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# CHEMISTRY

## 2010 National Qualifying Examination

TO BE COMPLETED BY THE STUDENT USE CAPITAL LETTERS

School Name: ..... State: .....

Student Name: .....

Home Address: .....

..... Post Code: .....

Telephone: (.....) ..... Mobile: .....

E-Mail: ..... Date of Birth: ...../...../.....

☐ Male ☐ Female

Year 10 ☐ Year 11 ☐ Other: .....

*Students competing in the 2010 National Qualifying Examinations must be in Year 11 or an earlier year in 2010.*

*The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Science Summer School. To be eligible for selection in one of the teams, students must have been schooled in Australia for the last two years, or hold an Australian passport.*

*Students who have finished their school examinations in the year of the competition can be members of the team as long as they have not commenced their university studies. Students must be under the age of twenty on 30 June of the year of the competition, and must not have started study at university as regular students.*

Signature: ..... Date: .....

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## CHEMISTRY

# 2010 NATIONAL QUALIFYING EXAMINATION

*Time Allowed*

*Reading Time: 15 minutes*

*Examination Time: 120 minutes*

### INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.
  - Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.  
[This section is worth 30 marks.]
  - Section B: Apportion your time equally on the questions in this section.  
Answer **ALLTHREE (3)** Questions.  
[This section is worth 90 marks.]
- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the spaces provided in the booklet.
- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable, except when you mark your multiple choice sheet.
- Rough working must be done only on pages 25 to 28 of this booklet.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.
- Do not staple the multiple choice answer sheet to this booklet.

## DATA

Avogadro constant (N)	$6.02 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c)	$2.998 \times 10^8 \text{ m s}^{-1}$
1 faraday	96,486 coulombs	Density of water at 25°C	$0.9971 \text{ g cm}^{-3}$
1 coulomb	$1 \text{ A s}^{-1}$	Acceleration due to gravity	$9.81 \text{ m s}^{-2}$
Universal gas constant (R)		1 newton (N)	$1 \text{ kg m s}^{-2}$
$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$			
$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$			
Planck's constant (h)	$6.626 \times 10^{-34} \text{ J s}$	1 pascal (Pa)	$1 \text{ N m}^{-2}$
Standard temperature and pressure (STP)		$\text{pH} = -\log_{10}[\text{H}^+]$ $\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$ $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$ $\text{PV} = nRT$ $E = h\nu$ $c = \nu\lambda$	
273 K and 100 kPa		Surface area of sphere $A = 4\pi r^2$	
0°C and 100 kPa			
0°C and 1 bar			
0°C and 750 mm Hg			
Molar volume of ideal gas at STP	22.7 L		
1 bar = 100 kPa			

## ATOMIC NUMBERS &amp; RELATIVE ATOMIC MASSES\*

1	H	1.008	23	V	50.94	45	Rh	102.9	67	Ho	164.9	89	Ac	(227)
2	He	4.003	24	Cr	52.00	46	Pd	106.4	68	Er	167.3	90	Th	232.0
3	Li	6.941	25	Mn	54.94	47	Ag	107.9	69	Tm	168.9	91	Pa	(231)
4	Be	9.012	26	Fe	55.85	48	Cd	112.4	70	Yb	173.0	92	U	238.0
5	B	10.81	27	Co	58.93	49	In	114.8	71	Lu	175.0	93	Np	(237)
6	C	12.01	28	Ni	58.69	50	Sn	118.7	72	Hf	178.5	94	Pu	(244)
7	N	14.01	29	Cu	63.55	51	Sb	121.8	73	Ta	180.9	95	Am	(243)
8	O	16.00	30	Zn	65.38	52	Te	127.6	74	W	183.9	96	Cm	(247)
9	F	19.00	31	Ga	69.72	53	I	126.9	75	Re	186.2	97	Bk	(247)
10	Ne	20.18	32	Ge	72.59	54	Xe	131.3	76	Os	190.2	98	Cf	(251)
11	Na	22.99	33	As	74.92	55	Cs	132.9	77	Ir	192.2	99	Es	(252)
12	Mg	24.31	34	Se	78.96	56	Ba	137.3	78	Pt	195.1	100	Fm	(257)
13	Al	26.98	35	Br	79.90	57	La	138.9	79	Au	197.0	101	Md	(258)
14	Si	28.09	36	Kr	83.80	58	Ce	140.1	80	Hg	200.6	102	No	(259)
15	P	30.97	37	Rb	85.47	59	Pr	140.9	81	Tl	204.4	103	Lw	(260)
16	S	32.07	38	Sr	87.62	60	Nd	144.2	82	Pb	207.2	104	Db	
17	Cl	35.45	39	Y	88.91	61	Pm	(145)	83	Bi	209.0	105	Jt	
18	Ar	39.95	40	Zr	91.22	62	Sm	150.4	84	Po	(209)	106	Rf	
19	K	39.10	41	Nb	92.91	63	Eu	152.0	85	At	(210)	107	Bh	
20	Ca	40.08	42	Mo	95.94	64	Gd	157.3	86	Rn	(222)	108	Hn	
21	Sc	44.96	43	Tc	(98) <sup>†</sup>	65	Tb	158.9	87	Fr	(223)	109	Mt	
22	Ti	47.88	44	Ru	101.1	66	Dy	162.5	88	Ra	226.0			

\* The relative values given here are to four significant figures.

<sup>†</sup> A value given in parentheses denotes the mass of the longest-lived isotope.

**SECTION A**

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section on the multiple choice answer sheet, using a 2B pencil. Only one choice is allowed per question. If you make a mistake **make sure that your incorrect answer is completely erased**.

**Please note the following:**

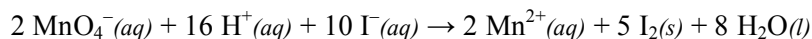
- It is recommended that you first record your answer on this question paper by circling **ONE** of the letters **A, B, C, D** or **E**.
- Then transfer these answers on to the computer sheet which will be computer marked for assessment.

**There are 15 multiple choice questions in Section A. The space for answers 16 to 30 is not used on the answer sheet.**

**Q1** In which one of the following pairs is the atomic radius of the second atom greater than that of the first atom?

- A** Be, B
- B** B, F
- C** Cl, Ar
- D** Ar, K
- E** Ne, He

**Q2** How many electrons are transferred from 10  $\Gamma^-$  ions to 2  $\text{MnO}_4^-$  ions in the following redox reaction?



- A** 2
- B** 5
- C** 8
- D** 10
- E** 16

**Q3** Which of the following acids is the strongest?

- A** perchloric acid,  $\text{HClO}_4$
- B** chloric acid,  $\text{HClO}_3$
- C** chlorous acid,  $\text{HClO}_2$
- D** hypochlorous acid,  $\text{HClO}$
- E** This can not be determined because not all the acids listed above exist.

**Q4** A gas **X** dissociates on heating to set up the following equilibrium:



A quantity of **X** was heated at constant pressure,  $p$ , at a certain temperature. The equilibrium partial pressure of **X** was found to be  $1/7 p$ . What is the equilibrium constant,  $K_p$  at this temperature?

- A  $6/7 p$
- B  $9/7 p$
- C  $36/7 p$
- D  $6 p$
- E  $9 p$

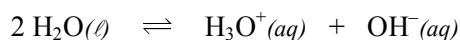
**Q5** In which one of the following compounds does manganese exist in the lowest oxidation state?

- A  $\text{Mn}_2\text{O}_7$
- B  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$
- C  $\text{KMnO}_4$
- D  $\text{MnO}_2\text{F}$
- E  $\text{K}_2\text{MnO}_4$

**Q6** How many structural isomers are possible for the molecular formula of  $\text{C}_4\text{H}_{10}\text{O}$ ?

- A 4
- B 5
- C 6
- D 7
- E 8

**Q7** Pure water undergoes self-ionisation according to the equation:



The equilibrium constant for the reaction is:

$$1.0 \times 10^{-14} \text{ at } 25^\circ\text{C and } 5.5 \times 10^{-13} \text{ at } 100^\circ\text{C}.$$

Which one of the following statements is correct?

- A At  $100^\circ\text{C}$  the  $\text{pH}$  of pure water is less than 7.0, but the  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ .
- B At  $100^\circ\text{C}$  the  $\text{pH}$  of pure water is less than 7.0, and therefore the  $[\text{H}_3\text{O}^+] > [\text{OH}^-]$ .
- C At  $100^\circ\text{C}$  the  $\text{pH}$  of pure water is greater than 7.0, and therefore the  $[\text{OH}^-] > [\text{H}_3\text{O}^+]$ .
- D At  $100^\circ\text{C}$  the  $\text{pH}$  of pure water must be 7.0 and the  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ .
- E At  $100^\circ\text{C}$  the  $\text{pH}$  of pure water is greater than 7.0, but the  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ .

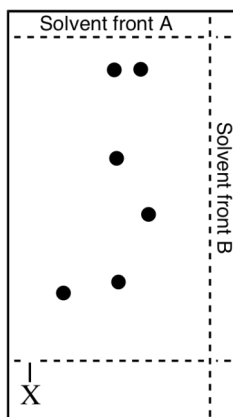
- Q8** A fuel/oxidant system consisting of monomethylhydrazine  $\text{CH}_3\text{NHNH}_2$  and  $\text{N}_2\text{O}_4$  (both liquids) is commonly used in space vehicle propulsion. Components are mixed stoichiometrically so that  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the only products (all gases under the same reaction conditions). How many moles of gases are produced from 100 mol of  $\text{CH}_3\text{NHNH}_2$ ?
- A 100  
B 125  
C 225  
D 400  
E 625
- Q9** Which one of the following is true for a solution of ammonia in water?
- A the solution contains ions only  
B the solution contains ions and large molecules  
C the solution contains small molecules and ions only  
D the solution contains small molecules and hydrogen bonded molecules only  
E the solution contains small molecules, hydrogen bonded molecules and ions
- Q10** The molecules listed below are of the general formula  $\text{XY}_n$ . Which one of the following compounds has the largest  $\text{Y-X-Y}$  bond angle?
- A  $\text{BF}_3$   
B  $\text{CH}_4$   
C  $\text{SCl}_2$   
D  $\text{NH}_3$   
E  $\text{PCl}_3$
- Q11** Trusty Dusty is up to his old tricks again – poisoning his mother’s pot plants with aqueous acid-laced fertiliser. Realising that the acid ( $\text{HX}$  – molar mass  $27.03 \text{ g mol}^{-1}$ ) is potentially incredibly dangerous to humans (quite volatile) he realises that he needs the free anion ( $\text{X}^-$ ) concentration in his fertiliser to be  $0.00340 \text{ mol L}^{-1}$ . First, he does a quick test. If, when he adds the equivalent of 0.560 g of  $\text{HX}$  to 50.0 mL of water, the  $\text{pH}$  is measured to be 3.67, how much  $\text{HX}$  should he add to 4.00 L in order to prepare his fatal fertiliser?
- A 6.96 kg  
B 8.91 kg  
C 11.3 kg  
D 22.8 kg  
E 0.368 g

- Q12** Samuel, a keen analytical chemist, was interested in determining the individual concentrations of two different weak acids found in fermented juices by titration with NaOH. Before he could begin, however, he wondered what the titration curve for a vessel containing **two** acids of variable  $pK_a$  values might look like. Indicate the correct titration curves for (a) a titration of a mixture of weak acids with substantially different  $pK_a$  values, and (b) a titration of a mixture of weak acids with very similar  $pK_a$  values?

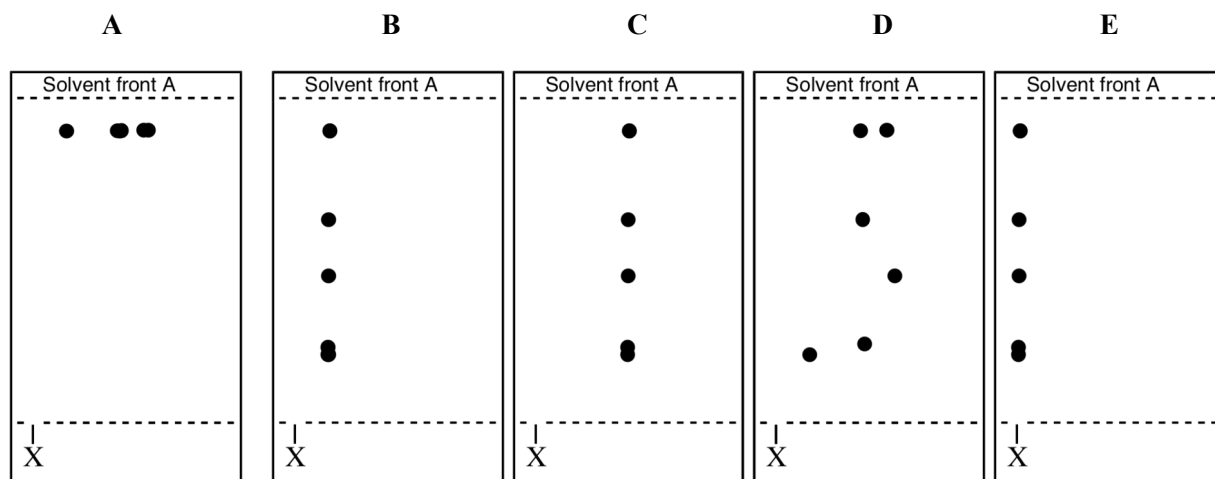
	(a) different $pK_a$ values	(b) similar $pK_a$ values
<b>A</b>		
<b>B</b>		
<b>C</b>		
<b>D</b>		
<b>E</b>		



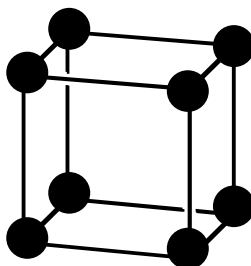
- Q13** TLC (thin layer chromatography) is used to separate mixtures of compounds based on the different polarities of the compounds. This is done based on the interactions between the polar stationary or solid phase and the less-polar mobile or liquid phase. A mixture of compounds is placed on the plate at position marked X, then through capillary action solvent A moves up the plate until the point shown. The plate is then dried, rotated 90° and the process repeated with solvent B until the point shown to give the following result.



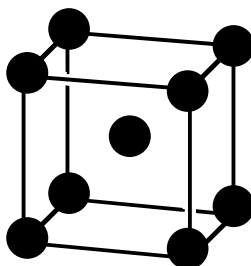
Which of the following plates would be the same as the plate you would expect after using solvent A as the mobile phase.



- Q14** A unit cell is the smallest possible repeating unit for a structure. The diagram below represents the unit cell of a simple (primitive) cubic structure. Repeating the unit cell in three dimensions gives the simple cubic structure. In the simple cubic structure, there is one atom per unit cell.



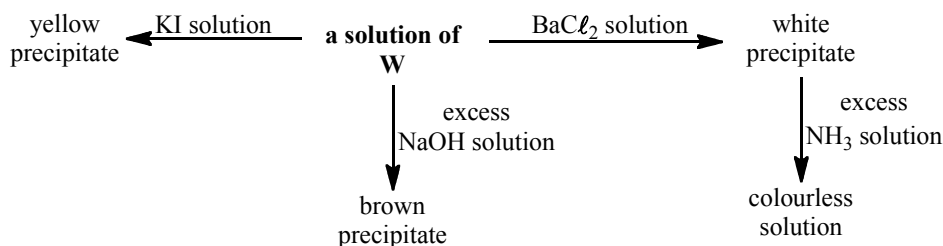
A unit cell of another important cubic lattice is the body-centred cubic. The diagram below represents the unit cell of a body-centred cubic structure.



How many atoms are there per unit cell in a **body-centred cubic** structure?

- A 1
- B 2
- C 3
- D 5
- E 9

- Q15** A solution of **W** reacts in the following ways:



What could be compound **W**?

- A AgNO<sub>3</sub>
- B Ag<sub>2</sub>SO<sub>4</sub>
- C CaCrO<sub>4</sub>
- D Pb(NO<sub>3</sub>)<sub>2</sub>
- E PbSO<sub>4</sub>

**SECTION B**

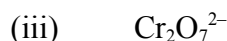
Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

**Answer ALL three of the questions in this section.**

**Q16**

The element chromium exists in a range of oxidation states and species, each of which has very different properties. The two primary uses of chromium today are in chrome-plating and the production of rust-resistant stainless steel. The most common source of chromium is ores containing the mineral chromite ( $\text{FeCr}_2\text{O}_4$ ), in which iron is present as Fe(II).

- (a) What is the oxidation state of chromium in each of the following species?



For the production of stainless steel, a chromium-iron alloy must first be formed. This is produced by reduction of chromite in a furnace with coke ( $\text{C}_{(s)}$ ).

- (b) Write a balanced redox equation for the reduction of chromite using carbon, given that the products are iron, chromium and carbon dioxide.

Chrome-plating requires a non-ferrous solution of chromium(III) ions (usually in acidic solution). A different method of extraction is therefore used. Firstly, the chromite is oxidised in air with molten sodium hydroxide to give sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). This is leached out with water, precipitated and then reduced with carbon to give  $\text{Cr}_2\text{O}_3_{(s)}$ . The chromium oxide can be dissolved in sulfuric acid to generate the desired solution.

- (c) (i) For the chromite ore ( $\text{FeCr}_2\text{O}_4$ ), write the half-equation for the oxidation of chromium species in basic solution.

- (ii) Write the reduction half-equation.

- (iii) Write the balanced redox equation.

As part of a prospector's assessment of a potential mining site, the chromite content of the ore must be determined. Because of the potential loss of material with multiple steps of extraction, the amount of chromium was determined by the titration of the sodium chromate solution obtained after the first step of the extraction. In order to find the concentration of the solution the prospector decided to use an iodometric method.

A 5.00 g sample of ore was oxidised to chromate and the product, in a sodium hydroxide solution, was quantitatively collected in a 1.00 L volumetric flask and made up to the mark with water to give a stock solution for analysis. A 25.00 mL aliquot of this solution was transferred into a 500 mL conical flask containing a buffer solution and approximately 100-150 mL of distilled water. KI (3 g) was then added. The flask was covered and placed in a cupboard to allow the reagents to react, forming triiodide ions ( $I_3^-$ ) and chromium(III) ions. The triiodide ions formed in the reactions were then titrated with  $0.1000 \text{ mol L}^{-1}$  potassium thiosulfate ( $K_2S_2O_3$ ) to give iodide ions and tetrathionate ( $S_4O_6^{2-}$ ) ions. Three titrations were performed and required an average of 23.10 mL of sodium thiosulfate solution.

- (d) Write the half-equations and the balanced redox equation for the reaction of chromate ions with iodide ions.

- (e) How many triiodide ions are generated for each chromate ion that is reduced?

- (f) Write two balanced half-equations and a redox equation for the reaction between triiodide ions and thiosulfate ions.

(g) What was the concentration of the stock sodium chromate solution?

(h)(i) What was the percentage chromite in the ore? (**Assume chromite was the only source of chromium**)

(ii) What was the percentage chromium in the ore?

## Q17

Amino acids are the building blocks of many biologically active compounds. This question concerns the ability of amino acids to react with one other and the analysis of the products of such reactions by tandem mass spectrometry.

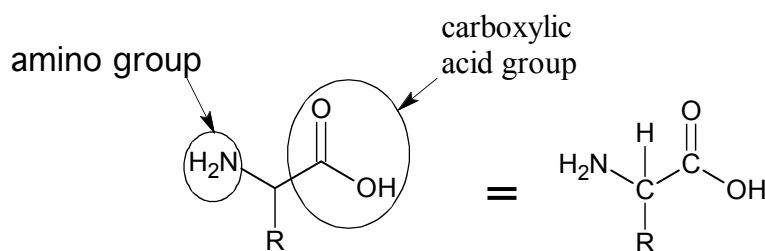
The tables below contain the name, abbreviation and relative formula mass (rounded to 1 decimal place) for common amino acids. The first table contains amino acids arranged alphabetically, the second by relative formula mass.

Amino acid name	Alanine	Arginine	Aspartic acid	Asparagine	Cysteine
Abbreviation	Ala	Arg	Asp	Asn	Cys
Relative formula mass	89.1	174.2	133.1	132.1	121.1
	Glutamic acid	Glutamine	Glycine	Histidine	Isoleucine
	Glu	Gln	Gly	His	Ile
	147.1	146.1	75.1	155.2	131.2
	Leucine	Lysine	Methionine	Phenylalanine	Proline
	Leu	Lys	Met	Phe	Pro
	131.2	146.2	149.2	165.2	115.1
	Serine	Threonine	Tryptophan	Tyrosine	Valine
	Ser	Thr	Trp	Tyr	Val
	105.1	119.1	204.2	181.2	117.1

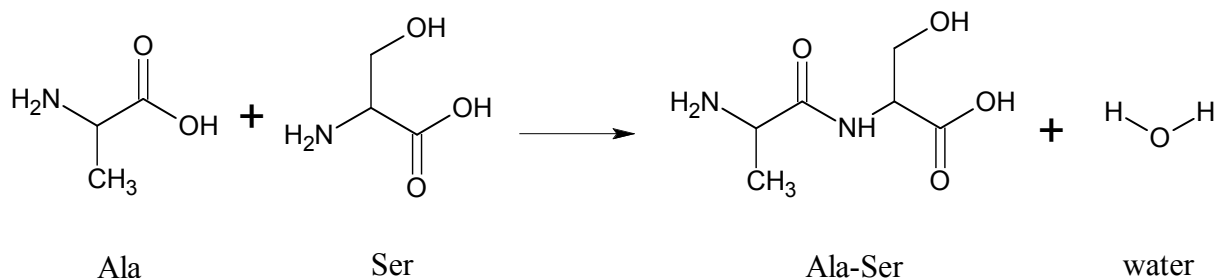
  

Abbreviation	Gly	Ala	Ser	Pro	Val
Relative formula mass	75.1	89.1	105.1	115.1	117.1
	Thr	Cys	Ile	Leu	Asn
	119.1	121.1	131.2	131.2	132.1
	Asp	Gln	Lys	Glu	Met
	133.1	146.1	146.2	147.1	149.2
	His	Phe	Arg	Tyr	Trp
	155.2	165.2	174.2	181.2	204.2

Amino acids, as their name suggests, are molecules possessing both an amino group ( $-\text{NH}_2$  or related derivative) and a carboxylic acid group ( $-\text{COOH}$ ). The structure of a general amino acid molecule is shown below; the 'R' represents a group of atoms that is different in each of the naturally-occurring amino acids.



The amino group ( $-\text{NH}_2$ ) from one amino acid can react with the carboxylic acid group ( $-\text{COOH}$ ) of a second amino acid, joining them together with the formation of a C-N bond. Water is also a product of this reaction, as shown below in the reaction of alanine with serine (abbreviated as Ala and Ser respectively, see the table above for abbreviations of other amino acids). The product (called a dipeptide) is directional: one end has a free amino group ( $-\text{NH}_2$ ) and the other has a free carboxylic acid group ( $-\text{COOH}$ ). When we report the sequence of amino acids in a polypeptide we do so starting at the end with the free amino group, as shown below.



- (a) Calculate the relative formula mass of water (to 1 decimal place).

- (b) Calculate the relative formula mass of the dipeptide Ala-Ser.

- (c) Name and draw the structure of another dipeptide that had the same relative formula mass as Ala-Ser.

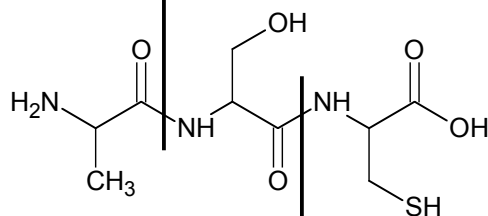
- (d) Calculate the relative formula mass of the tripeptide Ala-Ser-Ala.

- (e) Calculate the relative formula mass of the tetrapeptide Ala-Gly-Phe-Asp.

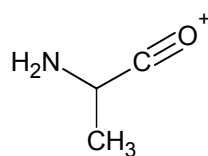
Tandem mass spectrometry is a high throughput method for determining the sequence of polypeptides. In this process, polypeptides are ionised to form a parent ion which then fragments further. The relative masses of the parent ion and all fragments are then measured.

One mode of fragmentation is by cleavage of the C-N bond between amino acids, leading to a series of 'b ions'. The formation of such ions for the tripeptide Ala-Ser-Cys is shown below:

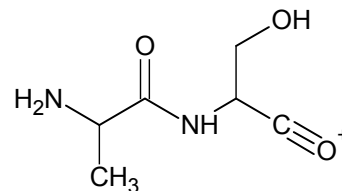
Fragmentation  
here gives b1 ion



Fragmentation  
here gives b2 ion



b1 ion



b2 ion

- (f) Calculate the relative formula mass of the b1 and b2 ions formed from the tetrapeptide Ala-Ser-Phe-Pro.

b1 ion mass:	b2 ion mass:

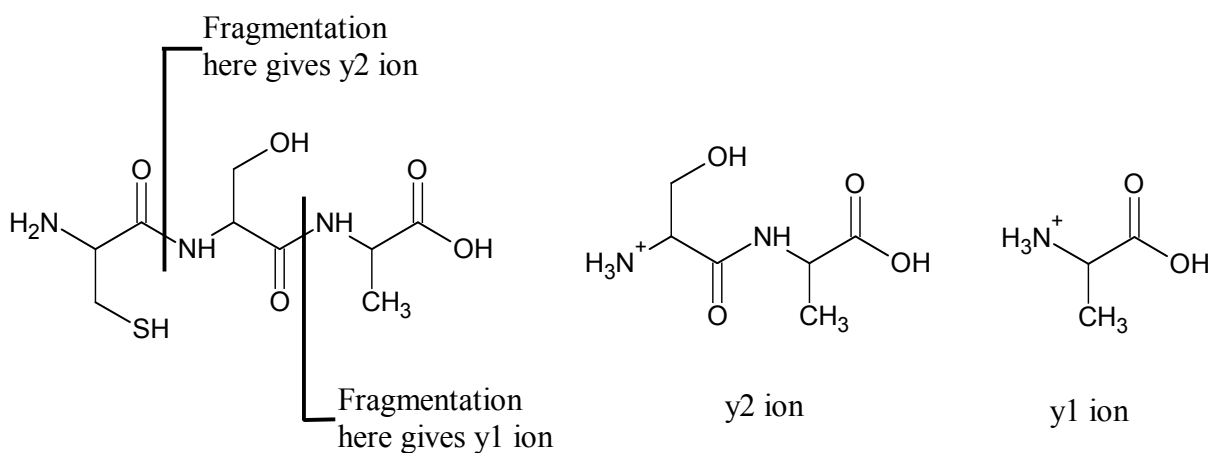
- (g) The masses of successive b ions from a tripeptide whose relative formula mass is 249.3 are tabulated below. Determine the sequence of amino acids in the tripeptide.

b ion	b1	b2	b3
mass	72.1	175.2	232.3

Number in sequence	1	2	3
Amino acid			



Another possible mode of fragmentation also involves C-N bond cleavage, but with protonation, and starting from the end of the peptide with the free  $-\text{COOH}$  group. This gives rise to so-called 'y ions', formation of which is shown below for a Cys-Ser-Ala tripeptide:



- (h) Calculate the relative formula mass of the y1 and y2 ions formed from the tetrapeptide Cys-Phe-Ser-Ala.

y1 ion mass:	y2 ion mass:
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- (i) The masses of successive y ions from a tripeptide whose relative formula mass is 409.5 are tabulated below. Determine the sequence of amino acids in the tripeptide.

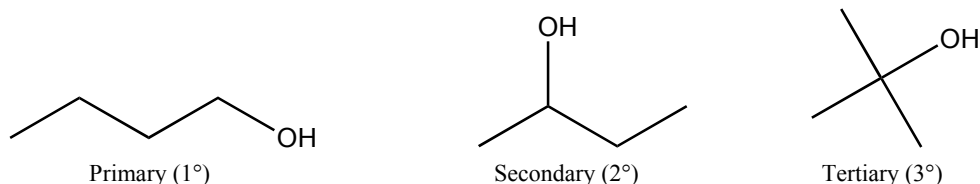
y ion	y1	y2	y3
mass	182.2	279.3	410.5

Number in sequence	1	2	3
Amino acid			

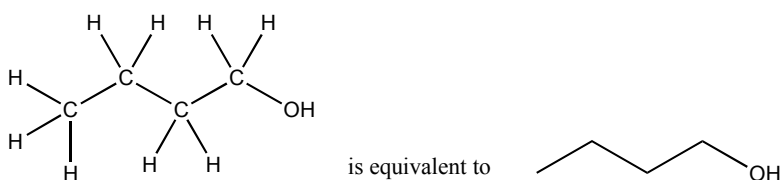


## Q18

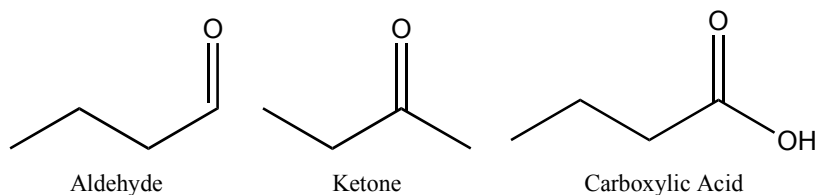
The alcohol functional group is well known for being a component of some beverages, along with its interesting chemical reactions! The reactivity is dependent on the carbon atom directly connected to the hydroxyl ( $\text{-OH}$ ) group, and the types of substituents present. Alcohols with two hydrogen atoms on the adjacent carbon atom are classified as primary, alcohols with one hydrogen atom on the adjacent carbon atom are secondary, and alcohols with no hydrogen atoms linked to the adjacent carbon atom are tertiary. Examples of these are shown below.



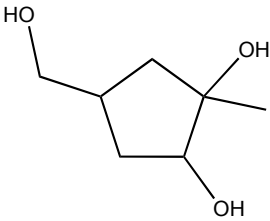
Note that in skeletal form, all hydrogen atoms are omitted and carbon atoms are represented by bends, such that

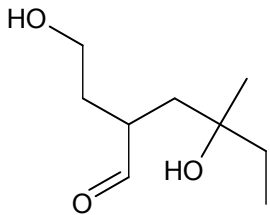
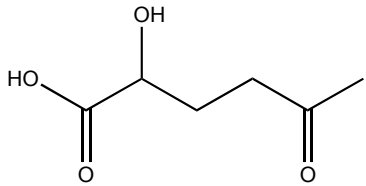


One common reaction of alcohols is oxidation. Whilst primary alcohols readily oxidise to form aldehydes and secondary alcohols oxidise to form ketones, tertiary alcohols do not undergo oxidation. Aldehydes can be further oxidised to form carboxylic acids. Usually this step occurs rapidly and the intermediate aldehyde cannot be easily isolated.



- (a) Circle the alcohol functional group in each of the following three compounds and indicate whether it is primary, secondary or tertiary. Draw the product of oxidation for each of these three compounds.

Original Compound	Product of Oxidation
(i) 	

Original Compound	Product of Oxidation
(ii) 	
Original Compound	Product of Oxidation
(iii) 	

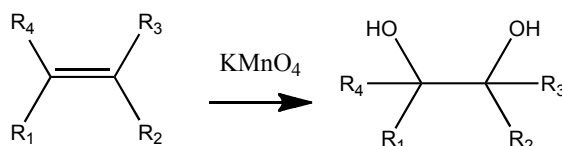
Compared to most other reactions that alcohols can undergo, oxidation is the easiest to visualise, with rapid and distinct colour changes occurring. Here, we will look at a number of qualitative tests that can be performed to determine the presence of certain functional groups.

### Tollens' Reagent

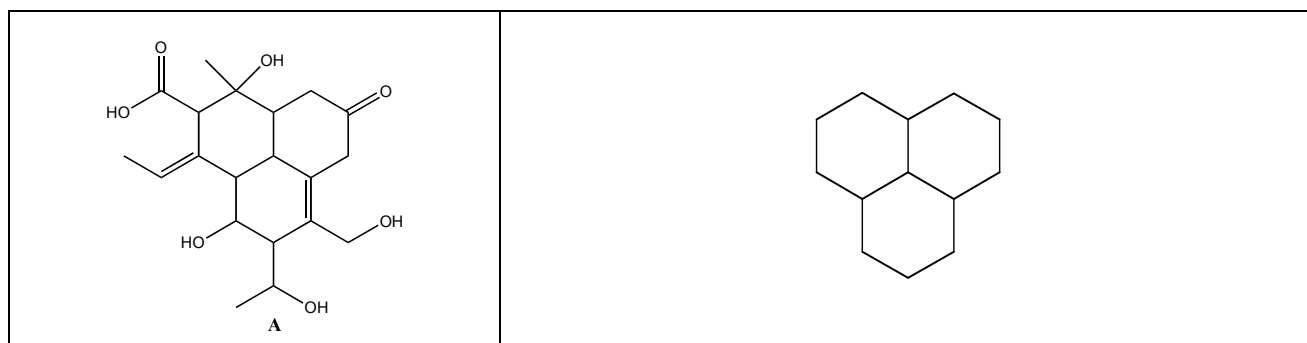
Ammoniacal silver nitrate solution (Tollens' reagent) is commonly employed in the oxidation of aldehydes. A positive test is characterised by the precipitation of silver to form a 'silver mirror'. Due to the high reactivity of aldehydes, only these functional groups can be readily detected using this method.

### Potassium Permanganate

Acidified potassium permanganate with heat is commonly used to oxidise alcohols but is also capable of adding diols across an alkene bond, as shown below. You should assume that a solution of acidified potassium permanganate oxidises all primary alcohols and aldehydes to carboxylic acids and C=C bonds to diols (and then further oxidation, if possible). Note that 'R' represents the rest of the molecule. Normally, the permanganate ion is purple but it is decolourised upon reduction.

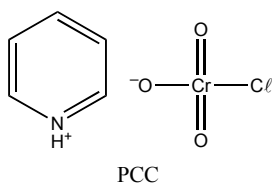


- (b) Draw the product when compound **A** (shown below) is treated with excess acidified potassium permanganate. A partial structure has been drawn for you.

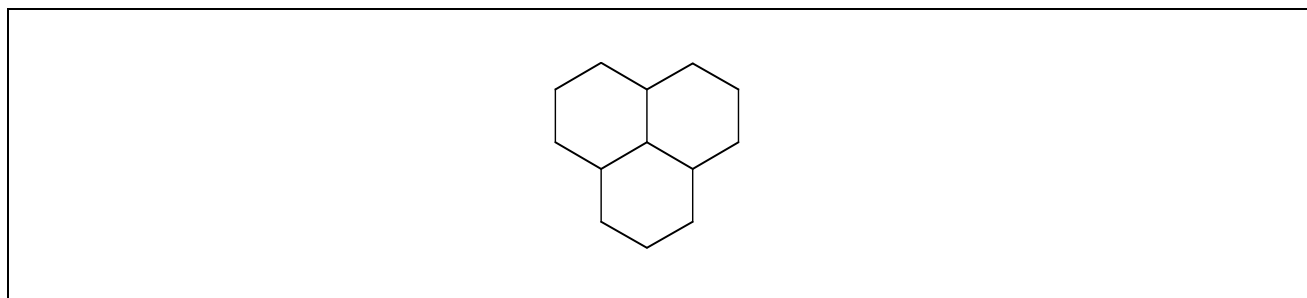


### Pyridinium Chlorochromate (PCC)

Pyridinium chlorochromate has the advantage over potassium permanganate of being more selective, allowing for one-step oxidations. Reactions with aldehydes and alkene bonds do not occur. The structure of PCC is shown below which appears red-orange, and is reduced to  $\text{Cr}_2\text{O}_3$  which appears green.

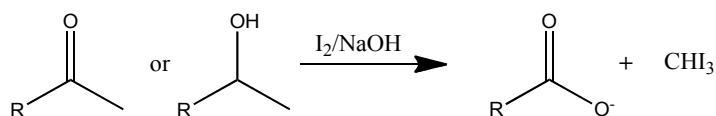


- (c) Draw the product formed when compound **A** is treated with PCC. A partial structure has been drawn for you.



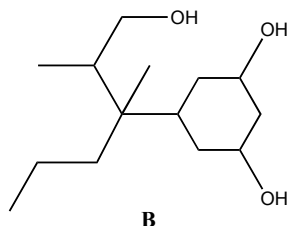
### Iodoform

The iodoform test is commonly used to test for the presence of methyl ketones and methyl secondary alcohols including ethanol and ethanal. Upon addition of  $\text{I}_2$  (in a basic solution), the alcohol is oxidised to the ketone which reacts further to produce the carboxylate ion and a yellow precipitate of iodoform ( $\text{CHI}_3$ ). Note that the addition of iodine across an alkene bond does not occur using these conditions.



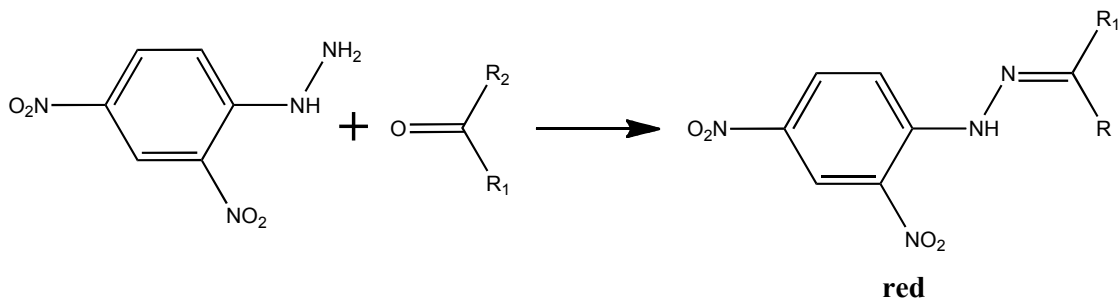
Iodine solution usually appears a brown-red colour which is decolourised with progression of the iodoform reaction, allowing for the yellow colour of iodoform to appear.

- (d) The iodoform test was performed on the following compound **B**. Decolourisation but no yellow precipitate was observed.



### 2,4-dinitrophenylhydrazine (DNP)

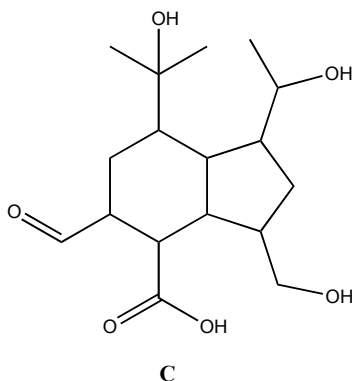
DNP (also known as Brady's Reagent) is used to detect the presence of aldehydes and ketones, which is affirmed by the presence of a red precipitate. The equation for the reaction which occurs is shown below.



### Identification of Functional Groups

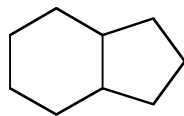
The above qualitative tests can be used in combination to elucidate the functional groups present in a compound.

- (e) A sample of compound **C** was oxidised, followed by treatment with DNP.

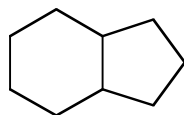


Draw the final product if **C** was oxidised first using each of the following three reagents. For simplification, you may write DNP at the sites where it reacts instead of drawing out the structure. A partial structure has been drawn for you.

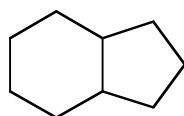
(i) acidified  $\text{KMnO}_4$



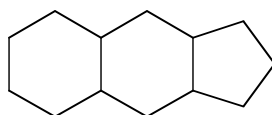
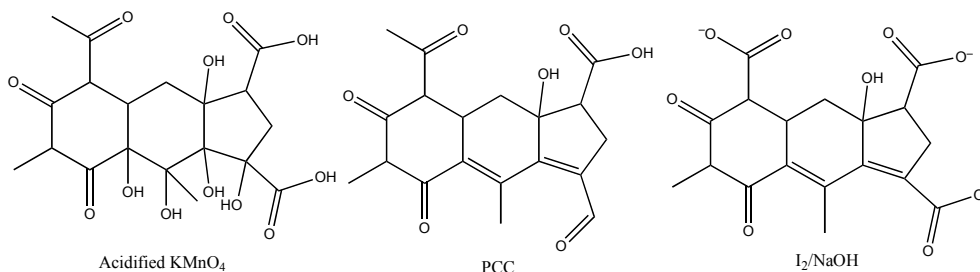
(ii) PCC



(iii)  $\text{I}_2/\text{NaOH}$



- (f) An unknown compound **D** was treated with each of the aforementioned three reagents, giving the compounds shown below. Treatment with Tollens' reagent showed no change, but a red precipitate was obtained with DNP. Suggest the structure of the original compound **D**. A partial structure has been drawn for you.

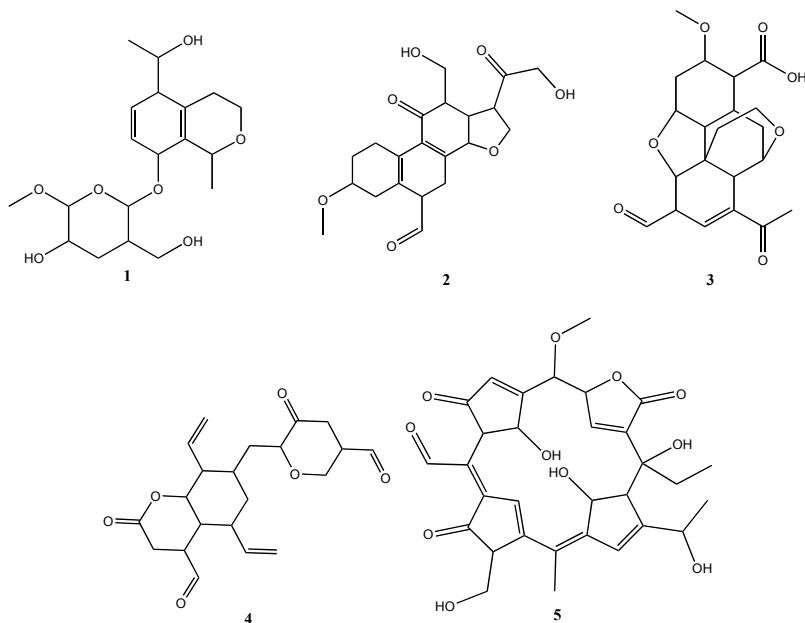




- (g) The above tests can also be used as a qualitative method of differentiating between compounds. An unknown compound **E** was treated with all of the aforementioned three tests and delivered results shown in the table below. Note that blue litmus turns red in acidic conditions.

Test	Result
Tollens' reagent	Silver mirror
Acidified $\text{KMnO}_4$	Colourless solution
PCC	Green solution
DNP	Red precipitate
Iodoform	Decolourisation
Blue litmus	No effect

Which of the following five structures could correspond to compound **E**? Justify your answer.

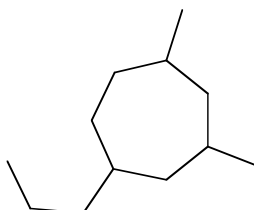
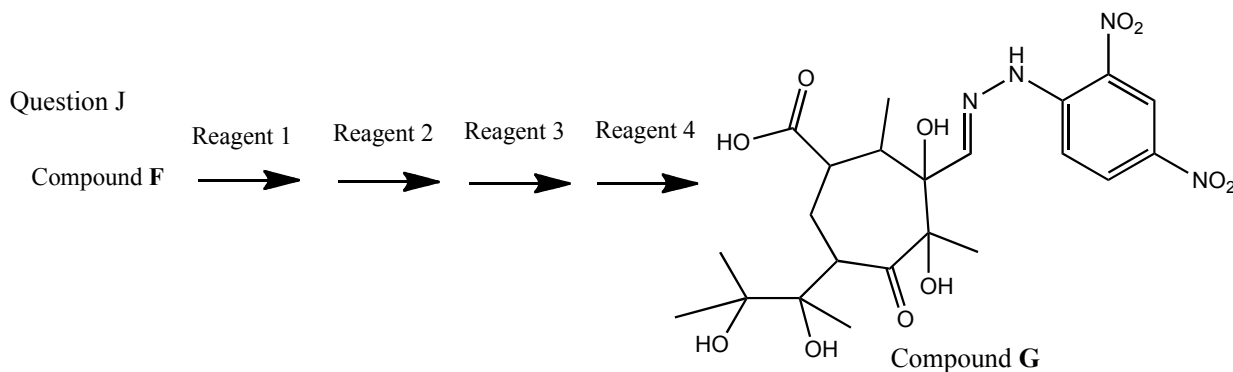


Compound **E** =

- (h) Alternatively, a compound can be tested sequentially with different reagents, as in the schematic shown below. This may be convenient in the identification of functional groups which have appeared following each treatment, such as the detection of a ketone following an oxidation reaction.

The compound **F** was treated with four different reagents sequentially, with the product formed after each step purified for the next reaction. These reagents include PCC,  $I_2/NaOH$  and acidified  $KMnO_4$  but not necessarily in this order. Each step yielded a positive result. The final product **G** is shown below.

Suggest what compound **F** could be and state the order in which the tests were performed. Justify your answer. A partial structure has been drawn for you.



Reagent 1 =

Reagent 2 =

Reagent 3 =

Reagent 4 =

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