + 2HI \rightarrow I_2 + 2H_2O$	1
9(c)(iii)	H_2O_2 = 1 AND I^- = 1 AND H^+ = 0	1

Q# 238/ Topic: **Chem 26** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(b)(i)	$2AuCl_3 + 3H_2O_2 \rightarrow 2Au + 3O_2 + 6HCl$	1
3(b)(ii)	**M1** 1st order w.r.t. $AuCl_3$ because rate ×2 / doubles when concentration ×2 / doubles **M2** First order H_2O_2 × 2; $AuCl_3$ × 3 rate × 6 so order = 1 for H_2O_2 **M3** rate = $k\,[AuCl_3]\,[H_2O_2]$	3
3(b)(iii)	$k = 1.53 \times 10^{-1} / (0.10 \times 0.50) = 3.06$ $dm^3\,mol^{-2}\,minute^{-1}$	2

Q# 239/ Topic: **Chem 26** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(b)(i)	(rate =) $k[ClNO_2][NO]$	1
2(b)(ii)	$mol^{-1}\,dm^3\,s^{-1}$	1
2(b)(iii)	Yes **AND** number of moles of reactants in overall equation is the same as order in rate equation	1
2(c)(i)	• straight line with a negative gradient • starting at 2.0×10^{-4} • reaches at 1.8×10^{-4} at 0.2 seconds Award 1 mark for two points, award 2 marks for all three points	2
2(c)(ii)	2×10^{-5} ($mol\,dm^{-3}$)	1
2(c)(iii)	The reaction has reached equilibrium	1

Q# 240/ Topic: **Chem 26** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	**M1**: using expt 2 and 3, $[NH_3]$ × 2, rate × 4 so order with respect to $[NH_3]$ = 2 **M2**: using expt 1 and 2, $[ClO^-]$ × 2 and $[NH_3]$ × 2, as rate × 8 (=2^2 * x) so order with respect to $[ClO^-]$ = 1	2
5(a)(ii)	rate = $k[NH_3]^2[ClO^-]$	1
5(a)(iii)	**M1:** $k = 0.256 / (0.200 \times 0.100^2)$ $k = 128$ **M2:** Units $dm^6\,mol^{-2}\,s^{-1}$	2

5(a)(iv)	curve / line showing *k* increasing as temperature increases	1
5(b)(i)	**M1:** plot a graph of $[I^-]$ against time **M2:** constant half-lives	2
5(b)(ii)	$ClO^- + I^- \rightarrow IO^- + Cl^-$	1

Q# 241/ Topic: **Chem 26** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	change in amount / mass / concentration of reactant / product per time	1
2(b)	decrease in volume or pressure	1
2(c)	8.13×10^4 / 81280 / 81300	1
	$mol^{-2}\,dm^6\,s^{-1}$	1
2(d)	$\sqrt{}(0.00231 / (0.0046 \times 81280)) = 2.49 \times 10^{-3}$	1
2(e)	2, 1, 3	1
2(f)(i)	2	1
2(f)(ii)	the total of steps 1 and 2 / the components of 2 are two NO and one H_2	1
2(g)(i)	time for amount or mass or concentration to halve	1
2(g)(ii)	0.02 at start and 0.01 after 2 seconds	1
	0.005 after 4 seconds and 0.0025 after 6 seconds	1
2(h)(i)	$NO + \frac{1}{2}O_2 \rightarrow NO_2$ or $NO + O_2 \rightarrow NO_2 + \frac{1}{2}O_2$ **AND** $NO_2 + SO_2 \rightarrow NO + SO_3$	1
2(h)(ii)	(NO is) regenerated / reformed	1
2(h)(iii)	$SO_3 + H_2O \rightarrow H_2SO_4$ **AND** acid rain or consequence of this described	1

Q# 242/ Topic: **Chem 26** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

<table>
<tr><td>4(f)</td><td>
<table>
<tr><th></th><th>heterogeneous</th><th>homogeneous</th></tr>
<tr><td>Fe in the Haber process</td><td>✓</td><td></td></tr>
<tr><td>Fe²⁺ in the I[−] / S₂O₈^{2−} reaction</td><td></td><td>✓</td></tr>
<tr><td>NO₂ in the oxidation of SO₂</td><td></td><td>✓</td></tr>
<tr><td>V₂O₅ in the Contact process</td><td>✓</td><td></td></tr>
</table>
</td><td>2</td></tr>
</table>

Q# 243/ Topic: **Chem 26** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

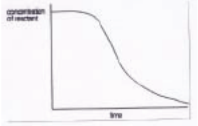
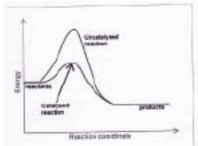
1(c)(i)	the power to which a concentration of a reactant is raised in the rate equation	1
1(c)(ii)	using expt. 2 and 3 a = 2 or [NO] 2nd order and conc × 3 rate × 9 or $6.1 \times 10^{-2} / 6.8 \times 10^{-3} = (0.09/0.03)^a$	1
	using expt. 1 and 2 b = 1 or $[Br_2]$ 1st order and conc × 2 rate × 2 or $6.8 \times 10^{-3} / 3.4 \times 10^{-3} = (0.04/0.02)^b$	1
(c)(iii)	initial rate = 0.16(32)	1
1(c)(iv)	$(0.0034 = k(0.03)^2(0.02))$ k = 188.9	1
	$mol^{-2}\,dm^6\,s^{-1}$	1
1(c)(v)	*k* decreases (as rate decreases)	1

1(d)	m = 2 and n = 0	1

Q# 244/ Topic: **Chem 26** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)	Any of the three methods possible. Any 4 of the 5 points for each method available for maximum 4 marks. Method 1 1 Ensure both solutions (A and B) at 40 °C before mixing 2 mix known volumes of A and B and start the clock 3 at known time take out a sample / X and add it to ice-cold solvent 4 titrate against HCl 5 repeat at time at known time intervals Method 2 1 Ensure both solutions (A and B) at 40 °C before mixing 2 mix known volumes of A and B and start the clock 3 at known time pour into ice-cold solvent or pour ice-cold solvent in 4 titrate against HCl 5 repeat with different concentrations of either A or B, or repeat using different times Method 3 1 Ensure both solutions (A and B) at 40 °C before mixing 2 mix known volumes of A and B and start the clock and add pH meter 3 at a known time . . . . 4 . . . . record the pH 5 repeat pH readings at known time intervals	4
6(b)(i)	from 1 and 3: when [RCl] is trebled, so is rate, so order w.r.t. [RCl] = 1	1
	from 1 and 2: when both concentrations are doubled, rate doubles so $[OH^-]$ has no effect on rate, so order w.r.t. $[OH^-]$ = 0	1
6(b)(ii)	rate = *k*[RCl] AND units: sec^{-1} 1 / s	1
6(b)(iii)	relative rate = 2.0	1

Q# 245/ Topic: **Chem 26** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

<table>
<tr><td>4(a)(i)</td><td>experiments 1 and 2: doubling [ClO$_2$] quadruples the rate, so second order</td><td></td><td>1</td></tr>
<tr><td></td><td>experiments 2 and 3: doubling [OH$^-$] doubles the rate, so first order</td><td></td><td>1</td></tr>
<tr><td></td><td>rate equation = k[ClO$_2$]^2[OH$^-$]</td><td></td><td>1</td></tr>
<tr><td>4(a)(ii)</td><td>from experimen t 2: $9.34 \times 10^{-4} = k(2.50 \times 10^{-2})^2 \times 1.30 \times 10^{-3}$
$k = 1.15 \times 10^3$</td><td></td><td>1</td></tr>
<tr><td></td><td>units: mol^{-2}dm^6 s^{-1}</td><td></td><td>1</td></tr>
<tr><td>4(b)(i)</td><td>heterogeneous catalysts are in different physical state from the reactants AND homogeneous catalysts are in the same physical state as the reactants</td><td></td><td>1</td></tr>
<tr><td>4(b)(ii)</td><td><table>
<tr><th>catalysed reaction</th><th>heterogeneous</th><th>homogeneous</th></tr>
<tr><td>manufacture of ammonia in the Haber process</td><td>✓</td><td></td></tr>
<tr><td>removal of nitrogen oxides from car exhausts</td><td>✓</td><td></td></tr>
<tr><td>oxidation of sulfur dioxide in the atmosphere</td><td></td><td>✓</td></tr>
</table></td><td></td><td>2</td></tr>
<tr><td>4(c)(i)</td><td>$2MnO_4^- + 6H^+ + 5(CO_2H)_2 \rightarrow 2Mn^{2+} + 10\ CO_2 + 8\ H_2O$
correct Mn : (CO$_2$H)$_2$ ratio
rest of equation</td><td>
1
1</td><td>2</td></tr>
<tr><td>4(c)(ii)</td><td>first section: flatter
second section: steeper, before flattening
 </td><td>1
1</td><td>2</td></tr>
<tr><td>.4(d)(i)</td><td>
diagram
catalyst lowers E$_a$ for both the forward and reverse reactions
so the process requires less energy/can occur at a lower temperature</td><td>1
1
1</td><td>3</td></tr>
</table>

Q# 246/ Topic: **Chem 26** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (i)	1st order	1
(ii)	1st order	1
(iii)	rate = k[CH$_3$CHO][OH$^-$]	1
(iv)	mol^{-1} dm^3 s^{-1} (or per any suitable time unit)	1
(v)	calculation from candidate's answer to **(iii)** (expected answer = 6)	1
(b) (i)	rate-determining step: step 1 explanation: both reactant species are in step 1 / rate-determining step	1 1

Q# 247/ Topic: **Chem 26** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

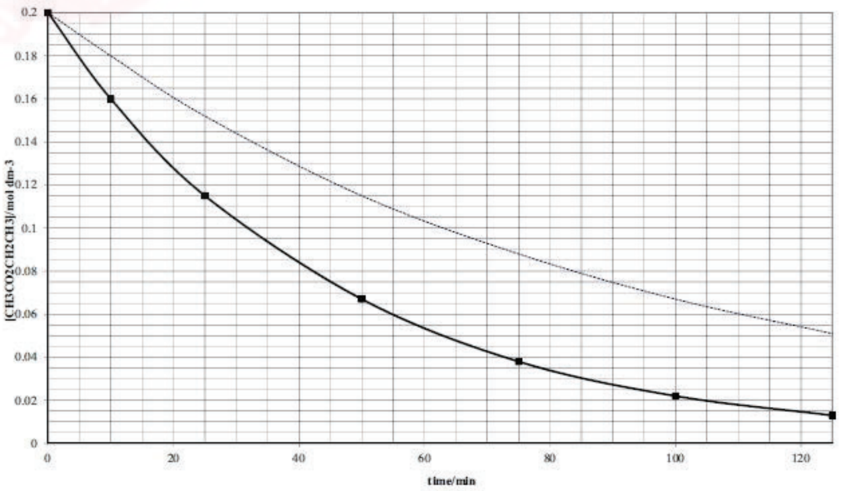
(b) (i)	time taken for the concentration of a reactant(s) to fall to half its original value	1
(ii)	evidence of a pair of construction lines on graph **and** $t_{½}$ = 49–53 s	1
(iii)	no effect/ change	1
(c) (i)	evidence of tangent at 80 s **and** data used, e.g. 0.42/ 152 = 0.00263 units mol dm^{-3} s^{-1}	2
(ii)	correct use of answer to (i)/0.19 **and** s^{-1}	1
		<u>9</u>

Q# 248/ Topic: **Chem 26** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) (i)	[NO] 2nd order **and** the concentration is ×2, rate × 4 [O$_2$] 1st order **and** evidence of using expt 1 & 2 when the concentration is ×2, rate doubles	1 1	
(ii)	(0.00408 × 27) rate = <u>**0.11**</u> (mol dm^{-3} s^{-1}) to **2sf**	1	
(iii)	(Rate =) k [O$_2$][NO]^2	1	
(iv)	k = 332(.03125) mol^{-2} dm^6 s^{-1}	1 1	[6]
(b) (i)	labelled axes *x*-axis: energy (KE) and *y*-axis: molecules or particles two curves: starts origin; not touching *x*-axis again; no levelling out; curves only intersecting once curves labelled and T2 is to the right and lower max than T1	1 1 1	
(ii)	rate increases **and** energy of the particles increases more particles have E_a	1 1	[5]
(c)	1 mole of F$_2$ and 1 mole NO reacting in the **slow** step a balanced mechanism consistent with overall equation e.g. $F_2 + NO \rightarrow NOF + F$ **OR** $F_2 + NO \rightarrow NOF_2$ $NO + F \rightarrow NOF$ $NO + NOF_2 \rightarrow 2NOF$	1 1	[2]
Total			[13]

Q# 249/ Topic: **Chem 26** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i)



plotting of points (–1 for any error – plotted to within ½ square) [1]
a good best fit curve [1]

(ii) construction lines for two half-lives **and** $t_{½} \approx 63$ m or 32 m (±3 min) / $t_{½}$ is constant
or
construction lines for two tangents **and** mention of two values / concentration doubled, rate doubled [1]

(iii) *either* ratio of (initial) rates (slopes) *or* ratio of $t_{½} = 2.0$ [1]

so reaction is first order w.r.t. [HC*l*] [1]

(iv) rate = k[$CH_3CO_2CH_2CH_3$][HC*l*] conditional on **(a)(iii) and** ecf from **(a)(iii)** [1]

(initial) rate = 0.2/95 *or* 0.2/47
$\approx 2.1 \times 10^{-3}$ *or* 4.3×10^{-3} (mol dm^{-3} min^{-1}) [1]

$k = 2.1 \times 10^{-3} / (0.2 \times 0.1)$ *or* $4.3 \times 10^{-3} / (0.2 \times 0.2)$
≈ 0.11 (mol^{-1} dm^3 min^{-1}) [1]
[8 max 7]

(b) (i) because H_2O is the solvent *or* its concentration cannot change [1]

(ii) because HC*l* is a catalyst [1]
[2]

[Total: 9]

Q# 250/ Topic: **Chem 26** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a) (i) heterogeneous: different states **<u>AND</u>** homogeneous: same state [1]

(ii) the correct allocation of the terms *heterogeneous* and *homogeneous* to common catalysts [1]

example of heterogeneous, e.g. Fe (in the Haber process) <u>linked</u> to correct system [1]
equation, e.g. $N_2 + 3H_2 \longrightarrow 2NH_3$ [1]

how catalyst works, adsorption (onto the surface) [1]
ecf for non-iron catalyst

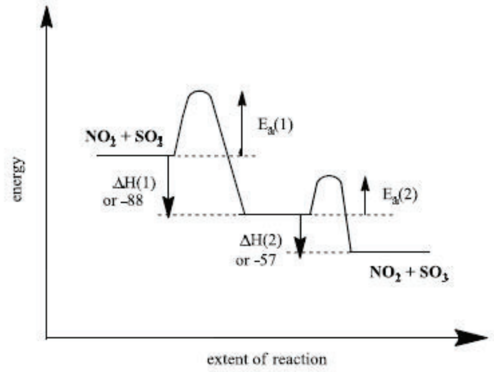
example of homogeneous, e.g. Fe^{3+} or Fe^{2+} (in $S_2O_8^{2-} + I^-$) linked to correct system [1]

equation, e.g. $S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$ [1]

how catalyst works, e.g. $Fe^{3+} + I^- \longrightarrow Fe^{2+} + ½I_2$ [1]
ecf for non-iron catalyst

[8]

(b)



both E_a shown, with $E_a(1) > E_a(2)$ [1]
both ΔH shown, with $\Delta H(1) > \Delta H(2)$ [1]
[2]

[Total: 10]

Q# 251/ Topic: **Chem 26** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(b) (i) (from 1 and 2:) as p(NO) halves, rate decreases to ¼ , **so order = 2** [1]
(from 1 and 3:) as $p(H_2)$ halves, so does rate, **so order = 1** [1]

(ii) rate = $k\, p_{NO}{}^2 . p_{H2}$ [1]
units (of k) are atm^{-2} s^{-1} [1]

(iii) add all three equations:
$NO + NO + H_2 + O + H_2 + N_2O \rightarrow N_2O + O + H_2O + N_2 + H_2O$ [1]
cross out all species common to both sides:
$NO + NO + H_2 + \cancel{O} + H_2 + \cancel{N_2O} \rightarrow \cancel{N_2O} + \cancel{O} + H_2O + N_2 + H_2O$ [1]
($\Rightarrow$ $2NO + 2H_2 \rightarrow N_2 + 2H_2O$)

(iv) *either:* **step 2** since it involves H_2 [1]
O formed from NO [1]
or: ***step 3*** *since it involves H_2* *[1]*
N_2O formed from NO *[1]*
[8]

Q# 252/ Topic: **Chem 26** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i) Order w.r.t. [CH_3CHO] = 1 [1]
Order w.r.t. [CH_3OH] = 1 [1]
Order w.r.t. [H^+] = 1 [1]

(ii) rate = k[CH_3CHO][CH_3OH][H^+] [1]

(iii) units = mol^{-2} dm^6 s^{-1} [1]

(iv) rate will be 2 × 4 = 8 times as fast as reaction 1 (relative rate = 8) [1]
[6]

(b)

	$[CH_3CHO]$ /mol dm^{-3}	$[CH_3OH]$ /mol dm^{-3}	$[H^+]$ /mol dm^{-3}	[acetal **A**] /mol dm^{-3}	$[H_2O]$ /mol dm^{-3}
at start	0.20	0.10	0.05	0.00	0.00
at equilibrium	(0.20 – x)	***(0.10 – 2x)***	***0.05***	x	***x***
at equilibrium	***0.175***	***0.05***	***0.05***	0.025	***0.025***

(i) 3 values in second row 3 x [1]

(ii) 4 values in third row 4 x [1]

(iii) $K_c = \{[\text{acetal } \mathbf{A}][H_2O]\}/\{[CH_3CHO][CH_3OH]^2\}$ [1]
units = $mol^{-1}dm^3$ [1]

(iv) $K_c = 0.025^2/(0.175 \times 0.05^2) = \mathbf{1.4(3)}\ (mol^{-1}\ dm^3)$ [1]

[max 9]

[Total: 15]

Q# 253/ Topic: **Chem 26** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) (i) SO_3 produces acid rain [1]

(ii) $NO + ½ O_2 \rightarrow NO_2$ [1]

(iii) $K_p = (p_{NO} \cdot p_{SO_3})/(p_{NO_2} \cdot p_{SO_2})$ [1]
units: dimensionless/none (don't accept just a blank!) [1]

(iv) $K_p = 99.8^2/0.2^2 = \mathbf{2.5 \times 10^5}$ [1]

(v) It will shift to the right (owtte) [1]
because the reaction is exothermic. NOT just Le Chatelier argument [1]

[Total: 11]

Q# 254/ Topic: Chem 27 ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	• barium carbonate / Ba / $BaCO_3$ • larger ionic radius OR smaller charge density of cation / M^{2+} [1] • anion / CO_3^{2-} / carbonate ion is less distorted / less polarised OR C-O / C=O less weakened [1]	2
4(b)	• calcium oxide / calcium hydroxide • $CaSO_4$ / calcium **sulfate** is more soluble OR $BaSO_4$ is less soluble [1] • ΔH_{latt} and ΔH_{hyd} are less exothermic / more endothermic (for $BaSO_4$) [1] • ΔH_{hyd} is dominant factor / ΔH_{hyd} change is greater OR ΔH_{latt} changes less [1]	3
4(c)(i)	mass of CO_2 = 0.02 × 44 = 0.88 g [1]	1
4(c)(ii)	(writes correct equation, deduces 3 CO_2 per mole) moles of propane = 0.02 / 3 OR 0.00667 OR 1 / 150 [1] mass of propane = 0.02 / 3 × 44 = 0.293 g [1] ecf M1 × 44 3sf needed	2

Q# 255/ Topic: **Chem 27** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(d)(ii)	$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$	1

Q# 256/ Topic: **Chem 27** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	**M1:** increases down the group **M2:** radius / size of (cat)ion / M^{2+} increases **M3:** less polarisation / distortion of anion / hydroxide ion / hydroxide group / OH^- / OH	3

Q# 257/ Topic: **Chem 27** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)	Co^{2+} = [Ar] $3d^7$ ($4s^0$) Co^{3+} = [Ar] $3d^6$ ($4s^0$)	1
1(b)	**M1/2:** Any two of: • Co^{3+} is **reduced** Co^{2+} • oxygen gas/O_2 is evolved • *E* of Co^{3+} **greater** than *E* of O_2 **M3:** no change (to $[Co(edta)]^-$) / not feasible **OWTTE**	3
1(c)	Any two of VISUAL observations: • condensation on tube / steam evolved • **brown** fumes / brown gas evolved • O_2 formed that relights a glowing splint • (solid) dissolves / turns to liquid	2

Q# 258/ Topic: **Chem 27** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(d)	**M1:** cationic radius / ion size increases (down the group) **M2:** less polarisation / distortion of nitrate ion / anion / NO_3^-	2

Q# 259/ Topic: **Chem 27** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(b)(ii)	**M1** (solubility) increases (down the group) [1] **M2** both ΔH_{latt} and ΔH_{hyd} become less exothermic / less negative [1] **M3** ΔH_{latt} changes more / is dominant factor [1] **M4** ΔH_{sol} becomes more negative / more exothermic [1]	4

Q# 260/ Topic: **Chem 27** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	**M1** solubility increases down the group **M2** ΔH_{latt} and ΔH_{hyd} both become less exothermic / less negative **M3** ΔH_{latt} changes **more** (than ΔH_{hyd} as OH^- being smaller than M^{2+}) **M4** ΔH_{sol} becomes more exothermic / more negative	4
2(a)(ii)	**M1** $Mg(OH)_2$ **AND** Mg^{2+} has a smaller ionic radii/ Mg^{2+} has a higher charge density **M2** OH^- ion is polarised/distorted more	2

Q# 261/ Topic: **Chem 27** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	**M1** (thermal stability) increases (down the group) **M2** size / radius of metal ion/M^{2+} increases **M3** polarisation / distortion of anion / CO_3^{2-} decreases	3
2(a)(ii)	**M1** lattice energy **AND** hydration enthalpy become less exothermic **M2** hydration enthalpy / ΔH_{hyd} becomes less exothermic more **M3** enthalpy change of solution / ΔH_{sol} becomes less exothermic / more endothermic	3

Q# 262/ Topic: **Chem 27** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(b)(iii)	**M1:** more stable (down the group) **M2:** cationic radius **increases** / charge density of M^{2+} decreases (down the group) **M3:** NO_3^- anion is less polarised / distorted	3
6(c)	**M1:** less soluble / decreases (down the group) **M2:** ΔH_{latt} and ΔH_{hyd} **both** decrease / less exothermic down the group **M3:** ΔH_{hyd} decreases by more (than ΔH_{latt}) **M4:** ΔH_{sol} becomes more endothermic / less exothermic	4

Q# 263/ Topic: **Chem 27** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	$Sr(NO_3)_2 \rightarrow SrO + 2NO_2 + ½O_2$	1
2(b)	**M1** increases **M2** cationic radius / ion size **increases** (down the group) **M3** less polarisation/distortion of anion / nitrate ion / NO_3^- / nitrate group	3
2(c)(i)	more readily **and** Ca^{2+} has a smaller ionic radius or more readily **and** Ca^{2+} has a greater charge density	1
2(c)(ii)	$3Ba(NH_2)_2 \rightarrow Ba_3N_2 + 4NH_3$	1

Q# 264/ Topic: **Chem 27** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 2/www.SmashingScience.org

2(a)(i)	**M1** ΔH_{latt} and ΔH_{hyd} both decrease OR ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic **M2** ΔH_{latt} decreases more than ΔH_{hyd} (as OH^- being smaller than M^{2+}) **M3** ΔH_{sol} becomes more exothermic / more negative	3
2(a)(ii)	(for MCO_3) change / decrease in ΔH_{hyd} is larger than decrease in ΔH_{latt}	1
2(a)(iii)	**M1** Sr and Ba could be used **AND** Mg could not be used **M2** solubility of $MgCO_3$ is more than $Mg(OH)_2$ OR $SrCO_3$ / $BaCO_3$ is less than $Sr(OH)_2$ / $Ba(OH)_2$	2

Q# 265/ Topic: **Chem 27** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	**M1** solubility decreases (down the Group) [1] **M2** because lattice energy and hydration energy **decreases** OR lattice energy and hydration energy become **less exothermic / more endothermic** [1] **M3** because hydration energy decreases to a greater extent (than does ΔH_{latt}) [1]	3

Q# 266/ Topic: **Chem 27** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(b)	• the temperature increases down the group • ionic radius increases / charge density decreases down the group • decreasing distortion / polarisation or decreasing weakening of bonds • of the anion / the CO_3^{2-} ion 2 points = 1 mark 3 points = 2 marks 4 points = 3 marks	3

Q# 267/ Topic: **Chem 27** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i)	(solubility) increases (down the group)	1
1(a)(ii)	*down the group:* lattice energy **or** hydration energy decrease lattice energy decreases more than hydration energy enthalpy change of solution becomes more negative / exothermic	3
1(c)(i)	$2\ SrO_2 \longrightarrow 2SrO + O_2$	1
1(c)(ii)	temperature will increase (down the group) charge density of cation decreases (down the group) this means less polarisation of the O_2^{2-} ion or weakens the O-O bond less	3
1(d)(i)	$BaC_2O_4 \longrightarrow BaO + CO + CO_2$	1

Q# 268/ Topic: **Chem 27** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(d)(i)	Mg^{2+} ion is smaller than Ba^{2+} ion or ionic radii increase down group ora	1
	(Mg^{2+}) distorts / polarises / the anion / nitrate group / nitrate ion / $NO_3^{(1)-}$ / NO_3 ion more easily (than Ba^{2+}) ora	1
2(d)(ii)	$Ba(NO_3)_2 \rightarrow BaO + 2NO_2 + ½O_2$	1
2(d)(iii)	$BaO + H_2O \rightarrow Ba(OH)_2$	1
	$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$	1

Q# 269/ Topic: **Chem 27** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	solubility increases down the group	1
	ΔH_{latt} and ΔH_{hyd} both decrease or ΔH_{latt} and ΔH_{hyd} both become less exothermic / more endothermic	1
	ΔH_{latt} decreases / changes more (than ΔH_{hyd} as OH^- being smaller than M^{2+})	1
	ΔH_{sol} becomes more exothermic / more negative / less endothermic / less positive	1

Q# 270/ Topic: **Chem 27** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	solid remains	1	1
2(b)	stability increases (down the group) as size / radius of (metal) ion / M^{2+} increases so polarisation / distortion of anion / carbonate ion decreases	1 1 1	3
2(c)(ii)	$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$ $CaCO_3$ correct equation	 1 1	2
	Total:		8

Q# 271/ Topic: **Chem 27** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1 (a) (i)	$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$	[1]
(ii)	$Ba(OH)_2$ is soluble, OR $BaCO_3$ is insoluble	[1]
(iii)	$Mg(OH)_2$ is insoluble / not very soluble will not form ppt. of $MgCO_3$	[1] [1]
(b)	carbonates are more stable down the group due to increase in cationic size / radius (causing) less polarisation of CO_3^{2-} ion	[1] [1] [1]
(c)	radius of Ni^{2+} = 0.070 nm; radius of Ca^{2+} = 0.099 nm so $NiCO_3$ decomposes more readily than $CaCO_3$	[1] [1]
		[Total: 9]

Q# 272/ Topic: **Chem 27** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6 (a) — 3

	identity or value	
V	nitrogen or	chlorine
X	NO / NO_2	ClO_2 / ClO_3
m	2, 3	1,2,3, or 4
W	sulfur	
Y	SO_2 or SO_3	
n	4, 3	

(b)	**M1**: (white precipitate is $BaSO_4$) descending the group ΔH_{sol} becomes more endothermic / positive;	1
	M2, M3 any **two** from: ΔH_{latt} decreases / becomes more endothermic / becomes less exothermic ΔH_{hyd} decreases / becomes more endothermic / becomes less exothermic ΔH_{hyd} decreases more than ΔH_{latt}	2

Q# 273/ Topic: **Chem 27** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) (i)	CaO **and** brown gas	1
(ii)	the (cat)ion size/radii increases decreasing its ability to polarise the nitrate ion/N-O bond	2

Q# 274/ Topic: **Chem 27** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b) (i)	nitrates become more stable (down the group) as the ionic radius increases ***or*** charge density on cation/ion decreases decreasing its ability to distort/polarise the NO_3^-/nitrate ion	1 1 1
(ii)	$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$	1
(iii)	the **charge density** of the other cations are too small (to polarise the anion sufficiently so the anion is more stable)	1
		[Total: 7]

Q# 275/ Topic: **Chem 27** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(b) (i) it would react (with H_2SO_4) [1]

(ii) $CaO + H_2O \longrightarrow Ca(OH)_2$ [1]

(iii) CaO absorbs more water *or* CaO has greater affinity for water [1]

[3]

(c) (i) $2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$ [1]

(ii) (Down the group, the nitrates)

become more stable/stability increases [1]

because the size/radius of **ion** (**M^{2+}**) increases [1]

thus causing less polarisation/distortion of the anion/NO_3^-/N-O bond [1]

[4]

[Total: 10]

Q# 276/ Topic: **Chem 27** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

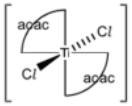
(e) solubility decreases down the group [1]
as M^{2+}/**ionic** radius increases [1]
both lattice energy **and** hydration(solvation) energy to decrease [1]
enthalpy change of solution becomes more endothermic [1]

[4]

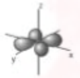
[Total: 18]

Q# 277/ Topic: Chem 28 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	(d-block) element that forms one or more stable ions with incomplete d subshell / incomplete d orbitals	1

3(a)(ii)	• variable oxidation states • behave as catalysts • form complex ions / complexes • form coloured compounds / ions *Any two for one mark*	1
3(b)(i)	Ti is in +4 oxidation state so no d electrons / d^0 OR Ti in TiO^{2+} has no d electrons / d^0 [1] cannot absorb photons / light in visible spectrum OR no wavelength / frequency absorbed in visible spectrum [1]	2
3(b)(ii)	$(1s^2)\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ (4s^0)$	1
3(b)(iii)	$2TiO^{2+} + 4H^+ + Zn \rightarrow 2Ti^{3+} + 2H_2O + Zn^{2+}$	1
3(c)(ii)	Ti^{3+} empty / vacant d orbitals can form dative bonds / accept a lone pair from a ligand OR Ti^{3+} has vacant d-orbitals which are energetically accessible	1
3(c)(iii)	the $E^\ominus$ of the half-cell must be greater than +1.23 V / $E^\ominus$ of the $O_2\|H^+$ half-cell as $E^\ominus_{cell} < 0$ and the reaction does not occur	1
3(d)(i)	the number of co-ordinate bonds being formed by the metal atom/ion	1
3(d)(ii)	$TiO_2 + 6HF \rightarrow TiF_6^{2-} + 2H_2O + 2H^+$ OR $TiO_2 + 6HF \rightarrow TiF_6^{2-} + 2H_3O^+$	1
3(d)(iii)	species with two lone pairs (of electrons) [1] that form dative covalent / co-ordinate bonds to a central metal atom/ion [1]	2
3(d)(iv)	mirror image of isomer I  trans isomer 	2
3(d)(v)	isomer I AND cis isomer drawn by candidate ecf [1] dipoles do not cancel / partial charges do not cancel [1]	2

Q# 278/ Topic: **Chem 28** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(c)(iii)	 $3d_{xy}$	1

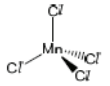
Q# 279/ Topic: **Chem 28** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

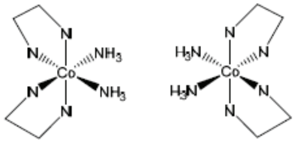
1(d)	*Reduction of Fe^{3+}*: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$ [1] *Regeneration of Fe^{3+}*: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$ [1]	2

Q# 280/ Topic: **Chem 28** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)	$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ OR $2CuSO_4 + 4NaI \rightarrow 2CuI + I_2 + 2Na_2SO_4$ [1]	1
6(b)(i)	M1: d-d orbital splitting occurs [1] M2: electron(s) promoted / excited [1] M3: wavelength / frequency of light is **absorbed** [1] M4: colour seen is complementary OR wavelength / frequency of light **not** absorbed is seen [1]	4
6(b)(ii)	(for Cu^+) $3d^{10}$ OR 3d subshell full [1]	1
6(c)	M1: $(Cu^{2+} / Cu^+)\ E^\ominus = (+)0.15$ V **AND** $(I_2 / I^-)\ E^\ominus = (+)0.54$ V [1] M2: <u>No</u>, since ($E^\ominus_{cell}$) negative / –0.39 V OR <u>No</u>, since (I_2 / I^-) is more positive than (Cu^{2+} / Cu^+) OR <u>No</u>, I_2 is more easily reduced OR No, I_2 stronger oxidant ORA [1]	2
6(d)	M1: Cu^{2+} / Cu^+ *E* becomes more positive as equilibrium shifts to the right [1] M2: The new E for Cu^{2+} / Cu^+ is more positive than 0.54 / $E^\ominus$ (I_2 / I^-) [1]	2

Q# 281/ Topic: **Chem 28** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	+2 [1]	1
5(a)(ii)	 [1] bond angle labelled 109.5° [1]	2

5(b)(i)	$[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(H_2O)_4(OH)_2 + 2H_2O$ OR $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ [1] **blue precipitate** [1]	2
5(b)(ii)	$[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ [1] yellow / brown / straw solution [1]	2
5(b)(iii)	$[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$ [1] blue solution [1]	2
5(b)(iv)	**ligand exchange** [1]	1
5(c)(i)	(a species) that **donates** <u>two</u> **lone pairs** to form <u>two</u> **dative bonds** [1] to a (transition) **metal atom / metal ion** [1]	2
5(c)(ii)	 M1 one correct 3D structure – trans or cis [1] M2 a correct optical isomer of M1 [must 3D] [1]	2

Q# 282/ Topic: **Chem 28** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

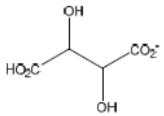
4(a)(i)	**M1:** blue solid / blue ppt **M2:** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ OR $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ **M3:** precipitation / acid-base	3
4(a)(ii)	**M1:** dark blue solution / deep blue solution **M2:** $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$ **M3:** ligand exchange / substitution / displacement / replacement	3
4(b)	**M1:** **X** $CuSO_4$ and **Y** Cu **M2:** *type of reaction* = redox / disproportionation	2

Q# 283/ Topic: **Chem 28** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(a)(i)	(an element) forming stable ion / ions / compound(s) / oxidation state(s) **AND** with partially filled / incomplete **AND** d orbitals / d subshell / d shell	1
3(a)(ii)	(melting point) higher **AND** (density) higher	1
3(b)(i)	**M1:** emf / potential difference / difference in electrode potential between two half-cells / two electrodes (in a cell) **M2:** (all solutions being) 1 mol dm^{-3} **AND either** 1 atm **OR** 298 K	2

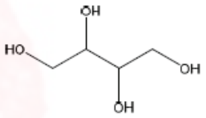
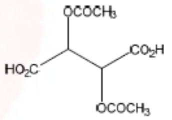
3(c)(i)	**M1:** $2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$ **M2:** $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$	2
3(c)(ii)	**M1:** I_2 / I^- +0.54 V **AND** Fe^{3+} / Fe^{2+} + 0.77 V **AND** $[Fe(CN)_6]^{3-} / [Fe(CN)_6]^{4-}$ +0.36 V **M2:** E° of I_2 / I^- is more positive / greater than E° of $[Fe(CN)_6]^{3-} / [Fe(CN)_6]^{4-}$ OR E°_{cell} = –0.18 V so no reaction occurs OR E° of Fe^{3+} / Fe^{2+} is more positive / greater than E° of I_2 / I^- OR E°_{cell} = 0.23 V so reaction occurs [1]	2
3(d)(i)	$S_2O_8^{2-}$ and tartrate ions are both negatively charged / both reactants same charge **AND** so repel each other OR have a high E_a	1

Q# 284/ Topic: **Chem 28** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3(e)(ii)	 $C_6H_5CH(NH_3^+)CH_3$ OR dianion of tartrate with two cations present	1

Q# 285/ Topic: **Chem 28** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

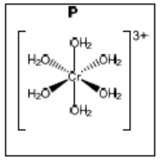
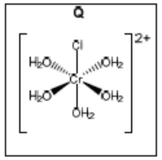
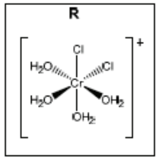
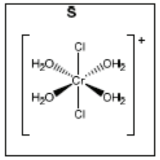
3(e)(i)	see below	3

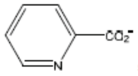
reagent	structure of organic product	type of reaction
an excess of $LiAlH_4$		reduction
an excess of CH_3COCl		condensation

M1: product with $LiAlH_4$
M2: product with CH_3COCl
M3: both types of reaction

Q# 286/ Topic: **Chem 28** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	**M1:** (complexes have two sets of) d orbital(s) of different energy / d-d splitting occurs OR d orbital(s) / d (sub)-shell splits OR (inferred from a movement of an electron) from a lower d to higher d orbital **M2:** electron(s) promoted / excited OR electron(s) moves to higher (d–)orbital OR electron(s) jumps up (to d–orbital) / jumps to higher (d–orbital) **M3:** wavelength / frequency / light / photon / hv absorbed OR radiation / energy from <u>visible</u> (region) absorbed **M4:** colour seen is complementary (to colour absorbed) OR wavelength / frequency / colour / light not absorbed is transmitted / reflected / seen	4

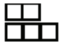
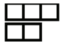
2(b)(i)	P  Q  R  S  **M1:** All charges **M2:** One octahedral with correct 3D **M3:** All formulae **M4:** R is cis, S is trans	4
2(b)(ii)	dipoles cancel	1
2(c)(i)	**M1:** (a species) that donates <u>two</u> lone pairs / forms two coordinate bonds / two dative bonds **M2:** to a metal atom / metal ion	2

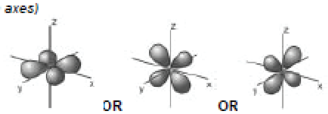
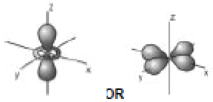
2(c)(ii)	 structure of the picolinate anion ligand	1
2(c)(iii)	(coordination number) six **AND** (geometry around Cr) octahedral	1
2(d)(i)	$(NH_4)_2Cr_2O_7$ +6 Cr_2O_3 +3	1

Q# 287/ Topic: **Chem 28** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

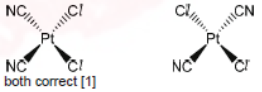
5(a)(ii)	square planar	1
5(a)(iii)	the distance between two coordinating oxygens is too small to bond trans OR atoms in a bidentate ligand can only bond 90° not 180°	1
5(a)(iv)	+4	1

Q# 288/ Topic: **Chem 28** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(a)	(element that forms one or more stable) ions with incomplete/ partially filled 3d-orbitals/d-subshell	1
4(b)(i)	O_h  **AND** T_d 	1

4(b)(ii)	**M1:** *lower energy level (in between axes)*  **M2:** *higher energy level (on the axes)* 	2
4(c)(i)	Circles round both N atoms and all four O⁻	1
4(c)(ii)	**M1:** (d–d) energy gap / Δ*E* is different **M2:** different frequency / wavelength (of light) absorbed	2
4(c)(iii)	ligand exchange / substitution / displacement / replacement	1
4(c)(iv)	$K_{stab} = \frac{[Fe(edds)^-]}{[Fe(H_2O)_6{}^{3+}][edds^{4-}]}$	1
4(c)(v)	$[Fe(edta)]^-$ is more stable as it has the higher K_{stab}	1
4(c)(vi)	$K_c = \frac{K_{stab}(edta)}{K_{stab}(edds)} = \frac{1.26\times10^{25}}{3.98\times10^{20}} = 3.17 \times 10^4$ **(31658)** min 2sf	1

Q# 289/ Topic: **Chem 28** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)	(a species) that donates <u>one</u> lone pair [1] to form a dative / coordinate to a central metal atom / metal ion [1]	2
6(a)(ii)	$[Ag(S_2O_3)_2]^{3-}$ [1]	1
6(b)(i)	$[Ag(S_2O_3)_2]^{3-} + 2CN^- \rightarrow [Ag(CN)_2]^- + 2S_2O_3{}^{2-}$ [1] OR $Ag(S_2O_3)_2]^{3-} + 2NaCN \rightarrow [Ag(CN)_2]^- + Na_2S_2O_3 + S_2O_3{}^{2-}$	1
6(b)(ii)	Q is more stable / has a larger K_{stab} than P [1]	1
6(b)(iii)	**ligand** exchange / displacement / substitution	1
6(c)(i)	 both correct [1]	1
6(c)(ii)	**square planar** [1]	1
6(c)(iii)	cis-trans OR geometric(al) [1]	1

Q# 290/ Topic: **Chem 28** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

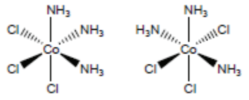
<table>
<tr><td>5(a)(i)</td><td>Kstab = $[(Cu(NH_3)_4)^{2+}] / [(Cu(H_2O)_6)^{2+}] [NH_3]^4$ [1]</td><td>1</td></tr>
<tr><td>5(a)(ii)</td><td>deep / dark / royal blue [1]</td><td>1</td></tr>
<tr><td>5(b)</td><td>$[Cu(NH_3)_4]^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2NH_4^+ + 2NH_3$ [1]
OR $[Cu(NH_3)_4]^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + 4NH_3$</td><td>1</td></tr>
<tr><td>5(c)</td><td>$Cu(OH)_2 + 4HCl \rightarrow [CuCl_4]^{2-} + 2H_2O + 2H^+$
OR $Cu(OH)_2 + 4Cl^- + 2H^+ \rightarrow [CuCl_4]^{2-} + 2H_2O$

$[CuCl_4]^{2-}$ complex including charge [1]
rest of equation fully correct [1]</td><td>2</td></tr>
<tr><td>5(d)</td><td><table>
<tr><td></td><td>Y</td><td>Z</td></tr>
<tr><td>colour of complex</td><td>yellow</td><td>blue / pale blue</td></tr>
<tr><td>geometry of complex</td><td>tetrahedral</td><td>octahedral</td></tr>
<tr><td>formula of complex</td><td></td><td>$[Cu(H_2O)_6]^{2+}$</td></tr>
</table>
one mark for any <u>three</u> cells [1] • • ✓
two marks for all five cells [2] • • ✓ • ✓</td><td>2</td></tr>
<tr><td>5(e)</td><td>M1: d orbitals splits into two sets of energy levels of different energy [1]
M2: wavelength / frequency / light / photon / hv absorbed [1]
M3: electron(s) promoted / excited [1]
M4: colour seen is complementary (to colour absorbed) [1]
M5: d–d energy gap / ΔE is different for Y and Z
AND so different frequency / wavelength of light <u>absorbed</u> • ✓ [1]</td><td>5</td></tr>
</table>

Q# 291/ Topic: **Chem 28** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10(a)	**+4 and** any of +1, +2, +3	1
10(b)	close similarity of energy of the 4s and 3d sub-shells	1

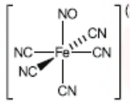
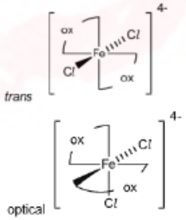
Q# 292/ Topic: **Chem 28** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i)	(a molecule or ion) formed by a (central) metal atom / ion surrounded by / bonded to (one or more) ligands	1
1(a)(ii)	M1: blue ppt/solid M2: $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$ OR $[Co(H_2O)_6]^{2+} + 2OH^- \rightarrow [Co(H_2O)_4(OH)_2] + 2H_2O$ M3: precipitation/ acid-base M4: blue solution M5: $[Co(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Co(NH_3)_6]^{2+} + 6H_2O$ M6: **ligand** exchange/displacement/substitution/replacement	6
1(b)	• solution turns blue → pink • a white ppt. of AgCl forms • equilibrium shifts to the left / [Cl⁻] decreases Two correct responses = 1 mark Three correct responses = 2 marks	2
1(c)	 geometric **ALLOW** cis-trans Two correct responses = 1 mark Three correct responses = 2 marks	2
1(d)(i)	**each nitrogen** / the four nitrogen's has a **lone pair of electrons** (to the metal ion) Two correct responses = 1 mark	1
1(d)(ii)	$[Co(H_2O)_6]^{2+} + C_6H_{18}N_4 \rightarrow [Co(C_6H_{18}N_4)]^{2+} + 6H_2O$ OR $[Co(H_2O)_6]^{2+} + C_6H_{18}N_4 \rightarrow [Co(C_6H_{18}N_4)(H_2O)_2]^{2+} + 4H_2O$	1

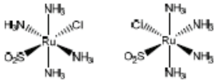
Q# 293/ Topic: **Chem 28** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(c)(iii)	$K_{stab} = \dfrac{[Ni(H_2O)_2Val_2]}{[Ni(H_2O)_6^{2+}][Val^-]^2}$	1
6(c)(iv)	equilibrium lies (well) to the right / towards the products **AND** (Z) is stable / more stable (than $[Ni(H_2O)_6]^{2+}$ in the presence of Val⁻)	1
6(c)(v)	bidentate	1

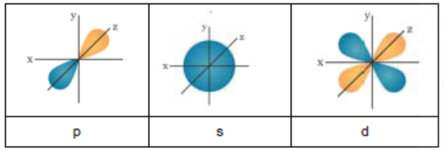
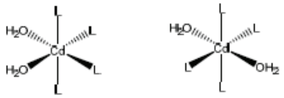
Q# 294/ Topic: **Chem 28** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i)	forms (one or more stable) ions with partially filled (3)d-subshell	1
1(a)(ii)	(Iron) has a higher (melting point) **AND** is denser/higher (density) (than calcium)	1
1(a)(iii)	$(1s^2)\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ (4s^0)$	1
1(a)(iv)	**M1** d sub-shell splits into two sets of d orbitals of different energy **M2** wavelength / frequency of light absorbed **M3** electron(s) promoted / excited **M4** colour seen is complementary (to colour absorbed)	4
1(b)(i)	octahedral	1
1(b)(ii)	$[Fe(H_2O)_6]^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-} + 6H_2O$	1
1(b)(iii)	$[Fe(CN)_6]^{4-}$ is (+)2 $[Fe(CN)_5NO]^{2-}$ is (+)3	1
1(b)(iv)	**M1** forms a single / one dative bond to a (central) metal atom / ion **M2** with lone pair (of electrons)	2
1(b)(v)		1
1(b)(vi)	**M1** d–d energy gap / ΔE is different **M2** different frequency / wavelength of light <u>absorbed</u>	2
1(c)(i)	the number of dative bonds formed with/by the (central) metal atom / ion **OR** number of bonds between the ligands and the (central) metal atom / ion	1
1(c)(ii)		2

Q# 295/ Topic: **Chem 28** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	forms one or more stable ions with incomplete / partially filled d-orbitals / d-subshell	1
7(b)(i)	purple to pale pink / colourless **AND** orange to green	1
7(b)(ii)	$3Sn^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Sn^{4+} + 2Cr^{3+} + 7H_2O$	1
7(c)(i)	• six • coordinate bonds / dative bonds / lone pairs donated • to the (central) metal ion award 1 mark for all three points	1
7(c)(ii)	$[Ru(NH_3)_4Cl(SO_2)]^+$	1
7(c)(iii)	 **M1:** six correct ligands around Ru, bonds are shown from S of SO_2 **M2:** 3-D bonds used correctly for octahedral **M3:** cis and trans isomers shown	3
7(c)(iv)	cis-trans or geometric(al) [1]	1
7(c)(v)	**M1:** complexes have two sets of **d orbital(s)** of different energy OR **d-orbitals** splits into two sets (of orbitals) **M2:** visible light **absorbed** (and complementary colour observed) **M3:** electron(s) promoted / excited OR electron(s) moves to higher (d–) orbital	3

Q# 296/ Topic: **Chem 28** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	 **All shapes required for mark**	1
4(b)	both cadmium ions have full d subshells	1
4(c)(i)	donates one lone pair to the central metal ion	1
4(c)(ii)	**M1** one 3D diagram of $[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}$ **M2** cis and trans structures 	2
4(d)(i)	equilibrium constant for the formation of a complex ion in solution / solvent [1]	1

<table>
<tr><td>4(d)(ii)</td><td>
<table>
<tr><td></td><td>decreases</td><td>no change</td><td>increases</td></tr>
<tr><td>K_{stab}</td><td>✓</td><td></td><td></td></tr>
<tr><td>$[[Cd(CH_3NH_2)_4(H_2O)_2]^{2+}]$</td><td>✓</td><td></td><td></td></tr>
</table>
M1 both ticks correct [1]
M2 equilibrium moves to the left as the (forward) reaction is exothermic [1]
</td><td>2</td></tr>
<tr><td>4(d)(iii)</td><td>$[CdEDTA]^{2-}$ and larger K_{stab} value</td><td>1</td></tr>
</table>

Q# 297/ Topic: **Chem 28** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

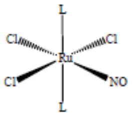
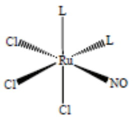
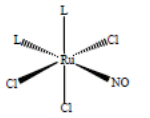
1(a)	**M1** $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ **M2** precipitation **M3** blue precipitate **M4** $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightarrow CuCl_4^{2-} + 6H_2O$ **M5** ligand exchange / displacement / substitution / replacement **M6** yellow solution	6
1(b)	**M1** amount of $Ag^+ = 0.050 \times 0.0224 = 1.12 \times 10^{-3}$ mol (in 25 cm³) amount of $Ag^+ = 1.12 \times 10^{-3} \times 4$ = **4.48×10^{-3} mol (in 100 cm³)** **M2** amount of $Cl^- = 4.48 \times 10^{-3}$ mol (in 100 cm³) mass of $Cl^- = 4.48 \times 10^{-3} \times 35.5 = 0.159$ g (in 100 cm³) mass of S = 0.303 – 0.159 = **0.144 g (in 100 cm³)** ecf **M3** moles of S = 0.144 / 32.1 = 4.49×10^{-3} molar ratio S : Cl 1:1 → **SCl** ecf	3

Q# 298/ Topic: **Chem 28** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	$(1s^22s^22p^6)3s^23p^63d^{10}4s^1$	1
4(a)(ii)	**M1** d orbitals / sub-shell split into two levels by repulsion of approaching ligands **M2** light absorbed and complementary colour observed **M3** (d) electron(s) promoted / excited OR (d) electron(s) moves to higher (d) orbital **M4** (in Cu(I) complexes) all the orbitals in Cu are full OR Cu(I) is d^{10}	4
4(b)	$n(S_2O_3^{2-}) = 28.35 \times 0.5 / 1000 = 0.0142$ (0.014175) this also equals $n(Cu^{2+})$ mass of Cu = 0.014175 × 63.5 = 0.90 g % of Cu = 100 × 0.90 / 1.5 = 60%	3
4(d)(i)	Cu^{2+}(aq) is (light) blue AND $[CuCl_4]^{2-}$(aq) is yellow	1
4(d)(ii)	ligand displacement / replacement / substitution / exchange	1
4(d)(iii)	$K_{stab} = [CuCl_4]^{2-} / ([Cu^{2+}][Cl^-]^4)$ units: $mol^{-4}\,dm^{12}$	2

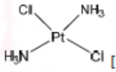
Q# 299/ Topic: **Chem 28** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

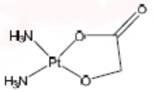
1(a)	natural: lightning, bacterial decomposition, volcanic emissions man-made: exhaust fumes, power stations, jet / car/ vehicle engines	1
1(b)(i)	$4NO \longrightarrow N_2O + N_2O_3$	1
1(b)(ii)	+2 to +1 **AND** +2 to +3	1
1(b)(iii)	$\Delta S = (\Delta H - \Delta G) / T$ $= (-195.2+102.8) / 298$ $= -0.310\ kJ\ mol^{-1}\ K^{-1}$ **M1** numerical answer **M2** units	2
1(b)(iv)	yes as there is a decrease in no. of moles of gas OR yes as moles of (gaseous) reactants is greater than moles of (gaseous) products	1
1(c)(i)	$K_p = p(NO)p(NO_2) / p(N_2O_3)$ **AND** units: atm OR Pa	1
1(c)(ii)	**M1** $p(NO) = p(NO_2) = 0.48$ atm $p(N_2O_3)_{eqm} = p(N_2O_3)_0 - 0.48 = 0.12$ atm **M2** $K_p = 0.48^2 / 0.12 = 1.92$ (atm)	2
1(d)(i)	**M1** from 3rd and 1st rows as [NO] × 2 , rate increases × 4, so order = 2 **M2** from 3rd and 2nd rows as $[O_2]$ × 2, rate also × 2, so order = 1	2
1(d)(ii)	rate = $k[NO]^2[O_2]$ k = rate / $([NO]^2[O_2]) = 3.5 / (0.01 \times 0.05) = 7000$ units: $mol^{-2}\ dm^6\ s^{-1}$	3

1(e)(i)	the number of dative bonds formed with / by the central metal atom / ion OR number of bonds between the ligands and the central metal atom / ion	1
1(e)(ii)	from 5 to 4	1
1(e)(iii)	tetrahedral	1
1(f)(i)	 (both L trans)  (cis L, but Cl opposite NO)  (cis L, but L opposite NO)	2
1(f)(ii)	geometric(al) OR cis-trans	1

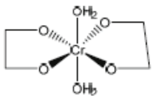
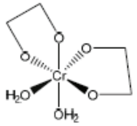
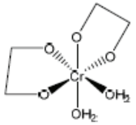
Q# 300/ Topic: **Chem 28** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

<table>
<tr><td>3(a)</td><td>[1] for each column
<table><tr><td></td><td colspan="2">number of unpaired electrons in</td></tr><tr><td>element</td><td>3d</td><td>4s</td></tr><tr><td>Cr</td><td>5</td><td>1</td></tr><tr><td>Mn</td><td>5</td><td>0</td></tr><tr><td>Fe</td><td>4</td><td>0</td></tr></table></td><td>2</td></tr>
<tr><td>3(b)</td><td>$2KMnO_4 \rightarrow K_2MnO_4 + O_2 + MnO_2$
formulae of K_2MnO_4 and O_2 [1]
rest of the equation [1]</td><td>2</td></tr>
<tr><td>3(c)</td><td>M1 d orbitals split into two levels / lower and upper orbitals [1]
M2 visible light is absorbed and the complementary colour observed [1]
M3 electron(s) promoted / excited [1]</td><td>3</td></tr>
<tr><td>3(d)(i)</td><td>precipitate A $[Cu(H_2O)_4(OH)_2]$ OR $Cu(OH)_2$ [1]
solution B $[Cu(NH_3)_4(H_2O)_2]^{2+}$ [1]
solution C $Cu(CH_3CO_2)_2$ [1]</td><td>3</td></tr>
<tr><td>3(d)(ii)</td><td>Na_2CO_3 or CO_3^{2-}</td><td>1</td></tr>
<tr><td>3(d)(iii)</td><td>$CuCO_3 + 2CH_3CO_2H \rightarrow Cu(CH_3CO_2)_2 + CO_2 + H_2O$</td><td>1</td></tr>
<tr><td>3(d)(iv)</td><td>any two for one mark
• fizzing / bubbles / effervescence
• solid disappears
• green / blue solution (formed)</td><td>1</td></tr>
</table>

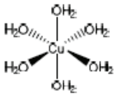
<table>
<tr><td>3(e)</td><td>sum of the charges of the (four) ligands equals the oxidation number / charge of Pt
OR a calculation Pt +2, NH_3 neutral / no charge, both Cl^-s –1 (so no overall charge)</td><td>1</td></tr>
<tr><td>3(f)(i)</td><td> [1]
square planar and 180° [1]</td><td>2</td></tr>
</table>

<table>
<tr><td>3(g)</td><td></td><td>1</td></tr>
</table>

Q# 301/ Topic: **Chem 28** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(a)	species that forms **dative bond**(s) to a (central) **metal atom / ion**	1
2(b)	   any two structures [1] × 2	2
2(c)(i)	$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$ [1] units $mol^2\ dm^{-6}$ [1]	2
2(c)(ii)	$[Ca^{2+}] = [C_2O_4^{2-}] = 6.65 \times 10^{-3}/128.1 = 5.19 \times 10^{-5}\ mol\ dm^{-3}$ [1] $K_{sp} = (5.19 \times 10^{-5})^2 = 2.7 \times 10^{-9}\ mol^2\ dm^{-6}$ [1]	2

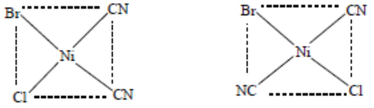
Q# 302/ Topic: **Chem 28** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)	$3s^23p^63d^{10}4s^1$	1
	$3s^23p^63d^{10}$	1
5(b)	*Cl*-Cu-*Cl*	1
	one minus charge	1
5(c)		1
	octahedral and 90° or 180° labelled correctly on diagram as appropriate	1
5(d)	reaction 1: blue ppt / blue **solid**	1
	$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2 + 6H_2O$ or $[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$ or $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow Cu(OH)_2(H_2O)_4 + 2NH_4^+$	1
	reaction 2: deep / dark / royal blue solution	1
	$Cu(OH)_2 + 4NH_3 + 2H_2O \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^-$ or $Cu(OH)_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 2OH^-$ or $Cu(OH)_2(H_2O)_4 + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$	1
5(e)(i)	ligand exchange / displacement / replacement / substitution	1
5(e)(ii)	K_{stab} =[$[CuEDTA]^{2-}$] / [$[Cu(H_2O)_6]^{2+}$][$[EDTA]^{4-}$]	1
5(e)(iii)	stable / more stable than $[Cu(H_2O)_6]^{2+}$	1
5(f)(i)	donates lone pairs / forms dative / co-ordinate bonds to (central) metal atom / metal ion	1
	donates two lone pairs / forms two (dative or coordinate) bonds	1
5(f)(ii)	$[Zr(C_2O_4)_4]^{4-}$	1
	not octahedral because 8 dative bonds to Zr or not octahedral because not 6 dative bonds to Zr or not octahedral because co-ordination number is 8 / is not 6	1

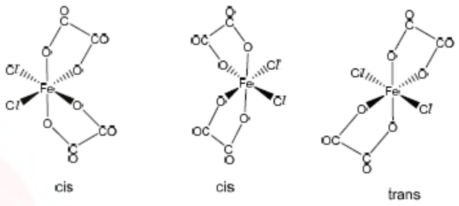
Q# 303/ Topic: **Chem 28** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	$1s^22s^22p^63s^2$**$3p^63d^64s^1$**	1
5(a)(ii)	(+)3 **and** (+)6	1
5(b)(i)	**H** is deep / dark / royal **and** blue (solution) **K** is yellow / yellow-green **M** is blue (precipitate) (allow pink)	2
5(b)(ii)	**L** is $[Co(NH_3)_6]^{2+}$ **N** is $[CoCl_4]^{2-}$	2
5(b)(iii)	(pale) blue **precipitate**	1

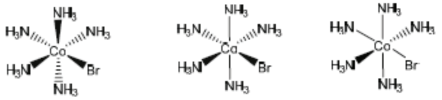
Q# 304/ Topic: **Chem 28** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(b)(i)	2-	1
3(b)(ii)	geometrical / cis-trans	1
3(b)(iii)	2 isomers  (must be clearly square planar)	3
3(c)	**C** is $Ni(CN)_2$ **D** is $K_2Ni(CN)_4$ **E** is $K_3Ni(CN)_5$	3

Q# 305/ Topic: **Chem 28** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

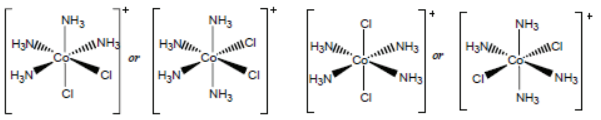
7(a)	Fe atom= $(1s^22s^22p^6)3s^23p^63d^64s^2$ Fe^{3+} ion= $(1s^22s^22p^6)3s^23p^63d^5$	1
7(b)	$([H^+]^2 = 8.9 \times 10^{-4} \times 0.25$ *or* $2.225 \times 10^{-4})$ $[H^+] = 0.0149$	1
	pH = –log(0.0149) = **1.83**	1
7(c)(i)	(K_{stab} is) the **equilibrium constant** for the formation of a complex (ion) (in a solvent from its constituent ions / molecules)	1
7(c)(ii)	$[Fe(H_2O)_5F]^{2+}$ **and** $[Hg(H_2O)_5Cl]^+$	1
7(d)	$K_{stab} = \dfrac{[Fe(ed)_2Cl_2^{3-}]}{[Fe(H_2O)_4Cl_2^{+}][ed]^2}$	1
	$mol^{-2} dm^6$	1
7(e)(i)	 cis cis trans	3
7(e)(ii)	any cis isomer and the trans isomer identified	1
7(e)(iii)	both correct cis isomers identified	1
7(e)(iv)	trans isomer identified	1

Q# 306/ Topic: **Chem 28** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	density is higher **and** melting point is higher	1
	(density) due to A_r being larger **and** smaller atomic radii or (Co) **atoms / ions** heavier **and** smaller	1
	(melting point) due to stronger attraction to cations as more delocalised electrons	1
4(b)	(a molecule or ion) formed by a central metal **atom / ion** surrounded by (one or more) **ligands**	1
4(c)(i)	same number and type of <u>atoms</u> and different structural formula	1
4(c)(ii)	octahedral **AND** 3D structure of $[Co(NH_3)_5Br]^{2+}$ e.g. 	1
4(c)(iii)	co-ordinate / dative covalent	1
4(c)(iv)	+3 for both	1
4(d)	(HNO_3) Ag^+ / $AgNO_3$ cream(–yellow) ppt. (of AgBr) **and** no reaction / white ppt. for other isomer	1
	$Ba(OH)_2$ / $Ba^{2+}(aq)$ / $BaCl_2$ / $Ba(NO_3)_2$ white ppt. (of $BaSO_4$) **and** no reaction for other isomer	1
4(e)	(d-d) energy gap / ΔE is different	1
	<u>**absorb**</u> **different** wavelength / frequency (of light)	1

Q# 307/ Topic: **Chem 28** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

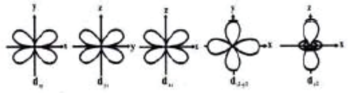
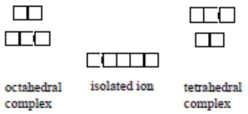
3(a)(i)	+3 or Co^{3+}	1
3(a)(ii)	oxidation	1
	ligand displacement / replacement / exchange / substitution	1

3(a)(iii)	 cis trans	1 + 1
	geometrical or cis-trans	1
3(b)(i)	The number of bonds / atoms bonded to **an atom / ion / species / metal**	1
3(b)(ii)	C 6 $[Cr(CN)_6]$ – D – $[Ni(NH_2CH_2CH_2NH_2)_3]$ 2+/+2 E 4 $[PtCl_4]$ – F 6 – 3–/–3	6
3(c)(i)	$K_{stab(1)} = [FeSCN^{2+}]/([Fe^{3+}][SCN^-])$ $mol^{-1}\ dm^3$ $K_{stab(2)} = [FeCl_4^-]/([Fe^{3+}][Cl^-]^4)$ $mol^{-4}\ dm^{12}$	3
3(c)(ii)	$K_{eq(3)} = K_{stab(1)} / K_{stab(2)}$	1
3(c)(iii)	$K_{eq(3)} = 1750$	1
	$mol^3\ dm^{-9}$	1
	Total:	19

Q# 308/ Topic: **Chem 28** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(d)(i)	*monodentate*: (a species that) forms **one dative / coordinate bond**	1
	ligand: a species that uses a lone pair of electrons to form a dative / coordinate bond to **a metal atom / metal ion**	1
2(d)(ii)	$[Ag(NCO)_2]^-$ or $[Ag(OCN)_2]^-$ correct formula	1
	correct charge	1

Q# 309/ Topic: **Chem 28** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)		1
6(a)(ii)	Ni : $[1s^22s^22p^63s^23p^6]$ $\mathbf{3d^84s^2}$ Ni^{3+} : $[1s^22s^22p^63s^23p^6]$ $\mathbf{3d^7}$	1
6(b)(i)		1
6(b)(ii)	energy / photon is absorbed in the visible region / light	1
	electron jumps from the lower to the upper energy level / is excited	1
6(b)(iii)	different frequency / wavelength of light are absorbed by the two complexes **OR** different size of energy gap	1
6(c)	colour of solution: green	1
	explanation: because the solution absorbs most strongly in the blue **AND** red regions	1
6(d)(i)		2

6(d)(ii)	cis-trans / geometrical	1
6(e)(i)		2
6(e)(ii)	optical	1
6(f)(i)	$K_{stab} = [Ni(NH_3)_6{}^{2+}]/([Ni(H_2O)_6{}^{2+}][NH_3]^6)$	1
6(f)(ii)	$[Ni(en)_3]^{2+}$ would be formed because it is much more stable / K_{stab} is much greater **OR** in the presence of both ligands the overall equilibrium $[Ni(NH_3)_6]^{2+} \rightleftharpoons [Ni(H_2O)_6]^{2+} \rightleftharpoons [Ni(en)_3]^{2+}$ would shift right	1
6(f)(iii)	cis-trans isomers identified	1
	two cis isomers identified	1

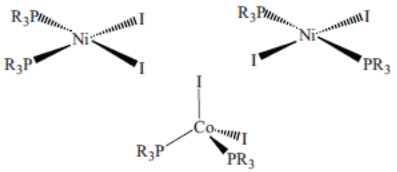
Q# 310/ Topic: **Chem 28** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	(an element) forming one or more (stable) **ions** or **compounds** or **oxidation states** with **partially filled / incomplete d orbitals**	1 1
4(b)(i)	A $Co(OH)_2$ OR $Co(H_2O)_4(OH)_2$ B $[CoCl_4]^{2-}$ C $[Co(NH_3)_6]^{2+}$ OR $[Co(NH_3)_6]^{3+}$ two correct = 1 mark three correct = 2 marks	2
4(b)(ii)	$[Co(H_2O)_6]^{2+}$ pink solution of B blue solution of C brown/yellow/orange	
	two correct = 1 mark three correct = 2 marks	2

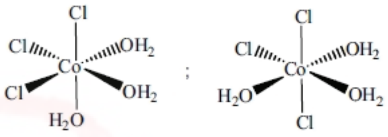
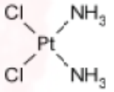
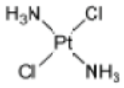
Q# 311/ Topic: **Chem 28** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)	Cu [Ar] $3d^{10}4s^1$ Cu^{2+} [Ar] $3d^9$ $(4s^0)$	1 1	2
1(b)(i)	ligand exchange / replacement / displacement / substitution	1	1
1(b)(ii)	$[Cu(H_2O)_6]^{2+}$ blue and $[CuCl_4]^{2-}$ yellow OR yellow / green OR green / yellow	1	1
1(b)(iii)	tetrahedral	1	1
1(b)(iv)	$K_{stab} = [CuCl_4^{2-}]/[Cu(H_2O)_6^{2+}][Cl^-]^4$	1	1
1(c)(i)	a species that contains two lone pairs that (each) form a co-ordinate / dative bond OR are donated (to a metal ion / atom)	1 1	2
1(c)(ii)	equilibrium 2 lies more to the RHS / favours forward reaction more	1	1
1(d)(i)	optical	1	1
1(d)(ii)	3D correct for octahedral one correct structure with 3D second correct with 3D	1 1 1	
			3

Q# 312/ Topic: **Chem 28** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i)	Co: $...3s^23p^63d^74s^2$ Co^{2+}: $...3s^23p^63d^7$	[1]
(ii)	solution starts pink turns blue pink is $[Co(H_2O)_6]^{2+}$ blue is $[CoCl_4]^{2-}$ this complex is tetrahedral	[1] [1] [1] [1] [1]
(b)		[1] [1] [1]
		[Total: 9]

Q# 313/ Topic: **Chem 28** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3 (a)	Co [Ar] $3d^74s^2$ Co^{2+} [Ar] $3d^7$	1 1
(b)		1
(c) (i)	$[Co(Cl)_3(H_2O)_3]^-$	1
(ii)		2
(d) (i)	$[Pt(Cl)_2(NH_3)_2]$	1
(ii)	**M1, M2**: diagrams **M3**: names  cis-platin / cis-diamminedichloroplatinum(II)  trans-platin / trans-diamminedichloroplatinum(II)	2 1
(iii)	(*cis* isomer) this can react / bond / bind with DNA; which prevents replication of the strand / prevents cell division;	1 1
(e) (i)	**M1**: formula **M2**: units (ecf from formula) $K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]^4}$ $mol^{-4}\,dm^{12}$	1 1
(ii)	(large value of K_{stab} shows that) the tetrammine complex is more stable	1

Q# 314/ Topic: **Chem 28** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 (a)	forms (one or more) ions with incomplete d orbital(s)/sub-shells/shells	1
(b) (i)	dative (covalent) *or* co-ordinate	1
(ii)	see table below	2
(c) (i)	see table below	5
		9

(b)(ii)

species	can act as a ligand	cannot act as a ligand
NO_3^-	✓	
BF_3		✓
$H_2NCH_2CH_2NH_2$	✓	
NH_4^+		✓

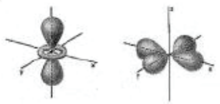
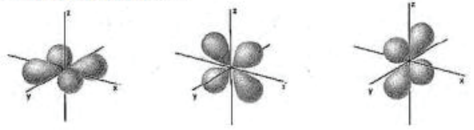
(c)(i)

	formula of manganese species formed	type of reaction
Mn^{2+} (aq) + NaOH (aq)	$Mn(OH)_2$ $Mn(H_2O)_4(OH)_2$ $Mn(OH)_3$	precipitation
Mn^{2+} (aq) + concentrated HC*l*	$MnCl_4^{2-}$ $MnCl_6^{4-}$	ligand exchange / substitution
Mn^{2+} (aq) + aqueous H_2O_2	Mn^{3+}	redox / oxidation

Q# 315/ Topic: **Chem 28** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(ii)	(molecule/ion/species) that **donates** a lone pair of electrons (to a central transition metal atom or ion)	1

Q# 316/ Topic: **Chem 28** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a)	see orbital boxes below	1 1	[2]
(b) (i)	degenerate	1	
(ii)	2 upper orbitals **and** 3 lower orbitals	1	
(iii)	**correct upper** orbital diagram  **correct lower** orbital diagram 	1 1	[4]
(c)	**electron(s)** move from lower to upper level **absorb** (red/blue) light/photon complementary colour (green) is seen **OR** green light is transmitted	1 1 1	[3]

2 (a)

	3d					4s
(Ni)	↑↓	↑↓	↑↓	↑	↑	↑↓
(Ni²⁺)	↑↓	↑↓	↑↓	↑	↑	

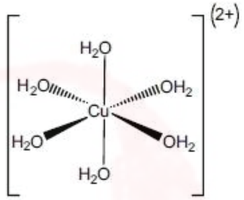
(d)	**A** $Ni(OH)_2$ **OR** $Ni(OH)_2(H_2O)_4$ **B** $[Ni(NH_3)_6]^{2+}$ **OR** $[Ni(NH_3)_n(H_2O)_{6-n}]^{2+}$ **OR** $[Ni(NH_3)_n(H_2O)_{4-n}]^{2+}$	1 1	
	$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2$ **OR** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6H_2O$ **OR** $[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow Ni(OH)_2 + 4H_2O + 2NH_4^+$ **OR** $[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2(H_2O)_4 + 2H_2O$	1	
	$Ni(OH)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+-} + 2OH^-$ **OR** $Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+-} + 6H_2O$	1	[4]
Total			[13]

Q# 317/ Topic: **Chem 28** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

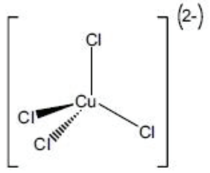
2 (a) (i) A *complex* is a compound/molecule/species/ion formed by a central metal atom/ion surrounded by/bonded to one or more ligands/groups/molecules/anions [1]

A *ligand* is a species that contains a **lone pair** of electrons that forms a **dative bond** to a metal atom/ion/*or* a lone pair donor to metal atom/ion [1]

(ii)

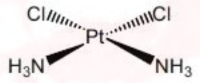


and

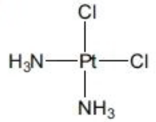


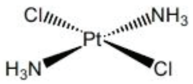
correct 3D structures: [1] + [1]
octahedral and tetrahedral [1]

(iii)

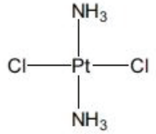


or





or



both structures [1]
geometric or cis-trans [1]

Q# 318/ Topic: **Chem 28** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

(c) (i) (colour change is) colourless to pink/pale purple
or (end point is the first) permanent (pale) pink/pale purple colour [1]

(ii) $\{n(MnO_4^-) = 0.02 \times 18.1/1000 = 3.62 \times 10^{-4}$ mol$\}$
$n(Fe^{2+}) = 5 \times n(MnO_4^-) =$ **1.81 × 10⁻³ mol** [1]

mass of Fe = 55.8 x 1.81 × 10^{-3} = 0.101 g (M2 × 55.8) ecf [1]

M_r = mass/moles = 0.500/1.81 × 10^{-3} = **276.2** ecf [1]

[Total: 16]

Q# 319/ Topic: **Chem 28** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(b)

reaction	acid-base	ligand exchange	precipitation	redox
$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 6H_2O$		✓		
$[Cu(H_2O)_6]^{2+} + 4HCl \rightarrow [CuCl_4]^{2-} + 4H^+ + 6H_2O$		✓		
$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$				✓
$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2 + 6H_2O$	✓		✓	
$2Fe(OH)_2 + ½O_2 + H_2O \rightarrow 2Fe(OH)_3$				✓
$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$	✓	✓		
$Cr(H_2O)_3(OH)_3 + OH^- \rightarrow [Cr(H_2O)_2(OH)_4]^- + H_2O$	✓	✓		
$[Cr(OH)_4]^- + 1½H_2O_2 + OH^- \rightarrow CrO_4^{2-} + 4H_2O$		✓		✓

(Where more than one tick appears on a line in the table above – these are alternatives – but allow the mark if both are given).

[8]

Q# 320/ Topic: **Chem 28** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

(c) **(i)** NO [1]

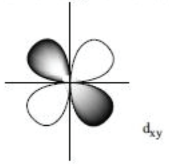
(ii) $3Fe^{2+} + 4H^+ + NO_3^- \longrightarrow 3Fe^{3+} + NO + 2H_2O$ [1]
(allow $Fe^{2+} + H^+ + HNO_2 \longrightarrow Fe^{3+} + NO + H_2O$)

(iii) dative/coordinate bonding [1]

(iv) $[Fe(H_2O)_{6-n}(NO)_n]^{2+}$ (n = 1-6) [1]
[4]

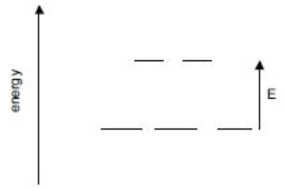
Q# 321/ Topic: **Chem 28** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** for example.... also allow d_{z2}



shape (4 lobes) [1]
correct label e.g. d_{xy} [1]
[2]

(b) **(i)**



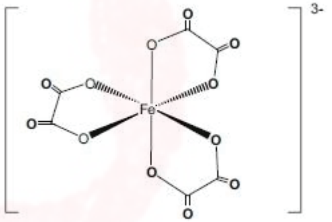
Marks are for 5 degenerate orbitals [1]
and 3:2 split [1]

(ii) colour due to the absorption of light NOT emitted light [1]
E = hf *or* photon's energy = E in above diagram [1]
electron promoted from lower to higher orbital [1]

size of ΔE depends on the ligand [1]
as ΔE changes, so does f in E = hf [1]
[7]

(ii) O.N. = +3 [1]

(iii)



[2]

Q# 322/ Topic: **Chem 28** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** **(i)** A ligand is a species that contains a lone pair of electrons, *or* that can form a dative bond (to a transition element) (1)

(ii)

species	can be a ligand	cannot be a ligand
OH^-	✓	
NH_4^+		✓
CH_3OH	✓	
CH_3NH_2	✓	

(4 × ½) **[3]**

(b) **(i)** **C** is $[Cu(NH_3)_6]^{2+}$ SO_4^{2-} (allow $[Cu(NH_3)_4]^{2+}$ SO_4^{2-} (1)
D is CuO (1)
E is Na_2SO_4 (1)
F is $BaSO_4$ (1)

(ii) acid-base *or* neutralisation (1) **[5]**

Q# 323/ Topic: **Chem 28** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 **(a)** coloured ions / compounds (1)
variable oxidation states (1)
formation of complexes (1)
catalytic activity (4 max 3) [3]

(b) (green is $[Ni(H_2O)_6]^{2+}$)
ppt is $Ni(OH)_2$ (1)

blue solution is $[Ni(NH_3)_6]^{2+}$ *or* $[Ni(NH_3)_4]^{2+}$ *or* $[Ni(NH_3)_4(H_2O)_2]^{2+}$ (1)

formed by ligand exchange (1)

$Ni^{2+} + 2OH^- \longrightarrow Ni(OH)_2$ (1)

$Ni(OH)_2 + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 2OH^-$ (1) [4]
(5 max 4)

(c) $M_r = 58.7 + 48 + 6 + 28 + 32 = \mathbf{172.7}$ (173) (1)

n(Ni) = 4.00 / 172.7 = **0.0232** mol (1)

mass(Ni) = 0.0232 × 58.7 = 1.36g

percentage = 100 × 1.36 / 3.4 = **40.0%** (1) [3]

[Total: 10]

Q# 324/ Topic: **Chem 28** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

3 **(a)** d-orbitals split into two / different levels
light is absorbed
electron is promoted from a lower to a higher level
colour observed is the complement of the colour absorbed
E = hf any 3 points [3]
[3]

(b) **(i)** $[Cu(H_2O)_6]^{2+}$ is pale blue [1]
$[Cu(NH_3)_4(H_2O)_2]^{2+}$ is deep / dark blue *or* purple [1]

(ii) because it has a larger absorbance peak *or* a larger ε_o value [1]
because λ_{max} is in the visible region (hence more visible light is absorbed) [1]

(iii) curve will have λ_{max} between >600 nm and 800 nm [1]
with maximum ε_o in between the other two [1]
[6]

(c) **(i)** $K_c = [CuCl_4^{2-}]/([Cu^{2+}][Cl^-]^4)$ units are $mol^{-4}\ dm^{12}$ [1] + [1]

(ii) $[CuCl_4^{2-}]/[Cu^{2+}] = K_c[Cl^-]^4 = 672$ (no units) [1]
[3]

[Total: 12]

Q# 325/ Topic: Chem 29 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	In F: (phenyl)amine **AND** carboxylic acid In J: phenol **AND** ester *Any two for one mark* *All four for two marks*	2

Q# 326/ Topic: **Chem 29** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	A = ester B = (2°) amide	2
4(a)(ii)	2	1

Q# 327/ Topic: **Chem 29** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)(ii)	**M1**: benzene (120°) <u>and</u> cyclohexane (109.5°) **M2**: as π-bonds are transformed into σ-bonds	2

Q# 328/ Topic: **Chem 29** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(a)	*Any two of:* chloro amine / amino alcohol / hydroxyl / phenol benzene / phenyl ring / aryl / arene	1

Q# 329/ Topic: **Chem 29** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(b)(i)	4-aminobenzoic acid	1

Q# 330/ Topic: **Chem 29** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)	nitrile; alkene; chloro; benzene / arene	2

Q# 331/ Topic: **Chem 29** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)	ibuprofen: carboxylic acid / carboxyl paracetamol: phenol and amide any two = 1 mark all three = 2 marks	

Q# 332/ Topic: **Chem 29** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8 (a)	P amide Q ketone R **secondary** alcohol Q = carbonyl and R = alcohol scores [1]	1 1 1

Q# 333/ Topic: **Chem 29** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b) (i)	σ-bonds = 14 π-bonds = 2	2

Q# 334/ Topic: **Chem 29** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(b)	lower doses of the drug required **OR** improved activity of the drug **OR** reduced side effects	1	[1]
(c)	decreases enzyme activity **OR** decreases rate at which product is formed	1	
	binds with the enzyme's active site **OR** has a complementary shape to active site **OR** similar shape to substrate	1	
	(competitive inhibition can be overcome by) increasing [substrate] **OR** increasing substrate concentration	1	[3]
(d)	**energy** source/carrier **OR** releases energy when hydrolysed	1	[1]
Total			7

Q# 335/ Topic: **Chem 29** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** **three** from phenol
(secondary) alcohol
(primary) amine
arene / aryl / benzene 3 × [1]

Q# 336/ Topic: **Chem 29** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) phenol [1]
ketone [1]

[2]

Q# 337/ Topic: **Chem 29** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(d) (i) (through its long chain of) delocalised electrons/mobile electrons [1]
free electrons is not sufficient

(ii) planar [1]

the π bonds/p-orbitals overlap (with each other) [1]

(iii) C_8H_6
C_4H_3 [2]

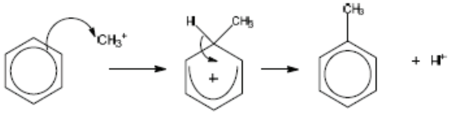
[5 max 4]

[Total: 10]

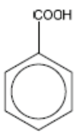
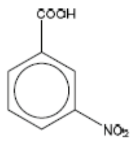
Q# 338/ Topic: **Chem 29** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(ii) ketone, alkene, amine, aryl (benzene/arene/phenyl) (any 3) [2]

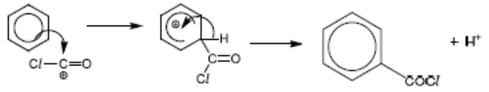
Q# 339/ Topic: Chem 30 ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(c)(i)	$CH_3Cl + AlCl_3 \rightarrow {}^+CH_3 + AlCl_4^-$ [1]	1
7(c)(ii)	 M1: arrow to CH_3^+ (arrow must come from inside the hexagon) [1] M2: correct structure of intermediate [1] M3: arrow <u>from</u> C-H bond into the ring AND H^+ seen [1]	3

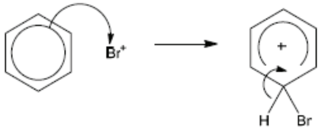
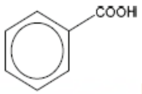
Q# 340/ Topic: **Chem 30** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)(i)	**M**  **N** 	2
7(a)(ii)	**M1:** step 1 hot $KMnO_4$ / MnO_4^- **M2:** step 2 conc. H_2SO_4 and conc. HNO_3 **M3:** step 3 Sn and conc. HCl (heat)	3

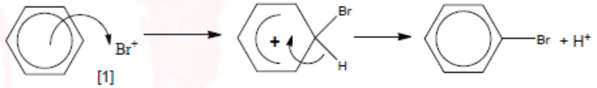
Q# 341/ Topic: **Chem 30** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(b)(iv)	 **M1:** curly arrow from inside hexagon to C of electrophile **M2:** correct intermediate **M3:** curly arrow from C—H bond **AND** formation/loss of H^+	3

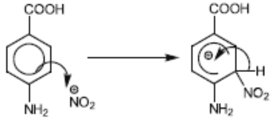
Q# 342/ Topic: **Chem 30** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)(i)	HBr / hydrogen bromide [1]	1
8(a)(ii)	 **M1** curly arrow to Br^+ **AND** curly arrow from C–H bond as shown [1] **M2** correct intermediate [1]	2
8(a)(iii)	**electrophilic substitution** [1]	1
8(b)(i)	reagent: chloroethane / bromoethane / iodoethane OR formula [1] catalyst: $FeCl_3$ / $AlCl_3$ etc. [1]	2
8(b)(ii)	 [1] **ALLOW** C_6H_5COONa	1
8(b)(iii)	step 3 = $LiAlH_4$ [1] step 4 = Pt AND H_2 [1]	2

Q# 343/ Topic: **Chem 30** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

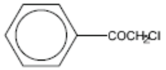
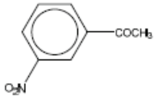
5(a)(i)	The substitution product is stabilised by delocalisation of (6)π-electrons OR The addition product is not stabilised by delocalisation of (6)π-electrons [1]	1
5(a)(ii)	 [1] intermediate [1] curly arrow + H^+ lost [1] • first curly arrow • intermediate • 2nd curly arrow, product and H^+ formed / lost	3
5(a)(iii)	$AlBr_4^- + H^+ \rightarrow AlBr_3 + HBr$	1

Q# 344/ Topic: **Chem 30** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

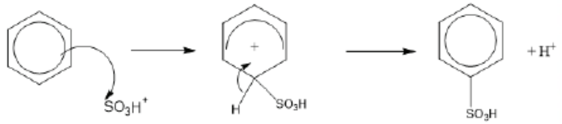
5(c)(i)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$ **OR** $HNO_3 + H_2SO_4 \rightarrow H_2O + NO_2^+ + HSO_4^-$	1
5(c)(ii)	 **M1** curly arrow from ring to N of NO_2^+ **M2** correct intermediate **AND** curly arrow from C—H back to ring	2
5(c)(iii)	electrophilic substitution	1

Q# 345/ Topic: **Chem 30** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

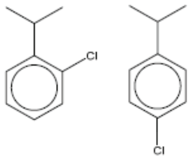
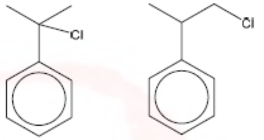
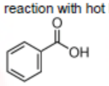
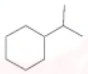
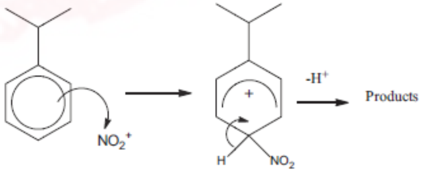
4(a)	**M1:** CH_3COCl or ethanoyl chloride **M2:** $AlCl_3$ catalyst	2
4(b)	see table below Award 1 mark for each correct entry to the table [5]	5

reagent	organic product	name of mechanism
Cl	 chlorine atom(s) in side chain only	free radical substitution
nitric / sulfuric	 one only –NO_2 group added at 3 position	electrophilic substitution
Br	no reaction with Br_2	

Q# 346/ Topic: **Chem 30** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)(i)	**M1**: reduction / hydrogenation **M2**: H_2 + Ni / Pt catalyst	2
7(b)(i)	 **M1**: first curly arrow to the sulfur atom **M2**: intermediate shown **M3**: 2nd curly arrow and H^+ formed / lost	3
7(b)(ii)	$HSO_4^- + H^+ \rightarrow H_2SO_4$	1
7(c)	**M1**: $C_{12}H_{25}Br$ and halogen carrier e.g. $AlBr_3$ (+ heat) **M2**: electrophilic substitution	2

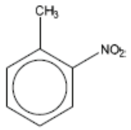
Q# 347/ Topic: **Chem 30** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)	D 2-chloropropane	1
	E hydrogen chloride	1
6(a)(ii)	(Friedel-Crafts) alkylation	1
6(b)(i)	$AlCl_3$ or $FeCl_3$	1
6(b)(ii)		1
6(b)(iii)	sunlight or UV OR T>100 °C	1
6(b)(iv)		1
6(c)	reaction with hot $KMnO_4$(aq) 	1
	reaction with H_2 + Ni, high pressure 	1
6(d)		
	attacking species is NO_2^+	1
	curly arrow starting within hexagon and going to NO_2^+	1
	correct intermediate	1
	2nd curly arrow from C-H bond into ring	1

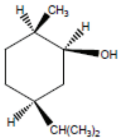
Q# 348/ Topic: **Chem 30** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(d)(i)	heat with (conc.) $KMnO_4$	1

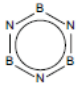
Q# 349/ Topic: **Chem 30** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)(i)		1
6(a)(ii)	$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + NO_2^+ + 2HSO_4^-$	1
6(a)(iii)	any three from: Point 1: bonds / electrons are partially delocalised in **T** or delocalised / π system / π bonding extends over only five carbons Point 2: four π-electrons in the (delocalised system of **T**) or methylbenzene has (two) more π-electrons / (two) more delocalised electrons Point 3: contains a carbon that is sp^3 hybridised in **T** *or* (all the) carbons are sp^2 hybridised in methylbenzene Point 4: one carbon has a bond angle of 109.5° / tetrahedral (in **T**) *or* (C-C) bond strengths / lengths are not all the same or not all the bond angles are 120° (in **T**)	3

Q# 350/ Topic: **Chem 30** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

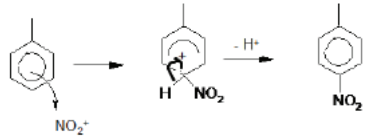
4(c)(i)	H_2 + Pt or H_2 + Ni + heat or pressure	1
4(c)(ii)	 $(CH_3)_2CH$, CH_3 and OH on the correct ring atoms i.e. structure is correct	1
	all Hs on the same side of the ring	1

Q# 351/ Topic: **Chem 30** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(d) (i)	*any four of* M1: σ-bonds between C–C **or** C–H M2: π-bonds formed from overlap of p-orbitals M3: (π-bonds/electrons) above and below the ring M4:bonds/electrons are delocalised M5: bond angle 120° M6: intermediate C–C bond length / all C–C same length / strength M7: carbons are sp^2 hybridised	3
(ii)	correct delocalised structure of borazine 	1
		<u>**10**</u>

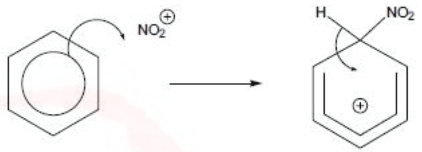
Q# 352/ Topic: **Chem 30** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (i)	$2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$ **OR** $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + NO_2^+ + H_2O$	1	

(ii)	**any three** of • curly arrow from inside the benzene ring to NO_2^+ group • intermediate – **penalise** NO_2 connectivity ***or*** missing methyl group (once) • curly arrow from C-H bond into ring • product + H^+ (or as diagram $-H^+$) **allow** 2- and 3-substituted nitromethylbenzene) 	3	**[4]**

Q# 353/ Topic: **Chem 30** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) **(i)** production of NO_2^+: $2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$ [1]
(accept $H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2O + NO_2^+$)



curly arrow from ring to NO_2^+ **and** from C-H bond to ring [1]
correct intermediate, including charge in the right place
Note charge area must be more than half ring [1]

(ii) **C** is $C_6H_5CO_2H$ [1]

(iii) step 1: reagent is hot acidified or alkaline $KMnO_4$ [1]
step 2: reagent is $Br_2 + FeBr_3/AlCl_3$ etc. (H_2O or light negates) [1]

(If **C** is given as 3-bromotoluene, then allow the last [2] marks if steps 1 and 2 are reversed.)

[Total: 12]

Q# 354/ Topic: Chem 31 ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(c)(i)	catalyst / halogen carrier	1
4(c)(ii)	**M1** —OH directs to 2,4 **AND** both 2 positions occupied / only position 4 is available **M2** —COOH directs to 3 position **AND** only position 3 is available / 5 is occupied	2

Q# 355/ Topic: **Chem 31** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(a)	**M1**: $CH_3COCl > CH_3CH_2Cl > C_6H_5Cl$ **M2 & M3 any two from:** • in C_6H_5Cl (no hydrolysis) C-Cl bond is part of delocalised system OR p-orbital on Cl overlaps with π system OR electrons from Cl overlap with π system • CH_3COCl carbon in C-Cl bond is more electron deficient since it is also attached to an oxygen atom (ora) or C-Cl bond strength is weakest in CH_3COCl (ora) • CH_3CH_2Cl carbon in C-Cl bond strengthened by positive inductive effect of alkyl group	3

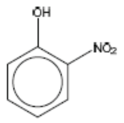
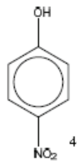
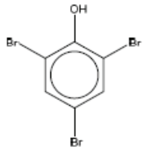
Q# 356/ Topic: Chem 32 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(e)	p-orbital on oxygen overlaps with ring / π system OR lone pair of e⁻ on oxygen is delocalised into the ring [1] electron density in ring increases [1] attracts/polarises electrophile better [1]	3

Q# 357/ Topic: **Chem 32** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(b)	M1: trend phenylethanoic acid > phenol > ethanol [1] M2: *why phenylethanoic acid is the strongest* • negative inductive electron withdrawing effect of C=O which weakens O-H bond / stabilises anion [1] M3: *why phenol is stronger than ethanol / weaker than phenylethanoic acid* • oxygen lone pair is delocalised into the ring system which weakens O-H bond / stabilises anion [1] M4: *why ethanol is the weakest* • electron donating alkyl / ethyl group which strengthens O-H bond / destabilises anion [1]	4

Q# 358/ Topic: **Chem 32** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	**M1:** HNO_2 OR $NaNO_2 + HCl$ [1] **M2:** T ⩾ 10 °C / warm **AND** water [1]	2
7(b)	 2-nitrophenol  4-nitrophenol 2 × [1]	2
7(c)(i)	 2,4,6-tribromophenol ✓✓ [2]	2
7(c)(ii)	bromine is decolourised **AND** white precipitate is formed BOTH [1]	1
7(d)	$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ [1] **ALLOW** any equation for phenol acting as an acid	1
7(e)	phenol>water>ethanol [1] • (phenol:) lone pair on oxygen is delocalised into the benzene ring • (ethanol:) positive inductive effect / electron donating effect of alkyl / ethyl group • correct statement about stabilisation of anion/ conjugate base OR weakening of O-H bonds once *in the context of phenol / ethanol* • correct statement about ease of proton/H^+ donation *in the context of phenol / ethanol* [2] Two correct statements = 1 mark	3

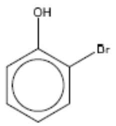
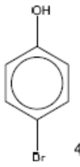
Q# 359/ Topic: **Chem 32** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(b)	lone pair of oxygen is delocalised into the ring any one from: • phenol has a higher electron density in the ring • phenol can polarise/induce a dipole in Br_2	2

Q# 360/ Topic: **Chem 32** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(a)	**M1** COOH is more acidic than phenol **AND** because the O-H bond in acid is weaker **OR** carboxylate ion is more stable **M2** O-H bond weakened / loses proton more easily **AND** by negative inductive effect of C=O / due to electronegative C=O **OR** carboxylate ion / anion is more stable **AND** due to delocalisation of minus charge by C=O / 2O	2

Q# 361/ Topic: **Chem 32** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	**M1** C-X / C-C*l* / C-O bond is stronger (in chlorobenzene / phenol) [1] **M2** p-orbital / lone pair on C*l* / O(H) / X (in chlorobenzene / phenol) [1] **M3** electrons of the (C*l* / O / electronegative atom) **AND** overlap / delocalise with π-electron cloud / delocalise into ring [1]	3
7(b)	 2-bromophenol  4-bromophenol structure and name correct [1]	2

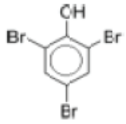
Q# 362/ Topic: **Chem 32** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8(c)	phenol	1
	ketone	1

Q# 363/ Topic: **Chem 32** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

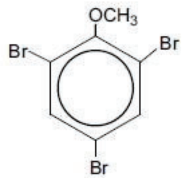
7(c)(i)	white precipitate	1
7(c)(ii)	$C_{14}H_{19}O_6N + 3NaOH \rightarrow C_{14}H_{16}O_6NNa_3 + 3H_2O$	2

Q# 364/ Topic: **Chem 32** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

<table>
<tr><td>7 (a) (i)</td><td>M1: phenol is more acidic than ethanol because the O–H bond in phenol is weakened / the phenoxide anion is stabilised / ethanol has an electron donating group
M2: p orbital / lone pair of electrons on O can be delocalised over / overlaps with ring</td><td>1
1</td></tr>
<tr><td>(ii)</td><td><table>
<tr><th>reagent</th><th>conditions</th><th>Structure</th></tr>
<tr><td>HNO₃</td><td>dilute, 5 °C</td><td> </td></tr>
<tr><td>Br₂</td><td>aqueous
(I: temperature)</td><td> </td></tr>
</table></td><td>3</td></tr>
<tr><td>(iii)</td><td>electrophilic substitution</td><td>1</td></tr>
</table>

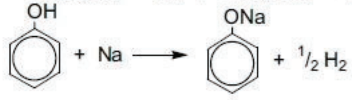
Q# 365/ Topic: **Chem 32** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i)

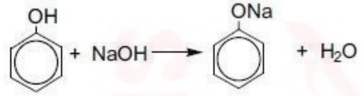


[1]

(ii) Na metal *or* NaOH [1]
Fizzes/gas given off with phenol *or* phenol dissolves (anisole doesn't) [1]
$C_6H_5OH + Na \rightarrow C_6H_5ONa + \frac{1}{2}H_2$ *or* $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$ [1]



or



(neutral) iron(III) chloride *[1]*
Solution goes purple/violet *[1]*
$3C_6H_5OH + FeCl_3 \rightarrow Fe(OC_6H_5)_3 + 3HCl$ *[1]*

[4]

Q# 366/ Topic: **Chem 32** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) (i) $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$ (*or* with $Na^+/H_2O/A^-$) [1]

(ii) pKa of nitrophenol is smaller/K_a is larger because it's a stronger acid/dissociates more than phenol [1]
stronger because the anionic charge is spread out moreover the NO_2 group *or* NO_2 is electron-withdrawing [1]

(iii) pKa = 1.0 [1]

(iv) Nitro group increases acidity / electron-withdrawing groups increase acidity [1]
[5]

(c) (i) **B** is phenyldiazonium cation, $C_6H_5{-}N^+{\equiv}N$ [1]

(ii)

reaction	reagent(s)	conditions
Step 1	**$NaNO_2$ + HC*l* or HNO_2** [1]	**T < 10°C** [1]
Step 2	**H_2O / aq**	**heat/boil/T > 10°** (both) [1]
Step 3	**HNO_3 NB HNO_3(aq) OK for both**	**dilute** (both) [1]

[4]
[5]

[Total: 14]

Q# 367/ Topic: **Chem 32** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (cyclohexanol & phenol) hydrogen bonding to (solvent) water molecules [1]
due to OH group [1]
[2]

(b) phenoxide anion is more stable (than cyclohexoxide) / OH bond is weaker [1]
due to delocalisation of charge / lone pair over the ring [1]
[2]

(c)

reagent	product with cyclohexanol	product with phenol
Na(s)	RONa *or* RO^-Na^+	ArONa *or* ArO^-Na^+
NaOH(aq)	***no reaction***	ArONa *or* ArO^-Na^+
Br_2(aq)	***no reaction***	tribromophenol
I_2(aq) + OH^-(aq)	***no reaction***	***no reaction***
an excess of acidified $Cr_2O_7^{2-}$(aq)	cyclohexanone	***no reaction***

five correct products 5 × [1]
five correct "no reaction"s [2]
(4 correct = [1]; 3 correct = [0])
[7]

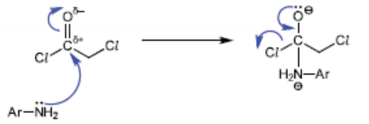
(d) *either* Br_2(aq): no reaction with cyclohexanol; decolourises *or* white ppt with phenol

or $Cr_2O_7^{2-} + H^+$: turns from orange to green with cyclohexanol; no reaction with phenol

correct reagent chosen **and** the correct "no reaction" specified [1]
correct positive observation [1]
[2]

[Total: 13]

Q# 368/ Topic: Chem 33 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)	$HOCH_2COOH + 2SOCl_2 \rightarrow ClCH_2COCl + 2SO_2 + 2HCl$	1
6(b)	to remove / neutralise excess H^+ / acid produced OR to react with any acidic by-products / HC*l* / SO_2 OR to react with any unreacted **W**	1
6(c)	 M1: curly arrow from **lone pair** on :NH_2 to carbonyl $C^{(\delta+)}{=}O$ M2: correct dipole on $^{\delta+}C{=}O^{\delta-}$ **AND** curly arrow from bond C=O to $O^{(\delta-)}$ M3: correct structure of the intermediate (inc. charges) M4: curly arrow from lone pair on :O^- to C=O **AND** curly arrow from C—C*l* to C*l*	4
6(d)	N / nitrogen can donate its lone pair / LP / pair of electrons	1

Q# 369/ Topic: **Chem 33** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(d)(iii)	• (CO)O—H bond weaker / more easy to donate H^+ in K • owing to negative inductive / electron withdrawing effect of C=O / COOH group • carboxylate anion stabilised / phenoxide anion is less stabilised *All three for two marks*	2

Q# 370/ Topic: **Chem 33** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

<table>
<tr><td>6(a)</td><td>M1: ethanoic acid > butanoic acid > water > ethanol

M2: a reason given in terms of an electron donating or an electron withdrawing group for one of:
strengthening of O–H bond OR weakening of O–H bond OR stability of anion

<i>Two out of the three alternatives M3, M4 and M5:</i>

M3: <u>ethanol</u>: positive inductive effect / electron donating effect of ethyl / alkyl / R group

M4: <u>butanoic acid</u>: positive inductive effect / electron donating effect of propyl / alkyl / R group

M5: (either ethanoic or butanoic) <u>acid</u>: negative inductive effect of either C=O or carbonyl OR negative charge delocalised over COO⁻</td><td>4</td></tr>
<tr><td>6(b)(i)</td><td>
<table>
<tr><th></th><th>reagents and conditions</th><th>observed change</th></tr>
<tr><td>test 1</td><td>Tollen’s reagent, warm
OR
Fehling’s solution, warm</td><td>silver mirror

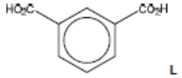
(brick) red ppt / solid</td></tr>
<tr><td>test 2</td><td>acidified MnO_4^-, warm</td><td>decolourises OR bubbles</td></tr>
</table>
M1 / M2: reagents and conditions × 2

M3: observations both correct</td><td>3</td></tr>
</table>

Q# 371/ Topic: **Chem 33** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(a)	CO_2 and H_2O / in words	1

Q# 372/ Topic: **Chem 33** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(b)(i)	 L	1
5(b)(ii)	**M1**: heat / reflux with acidified / alkaline KMnO4 (then acidify) **M2**: PCl_5 OR $SOCl_2$ / (heat with) PCl_3	2
5(b)(iii)	$C_8H_6O_4 + 2PCl_5 \rightarrow C_8H_4O_2Cl_2 + 2POCl_3 + 2HCl$ OR $C_8H_6O_4 + 2SOCl_2 \rightarrow C_8H_4O_2Cl_2 + 2SO_2 + 2HCl$ OR $3C_8H_6O_4 + 2PCl_3 \rightarrow 3\ C_8H_4O_2Cl_2 + 2H_3PO_3$	1

Q# 373/ Topic: **Chem 33** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

<table>
<tr><td>6(a)</td><td>M1 2-chloropropanoic acid > 3-chloropropanoic acid > propanoic acid [1]

M2 $CH_3CHClCO_2H$ / $ClCH_2CH_2CO_2H$ (are more acidic) as they contain an electronegative <i>Cl</i> atom so weaken O-H bond / stabilise carboxylate anion [1]

M3 $CH_3CHClCO_2H$ (is more acidic than $ClCH_2CH_2CO_2H$) as the <i>Cl</i> atom is closer to CO_2H so weaken O-H bond more / stabilise carboxylate anion more [1]</td><td>3</td></tr>
<tr><td>6(c)</td><td>
<table>
<tr><th></th><th>reagents and conditions</th><th>observed change</th></tr>
<tr><td>test 1</td><td>M1 Tollen’s reagent, warm
OR
Fehling’s solution, warm</td><td>silver mirror

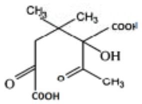
(brick)-red ppt.</td></tr>
<tr><td>test 2</td><td>M2 aqueous alkaline iodine
OR
2,4-DNPH</td><td>yellow ppt.

orange ppt.</td></tr>
<tr><td>test 3</td><td>M3 acidified MnO_4^-, warm</td><td>decolourises (and bubbles)</td></tr>
</table>
Two correct observations = 1 mark
Three correct observations = 2 marks</td><td>5</td></tr>
</table>

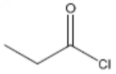
Q# 374/ Topic: **Chem 33** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

<table>
<tr><td>1(c)(iii)</td><td>
<table>
<tr><th>reactant</th><th>observation with $(CO_2H)_2$</th></tr>
<tr><td>warm H^+/MnO_4^-</td><td>decolourised
OR effervescence / bubbling / fizzing</td></tr>
<tr><td>2,4-DNPH</td><td>none / no reaction</td></tr>
<tr><td>warm Tollens’ reagent</td><td>none / no reaction</td></tr>
</table></td><td>2</td></tr>
</table>

Q# 375/ Topic: **Chem 33** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(b)	$C_{15}H_{22}O_4$	1
8(c)(i)		1
8(c)(ii)	CO_2	1
	oxidation / oxidative cleavage	1
8(c)(iii)	CH_3COCO_2H	1

Q# 376/ Topic: **Chem 33** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(b)(i)	propanoic acid, phenol, propan-1-ol	1
7(b)(ii)	• propan-1-ol: O-H bond strengthened by positive inductive effect of alkyl group OR propoxide ion is destabilised by positive inductive effect of alkyl group • phenol: O-H bond weakened by negative inductive effect of ring OR phenoxide ion is stabilised by delocalisation of oxygen lone pair into ring • propanoic acid: O-H bond weakened by negative inductive effect of C=O OR propanoate ion is stabilised by delocalisation of minus charge by C=O 1 mark for a correct explanation, max 2 marks	2
7(c)	Tollens’ reagent or Fehling’s reagent	1
	methanoic acid gives a silver mirror/solid with Tollen’s reagent OR red / orange ppt / solid with Fehlings’ reagent	1
7(d)	PCl_5 or PCl_3 (+heat) or $SOCl_2$ (added to propanoic acid)	1
	product of first step: 	1
	add product of first step to phenol in NaOH	1

Q# 377/ Topic: **Chem 33** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9(b)	benzoic acid > methylphenol > phenylmethanol methylphenoxide anion has delocalisation of the lone pair on oxygen over the ring benzoic acid has an (extra) electronegative oxygen or electron withdrawing C=O	3

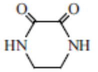
Q# 378/ Topic: **Chem 33** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

1(d)(ii)	the $KMnO_4$ would decolourise bubbles / gas evolution would be seen	2

Q# 379/ Topic: **Chem 33** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(b)(i)	$H^+(aq)$ + heat	1
7(b)(ii)	hydrolysis	1
7(b)(iii)	CH_3OH	1

Q# 380/ Topic: **Chem 33** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10 (a)	n(MnO_4^-) = 0.02 × 15.2/1000 = 3.04 × 10^{-4} mol n($C_2O_4H_2$) = 3.04 × 10^{-4} × 5/2 = 7.6 × 10^{-4} (in 25cm^3) = 3.04 × 10^{-3}mol in 100cm^3 M_r = 24 + 64 + 2 = 90 mass of $C_2O_4H_2$ = 3.04 × 10^{-3} × 90 = 0.2736 g (0.274) percentage = 0.2736 × 100/40 = 0.68%	[1] [1] [1]
(b) (i)	$SOCl_2$ *or* PCl_5 *or* PCl_3	[1]
(ii)	**J** is $CH_3OCO–COOCH_3$ **K** is 	[1] [1]

Q# 381/ Topic: **Chem 33** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2 (a) (i)	hydrogen chloride ***or*** HC*l*	**1**
(ii)	***either*** (RCOC*l*) has two electron-withdrawing groups/atoms, making the **more** δ+/electron deficient ***or*** (RCOC*l*) has an oxygen, making the **carbon more** δ+/electron deficient ***or*** (RCOC*l*) has two electron-withdrawing groups, **weakening** the **C–C*l*** bond	**1**

Q# 382/ Topic: **Chem 33** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

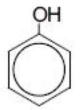
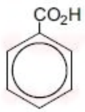
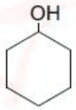
5 (a)	$CH_3CH_2COCl > CH_3CH_2CH_2Cl > C_6H_5Cl$	1	
	any two *of:* • C-C*l* bond strength is weakest in CH_3CH_2COCl ora • In C_6H_5Cl (no hydrolysis) C-C*l* bond is part of delocalised system **OR** p-orbital on C*l* overlaps with π system **OR** electrons from C*l* overlap with π system • CH_3CH_2COCl carbon in C-C*l* bond is more electron deficient since it is also attached to an oxygen atom ora	1+1	[3]

Q# 383/ Topic: **Chem 33** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) (i)	acidity of $ClCH_2CO_2H > CH_3CO_2H$ **AND** ($ClCH_2CO_2H$) as an electronegative/electron withdrawing C*l*	1	
(ii)	acidity of phenol > CH_3CH_2OH **AND** electrons on oxygen (on phenol) delocalised into ring **OR** benzene ring withdraws electrons from oxygen	1	
	stronger acid linked to weakening O-H bond/anion being stabilised	1	[3]

Q# 384/ Topic: **Chem 33** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a)

	H_2O			
Na	H_2	**H_2**	**H_2**	**H_2**
KOH(aq)	X	**X**	**X**	**X**
Na_2CO_3(aq)	X	**X**	**CO_2**	**X**

[5]

Q# 385/ Topic: **Chem 33** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a) (i) $SOCl_2$ *or* PCl_5 *or* PCl_3 (1)

(ii) $CH_3CO_2H + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$
or $CH_3CO_2H + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$
or $3CH_3CO_2H + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$ (1)
[2]

(b) (i) A is $C_6H_5CO_2C_2H_5$ (1)
B is $C_6H_5CONH_2$ (1)

(ii) ester (1)
amide (1)

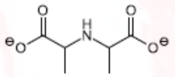
(iii) nucleophilic substitution / condensation (1) [5]

(c) (i) C is $ClCOCOCl$ (1)
D is $ClCOCOCOCl$ (1)

(iv) condensation (polymer) *or* polyester (1) [5]

[Total: 12]

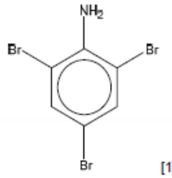
Q# 386/ Topic: Chem 34 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(c)(vi)		1

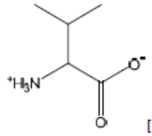
Q# 387/ Topic: **Chem 34** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

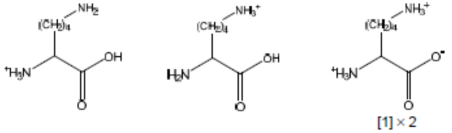
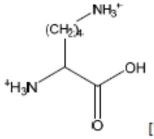
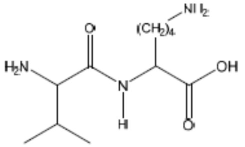
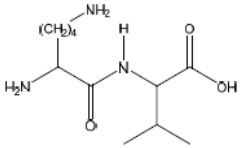
5(a)(i)	$CH_3CHClCOOH + H_2O \rightleftharpoons CH_3CHClCOO^- + H_3O^+$ OR $CH_3CHClCOOH \rightleftharpoons CH_3CHClCOO^- + H^+$	1
5(a)(ii)	M1: $[H^+] = 10^{-1.51} = 0.0309$ (mol dm^{-3}) M2: $K_a = 0.0309^2/0.60 = 1.592 \times 10^{-3}$ ecf $pK_a = –\log 1.592 \times 10^{-3} = 2.80$ ecf	2

Q# 388/ Topic: **Chem 34** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

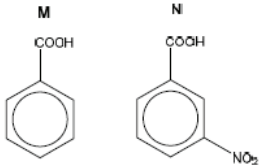
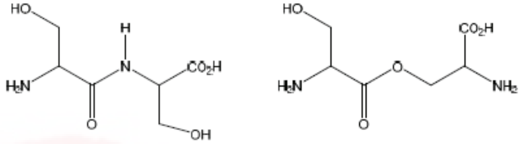
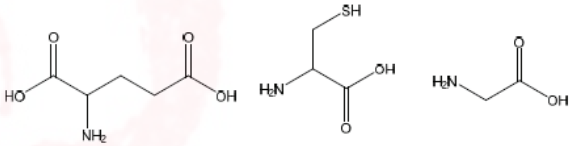
8(a)	bromine decolourised OR orange / brown to colourless [1] white precipitate [1]	2
8(b)	no change [1]	1
8(c)	 [1]	1
8(d)	2,4,6-tribromophenylamine [1] ECF 8(c) for a bromophenylamine	1

Q# 389/ Topic: **Chem 34** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10(a)	 [1]	1

10(b)	A and B any two from: [all net single positive charge]  [1] × 2 C at pH 1.0 [2+ positive charge]  [1]	3
10(c)	M1: peptide link correct and displayed unit including C=O M2: everything else correct  OR  [2]	2

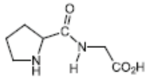
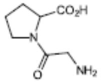
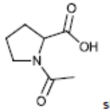
Q# 390/ Topic: **Chem 34** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

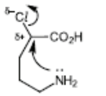
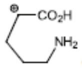
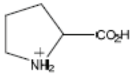
7(a)(i)		2
7(a)(ii)	**M1:** step 1 hot KMnO$_4$ / MnO$_4^-$ **M2:** step 2 conc. H$_2$SO$_4$ and conc. HNO$_3$ **M3:** step 3 Sn and conc. HC*l* (heat)	3
7(b)(i)	 **M1 / M2:** each structure **M3:** both displayed linkage	3
7(b)(ii)	molecular formula | number of structural isomers formed C$_9$H$_{19}$N$_3$O$_4$ | 4	1
7(c)(ii)	 one mark for two correct two marks for three correct	2

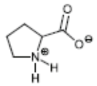
Question	Answer	Marks
8(a)(i)	**M1:** CH$_3$CO$_2$H and CH$_3$CO$_2^-$	3

7(c)(iii) is [1] mark, but the mark scheme is not given in the published mark scheme. Only 12 marks for Q7 are accounted for in the mark scheme.

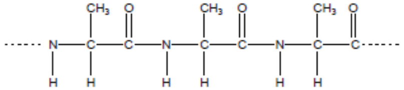
Q# 391/ Topic: **Chem 34** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(a)(i)	 **OR**  **M1**: peptide link shown **M2**: rest of Pro–Gly correct	2
7(a)(ii)	condensation **ALLOW** substitution / addition–elimination	1
7(b)(i)	(C$_4$H$_7$NHCO$_2$H +) NaOH → C$_4$H$_7$NHCO$_2$Na + H$_2$O	1
7(b)(ii)	 skeletal only	1

7(b)(iii)	$LiAlH_4$	1
7(c)(i)	$CH_2(CO_2C_2H_5)_2$: • (di)ester CH_2=CHCN: • alkene • nitrile/cyanide All three correct for two marks	2
7(c)(ii)	addition	1
7(c)(iii)	H_2 / Ni **OR** H_2 / Pt **OR** H_2 / Pd	1
7(c)(iv)	condensation / (nucleophilic) substitution / elimination	1
7(c)(v)	ethanol / C_2H_5OH / CH_3CH_2OH	1
7(c)(vi)	 **M1/2**: All four correct: • lone pair on NH_2 • curly arrow from N: to C of C—Cl • correct dipole on C—Cl • curly arrow from C—Cl to Cl **M3**: intermediate =  **OR** 	3
7(c)(vii)	Asterisk on *$CHCO_2H$	1

7(d)	9	1
7(e)(i)	**M1**:  **M2**: proton / H^+ transferred from carboxylic acid to amine	2
7(e)(ii)	 **M1**: glutamic acid towards + end (from the diagram) **M2**: proline and alanine towards – end (from the diagram) **M3**: Glu moves towards positive (pole) as negatively charged / contains a COO^- OR Pro/Ala move towards negative (pole) as positively charged / contains a NH_2^+ / contains a NH_3^+ **M4**: Ala moves farther than Pro because of lower M_r / size (with positive charge) ORA	4

Q# 392/ Topic: **Chem 34** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

10(b)(i)	 $\cdots\cdots\underset{H}{N}-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\overset{CH_3}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}\cdots\cdots$ • amide links displayed correct (NHCO OR CONH) • three monomers of Ala only • one repeat unit correctly identified • continuation bonds (with a polypeptide involving Ala only) mark as • ✓ ✓ ✓ [3]	3

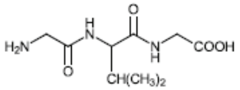
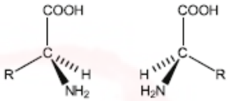
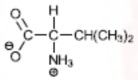
Q# 393/ Topic: **Chem 34** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)	**M1** phenylmethanamine / **U** > phenylamine / **T** > benzamide / **S** [1] any two from: • alkyl group is electron donating so lone pair more able to accept a proton • lone pair on N overlaps with delocalised system so less able to accept a proton • presence of electron-withdrawing oxygen / carbonyl group means lone pair is not available to accept a proton OR amides are neutral	3

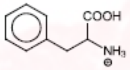
Q# 394/ Topic: **Chem 34** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(b)(i)	reaction 1 $LiAlH_4$ reaction 2 heat NH_3 under pressure/ heat NH_3 in a sealed tube	2
4(b)(ii)	reaction 1 reduction reaction 2 nucleophilic substitution	2

Q# 395/ Topic: **Chem 34** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

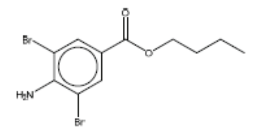
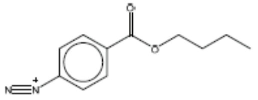
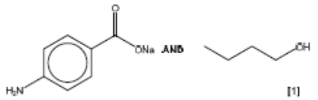
6(b)	 **M1** one peptide link fully displayed (but not contradicted by the other peptide link) **M2** rest of structure correct	2
6(c)(i)	**M1** optical isomerism **M2** 	2
6(c)(ii)	 $^{\ominus}O-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{NH_3^{\oplus}}{C}}-CH(CH_3)_2$	1

Q# 396/ Topic: **Chem 34** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

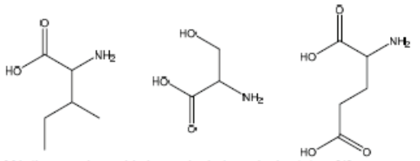
4(a)(i)	A = ester B = (2°) amide	2
4(a)(ii)	2	1
4(b)	 **M1** phenylalanine **M2** protonated amine **M3** (ethanol) CH_3CH_2OH	3
4(c)(i)	catalyst / halogen carrier	1
4(c)(ii)	**M1** —OH directs to 2,4 **AND** both 2 positions occupied / only position 4 is available **M2** —COOH directs to 3 position **AND** only position 3 is available / 5 is occupied	2
4(d)(i)	x = 14.4 / 100 × 100 / 1.1 = 13.1 13 carbon atoms (some working required)	1
4(d)(ii)	(250 – 205 = 45, so) CO_2H / C_2H_5O	1

Q# 397/ Topic: **Chem 34** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

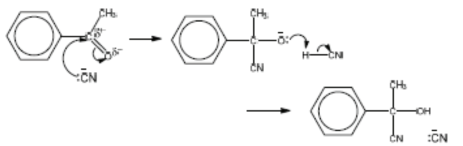
9(a)(i)	$RNH_2 + H^+ \rightarrow RNH_3^+$ OR $RNH_2 + HCl \rightarrow RNH_3Cl$ [1]	1
9(a)(ii)	weaker **AND** lone pair of N delocalised into benzene ring [1]	1

9(b)	 [1]  [1]  [1]	3

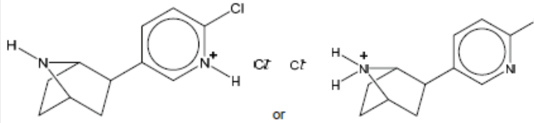
Q# 398/ Topic: **Chem 34** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(a)(i)	any one from: • OH⁻ / NaOH; aqueous / dilute; heat under reflux • H⁺ / HC*l* / H_2SO_4, aqueous / dilute; heat under reflux • protease or named protease; water; T = 30° – 40°C all three points in each bullet [1]	1
8(a)(ii)	 M1: three amino acids in any ionic / non-ionic states [1] M2: three amino acids in the correct ionic state for their conditions [1]	2

Q# 399/ Topic: **Chem 34** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(c)(ii)	 **M1 and M2:** first structure – award one mark for two points correct, award two marks for four points correct. • correct polarity shown on C=O bond • curly arrow from double bond to O of the C=O • lone pair shown on C of CN⁻ ion • curly arrow from C (on CN⁻ ion) to C of C=O M3: middle structure • correct intermediate **AND** curly arrow from lone pair on O⁻ to H⁺ or H of H_2O or HCN M4: third structure • correct product **AND** either CN⁻ reformed (if HCN seen in step 2) OR curly arrow on H-CN bond towards CN in step 2	4

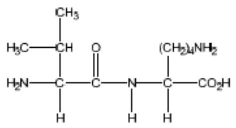
Q# 400/ Topic: **Chem 34** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

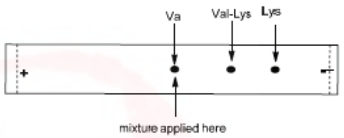
9(b)(i)	partially ionised and proton acceptor	1
9(b)(ii)		1

Q# 401/ Topic: **Chem 34** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

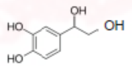
4(f)(i)	$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$ **M1** Correct formulae of CH_3COCl or $CH_3CONHCH_3$ **M2** rest of the equation	2
4(f)(ii)	condensation or addition-elimination	1

Q# 402/ Topic: **Chem 34** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(a)	 **M1** amide bond displayed [1] **M2** rest of the structure [1]	2

6(b)	 **M1** valine on the cross [1] **M2** Val-Lys and Lys on the right of the cross (in any order) [1] **M3** relative order of Val-Lys and Lys (on the same side of the cross) [1] **Explanation** • Val does not move as it is a zwitterion / neutral (at pH6) OR Lys / Val-Lys move towards **negative** (pole) as they are **positively charged** • Lys moves the **furthest** as it has the **lowest** M_r (with the same positive charge) OR Val-Lys moves the **least** as it has the **largest** M_r (with the same positive charge) [1] × 2	5

Q# 403/ Topic: **Chem 34** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(c)(i)	(phenyldiazonium ion is stabilised because) positive charge is delocalised by ring / positive charge is spread over ring	1
9(c)(ii)		1
	N_2	1

Q# 404/ Topic: **Chem 34** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(b)(i)	($RCO_2H + H_2NR' \longrightarrow$) $RCONHR' + H_2O$	1
7(b)(ii)	*broken:* C-O, N-H *formed:* C-N, O-H	2
7(b)(iii)	bonds formed: 305 + 460 or 765 bonds broken: 360 + 390 or 750 (both) $\Delta H = 750 - 765 = \mathbf{-15}$ (kJ)	2
7(c)	(If $\Delta G = 0$, then) $\Delta H = T\Delta S$ $\Delta S = \Delta H / T = -6000 / 298 = \mathbf{-20.1}$ (J mol^{-1} K^{-1})	2

Q# 405/ Topic: **Chem 34** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(d)(ii)	Sn and HC*l* heat + conc. (then add NaOH)	2

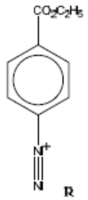
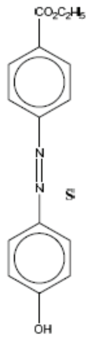
Q# 406/ Topic: **Chem 34** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 4/www.SmashingScience.org

4(b)(i)	nitrogen has a lone pair which can accept a proton or can be donated to a proton	1
4(b)(ii)	e.g. $C_4H_9NH_2 + HCl \rightleftharpoons C_4H_9NH_3^+ + Cl^-$ etc.	1
4(b)(iii)	butanamide is non-basic / neutral *or* (much) less basic than butylamine	1
4(b)(iv)	$LiAlH_4$ (in dry ether)	1

Q# 407/ Topic: **Chem 34** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 3/www.SmashingScience.org

3(a)(iv)	**A** is CH_3NH_2 **B** is HCO_2H	2

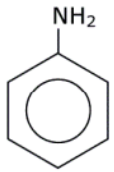
Q# 408/ Topic: **Chem 34** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(e)(ii)	 **R**  **S**	
	structure of diazonium salt **R**	1
	structure of azo dye **S**	1

Q# 409/ Topic: **Chem 34** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(c)	(benzocaine) is less (basic than ethylamine) **AND** **lone pair** (on N) is less available to **accept** a proton / H^+ since (lone pair on N) is delocalised over the ring *or* phenyl ring is electron withdrawing group OR ethylamine is more basic (than benzocaine) **AND** **lone pair** (on N) is more available to **accept** a proton / H^+ since ethyl / alkyl group is electron-donating group	2

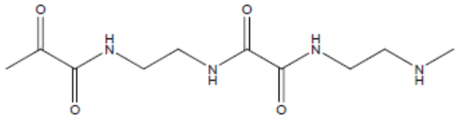
Q# 410/ Topic: **Chem 34** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

2(e)(i)	$n(BaCO_3) = 1.66 / 197.3 = 8.4(1) \times 10^{-3}$ mol	1
2(e)(ii)	$n(RNCO) = 8.41 \times 10^{-3}$ mol, so $M_r = 1 / (8.41 \times 10^{-3}) = \mathbf{119}$	1
2(e)(iii)	molecular formula = C_7H_5NO	1
2(e)(iv)		1
	Total:	23

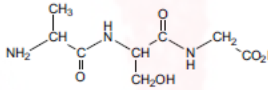
Q# 411/ Topic: **Chem 34** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(b)	$C_{10}H_{13}NH_2 + H_3O^+ \rightleftharpoons C_{10}H_{13}NH_3^+ + H_2O$	1
5(c)	in compound **H**, the alkyl groups are electron donating / have a positive inductive effect, so it is more basic than NH_3	1
	in phenylamine, the lone pair (of N) is delocalised over the aryl group / benzene ring, so phenylamine is less basic than NH_3	1

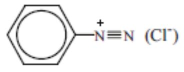
Q# 412/ Topic: **Chem 34** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(e)(i)	lone pair receive / accepts a proton / H^+	1 1	2
1(e)(ii)	$H_2NCH_2CH_2NH_2 + 2HCl \rightarrow ClH_3NCH_2CH_2NH_3Cl$ OR $H_2NCH_2CH_2NH_2 + 2H^+ \rightarrow H_3N^+CH_2CH_2N^+H_3$	1	1
1(f)(i)	amide bond, displayed or –CONH– rest of the molecule with continuation bonds 	1 1	2
1(f)(ii)	condensation / addition – elimination	1	1
1(f)(iii)	any named polyalkene / eg polyethene, PVC allow Bakelite or Kevlar	1	1
	Total:		20

Q# 413/ Topic: **Chem 34** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 (a) (i)		[2]
(ii)	$M_r = 233$	[1]
(b) (i)	$NH_2CH(CH_2OH)CO_2^-$	[1]
(ii)	**F** is a DC power supply **G** is the anode OR positive electrode **I** is the cathode OR negative electrode **H** is filter paper (OR gel) soaked in **buffer** solution	[4]
(iii)	**P** is $NH_2CH_2CO_2^-$ *or* $NH_2CH_2CO_2H$ *or* glycine **S** is $[ala–ser–gly]^{(-)}$ glycine is the smallest, so travels fastest; tripeptide is the largest, so travels slowest	[1] [1] [1]
(c) (i)	heat with H_3O^+ OR heat with $OH^-(aq)$	[1]
(ii)	hydrolysis	[1]
		[Total: 13]

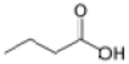
Q# 414/ Topic: **Chem 34** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a) (i)	$C_6H_5NO_2$ + $6e^-$ + $6H^+$ $\longrightarrow$ $C_6H_5NH_2$ + $2H_2O$	[1]
(ii)	$2C_6H_5NO_2 + 14HCl + 3Sn \rightarrow 2C_6H_5NH_3Cl + 3SnCl_4 + 4H_2O$	[2]
(b)	(M_r values: $C_6H_5NO_2$ = 123 $C_6H_5NH_3Cl$ = 129.5) theoretical yield = 5.0 × 129.5/123 = 5.26 g percentage yield = 100 × 4.2/5.26 = 79.8% (80%)	[1] [1]
(c) (i)	$C_6H_5NH_2$ = 93 yield of phenylamine = 4.2 × 93/129.5 = 3.016 g	[1]
(ii)	mass left in water = 3.016 – 2.68 = 0.336g K_{part} = (2.68/50)/(0.336/25) = 3.99	[1] [1]
(d)	phenylamine is less basic that ethylamine the lone pair on N is delocalised over the ring… …making it less available for reaction with a proton/δ+ H	[2]
(e) (i)	step 1: HNO_2 OR ($NaNO_2$ + HCl) at $T \leqslant 10\,°C$ step 2: boil/heat in water	[1] [1]
(ii)	**E** is 	[1]
		[Total: 13]

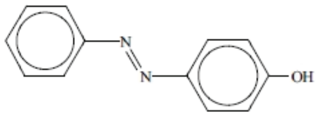
Q# 415/ Topic: **Chem 34** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

(c) (i)	V: it has two amine/NH_2 groups (which can be protonated) *or* it has an amine/NH_2 group on its side chain/R group	1
(ii)	four (TT, TU, UT, UU)	1

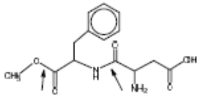
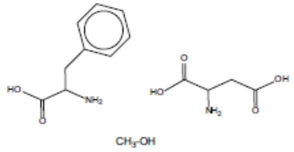
Q# 416/ Topic: **Chem 34** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

(c) (i)	see line on diagram in **(b)**	1
(ii)		1

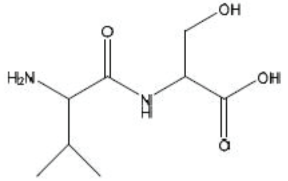
Q# 417/ Topic: **Chem 34** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(b) (i)	white precipitate/solid	1
(ii)	between 0° C and 10 °C	1
(iii)	**M1**: double bond between nitrogen atoms **M2**: rest of molecule 	1 1

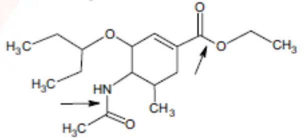
Q# 418/ Topic: **Chem 34** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

(ii)		2
(iii)		3
(b)	M1: hydrogen bonding M2: between the NH_2 groups and water **or** CO_2/C=O/–OH groups and water (allow names) **or** lone pair on N/O with water	2

Q# 419/ Topic: **Chem 34** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 (a) (i)	condensation	1
(ii)		2

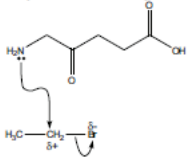
Q# 420/ Topic: **Chem 34** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 (a)	amide group circled **OR** indicated as diagram ester group circled **OR** indicated as diagram 	1 1	[2]

Q# 421/ Topic: **Chem 34** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 (a)	• (move in different directions) some amino acids have a different charge • (move at different speeds) some amino acids have a different size/different charge • (some amino acids do not move at all) some amino acids exist as a zwitterions/have no net(overall) charge/neutral/both NH_2/COOH are charged in amino acids	1 1 1	[3]

Q# 422/ Topic: **Chem 34** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(c) (i)	dipole on C-Br curly arrow breaking C-Br bond curly arrow from **lone pair** on N to carbon in C-Br bond 	1 1 1	
(ii)	nucleophilic substitution	1	
(iii)	HBr or hydrogen bromide	1	[5]

Q# 423/ Topic: **Chem 34** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

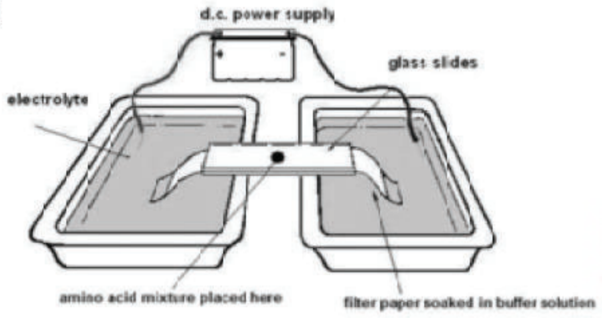
3 **(a)** heat in dilute HC*l*(aq) (or H_2SO_4(aq)) [1]

Q# 424/ Topic: **Chem 34** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(iv) piperidine should be a **stronger base/more basic** than ammonia because of the electron-donating (alkyl/CH_2) groups [1]

Q# 425/ Topic: **Chem 34** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)**



power supply (idea of complete circuit)
electrolyte/buffer solution
gel/filter paper/absorbent paper
(amino acid) sample/mixture [centre of plate] 4 × [1]

[4]

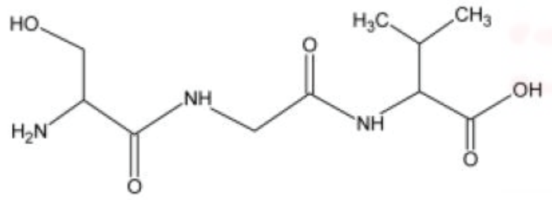
(b) *any two from:*
size/M_r (of the amino acid species)
charge (on the amino acid species)
temperature 2 × [1]

[2]

Q# 426/ Topic: **Chem 34** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** **(i)** **six/6** (gsv, sgv, gvs, vgs, svg,vsg) [1]

(ii)



two **displayed** peptide bonds [1]
correct formula of peptide [1]

(iii) valine (**allow** glycine) [1]

Q# 427/ Topic: **Chem 34** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c) (base is a) proton acceptor [1]

basicities: ethylamine > NH_3 > phenylamine [1]

ethylamine (more basic) due to electron donating ethyl group [1]

phenylamine (less basic) due to lone pair being delocalised into the ring [1]
[4]

Q# 428/ Topic: **Chem 34** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(c)

Addition OR	**condensation**
requires C=C/double bond	does not need C=C/double bond
uses the same functional group	needs two different functional groups
same general (empirical) formula as monomer	different formula
no loss of small molecule/H_2O/HCl	small molecule /H_2O/HCl is formed

Any two differences [1]
[2]

Q# 429/ Topic: **Chem 34** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)**

Glutamic acid between + and start point [1]
Lysine between – and start point [1]
Glycine at, or *very* close to, start point [1]
[3]

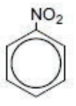
Q# 430/ Topic: **Chem 34** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** **(i)** Condensation [1]

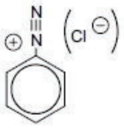
(ii) ala-ala, gly-gly, ala-gly [2]
[3]

Q# 431/ Topic: **Chem 34** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) (i)



D



E

[1] + [1]

(ii) step 2: Sn + HC*l* conc. + reflux — **NOT** LiA*l*H$_4$, NaBH$_4$ *(warm is insufficient)* [1] [1]

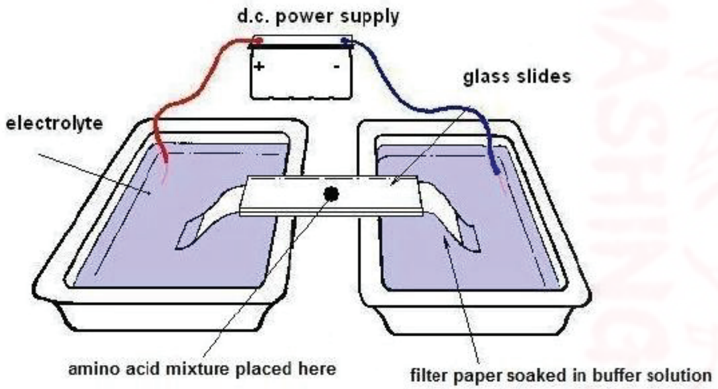
step 4 is conditional of structure E

step 4: warm + in H$_2$O [1]

[5 max 4]

Q# 432/ Topic: **Chem 34** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 (a) Sketch and label the apparatus used to carry out electrophoresis e.g



Marks: power supply / electrolyte + filter paper / buffer / acid mixture central 4 × [1]

[4]

(b) (i) pH of the buffer [1]

Charge on the amino acid species [1]

(ii) Size of the amino acid species / M$_r$ [1]

Voltage applied [1]

Magnitude of the charge (on the amino acid species) [1]

Temperature [1]

(max 3)

[max 3]

Q# 433/ Topic: **Chem 34** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) (i) $C_2H_5NH_2 + HA \rightarrow C_2H_5NH_3^+ + A^-$ (HA can be H$_2$O, HC*l* etc.) [1]

Allow $\rightleftharpoons$ instead of arrow

(ii)

most basic		least basic
ethylamine	**ammonia**	**phenylamine**

[1]

(iii) ethylamine > NH$_3$ due to electron-donating ethyl/alkyl group [1]

phenylamine < NH$_3$ due to delocalisation of lone pair over ring [1]

[4]

Q# 434/ Topic: **Chem 34** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(ii) hydrogen bonding (1)

(iii) because it's an amide *or* not an amine *or* its lone pair is delocalised (over C=O) or less available due to electronegative oxygen [NOT: **E** is neutral, but the diamine is basic] (1)

Q# 435/ Topic: **Chem 34** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 (a) hydrogen bonding (1)

diag: NH$_2$CH$_2$CH$_2$OH---OHCH$_2$CH$_2$NH$_2$ *or* NH$_2$CH$_2$CH$_2$OH---NH$_2$CH$_2$CH$_2$OH
(i.e. H-bond from OH group to either OH or NH$_2$) (1) [2]

(b) propylamine is more basic than phenylamine (1)

because lone pair on N is delocalised over ring in phenylamine (so less available for protonation)

or the propyl group is electron-donating, so the lone pair is more available (1) [2]

(c) $HOCH_2CH_2NH_2 + H^+ \longrightarrow HOCH_2CH_2NH_3^+$

or $HOCH_2CH_2NH_2 + HCl \longrightarrow HOCH_2CH_2NH_3^+Cl^-$

or $HOCH_2CH_2NH_2 + H_2O \longrightarrow HOCH_2CH_2NH_3^+OH^-$

(reaction with any acceptable Bronsted acid accepted) [1]

(e) ethanolamine:

	Na		effervescence / bubbles produced	
or	$Cr_2O_7^{2-}$ / H$^+$		colour turns from orange to green	
or	MnO_4^- / H$^+$		purple colour disappears	
or	PC*l*$_3$ / PC*l*$_5$ / SOC*l*$_2$	(1)	steamy fumes	(1)

phenylamine:

	Br$_2$(aq)		decolourises / white ppt formed		
or	HNO$_2$ / H$^+$ at T<10°C, then phenol in NaOH	(1)	coloured dye formed	(1)	[4]

[Total: 12]

Q# 436/ Topic: **Chem 34** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

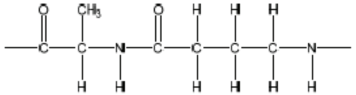
(e) **(i)** A species having positive and negative ionic centres / charges, with no overall charge [1]

(ii) $^{-}O_2C\text{-}C_6H_4\text{-}NH_3^{+}$ [1]

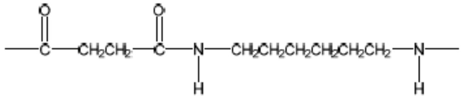
[2]

[Total: 16]

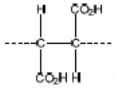
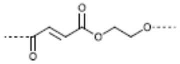
Q# 437/ Topic: Chem 35 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(b)(iv)	 middle amide group shown displayed [1] rest of structure correct [1]	2
5(b)(v)	condensation	1
5(b)(vi)	C is biodegradable / easily hydrolysed	1

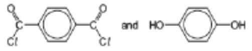
Q# 438/ Topic: **Chem 35** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(d)	 **M1:** correct displayed amide linkage **M2:** the rest of the repeat unit correct including trailing bonds	2

Q# 439/ Topic: **Chem 35** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(b)(i)	 if more than one unit drawn **ALLOW** one repeat unit identified	1
6(b)(ii)	 **M1:** presence of an ester group from the diol and COOH **OR** presence of an ester group from the fumaric acid and OH **M2:** rest of repeat unit including 'dangling' bonds	2
6(b)(iii)	C—C bonds are non-polar / polyalkenes cannot be hydrolysed OR polyesters / they can be broken down by hydrolysis	1

Q# 440/ Topic: **Chem 35** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

<table>
<tr><td>10(a)</td><td><table><tr><th>pair of monomers</th><th>type of polymerisation</th></tr><tr><td>HOCH₂CH₂OH and HO₂CCH₂CO₂H</td><td>condensation</td></tr><tr><td></td><td>condensation</td></tr><tr><td>CH₂CHCF₃ and CH₃CHCH₂</td><td>addition</td></tr></table>ALL correct [1]</td><td>1</td></tr>
<tr><td>10(c)(i)</td><td>epoxy resin [1] ALLOW Super Glues</td><td>1</td></tr>
<tr><td>10(c)(ii)</td><td>compound with two amine groups per molecule, amine groups must not be on the same carbon atom [1]
e.g. $H_2NCH_2CH_2NH_2$</td><td>1</td></tr>
</table>

Q# 441/ Topic: **Chem 35** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

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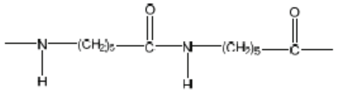
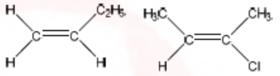
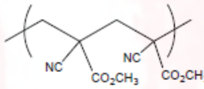
8(c)(i)	any structure containing one COOH / COCl and NH_2 groups in the same molecule [1]	1
8(c)(ii)	$HOCH_2CH_2OH$ [1] ethan(e)-1,2-diol [1] ecf for diols HO_2CCO_2H or $ClOCCOCl$ [1] ethan(e)dioic acid or ethan(e)dioyl chloride [1] ecf for diacids / diacyl chlorides	4

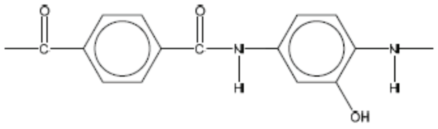
Q# 442/ Topic: **Chem 35** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

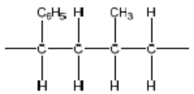
<table>
<tr><td>9(c)(i)</td><td><table><tr><th></th><th>σ-bonds only</th><th>π-bonds only</th><th>both σ- and π-bonds</th></tr><tr><td>bonds broken</td><td></td><td></td><td>✓</td></tr><tr><td>bonds formed</td><td></td><td></td><td>✓</td></tr></table>Both ticks correct</td><td>1</td></tr>
<tr><td>9(c)(ii)</td><td>M1: amide link
M2: rest of the structure</td><td>2</td></tr>
<tr><td>9(d)</td><td>or CH₃CCl=CH₂ and C₂H₅CH=CHCH₃ each correct structure scores one mark</td><td>2</td></tr>
<tr><td>9(e)</td><td>C-C bonds are non-polar / polyalkenes cannot be hydrolysed and polyamides can be broken down by hydrolysis</td><td>1</td></tr>
</table>

Q# 443/ Topic: **Chem 35** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	 **M1** correct C–C backbone (with correct side groups) **M2** continuation bonds and two repeat units	2
5(a)(ii)	addition	1
5(a)(iii)	*Any two of:* permanent dipole (attraction): C, N, O, OR CO, CN, CO_2CH_3, OCH_3 H-bonding: N, O OR CO, CN London/van der Waals: N, C, H, O OR CH_3, CN, CO_2CH_3, C–C chains	2

Q# 444/ Topic: **Chem 35** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

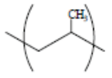
<table>
<tr><td>5(a)(ii)</td><td>one amide bond displayed in full [1]
rest of the structure – one repeat unit only [1]</td><td>2</td></tr>
<tr><td>5(b)</td><td>[1] for each correct tick<table><tr><th></th><th>σ-bonds only</th><th>π-bonds only</th><th>both σ- and π-bonds</th></tr><tr><td>bonds broken</td><td></td><td>✓</td><td></td></tr><tr><td>bonds formed</td><td>✓</td><td></td><td></td></tr></table></td><td>2</td></tr>
</table>

<table>
<tr><td>5(c)</td><td>

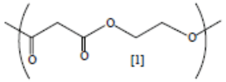
$-\overset{C_6H_5}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$

M1 length of chain with both monomers [1]
M2 continuation bonds [1]</td><td>2</td></tr>
<tr><td>5(d)(i)</td><td>C-C bonds are non-polar / have no dipole so cannot be hydrolysed [1]</td><td>1</td></tr>
<tr><td>5(d)(ii)</td><td>M1 <u>Hydrolysis</u> using acid / base / alkali / enzymes [1]
M2 action of UV light [1]</td><td>2</td></tr>
</table>

Q# 445/ Topic: **Chem 35** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

<table>
<tr><td>7(a)(i)</td><td>

[1]



[1]

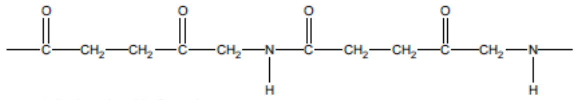
+ H_2O

[1]</td><td>3</td></tr>
<tr><td>7(a)(ii)</td><td>• <i>for addition polymerisation:</i>
ΔS will be negative, as many gas molecules are combining to form one (large) molecule
• <i>for condensation polymerisation:</i>
ΔS likely to be positive, (as each pair of monomer molecules join to chain, two molecules of) <u>water</u> forms</td><td>2</td></tr>
</table>

Q# 446/ Topic: **Chem 35** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

<table>
<tr><td>9 (a) (i)</td><td>polyester : <i>Terylene</i> / polylactic acid (PLA) /
polyamide : nylon / <i>Kevlar</i> / Nomex</td><td>1</td></tr>
<tr><td>(ii)</td><td>water <i>or</i> hydrochloric acid / hydrogen chloride</td><td>1</td></tr>
<tr><td>(b) (i)</td><td>
<table>
<tr><th>polymer</th><th>biodegradable</th></tr>
<tr><td>A</td><td>yes</td></tr>
<tr><td>B</td><td>yes</td></tr>
<tr><td>C</td><td>no</td></tr>
<tr><td>D</td><td>yes</td></tr>
</table>
</td><td>2</td></tr>
<tr><td>(ii)</td><td>$HOCH_2CH_2OH$ and  or equivalent 1,4-diacyl chloride
or equivalent 1,4-diester</td><td>2</td></tr>
</table>

Q# 447/ Topic: **Chem 35** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

<table>
<tr><td>(e)</td><td>

$-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\underset{H}{\underset{|}{N}}-$

correct displayed amide formula
correct polyamide with two repeat units</td><td>1
1</td><td>[2]</td></tr>
<tr><td>Total</td><td></td><td></td><td>15</td></tr>
</table>

Q# 448/ Topic: **Chem 35** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

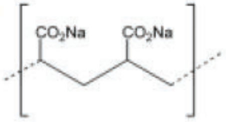
5 (a) (i) **many** monomers form a polymer [1]

(ii) addition [1]

(iii) C=C/double/π bond is broken **and** new C-C single bond**<u>s</u>** are formed
or double bond breaks and forms single bonds with other monomers [1]

[3]

(c) (i)

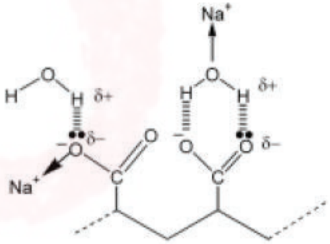


carbon chain **and** CO_2H [1]
at least one sodium salt [1]

(ii) 120° to 109(.5)° [1]
due to the change from a trigonal/sp^2 carbon to a tetrahedral/sp^3 carbon [1]

[4]

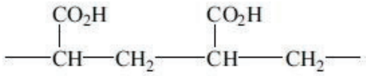
(d) (i)



Any four:
hydrogen bond **labelled**
water H-bonded to O through H atom
δ+/δ- shown on each end of a H-bond
lone pair shown on O^- *or* C=O *or* H_2O on a **correct H-bond**
Na^+ shown as coordinated to a water molecule [3]

Q# 449/ Topic: **Chem 35** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 (a) (i)



$$-\overset{CO_2H}{\overset{|}{CH}}-CH_2-\overset{CO_2H}{\overset{|}{CH}}-CH_2-$$

[1]

(ii) Addition [1]

(iii) Hydrogen bonding [1]
[3]

(b) (i) more / increase water absorbing properties (allow attracts water more) [1]

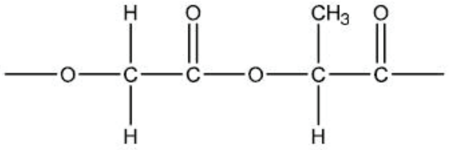
more polar(ity)/more hydrophilic / has ionic side-chains (as well as hydrophilic ones) [1]

(ii) It should be biodegradable/decompose [1]
[3]

Q# 450/ Topic: **Chem 35** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(ii) condensation [1]

(d) (i)



ester linkage shown [1]
rest of repeat unit correct (ONE) [1]

Q# 451/ Topic: **Chem 35** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

(b) Reasons: Plastics/polymers pollute the environment for a long time do not decompose/ biodegrade quickly [1]
They are mainly produced from oil [1]
Produce toxic gases on burning [1]
max two

Strategy 1: Recycle polymer waste / use renewable resources [1]
Strategy 2: Develop biodegradable polymers [1]
[max 3]

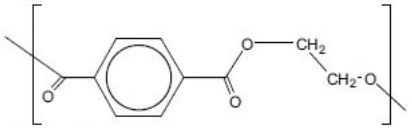
Q# 452/ Topic: **Chem 35** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(b) Any TWO from:
addition needs unsaturated/double bonds/alkene
condensation eliminates a small molecule
condensation needs a molecule other than a hydrocarbon
empirical formula of addition polymer is the same as that of its monomer
condensation needs two different functional groups

(**NOT** – "condensation needs two different monomers") 2 × [1]

(c) (i) Water [1]

(ii)



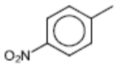
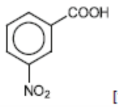
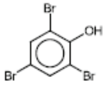
Correct 'ester' bond [1]
'sticks' to rest of molecule [1]
Note : candidates need only show 'brackets' if more than one repeat unit shown

(iii) Polyesters [1]

(d) Monomers in *Terylene* have to alternate in order to condense out water (owtte) [1]

Alkenes can link in any order (and still form a polyalkene) (***or*** diagram showing this) [1]

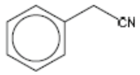
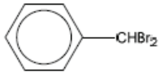
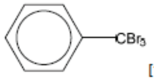
Q# 453/ Topic: Chem 36 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	In F: (phenyl)amine **AND** carboxylic acid In J: phenol **AND** ester *Any two for one mark* *All four for two marks*	**2**
4(a)(ii)	0 (zero) in **F AND** 2 (two) in J	**1**
4(b)(i)	step 1 CH_3Cl **AND** $AlCl_3$ [1] step 2 D =  [1] step 4 (hot) Sn **AND** concentrated **AND** HC*l* [1]	**3**
4(b)(ii)	 [1] COOH group is electron-withdrawing group and 3,5-/meta- directing [1]	**2**
4(c)(i)	$C_9H_{18}O$	**1**
4(c)(ii)	hydrolysis [1] acid–base / neutralisation [1]	**2**
4(d)(i)	$C_6H_5OH + Na \rightarrow C_6H_5O^{(-)}Na^{(+)} + ½H_2$	**1**
4(d)(ii)		**1**

Q# 454/ Topic: **Chem 36** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(a)	PCl_5 OR PCl_3 OR $SOCl_2$ [1]	1
9(b)(i)	amide [1]	1
9(b)(ii)	HCl / hydrogen chloride OR $C_2H_5NH_3Cl$ / ethylammonium chloride [1]	1
9(c)(i)	$LiAlH_4$ [1]	1
9(c)(ii)	reduction [1]	1

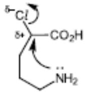
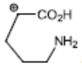
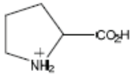
Q# 455/ Topic: **Chem 36** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(d)(i)	Br_2 + UV light [1]	1
7(d)(ii)	 [1]	1
7(d)(iii)	**CHECK** Q is correct step 2 – KCN in ethanol + heat [1] step 3 – HCl(aq) + heat/reflux/boil [1]	2
7(d)(iv)	 OR  [1] **ALLOW** any viable organic by-product from this radical substitution reaction, e.g. $C_6H_5CH_2CH_2C_6H_5$	1

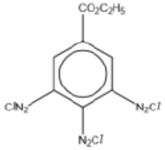
Q# 456/ Topic: **Chem 36** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(c)(i)	G = $HOCH_2CH_2CH_2CH_2OH$ H = $NCCH_2CH_2CH_2CH_2CN$	2
6(c)(ii)	**M1:** step 1 NaOH(aq) + heat **M2:** step 2 acidified $KMnO_4$ + heat / acidified $K_2Cr_2O_7$ + heat **M3:** step 3 CN^- / KCN / NaCN + heat **M4:** step 4 $LiAlH_4$ **ALLOW** Na in ethanol or H_2 + Ni / Pd / Pt	4

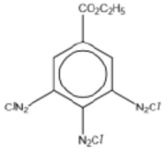
Q# 457/ Topic: **Chem 36** ALvl Chemistry/2021/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(c)(i)	$CH_2(CO_2C_2H_5)_2$: • (di)ester CH_2=CHCN: • alkene • nitrile/cyanide All three correct for two marks	2
7(c)(ii)	addition	1
7(c)(iii)	H_2 / Ni **OR** H_2 / Pt **OR** H_2 / Pd	1
7(c)(iv)	condensation / (nucleophilic) substitution / elimination	1
7(c)(v)	ethanol / C_2H_5OH / CH_3CH_2OH	1
7(c)(vi)	 **M1/2:** All four correct: • lone pair on NH_2 • curly arrow from N: to C of C—Cl • correct dipole on C—Cl • curly arrow from C—Cl to Cl **M3:** intermediate =  OR 	3

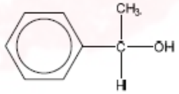
Q# 458/ Topic: **Chem 36** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(c)(iv)	**M1** Sn and HCl **M2** heat and concentrated (dependent on metal (Fe / Sn) and acid seen for M1)	2
5(c)(v)	 **M1** 1 × diazonium salt with ester group unchanged **M2** 3 × diazonium salt (to match formula)	2
5(c)(vi)	warm / T ⩾ 30 °C **AND** H_2O / named aqueous acid	1

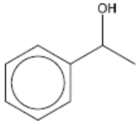
Q# 459/ Topic: **Chem 36** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(c)(iv)	**M1** Sn and HCl **M2** heat and concentrated (dependent on metal (Fe / Sn) and acid seen for M1)	2
5(c)(v)	 **M1** 1 × diazonium salt with ester group unchanged **M2** 3 × diazonium salt (to match formula)	2
5(c)(vi)	warm / T ⩾ 30 °C **AND** H_2O / named aqueous acid	1
5(d)(i)	5	1
5(d)(ii)	**M1** only one peak **M2** singlet at δ 6.0–9.0 ppm **OR** **M1** singlet(s) only **M2** only one peak at δ 6.0–9.0 ppm	2

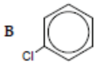
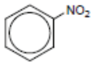
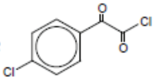
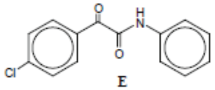
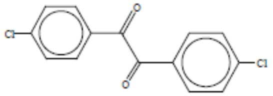
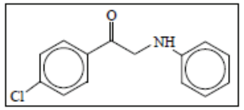
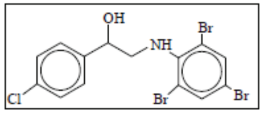
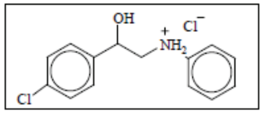
Q# 460/ Topic: **Chem 36** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(d)(i)		1
4(d)(ii)	$LiAlH_4$ or $NaBH_4$	1
4(d)(iii)	conc H_2SO_4 / conc H_3PO_4 / Al_2O_3	1

Q# 461/ Topic: **Chem 36** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(f)(i)		1
9(f)(ii)	**M1:** step 1: CH_3COCl + $AlCl_3$ [1] **M2:** step 2: $NaBH_4$ / $LiAlH_4$ [1] **M3:** step 3: conc. H_2SO_4, heat [1]	3

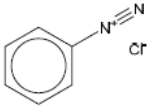
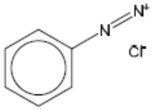
Q# 462/ Topic: **Chem 36** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(a)(i)	$HO_2C–CO_2H$ OR $HO_2C–COCl$	1
7(a)(ii)	$SOCl_2$ OR PCl_5	1
7(b)(i)	B  D  C   E	4
7(b)(ii)	**M1** step 1: $Cl_2 + AlCl_3$ **M2** step 3: conc. $HNO_3 + H_2SO_4$ **M3** step 4: Sn + conc. HCl **M4** step 6: $LiAlH_4$ **M5** *any two of:* heat / T ⩾ 60 °C / reflux for step 1 T⩽ 60 °C / warm for step 3 heat / T ⩾ 60 °C / reflux for step 4	5
7(b)(iii)		1
7(b)(iv)	steps 1, 2 and 3	1
7(c)	 no reaction  	4

Q# 463/ Topic: **Chem 36** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(b)(i)	**Y** $CH_3COCO_2CH_3$ **Z** $CH_3C(OH)(CN)CO_2CH_3$	2
5(b)(ii)	**M1/M2** step 1: CH_3OH and (conc) H_2SO_4 + heat **M3** step 2: HCN + NaCN catalyst **M4** step 3: T > 100°C / heat with Al_2O_3 (or heat with c. H_2SO_4)	4

Q# 464/ Topic: **Chem 36** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(c)(i)	step 1 conc. HNO_3 + H_2SO_4 (and temperare 50–55 °C) [1] step 2 Sn + HCl AND one of conc.HCl + heat [1] step 4 H_2O warm / heat [1]	3
7(c)(ii)	 OR 	1
7(c)(iii)	step 1 electrophilic substitution	1
7(c)(iv)	$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$	1

Q# 465/ Topic: **Chem 36** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9(c)	step 1 treat benzoic acid with $SOCl_2$ *or* PCl_5 to make the acyl chloride formula is **C_6H_5COCl** step 2 dissolve the methylphenol in NaOH(aq) (and shake with the benzoyl chloride)	3

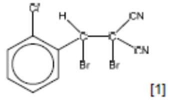
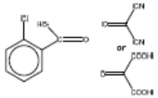
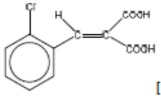
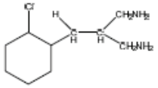
Q# 466/ Topic: **Chem 36** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8(b)(i)	step 1 heat with $AlCl_3$ + $(CH_3)_2CHCl$ *or* $CH_3CH{=}CH_2$ step 2 heat with $AlCl_3$ + CH_3COCl step 3 NaOH + I_2 (*or* Cl_2) (then H^+) step 4 $LiAlH_4$ (in dry ether)	4
8(b)(ii)	step 2 electrophilic (aromatic) substitution step 4 reduction	2

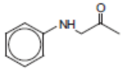
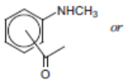
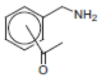
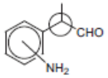
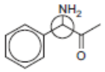
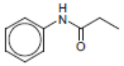
Q# 467/ Topic: **Chem 36** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(b)(ii)	step 1 Sn + HCl [1] concentrated / reflux / heat [1] step 2 CH_3COCl [1] step 3 $KMnO_4$ / manganate(VII) / MnO_4^- (acidified / alkaline) and heat [1] step 4 aqueous HCl and heat [1] step 5 ethanol, H_2SO_4, concentrated / reflux / heat [1]	6

Q# 468/ Topic: **Chem 36** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(c)	reagent	structure of product	type of organic reaction	8
	excess Br_2(aq)	 [1]	(electrophilic) addition	
	excess hot, conc. MnO_4^-(aq)	 [1] + [1]	oxidation	
	excess hot, aqueous HCl	 [1]	hydrolysis	
	excess H_2 / Pt catalyst	 both CH_2NH_2 formed [1] both arene and alkene reduced [1]	reduction / hydrogenation	
		structures [6]	2 correct for 1 mark total [2]	

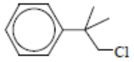
Q# 469/ Topic: **Chem 36** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

<table>
<tr><td>5(a)</td><td><table><tr><th>J</th><th>K</th><th>L</th><th>M</th></tr><tr><td>amine
methyl ketone</td><td>aromatic amine
aldehyde</td><td>amine
methyl ketone</td><td>amide</td></tr></table></td><td></td></tr>
<tr><td></td><td>J and L correct</td><td>1 + 1</td></tr>
<tr><td></td><td>K correct</td><td>1 + 1</td></tr>
<tr><td></td><td>M correct</td><td>1</td></tr>
<tr><td>5(b)(i)</td><td>hydrolysis</td><td>1</td></tr>
<tr><td>5(b)(ii)</td><td>P is $C_6H_5NH_2$</td><td>1</td></tr>
<tr><td></td><td>Q is $CH_3CH_2CO_2Na$</td><td>1</td></tr>
<tr><td>5(c)</td><td>J is  or  or </td><td>1</td></tr>
<tr><td></td><td>K is </td><td>1</td></tr>
<tr><td></td><td>L is </td><td>1</td></tr>
<tr><td></td><td>M is </td><td>1</td></tr>
<tr><td></td><td>**K&L only:** two chiral atoms shown</td><td>1</td></tr>
<tr><td>5(d)</td><td>W is $C_6H_5CO_2Na$</td><td>1</td></tr>
<tr><td></td><td>Total:</td><td>14</td></tr>
</table>

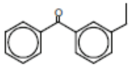
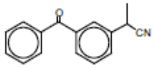
Q# 470/ Topic: **Chem 36** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(a)(i)	optical, because it contains a / one chiral C-atom or chiral C-atoms or chiral atom / centre or C* indicated or C with 4 **different** groups	1
4(a)(ii)	$C_{10}H_{14}O + 3H_2 \longrightarrow C_{10}H_{20}O$ correct formulae	1
	balancing	1
4(b)(i)	electrophilic substitution	1
4(b)(ii)	step 3 reduction	1
	step 5 substitution / hydrolysis	1
4(b)(iii)	step 1 $(CH_3)_2CHCl + AlCl_3 / AlBr_3 / FeCl_3 / FeBr_3$	1 + 1
	step 2 $HNO_3 + H_2SO_4$ conc (T < 55 °C)	1
	step 3 Sn + HC*l*	1
	step 4 HNO_2 (*or* $NaNO_2 + HCl$) (at T < 10 °C)	1
	the two temperatures for steps 2 and 4	1

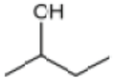
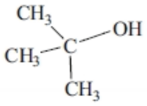
Q# 471/ Topic: **Chem 36** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	$(CH_3)_3C\text{-}Cl$ / $(CH_3)_2C=CH_2$	1
	$AlCl_3$ + heat	1
5(a)(ii)	(UV) light	1
5(a)(iii)		1
5(a)(iv)	ammonia / NH_3	1
	heat in sealed tube / heat under pressure	1

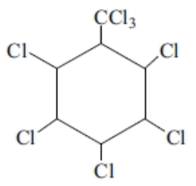
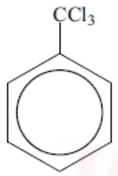
Q# 472/ Topic: **Chem 36** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 (a)	T is  U is 	[1] [1]
(b)	step 1: C_6H_5COCl + $AlCl_3$ (+ heat) step 2: CH_3CH_2Cl + $AlCl_3$ (+ heat) step 3: Br_2 + light (*or* heat) step 4: KCN + heat (in ethanol) step 5: H_3O^+ OR H^+ in H_2O OR HC*l* (aq) etc AND heat / boil / reflux	[1] [1] [1] [1] [1]
(c)	step 1: electrophilic substitution OR nucleophilic substitution step 5: hydrolysis OR nucleophilic substitution	[1] [1]
		[Total: 9]

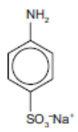
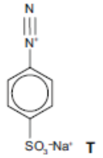
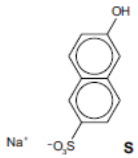
Q# 473/ Topic: **Chem 36** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

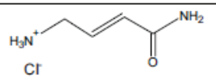
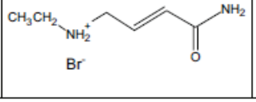
<table>
<tr><td>(d)</td><td><table><tr><th>reagent</th><th>observation</th></tr><tr><td>alkaline iodine solution</td><td>yellow ppt. formed</td></tr><tr><td>universal indicator</td><td>blue / purple colour formed</td></tr><tr><td>2,4-dinitrophenylhydrazine</td><td>yellow / orange ppt formed</td></tr><tr><td>Tollens' reagent</td><td>no reaction</td></tr></table></td><td>3</td></tr>
<tr><td>(e) (i)</td><td>$LiAlH_4$</td><td>1</td></tr>
<tr><td>(ii)</td><td>
(must be skeletal)</td><td>1</td></tr>
<tr><td>(iii)</td><td></td><td>1</td></tr>
</table>

Q# 474/ Topic: **Chem 36** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 1/www.SmashingScience.org

(b) **(i)**	sp^2	**1**
(ii)	$x = 60$ / $C_{60}H_{60}$	**1**
(c) **(i)**	reaction 1: Cl_2 and UV light; reaction 2: $AlCl_3$, Cl_2 (NOT aqueous);	**1** **1**
(ii)	(free) radical substitution	**1**
(iii)	 *or* 	**1**

Q# 475/ Topic: **Chem 36** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** **(i)**	 **R**  **T**  **S**	**3**
(ii)	Sn + HCl HNO_2 or $NaNO_2$ + HCl step 1 (linked to a reduction) reflux/heat/ >50 °C **or** conc/6M (HCl) **and** step 2 ≤10°C	**3**
(iii)	diazonium (group)	**1**
7		**3**
		<u>**12**</u>

reagent	structure of product	type of reaction
HCl		acid-base **or** neutralisation
CH_3CH_2Br		(nucleophilic) substitution

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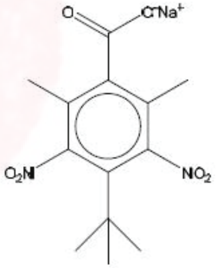
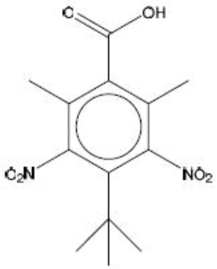
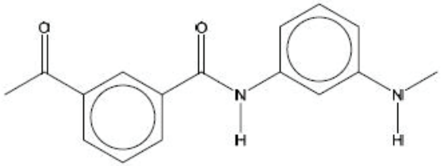
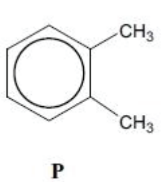
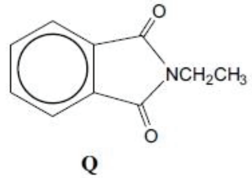
Q# 476/ Topic: **Chem 36** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 **(a)** **(i)**	heat with catalyst ***or*** heat with Al_2O_3/SiO_2	**1**
(ii)	**B** is $CH_3CH_2CH_3$	**1**
(iii)	**C** is $CH_2{=}CHCH_2CH_2CH_3$ **D** and **E** are $CH_3CH{=}CHCH_2CH_3$ (one shown as cis, the other as trans) **F** is $CH_3CH_2CH_2CO_2H$ **G** is CH_3CO_2H **H** is $CH_3CH_2CO_2H$	**1** **1** **1**
(iv)	geometrical *or* cis-trans *or E–Z*	**1**

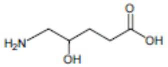
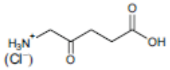
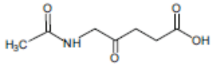
Q# 477/ Topic: **Chem 36** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6 **(a)** **(i)**	CH_3COCl ***or*** ethanoyl chloride	**1**
(ii)	electrophilic substitution	**1**
(iii)	conc HNO_3 **and** conc H_2SO_4	**1**
(iv)	CHI_3  or 	**1** **1**
(b) **(i)**		**1**
(ii)	polyamide ***or*** condensation	**1**
(iii)	H_2O / water	**1**
(iv)	Sn / Fe + HCl + conc / aq / heat/warm	**1**

Q# 478/ Topic: **Chem 36** ALvl Chemistry/2015/s/TZ 1/Paper 4/Q# 2/www.SmashingScience.org

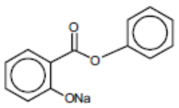
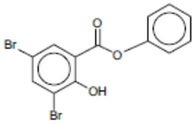
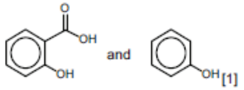
(b) (i)	 **P**  **Q**	**1** **1**
(ii)	step 1: heat with $MnO_4^-/KMnO_4$ (+ acid or alkali) step 2: PCl_3 + heat **or** $SOCl_2$ **or** PCl_5 step 4: $LiAlH_4$ (in dry ether)	**1** **1** **1**
		[Total: 7]

Q# 479/ Topic: **Chem 36** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(d)	Y =  W =  X =  each structure 1 mark	3	[3]

Q# 480/ Topic: **Chem 36** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(c)

Na	 (or ionic)	redox/reduction
Br$_2$		(electrophilic) substitution
NaOH	 [1] or ionic 	hydrolysis/ acid-base/

1 mark for each correct structure
for reaction types, 2 correct = 1 mark, 3 correct = 2 marks

4
2

[6]

Q# 481/ Topic: **Chem 36** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** **(i)** –OH *or* hydroxyl groups (allow alcohol groups) [1]

(ii) alkenes *or* C=C (double) bonds *or* carbon double bonds [1]

(iii) $CH_3CH(OH)$ *or* CH_3CO- groups [1]

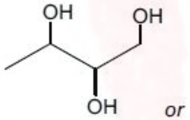
(b) **V** is $CH_3CH(OH)CH{=}CH_2$ [1]

W is $CH_3CH{=}CHCH_2OH$ [1]

(c) compound **V** shows **optical** isomerism

(**ecf** for 'geometric(al)' if candidate's **V** is capable of cis-trans) [1]

[1]

(d) 

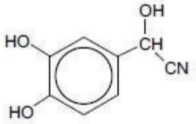
or $CH_3CH(OH)CH(OH)CH_2OH$ [1]

[Total: 8]

Q# 482/ Topic: **Chem 36** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(b) **(i)**

Compound **Z** is

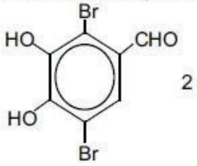


[1]

step 1: HCN + NaCN *or* HCN + base [1]
step 2: H_2 + Ni *or* $LiAlH_4$ *or* Na + ethanol [1]

(ii) bromine decolourises *or* goes from orange to colourless *or* white ppt. formed [1]

e.g.

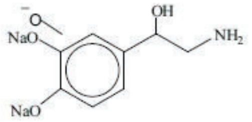


2 or 3 bromines in ring

[1]

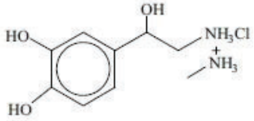
(c)

(i)



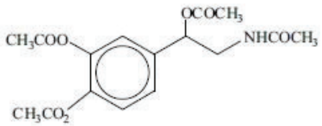
(*or* ionic) [1]

(ii)



(*or* ionic) [1]

(iii)



M1: amide [1]
M2: alcoholic ester [1]
M3: <u>both</u> phenolic esters [1]
[5] max [4]

(d) amide [1]
ester [1]

[Total: 14]

Q# 483/ Topic: **Chem 36** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(e) **(i)** alkene(1), amide(1) [2]

(ii) NH_3 [1]

(iii) H_2O [1]

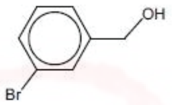
(iv) HCl (aq)/H_3O^+ **and** heat/reflux (**not** warm) [1]
or OH^- (aq), heat and acidify

[5]

[Total: 17]

Q# 484/ Topic: **Chem 36** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) $Cl\text{-}CH_2CH_2\text{-}CO_2H$ [1]
$HO\text{-}CH_2CH_2CH_2\text{-}Cl$ [1]



[1]

[3]

Q# 485/ Topic: **Chem 36** ALvl Chemistry/2013/w/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

(e) **G** is CH_3CH_2COCl
H is $SOCl_2$ *or* PCl_5
J is $NaCl$ [2]
(or corresponding Br compounds for **G**, **H** and **J**; CH_3CH_2COBr, $SOBr_2$, NaBr)

[Total: 18]

Q# 486/ Topic: **Chem 36** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

(b) **(i)** $(CH_3)_3C\text{–}Cl$ (any unambiguous structure *or* name) [1]

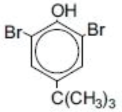
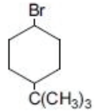
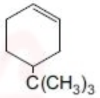
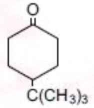
(ii) reduction *or* hydrogenation [1]

(iii) *either* CH_3CO_2H **and** heat with (conc) H_2SO_4
or
CH_3COCl [1]

(iv) reflux [1]

dilute HCl [1]
[5]

(c) **(i)**

reagent and conditions	product with **A**	product with **B**
$Br_2(aq)$		no reaction
heat with HBr	no reaction	
pass vapour over heated Al_2O_3	no reaction	
heat with acidified $K_2Cr_2O_7$	no reaction	

[6]

(ii) *either:* $Cr_2O_7^{2-}/H^+$: no observation with **A and** goes from orange to green with **B.**
or:
$Br_2(aq)$: white ppt. with **A and** no observation/ppt with **B** [1]

[7]

[Total: 17]

Q# 487/ Topic: **Chem 36** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

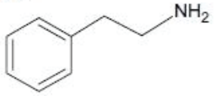
(d) **(i)** step 1: nucleophilic substitution [1]

step 2: hydrolysis [1]

(ii) step 1: KCN (in ethanol) **and** reflux [1]

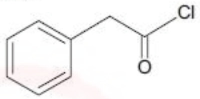
step 2: H_3O^+ / aqueous acid **and** reflux [1]

(iii) **T** is



[1]

W is



[1]
[6]

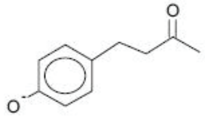
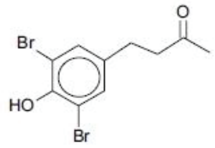
[Total: 15]

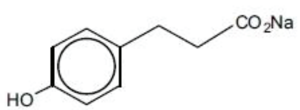
Q# 488/ Topic: **Chem 36** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** phenol [1]
ketone [1]

[2]

(b)

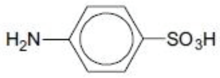
reagent	observation	structure of product	type of reaction
sodium metal	**effervescence /bubbles/fizzing**		*redox*
aqueous bromine	**decolourises** *or* **white ppt.**		*electrophilic substitution*

aqueous alkaline iodine	**yellow ppt.**		*oxidation*

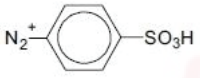
[2]

[8]

(c) **(i)**



J



K

[1] + [1]

(ii) step 1: $NaNO_2$ + HC*l* *or* HNO_2 [1]

at T < 10°C [1]

step 2: (add **K** to a solution of **G)** in aqueous NaOH [1]

[5]

(d) $(CH_3CH_2CO_2H) \xrightarrow[\text{[1]}]{SOCl_2/PCl_5\ /PCl_3\ +\ \text{heat}} \underset{\text{[1]}}{CH_3CH_2COCl} \xrightarrow[\text{[1]}]{\text{add to } \mathbf{G} \text{ (in NaOH(aq))}} \mathbf{L}$

ecf from CH_3COOH **[3]**

[Total: 18]

Q# 489/ Topic: **Chem 36** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4 **(a)** $K_2Cr_2O_7 + H^+$ + heat under reflux [1]

(b) nucleophilic substitution [1]

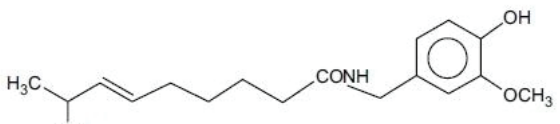
(c) heat under reflux + aqueous HC*l* [1]

(d) alkene [1]

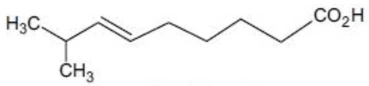
(e) amide *or* ester [1]

[5]

(f)

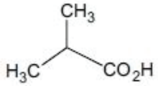


capsaicin



C (cis/trans)

D

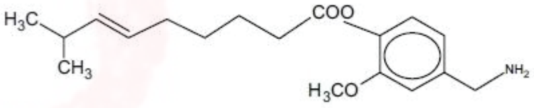


E

(-1 for CN- bond attachment)

F

alternative structure for capsaicin



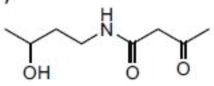
ecf 5 × [1]

[5]

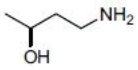
[Total: 10]

Q# 490/ Topic: **Chem 36** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

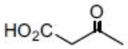
(c) **(i)**



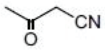
F



G



H



J

F must be an **amide**

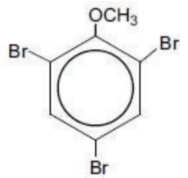
[4]

(ii) reaction 1: H_2 + Ni *or* $LiAlH_4$ [1]
reaction 2: heat + aqueous HC*l* [1]
[6]

[Total: 14]

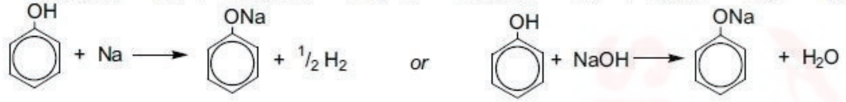
Q# 491/ Topic: **Chem 36** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i)



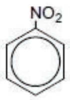
[1]

(ii) Na metal *or* NaOH [1]
Fizzes/gas given off with phenol *or* phenol dissolves (anisole doesn't) [1]
$C_6H_5OH + Na \rightarrow C_6H_5ONa + \frac{1}{2} H_2$ *or* $C_6H_5OH + OH^- \rightarrow C_6H_5O^- + H_2O$ [1]

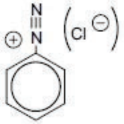


(neutral) iron(III) chloride *[1]*
Solution goes purple/violet *[1]*
$3C_6H_5OH + FeCl_3 \rightarrow Fe(OC_6H_5)_3 + 3HCl$ *[1]*
[4]

(b) (i)



D



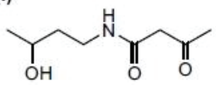
E

[1] + [1]

(ii) step 2: Sn + HC*l* **NOT** LiA*l*H$_4$, NaBH$_4$ [1]
conc. + reflux *(warm is insufficient)* [1]

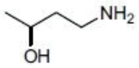
step 4 is conditional of structure E
step 4: warm + in H_2O [1]
[5 max 4]

(c) (i)

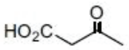


F

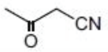
F must be an **amide**



G



H



J

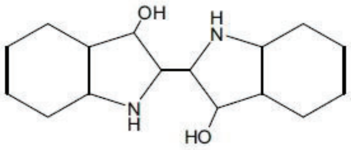
[4]

(ii) reaction 1: H_2 + Ni *or* LiA*l*H$_4$ [1]
reaction 2: heat + aqueous HC*l* [1]
[6]

[Total: 14]

Q# 492/ Topic: **Chem 36** ALvl Chemistry/2012/s/TZ 1/Paper 4/Q# 3/www.SmashingScience.org

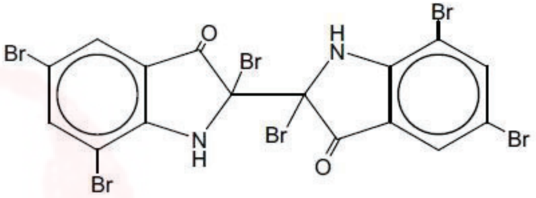
(d) (i)



[1]

(ii) $M_r = 262$, so 2.5 g = 2.5/262 = 9.54×10^{-3} mol [1]
(1 mol indigo absorbs 9 mol of H_2)
so volume of $H_2 = 9 \times 24 - 9.54 \times 10^{-3}$ = **2.06 dm^3** (2060 cm^3) [1]
[3]

(e)



2 x Br **on C=C** [1]
a Br on each ring [1]
TWO non-adjacent Br on **each ring** [1]
[3]

Q# 493/ Topic: **Chem 36** ALvl Chemistry/2011/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

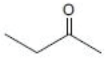
5 (a) (i) C=C double bonds / alkenes

(ii) –OH groups / accept alcohols or acids

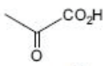
(iii) CH_3CO– or $CH_3CH(OH)$– groups

(iv) carbonyl, >C=O, groups / accept aldehydes <u>and</u> ketones 4 × [1]
[4]

(b)



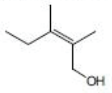
D



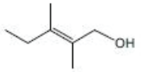
E

2 × [1]
[2]

(c) isomers of **C**



cis

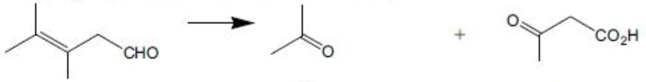


trans

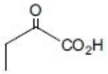
correct structure (excl. stereochemistry) [1]
cis and trans drawn correctly [1]
type of isomerism is **cis-trans *or* geometrical isomerism** [1]
[3]

Q# 494/ Topic: **Chem 36** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

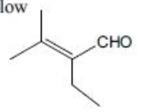
(b) (allow displayed, skeletal *or* structural formulae)



D **E** **F**

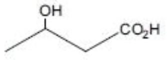
(**no mark** for )

for **D** allow



(D + E + F): 3 × [1]

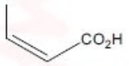
(c) (allow displayed, skeletal ***and*** structural formulae)
Must be consistent with **F**



G

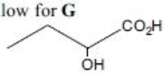
H
(only allow mark for **H** if **G** is the 3-OH acid)

J



K

allow for **G**



(N.B. letters **H**, **J**, **K** can be swapped around) (G + H + J + K): 4 × [1]

geometrical *or* cis-trans isomerism [1]

[Total: 14]

Q# 495/ Topic: **Chem 36** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

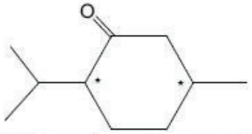
5 (a)

transformation	reagent + conditions
$C_2H_4 \rightarrow C_2H_5Cl$	**HC*l*, no light or catalyst**
$C_2H_5OH \rightarrow C_2H_5Cl$	**conc HC*l* + ZnC*l*$_2$ *or* SOC*l*$_2$ *or* PC*l*$_5$ *or* PC*l*$_3$ and heat**
$C_2H_6 \rightarrow C_2H_5Cl$	**C*l*$_2$ + light**
$C_2H_4 \rightarrow C_2H_4Cl_2$	**C*l*$_2$, no light or catalyst**
$CH_3CO_2H \rightarrow CH_3COCl$	**SOC*l*$_2$ *or* PC*l*$_5$ *or* PC*l*$_3$ and heat**
 H3C— → H3C— —Cl	**C*l*$_2$ + A*l*C*l*$_3$**
 —CH3 → —CH2Cl	**C*l*$_2$ + light or heat**

[6]

Q# 496/ Topic: **Chem 36** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

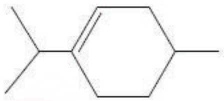
6 (a)



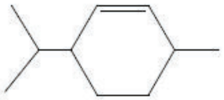
(1) for each centre – more than 2 centres shown deduct 1 mark [2]

(b) (i) step 1 LiA*l*H$_4$ *or* NaBH$_4$ *or* Na + ethanol *or* H$_2$ + Ni (1)
step 2 heat with A*l*$_2$O$_3$ / porous pot or conc. H$_2$SO$_4$ / H$_3$PO$_4$ (1)

(ii)



L (1)

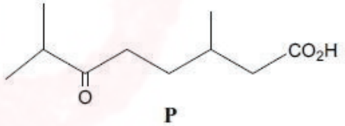


M (1)

(letters may be reversed) [4]

(c) (i) **M** (no mark)

(ii)



P

i.e. 3,7-dimethyl-6-oxo-octanoic acid (1)

(iii) 2,4-DNPH (1) orange ppt. with **P** (none with **N**) (1)
Mark ecf from candidates' P [3]

Q# 497/ Topic: **Chem 36** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 (a) (i) ester (1)

(ii) H is nitrobenzene – structure needed here (1)
J is phenyldiazonium chloride – structure needed here (1)

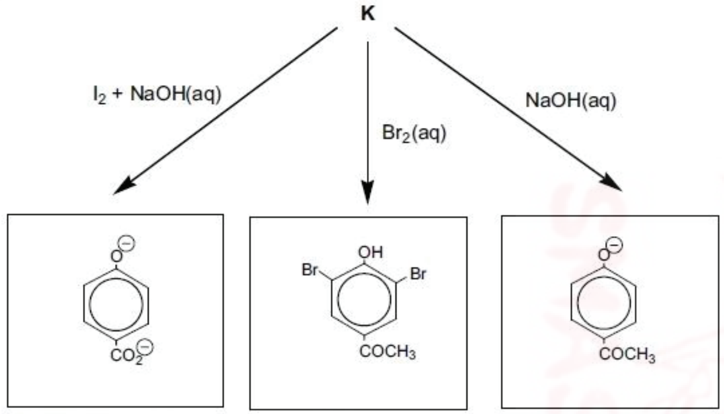
(iii) step 2 Sn/Zn + HC*l* / H$_2$ + named cat / NaBH$_4$ / LiA*l*H$_4$ / Na + ethanol (1)
step 3 HNO$_2$/NaNO$_2$ + HC*l* at T = 10°C or less (1)
step 4 heat/warm to T > 10°C (1)
step 5 CH_3COCl / $CH_3COCOCOCH_3$ (1) [7]

(b) **(i)** compounds that have the same molecular formula, but different structures (1)

(ii) phenol (NOT hydroxy) (1)
(methyl) ketone *or* carbonyl (1)

(iii) K is 4-ethanoylphenol, HO-C_6H_4-$COCH_3$ (must be 1,4- disubstituted isomer) (1)

(iv)



((1) for CO_2^-; (1) for –O⁻)
In any positions

(2 × Br needed)

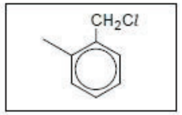
(anion needed)

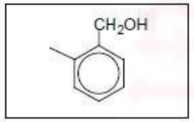
[4]
[8 max 7]

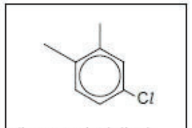
[Total: 14]

Q# 498/ Topic: **Chem 36** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

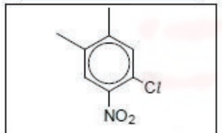
7



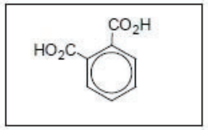


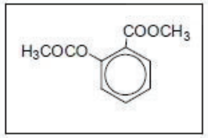


(ignore orientation)



(ignore orientation of both)





[6]

[Total: 6]

Q# 499/ Topic: **Chem 36** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

(d) **(i)** X is CH_3CH_2CN (1)

(ii) step 1 is KCN in ethanol, heat [HCN negates] (1)
step 2 is H_2+Ni / Pt or $LiAlH_4$ or Na in ethanol [NOT $NaBH_4$ or Sn/HC*l*] (1) [3]

Q# 500/ Topic: **Chem 36** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5 **(a)** **(i)** I: $KMnO_4$ [1]
heat with H^+ *or* OH^- [1]
II: $SOCl_2$ *or* PCl_5 *or* PCl_3 (NOT aq) [1]

(ii) -[-CO-C_6H_4-CO-NH-C_6H_4-NH-]- (Peptide bond must be displayed for minm) [1]
[4]

(b) **(i)** CH_3NHCO-C_6H_4-$CONHCH_3$ (1 mark for each end) [1] + [1]

(ii) $HOCH_2CH_2O$-CO-C_6H_4-CO-OCH_2CH_2OH for [1]
or the polymer -[- OCH_2CH_2O-CO-C_6H_4-CO-]- for [2]
[4 max 3]

(c) **(i)** Cl^- $^+NH_3$-C_6H_4-NH_3^+ Cl^- (1 mark for each end) [1] + [1]

(ii) H_2N-$C_6H_2Br_2$-NH_2 *or* H_2N-$C_6H_2Br_3$-NH_2 *or* H_2N-C_6Br_4-NH_2 [1]
[3]

(d) I: HNO_2 (*or* $NaNO_2$ + HCl/H_2SO_4) [1]
at T < 10°C [1]

II: *m*-prop-2-yl phenol, $(CH_3)_2CH$-C_6H_4OH [1]
+ NaOH(aq) [1]
[4]

Q# 501/ Topic: Chem 37 ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(e)(i)	mobile = ethyl ethanoate stationary = SiO_2 / silica or Al_2O_3 / alumina	1
6(e)(ii)	*R*$_f$ = distance travelled by solute / substance / compound / component ÷ distance travelled by solvent (front)	1
6(e)(iii)	X is more attracted / more affinity / adsorbed more to the **stationary phase** OR lidocaine dissolves better in the solvent ORA	1

Q# 502/ Topic: **Chem 37** ALvl Chemistry/2022/m/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(f)(i)	quartet AND triplet	1
6(f)(ii)	• δ 7.1 = attached to aromatic ring / **H—Ar** • δ 3.0 = alkyl next to C=O / —$CH_{(2)}$–C=O • δ 2.3 = alkyl next to aromatic ring / $H_{(3)}$C–Ar *All three correct for two marks*	2
6(f)(iii)	9 (nine)	1

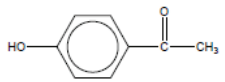
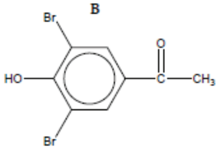
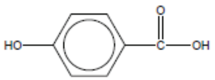
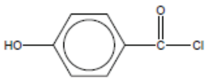
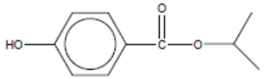
Q# 503/ Topic: **Chem 37** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

	$C_6H_5CH_2^+$ [1]	
9(e)(i)	a [1]	1
9(e)(iii)	d [1]	1
9(e)(iii)	b, c, f [1]	1
9(e)(iv)	f [1]	1

Q# 504/ Topic: **Chem 37** ALvl Chemistry/2021/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(a)	6 [1]	1

Q# 505/ Topic: **Chem 37** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

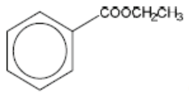
9(a)	**A**  **B**  **C** CHI_3 **D**  **E**  **F**  one mark for each structure	6

Not sure why 9(a) is given this numbering system, no other question part is present for Q# 9 in the question paper, nor any other part is given in the mark scheme published.

Q# 506/ Topic: **Chem 37** ALvl Chemistry/2021/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(b)(ii)	compound	number of peaks in proton NMR	number of peaks in carbon-13 NMR	2
	HCO_2H	2	1	
	HO_2CCO_2H	1	1	
	$HO_2CCH_2CH_2CO_2H$	2	2	
	one mark for three, four or five correct two marks for six correct			
6(b)(iii)	OH peak disappears **AND** proton / H exchanges with deuterium			1

Q# 507/ Topic: **Chem 37** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(a)	(because $CDCl_3$ / it) does not give a peak [1] OR because $CHCl_3$ does give a peak	1
9(b)	as a **standard** / **reference** for (chemical shift measurements) [1]	1
9(c)	ester [1]	1
9(d)(i)	• (δ = 1.4) triplet • (δ = 1.4) two H on neighbouring C atom • (δ = 4.3) quartet / quadruplet • (δ = 4.3) three H on neighbouring C atom mark as • ✓ • ✓ [2]	2
9(d)(ii)	aryl group / arene / phenyl [1]	1
9(d)(iii)	 OR $C_6H_5CO_2C_2H_5$ [1]	1
9(e)	$CH_3CH_2^+$ / $C_2H_5^+$ [1] $C_6H_5^+$ [1]	2

Q# 508/ Topic: **Chem 37** ALvl Chemistry/2020/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

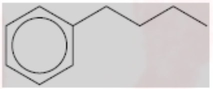
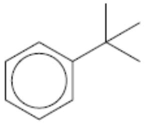
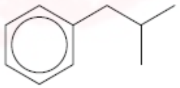
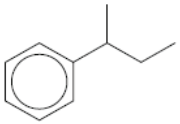
8(b)(iv)	5 / five [1]	1

Q# 509/ Topic: **Chem 37** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(d)	chemical shift (δ)	environment of the carbon atom	hybridisation of the carbon atom	2
	27	CH_3 circled	sp^3	
	163	COOH circled	sp^2	
	192	C=O(COOH) circled	sp^2	
	Award one mark for each correct column			

6(e)	chemical shift (δ)	group responsible for the peak	splitting pattern	number of ^1H atoms responsible for the peak	3
	1.3	alkane / CH / CH_3	triplet	3	
	2.2	CH_3CO or alkyl / CH next to C=O	singlet	3	
	4.0	CH_2O or alkyl / CH next to electronegative atom / C=O	quartet / quadruplet	2	
	Award one mark for every three correct responses.				
6(f)	CH **AND** CH_3 **circled** these protons do not exchange with D_2O OR OH and NH protons exchange with D_2O				2

Q# 510/ Topic: **Chem 37** ALvl Chemistry/2020/s/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(c)(i)	$CH_3CH_2CH^+CH_3$ $(CH_3)_2CHCH_2^+$ $(CH_3)_3C^+$ Each correct structure = 1 mark		3
5(c)(ii)	 number of peaks in carbon-13 NMR = 8	 number of peaks in carbon-13 NMR = 6	4
	 number of peaks in carbon-13 NMR = 7	 number of peaks in carbon-13 NMR = 8	
	Two correct organic products = 1 mark three correct organic products = 2 marks all products linked correctly to NMR = 2 marks		

Q# 511/ Topic: **Chem 37** ALvl Chemistry/2020/m/TZ 2/Paper 4/Q# 5/www.SmashingScience.org

5(d)(i)	5	1
5(d)(ii)	**M1** only one peak **M2** singlet at δ 6.0–9.0 ppm **OR** **M1** singlet(s) only **M2** only one peak at δ 6.0–9.0 ppm	2

Q# 512/ Topic: **Chem 37** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9(a)(i)	$RNH_2 + H^+ \rightarrow RNH_3^+$ OR $RNH_2 + HCl \rightarrow RNH_3Cl$ [1]	1
9(a)(ii)	weaker **AND** lone pair of N delocalised into benzene ring [1]	1

9(c)(i)	2 [1]	1
9(c)(ii)	CH_2 next to ester and terminal CH_3 are circled [1]	1
9(c)(iii)	• one less peak • the lost peak is NH_2 / aryl amine • protons exchange with D OR protons are labile OR valid equation •✓✓ for two marks [2]	2

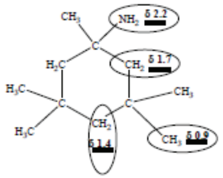
Q# 513/ Topic: **Chem 37** ALvl Chemistry/2019/w/TZ 1/Paper 4/Q# 4/www.SmashingScience.org

4(d)(iv)	6	1
4(d)(v)	• 25–50 • 110–160 • 190–220 Award 1 mark for two points, award 2 marks for three points	2

Q# 514/ Topic: **Chem 37** ALvl Chemistry/2019/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8(b)	TMS: Reference $CDCl_3$: Solvent	1
8(c)(i)	**M1**: CH_3CO **M2**: CH_3CH_2O **M3**: $(CO)CH_2O$	3
8(c)(ii)	$CH_3COCH_2OCH_2CH_3$	1
8(d)	$HCO_2C(CH_3)_3$	1
8(e)(i)	this is a (carbon) atom which has four different atoms or groups attached to it	1
8(e)(ii)	$CH_3CH_2CH(CH_3)COOH$	1

Q# 515/ Topic: **Chem 37** ALvl Chemistry/2019/m/TZ 2/Paper 4/Q# 6/www.SmashingScience.org

6(c)(i)	six	1
6(c)(ii)	**M1** peak at δ 0.9 is due to **12 H** **M2** peak at 2.2 is due to **2 H** **M3/M4** peaks at 1.2, 1.4 and 1.7 are **all singlets**	4
6(c)(iii)		2
6(c)(iv)	NH / NH_2 protons **AND** exchange with D_2O / D OR $–NH_2 + D_2O \rightarrow –ND_2 + H_2O$	1

Q# 516/ Topic: **Chem 37** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i) — 2

[1] for each correct answer

	number of peaks
F	3
G	6

Q# 517/ Topic: **Chem 37** ALvl Chemistry/2018/w/TZ 1/Paper 4/Q# 1/www.SmashingScience.org

1(a)(i) — 2

peak	organic compound	explanation
X	alkane	London forces only OR no hydrogen bonding
Y	aldehyde	(Permanent dipole-dipole and London forces)
Z	carboxylic acid	(contains) hydrogen bonding

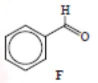
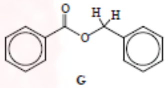
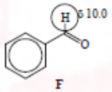
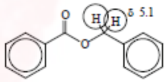
M1 peak assignments [1]
M2 explanation of Z OR X [1]

1(a)(ii)	**% of Z = 47/98 = 48%**	1

Q# 518/ Topic: **Chem 37** ALvl Chemistry/2018/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7(e)(i)	propanoic acid	1
7(e)(ii)	propan-1-ol would have peak at 0.5–6.0 because of OH group	1
	propanal would have peak at 9.3–10.5 because of CHO / aldehyde	1

Q# 519/ Topic: **Chem 37** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

9(a)(i)	n = (100 / 1.1)(8 / 100) = 7.3 (⇒ 7 C atoms)	1
9(a)(ii)	$C_7H_7^{+}$	1
9(a)(iii)	F is C_7H_6O G is $C_{14}H_{12}O_2$	2
9(a)(iv)	 F  G	2
9(a)(v)	 F  G	1
9(a)(vi)	hydrolysis	1

Q# 520/ Topic: **Chem 37** ALvl Chemistry/2018/m/TZ 2/Paper 4/Q# 8/www.SmashingScience.org

8(a)(i)	7 peaks	1

8(a)(ii) — 2

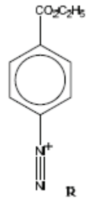
C=O	1670–1740	▨
OH	▨	3200–3600
Or C-O	▨	1000–1260

Q# 521/ Topic: **Chem 37** ALvl Chemistry/2017/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(d)(i)	7 peaks	1
6(d)(ii)	$CDCl_3$ will produce no signal in the spectrum or $CHCl_3$ would produce a signal / would be detected	1

6(d)(iii) — 4

δ/ppm	group responsible for the peak	number of H atoms responsible for the peak	splitting pattern
1.2	$CH_{(3)}$	3	triplet
3.5	$CH_{(2)}O$	2	quartet
5.5	NH_2	2	singlet (broad)
7.1–7.4	H attached to aromatic / benzene ring	4	*multiplet*

6(d)(iv)	neighbouring / adjacent carbon atom has two protons / H (attached to it) or there is an adjacent $CH_2(O)$ group	1
6(d)(v)	peak at 5.5 / NH_2 peak will disappear and NH_2 / protons exchange / swap with deuterium	1
6(e)(i)	$NaNO_2$ + HC*l* or HNO_2	1
6(e)(ii)	 R  S	
	structure of diazonium salt **R**	1
	structure of azo dye **S**	1

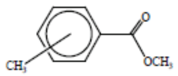
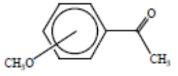
Q# 522/ Topic: **Chem 37** ALvl Chemistry/2017/s/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(d)(i)

δ value	number of H atoms	group	splitting	result with D_2O
1.4	3	**CH_3 / methyl**	**doublet**	**peak remains**
2.7	1	**OH / hydroxyl / alcohol**	**singlet**	**peak disappears**
4.0	1	**CH**	**quartet**	**peak remains**

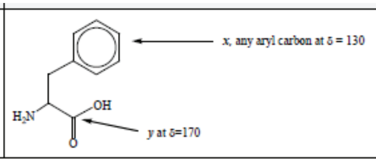
6(d)(i)	the three groups are in their correct places wrt the δ values	1
	no. of H atoms for each peak agrees with group column	1
	splitting patterns doublet, singlet and quartet are assigned to correct groups	1
	peak identified as OH disappears with D_2O, no other peak disappears	1
	Total:	**16**

Q# 523/ Topic: **Chem 37** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 9/www.SmashingScience.org

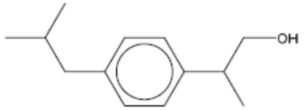
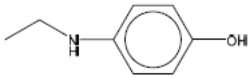
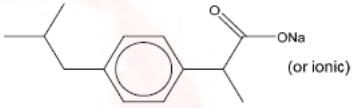
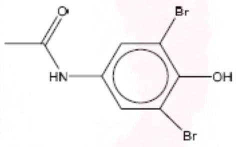
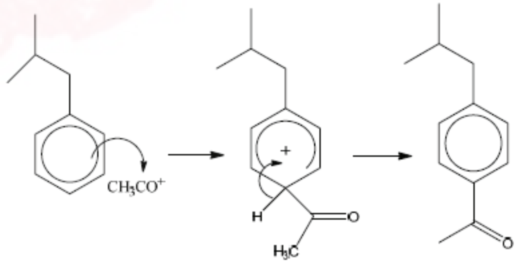
9(a)(i)	n = 100 × (M+1)/(1.1 × M) = 100 × 3.4/(1.1 × 33.9) = 9.1	1
	hence 9 carbons atoms	1
9(a)(ii)	$C_9H_{10}O_2$	1
9(a)(iii)	(150 – 119 = 31), hence fragment is CH_3O	1
9(b)	**V** is C=O **AND W** is C–O	1
9(c)(i)	δ 3.9 is CH or alkyl / CH_3 next to oxygen **AND** δ 7.2–7.9 is CH / aryl hydrogens	1
9(c)(ii)	alkyl H next to C=O **AND** alkyl H next to aryl ring	1
9(c)(iii)	none of the functional groups in **T** contains a labile proton / **T** does not contain –OH or –NH groups.	1
9(d)	 	2

Q# 524/ Topic: **Chem 37** ALvl Chemistry/2017/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

7(e)(i)	seven	1

7(e)(ii)		1

Q# 525/ Topic: **Chem 37** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

6(c)	  with ibuprofen with paracetamol	1 1	2
6(d)(i)	(reagent D) Na_2CO_3 / any carbonate (reagent E) Cl_2 / Br_2	1 1	2
6(d)(ii)		1	1
6(d)(iii)		1	1
6(e)(i)	$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$	1	
6(e)(ii)	 curly arrow from ring system to CH_3CO^+ correct intermediate curly arrow from C–H bond into ring	1 1 1	3
6(e)(iii)	electrophilic substitution	1	1
	Total:		**16**

Q# 526/ Topic: **Chem 37** ALvl Chemistry/2016/w/TZ 1/Paper 4/Q# 5/www.SmashingScience.org

5(a)(i)	(100/22.1)×(0.7/1.1) or $\frac{100\times0.7}{22.1\times1.1}$ or 2.87/2.88/2.9 3 carbon atoms	1 1	2
5(a)(ii)	$C_3H_6O_3$	1	1

5(b)

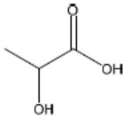
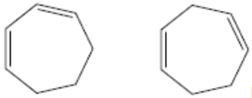
absorption/ cm^{-1}	appearance of the peak	type of bond	functional group
3350	broad and strong	OH or O–H	alcohol/ROH
2680	very broad and strong	OH or O–H	(carboxylic) acid/CO_2H
1725	strong	C=O	(carboxylic) acid/CO_2H

2

5(c)(i)

δ/ppm	type of proton	relative peak area
1.4	$–CH_3$ or $–CH_2$ or –CH or alkane	3
3.9	–OCH or $–OCH_2$ or $–OCH_3$ or CH or alkyl next to electronegative atom/oxygen	1
4.7	–OH or alcohol	1
12.9	–OH or $–CO_2H$ or carboxylic acid	1

4

5(c)(ii)	doublet and 1/one H/proton on neighbouring OR adjacent carbon	1	1
5(c)(iii)	4.7 and 12.9 OR –OH and $–CO_2H$	1	1
5(c)(iv)		1	1
5(d)(i)	 both required for 1 mark	1	1

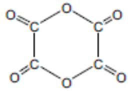
5(d)(ii)

isomer	number of peaks
P	4
Q	4

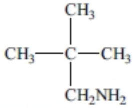
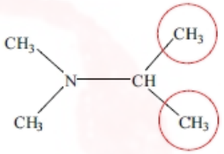
1
1
2

Total: 15

Q# 527/ Topic: **Chem 37** ALvl Chemistry/2016/s/TZ 1/Paper 4/Q# 10/www.SmashingScience.org

(c) (i)	CH_3 at δ 15 CH_2O at δ65	[1] [1]
(ii)	Only one peak, so only one type/environment of C atom	[1]
(d) (i)	**M** is $HO_2C–CO_2H$ **N** is $CH_3OCO–CO_2H$ **O** is $CH_3OCO–COOCH_3$	[3]
(ii)	**L** is 	[1]
		[Total: 13]

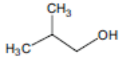
Q# 528/ Topic: **Chem 37** ALvl Chemistry/2016/m/TZ 2/Paper 4/Q# 7/www.SmashingScience.org

(c) (i)		1
(ii)	 either one or both CH_3 groups circled	1

Q# 529/ Topic: **Chem 37** ALvl Chemistry/2015/w/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

(d) (i)	**E** = CH and **F** = CH_2	1
(ii)	**E** = triplet and adjacent 2H **F** = doublet and adjacent 1H	2
		11

Q# 530/ Topic: **Chem 37** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 (a)	M:M+1 = 100/(1.1 x n) 20.4/0.9 = 100/(1.1 x n) x = 4	1 1	
(ii)	$C_4H_{10}O$	1	[3]
(b) (i)	2-methylpropan-1-ol **OR** correct structure 	1	
(ii)	0.9-1.0 is (2 x)$CH_3R/CH_3/RCH$ multiplet/1.8 is CHR/R_3CH singlet/2.5 is OH 3.4 is CH_2O/CH_3O	1 1 1 1	
(iii)	doublet 1H/one proton on adjacent carbon	1 1	
(iv)	OH peak or one peak disappears OH proton is labile ***or*** exchanges for D of D_2O ***or*** as an equation e.g. $D_2O + OH \rightarrow DOH + OD$ as a minimum	1 1	[9]
Total			12
			100

Q# 531/ Topic: **Chem 37** ALvl Chemistry/2014/w/TZ 1/Paper 4/Q# 6/www.SmashingScience.org

(b) (i)	mobile – solvent **or** water stationary – alumina/silica (supported on glass/plastic/Al)	1 1	
(ii)	by adsorption	1	[3]

Q# 532/ Topic: **Chem 37** ALvl Chemistry/2014/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

7 (a) Expression: $n = \frac{100 \times 2.5}{1.1 \times 74}$ or equivalent [1]

$n = 3.1$ hence **G** has three carbon atoms [1]

(b) (i) (δ 1.1) RCH_3 *or* RCH_2R *or* methyl *or* CH_3

(δ 2.2) $(R)CH_2CO(R)$ *or* $CH_3CO(R)$

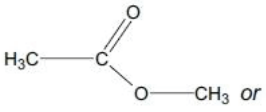
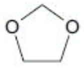
(δ 11.8) $(R)COOH$ or $(R)CONH(R)$ 3 × [1]

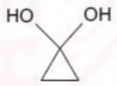
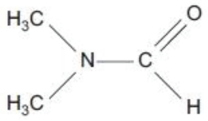
(ii) The (–OH) peak at δ 11.8 (disappears) [1]

because of (O)H-D exchange *or* equation showing this
(e.g. $R\text{-}OH + D_2O \rightleftharpoons R\text{-}OD + HOD$) [1]

(iii) $CH_3CH_2CO_2H$ [1]

(c) (i)


or

or

or

or


[1]

(ii) If methyl ethanoate: δ 2.0–2.1 [1]
δ 3.3–4.0 [1]

Or if 1, 3-dioxolane: δ 3.3–4.0 [1]
δ 3.3–5.0 [1]

Or if 1, 2-dioxolane: δ 0.9–1.4 [1]
δ 3.3–4.0 [1]

Or if dihydroxycyclopropane: δ 0.9–1.4 [1]
δ 0.5–6.0 [1]

[Total: 11]

Q# 533/ Topic: **Chem 37** ALvl Chemistry/2013/s/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) insecticides: gas-liquid *or* thin-layer chromatography [1]

dyes : paper *or* thin-layer chromatography [1]

drugs: gas-liquid
or
thin-layer chromatography [1]
[3]

[Total: 10]

Q# 534/ Topic: **Chem 37** ALvl Chemistry/2012/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) P is $CH_3CO_2CH_2CH_3$ [1]

any four of:

- 3 different (proton) environments
- (M and M+1 data shows no of carbons present is) (100 × 0.22)/(1.1 × 5.1) = **4 carbons**
- the NMR spectrum shows 8 hydrogens leaving 32 mass unit or 2 oxygen ***or*** M_r = 88 **and** (molecular formula is) $C_4H_8O_2$
- 4 peaks/quartet (at 4.1) shows an adjacent $3H/CH_3$
- 3 peaks/triplet (at 1.3) shows an adjacent $2H/CH_2$
- (peak at) 2.0/singlet shows CH_3CO (group)
- (peak at) 4.1/quartet **and** 1.3/triplet shows presence of ethyl/CH_3CH_2 (group)

4 × [1]

[5]

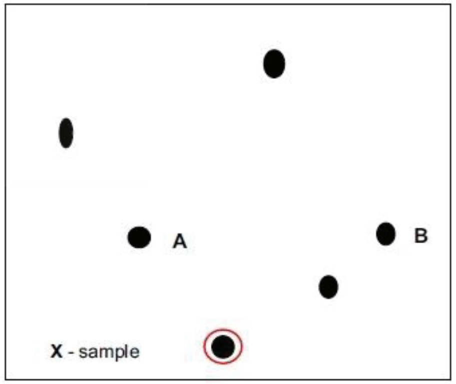
[Total: 10]

Q# 535/ Topic: **Chem 37** ALvl Chemistry/2011/s/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 (a) **partition** – separation due to the different solubilities of compounds in two solvents/phases [1]

adsorption – separation due to the different attractions between the compounds and the stationary phase, relative to their solubility in the solvent [1]
Note, if candidates do not refer to different solubilities and different attractions max 1

(b)



Ring: [1]
A + B: [1]

Q# 536/ Topic: **Chem 37** ALvl Chemistry/2010/w/TZ 1/Paper 4/Q# 8/www.SmashingScience.org

8 **(a)** Protons (1)
in NMR, energy is absorbed due to the two spin states (1)
Electrons (1)
in X-ray crystallography, X-rays are diffracted (by regions of high electron density) (1) **[4]**

(b) **(i)** 1 – no mark
The spectrum of alcohol / **Y** contains different peaks
Alcohol / **Y** contains different chemical environments
Spectrum 2 contains only one peak (1)

(ii) Spectrum 2 only shows 1 peak so **Z** must be a ketone (1)

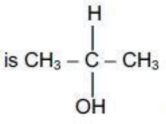
Hence **Y** must be a 2° alcohol (1)

Number of carbon atoms present $= \dfrac{0.6 \times 100}{17.6 \times 1.1} = 3$ (1)

Thus **Z** must be CH_3COCH_3 (1)

Hence **Y** must be propan-2-ol, $CH_3CH(OH)CH_3$ (1)

(iii)

Y is 
$CH_3-\overset{\displaystyle H \atop |}{\underset{| \atop \displaystyle OH}{C}}-CH_3$ (1)

(iv) All of the protons in **Z** are in the same chemical environment (1) **[8] max [7]**

[Total: 11]

Q# 537/ Topic: **Chem 37** ALvl Chemistry/2010/s/TZ 1/Paper 4/Q# 9/www.SmashingScience.org

9 **(a)** spinning proton produces two spin states / magnetic moments (1)
these can align with or against an applied magnetic field (1) [2]

(b) field experienced by protons is influenced by adjacent atoms / protons are in two different chemical environments (1)
peaks are in the area ratio 3 : 1 (methyl to –OH protons)
or are at 0.5 – 6.0δ and 3.3 – 4.0δ (1) [2]

(c) **(i)**

$CH_3CH_2CO_2H$	$CH_3CO_2CH_3$	$HCO_2CH_2CH_3$
propanoic acid	methyl ethanoate	ethyl methanoate

all for (2) two for (1)

(ii) compound is $CH_3CO_2CH_3$ *or* methyl ethanoate (1)
the other two compounds each have 3 different proton environments, but the spectrum shows only 2 peaks. (1)

A is OCH_3, B is CH_3CO (1)

(iii) compound – propanoic acid *or* ethyl methanoate
the –OH proton *or* the H–CO proton (1) [6]

Q# 538/ Topic: **Chem 37** ALvl Chemistry/2009/w/TZ 1/Paper 4/Q# 7/www.SmashingScience.org

(c) **(i)** Nuclear spin (1)

(ii) (If M : M+1 gives a ratio 15 : 2)

Then $x = \dfrac{100 \times 2}{1.1 \times 25} = 7$ (1)

Single peak at 3.7 δ due to $–O\text{-}CH_3$ (1)

Single peak at 5.6 δ due to phenol / OH (1)

1,2,1 peak at 6.8 δ due to hydrogens on benzene ring (1)

Pattern suggests 1,4 subsitution (1)

(x = 7,) y = 8, z = 2 (1)

Compound is 4-methoxylphenol (1)
Max 5 [6]

[Total: 10]

2016 Data Booklet and Periodic Table

The Data Booklet was used for all Paper 1, 2 and 4 exams until and including winter 2021.

Two Data Booklets cover the time period of this Work Book, one for exams after 2009 and the other for exam safter 2016. Only the data booklet for 2016 is given here, but for exam questions for years 2009 to 2015 care should be taken checking the mark schemes, sometimes constants change from one edition of a Data Booklet to another, so **answers to calculations using data from an unintended Data Booklet might be a little out** as a result. If unsure, check out the earlier data booklet for questions 2015 and before (Google: "2009 data booklet 9701").

Contents: Tables of Chemical Data

1 Important values, constants and standards

molar gas constant	$R = 8.31\ J\,K^{-1}\,mol^{-1}$
the Faraday constant	$F = 9.65 \times 10^{4}\ C\,mol^{-1}$
the Avogadro constant	$L = 6.02 \times 10^{23}\ mol^{-1}$
the Planck constant	$h = 6.63 \times 10^{-34}\ J\,s$
speed of light in a vacuum	$c = 3.00 \times 10^{8}\ m\,s^{-1}$
rest mass of proton, ${}^{1}_{1}H$	$m_p = 1.67 \times 10^{-27}\ kg$
rest mass of neutron, ${}^{1}_{0}n$	$m_n = 1.67 \times 10^{-27}\ kg$
rest mass of electron, ${}^{0}_{-1}e$	$m_e = 9.11 \times 10^{-31}\ kg$
electronic charge	$e = -1.60 \times 10^{-19}\ C$
molar volume of gas	$V_m = 22.4\ dm^3\,mol^{-1}$ at s.t.p. $V_m = 24.0\ dm^3\,mol^{-1}$ under room conditions (where s.t.p. is expressed as 101 kPa, approximately, and 273 K [0 °C])
ionic product of water	$K_w = 1.00 \times 10^{-14}\ mol^2\,dm^{-6}$ (at 298 K [25 °C])
specific heat capacity of water	$= 4.18\ kJ\,kg^{-1}\,K^{-1}$ $(= 4.18\ J\,g^{-1}\,K^{-1})$

2 Ionisation energies (1st, 2nd, 3rd and 4th) of selected elements, in $kJ\,mol^{-1}$

	Proton number	First	Second	Third	Fourth
H	1	1310	–	–	–
He	2	2370	5250	–	–
Li	3	519	7300	11800	–
Be	4	900	1760	14800	21000
B	5	799	2420	3660	25000
C	6	1090	2350	4610	6220
N	7	1400	2860	4590	7480
O	8	1310	3390	5320	7450
F	9	1680	3370	6040	8410
Ne	10	2080	3950	6150	9290
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600
Si	14	786	1580	3230	4360
P	15	1060	1900	2920	4960
S	16	1000	2260	3390	4540
Cl	17	1260	2300	3850	5150
Ar	18	1520	2660	3950	5770
K	19	418	3070	4600	5860
Ca	20	590	1150	4940	6480
Sc	21	632	1240	2390	7110
Ti	22	661	1310	2720	4170
V	23	648	1370	2870	4600
Cr	24	653	1590	2990	4770
Mn	25	716	1510	3250	5190
Fe	26	762	1560	2960	5400
Co	27	757	1640	3230	5100
Ni	28	736	1750	3390	5400
Cu	29	745	1960	3350	5690
Zn	30	908	1730	3828	5980
Ga	31	577	1980	2960	6190
Br	35	1140	2080	3460	4850
Rb	37	403	2632	3900	5080
Sr	38	548	1060	4120	5440
Ag	47	731	2074	3361	5000
I	53	1010	1840	3000	4030
Cs	55	376	2420	3300	4400
Ba	56	502	966	3390	4700

3 Bond Energies

3(a) Bond energies in diatomic molecules (these are exact values)

Homonuclear

Bond	Energy / kJ mol^{-1}
H—H	436
D—D	442
N≡N	944
O=O	496
P≡P	485
S=S	425
F—F	158
Cl—Cl	242
Br—Br	193
I—I	151

Heteronuclear

Bond	Energy / kJ mol^{-1}
H—F	562
H—Cl	431
H—Br	366
H—I	299
C≡O	1077

3(b) Bond energies in polyatomic molecules (these are average values)

Homonuclear

Bond	Energy / kJ mol^{-1}
C—C	350
C=C	610
C≡C	840
C⋯C (benzene)	520
N—N	160
N=N	410
O—O	150
Si—Si	225
P—P	200
S—S	265

Heteronuclear

Bond	Energy / kJ mol^{-1}
C—H	410
C—Cl	340
C—Br	280
C—I	240
C—N	305
C=N	610
C≡N	890
C—O	360
C=O	740
C=O in CO_2	805
N—H	390
N—Cl	310
O—H	460
Si—Cl	360
Si—H	320
Si—O (in SiO_2(s))	460
Si=O (in SiO_2(g))	640
P—H	320
P—Cl	330
P—O	340
P=O	540
S—H	340
S—Cl	250
S—O	360
S=O	500

4 Standard electrode potential and redox potentials, $E^{\ominus}$ at 298 K (25 °C)

For ease of reference, two tables are given:

(a) an extended list in alphabetical order;
(b) a shorter list in decreasing order of magnitude, i.e. a redox series.

(a) $E^{\ominus}$ in alphabetical order

Electrode reaction	$E^{\ominus}$/V
$Ag^{+} + e^{-} \rightleftharpoons Ag$	+0.80
$Al^{3+} + 3e^{-} \rightleftharpoons Al$	–1.66
$Ba^{2+} + 2e^{-} \rightleftharpoons Ba$	–2.90
$Br_2 + 2e^{-} \rightleftharpoons 2Br^{-}$	+1.07
$Ca^{2+} + 2e^{-} \rightleftharpoons Ca$	–2.87
$Cl_2 + 2e^{-} \rightleftharpoons 2Cl^{-}$	+1.36
$2HOCl + 2H^{+} + 2e^{-} \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$ClO^{-} + H_2O + 2e^{-} \rightleftharpoons Cl^{-} + 2OH^{-}$	+0.89
$Co^{2+} + 2e^{-} \rightleftharpoons Co$	–0.28
$Co^{3+} + e^{-} \rightleftharpoons Co^{2+}$	+1.82
$[Co(NH_3)_6]^{2+} + 2e^{-} \rightleftharpoons Co + 6NH_3$	–0.43
$Cr^{2+} + 2e^{-} \rightleftharpoons Cr$	–0.91
$Cr^{3+} + 3e^{-} \rightleftharpoons Cr$	–0.74
$Cr^{3+} + e^{-} \rightleftharpoons Cr^{2+}$	–0.41
$Cr_2O_7^{2-} + 14H^{+} + 6e^{-} \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cu^{+} + e^{-} \rightleftharpoons Cu$	+0.52
$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^{-} \rightleftharpoons Cu^{+}$	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^{-} \rightleftharpoons Cu + 4NH_3$	–0.05
$F_2 + 2e^{-} \rightleftharpoons 2F^{-}$	+2.87
$Fe^{2+} + 2e^{-} \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^{-} \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^{-} \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^{-} \rightleftharpoons Fe(OH)_2 + OH^{-}$	–0.56
$2H^{+} + 2e^{-} \rightleftharpoons H_2$	0.00
$2H_2O + 2e^{-} \rightleftharpoons H_2 + 2OH^{-}$	–0.83
$I_2 + 2e^{-} \rightleftharpoons 2I^{-}$	+0.54
$K^{+} + e^{-} \rightleftharpoons K$	–2.92
$Li^{+} + e^{-} \rightleftharpoons Li$	–3.04
$Mg^{2+} + 2e^{-} \rightleftharpoons Mg$	–2.38
$Mn^{2+} + 2e^{-} \rightleftharpoons Mn$	–1.18
$Mn^{3+} + e^{-} \rightleftharpoons Mn^{2+}$	+1.49
$MnO_2 + 4H^{+} + 2e^{-} \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^{-} + e^{-} \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^{-} + 4H^{+} + 3e^{-} \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^{-} + 8H^{+} + 5e^{-} \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$NO_3^{-} + 2H^{+} + e^{-} \rightleftharpoons NO_2 + H_2O$	+0.81
$NO_3^{-} + 3H^{+} + 2e^{-} \rightleftharpoons HNO_2 + H_2O$	+0.94
$NO_3^{-} + 10H^{+} + 8e^{-} \rightleftharpoons NH_4^{+} + 3H_2O$	+0.87

Electrode reaction	$E^\ominus$/V
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	–0.25
$[Ni(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Ni + 6NH_3$	–0.51
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^-$	+0.88
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68
$O_2 + H_2O + 2e^- \rightleftharpoons HO_2^- + OH^-$	–0.08
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$V^{2+} + 2e^- \rightleftharpoons V$	–1.20
$V^{3+} + e^- \rightleftharpoons V^{2+}$	–0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76

All ionic states refer to aqueous ions but other state symbols have been omitted.

(b) $E^\ominus$ in decreasing order of oxidising power

(a selection only – see also the extended alphabetical list on the previous pages)

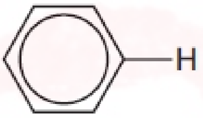
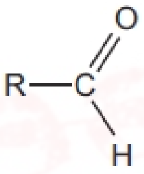
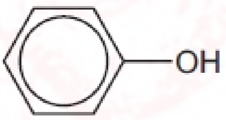
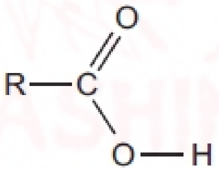
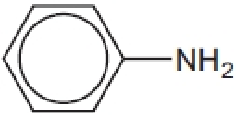
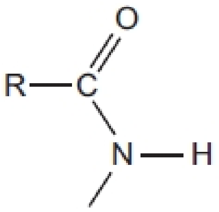
Electrode reaction			$E^\ominus$/V
$F_2 + 2e^-$	$\rightleftharpoons$	$2F^-$	+2.87
$S_2O_8^{2-} + 2e^-$	$\rightleftharpoons$	$2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^-$	$\rightleftharpoons$	$2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^-$	$\rightleftharpoons$	$Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightleftharpoons$	$2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^-$	$\rightleftharpoons$	$2H_2O$	+1.23
$Br_2 + 2e^-$	$\rightleftharpoons$	$2Br^-$	+1.07
$ClO^- + H_2O + 2e^-$	$\rightleftharpoons$	$Cl^- + 2OH^-$	+0.89
$NO_3^- + 10H^+ + 8e^-$	$\rightleftharpoons$	$NH_4^+ + 3H_2O$	+0.87
$NO_3^- + 2H^+ + e^-$	$\rightleftharpoons$	$NO_2 + H_2O$	+0.81
$Ag^+ + e^-$	$\rightleftharpoons$	Ag	+0.80
$Fe^{3+} + e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77
$I_2 + 2e^-$	$\rightleftharpoons$	$2I^-$	+0.54
$O_2 + 2H_2O + 4e^-$	$\rightleftharpoons$	$4OH^-$	+0.40
$Cu^{2+} + 2e^-$	$\rightleftharpoons$	Cu	+0.34
$SO_4^{2-} + 4H^+ + 2e^-$	$\rightleftharpoons$	$SO_2 + 2H_2O$	+0.17
$Sn^{4+} + 2e^-$	$\rightleftharpoons$	Sn^{2+}	+0.15
$S_4O_6^{2-} + 2e^-$	$\rightleftharpoons$	$2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^-$	$\rightleftharpoons$	H_2	0.00
$Pb^{2+} + 2e^-$	$\rightleftharpoons$	Pb	–0.13
$Sn^{2+} + 2e^-$	$\rightleftharpoons$	Sn	–0.14
$Fe^{2+} + 2e^-$	$\rightleftharpoons$	Fe	–0.44
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	–0.76
$2H_2O + 2e^-$	$\rightleftharpoons$	$H_2 + 2OH^-$	–0.83
$V^{2+} + 2e^-$	$\rightleftharpoons$	V	–1.20
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	–2.38
$Ca^{2+} + 2e^-$	$\rightleftharpoons$	Ca	–2.87
$K^+ + e^-$	$\rightleftharpoons$	K	–2.92

5 Atomic and ionic radii

(a)	**Period 1**	**atomic / nm**		**ionic / nm**			
	single covalent	H	0.037	H^-	0.208		
	van der Waals	He	0.140				
(b)	**Period 2**	**atomic / nm**		**ionic / nm**			
	metallic	Li	0.152	Li^+	0.060		
		Be	0.112	Be^{2+}	0.031		
	single covalent	B	0.080	B^{3+}	0.020		
		C	0.077	C^{4+}	0.015	C^{4-}	0.260
		N	0.074			N^{3-}	0.171
		O	0.073			O^{2-}	0.140
		F	0.072			F^-	0.136
	van der Waals	Ne	0.160				
(c)	**Period 3**	**atomic / nm**		**ionic / nm**			
	metallic	Na	0.186	Na^+	0.095		
		Mg	0.160	Mg^{2+}	0.065		
		Al	0.143	Al^{3+}	0.050		
	single covalent	Si	0.117	Si^{4+}	0.041	Si^{4-}	0.271
		P	0.110			P^{3-}	0.212
		S	0.104			S^{2-}	0.184
		Cl	0.099			Cl^-	0.181
	van der Waals	Ar	0.190				
(d)	**Group 2**	**atomic / nm**		**ionic / nm**			
	metallic	Be	0.112	Be^{2+}	0.031		
		Mg	0.160	Mg^{2+}	0.065		
		Ca	0.197	Ca^{2+}	0.099		
		Sr	0.215	Sr^{2+}	0.113		
		Ba	0.217	Ba^{2+}	0.135		
		Ra	0.220	Ra^{2+}	0.140		

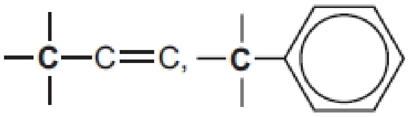
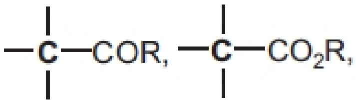
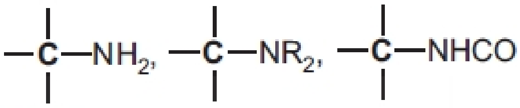
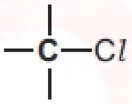
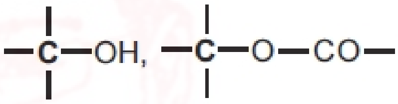
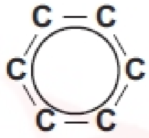
(e)	**Group 14**	**atomic / nm**		**ionic / nm**			
	single covalent	C	0.077				
		Si	0.117	Si^{4+}	0.041		
		Ge	0.122	Ge^{2+}	0.093		
	metallic	Sn	0.162	Sn^{2+}	0.112		
		Pb	0.175	Pb^{2+}	0.120		
(f)	**Group 17**	**atomic / nm**		**ionic / nm**			
	single covalent	F	0.072	F^{-}	0.136		
		Cl	0.099	Cl^{-}	0.181		
		Br	0.114	Br^{-}	0.195		
		I	0.133	I^{-}	0.216		
		At	0.140				
(g)	**First row transition elements**	**atomic / nm**		**ionic / nm**			
	metallic	Sc	0.164			Sc^{3+}	0.081
		Ti	0.146	Ti^{2+}	0.090	Ti^{3+}	0.067
		V	0.135	V^{2+}	0.079	V^{3+}	0.064
		Cr	0.129	Cr^{2+}	0.073	Cr^{3+}	0.062
		Mn	0.132	Mn^{2+}	0.067	Mn^{3+}	0.062
		Fe	0.126	Fe^{2+}	0.061	Fe^{3+}	0.055
		Co	0.125	Co^{2+}	0.078	Co^{2+}	0.053
		Ni	0.124	Ni^{2+}	0.070	Ni^{3+}	0.056
		Cu	0.128	Cu^{2+}	0.073		
		Zn	0.135	Zn^{2+}	0.075		

6 Typical proton (^{1}H) chemical shift values (δ) relative to TMS = 0

type of proton	environment of proton	example structures	chemical shift range (δ)
C–H	alkane	$-CH_3$, $-CH_2-$, $>CH-$	0.9–1.7
	alkyl next to C=O	$CH_3-C=O$, $-CH_2-C=O$, $>CH-C=O$	2.2–3.0
	alkyl next to aromatic ring	CH_3-Ar, $-CH_2-Ar$, $>CH-Ar$	2.3–3.0
	alkyl next to electronegative atom	CH_3-O, $-CH_2-O$, $-CH_2-Cl$, $>CH-Br$	3.2–4.0
	attached to alkyne	$\equiv C-H$	1.8–3.1
	attached to alkene	$=CH_2$, $=CH-$	4.5–6.0
	attached to aromatic ring		6.0–9.0
	aldehyde		9.3–10.5
O-H (see note below)	alcohol	RO–H	0.5–6.0
	phenol		4.5–7.0
	carboxylic acid		9.0–13.0
N-H (see note below)	alkyl amine	R–NH–	1.0–5.0
	aryl amine		3.0–6.0
	amide		5.0–12.0

Note: δ values for –O-H and –N-H protons can vary depending on solvent and concentration

7 Typical carbon (^{13}C) chemical shift values (δ) relative to TMS = 0

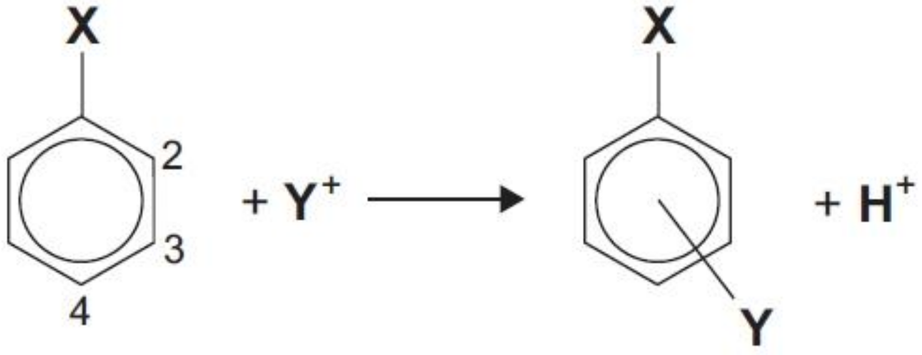
hybridisation of the carbon atom	environment of carbon atom	example structures	chemical shift range (δ)
sp^3	alkyl	CH_3-, $-CH_2-$, $-CH<$, $>C<$	0–50
sp^3	next to alkene/arene		10–40
sp^3	next to carbonyl/carboxyl	 $-\underset{\vert}{\overset{\vert}{C}}-COR$, $-\underset{\vert}{\overset{\vert}{C}}-CO_2R$,	25–50
sp^3	next to nitrogen	 $-\underset{\vert}{\overset{\vert}{C}}-NH_2$, $-\underset{\vert}{\overset{\vert}{C}}-NR_2$, $-\underset{\vert}{\overset{\vert}{C}}-NHCO$	30–65
sp^3	next to chlorine (-CH_2-Br and -CH_2-I are in the same range as alkyl)	 $-\underset{\vert}{\overset{\vert}{C}}-Cl$	30–60
sp^3	next to oxygen	 $-\underset{\vert}{\overset{\vert}{C}}-OH$, $-\underset{\vert}{\overset{\vert}{C}}-O-CO-$	50–70
sp^2	alkene or arene	$>C=C<$, 	110–160
sp^2	carboxyl	$R-CO_2H$, $R-CO_2R$	160–185
sp^2	carbonyl	R–CHO, R–CO–R	190–220
sp	alkyne	R–C≡C–	65–85
sp	nitrile	R–C≡N	100–125

8 Characteristic infra-red absorption frequencies for some selected bonds

bond	functional groups containing the bond	absorption range (in wavenumbers) /cm^{-1}	appearance of peak (*s* = strong, *w* = weak)
C–O	alcohols, ethers, esters	1040–1300	*s*
C=C	aromatic compounds, alkenes	1500–1680	*w* unless conjugated
C=O	amides, ketones and aldehydes, carboxylic acids, esters	1640–1690 1670–1740 1680–1730 1710–1750	*s* *s* *s* *s*
C≡C	alkynes	2150–2250	*w* unless conjugated
C≡N	nitriles	2200–2250	*w*
C–H	alkanes, CH_2–H alkenes/arenes, =C–H	2850–2950 3000–3100	*s* *w*
N–H	amines, amides	3300–3500	*w*
O–H	carboxylic acids, RCO_2–H H–bonded alcohol, RO–H free alcohol, RO–H	2500–3000 3200–3600 3580–3650	*s* and very broad *s* *s* and sharp

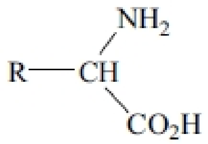
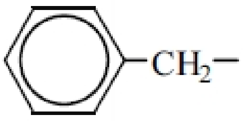
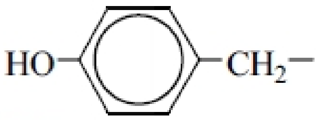
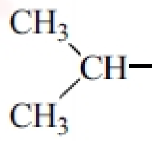
9 The orientating effect of groups in aromatic substitution reactions.

The position of the incoming group, **Y**, is determined by the nature of the group, **X**, already bonded to the ring, and not by the nature of the incoming group **Y**.



X- groups that direct the incoming **Y** group to the 2- or 4- positions	**X**- groups that direct the incoming **Y** group to the 3- position
$-NH_2$, $-NHR$ or $-NR_2$	$-NO_2$
$-OH$ or $-OR$	$-NH_3^+$
$-NHCOR$	$-CN$
$-CH_3$, –alkyl	$-CHO$, $-COR$
$-Cl$	$-CO_2H$, $-CO_2R$

10 Names, structures and abbreviations of some amino acids

name	3-letter abbreviation	1-letter symbol	structure of side chain R- in 
alanine	Ala	A	CH_3–
aspartic acid	Asp	D	HO_2CCH_2–
cysteine	Cys	C	$HSCH_2$–
glutamic acid	Glu	E	$HO_2CCH_2CH_2$–
glycine	Gly	G	H–
lysine	Lys	K	$H_2NCH_2CH_2CH_2CH_2$–
phenylalanine	Phe	F	
serine	Ser	S	$HOCH_2$–
tyrosine	Tyr	Y	
valine	Val	V	

Important values, constants and standards (2022 and after)

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C}\,\text{mol}^{-1}$
Avogadro constant	$L = 6.022 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ}\,\text{kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J}\,\text{g}^{-1}\,\text{K}^{-1}$)

9701/41/O/N/23

Periodic table

The Periodic Table of Elements

Group																	
1	2											13	14	15	16	17	18
				Key			1 H hydrogen 1.0										2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0			atomic number atomic symbol name relative atomic mass								5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.4	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –