3

Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/01

Paper 1 Multiple Choice

September 2021

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, class and NRIC/FIN number on the Answer Sheet in the spaces provided.

There are **thirty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

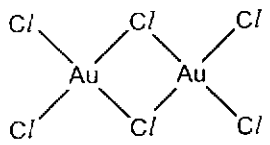
This document consists of **12** printed pages.

1 Nitrogen exists as a diatomic molecule, N_2. Hydrazine, N_2H_4, and dinitrogen difluoride, N_2F_2, are compounds of nitrogen.

Which of the following gives the correct number of π bonds in N_2, N_2H_4 and N_2F_2?

	number of π bonds in N_2	number of π bonds in N_2H_4	number of π bonds in N_2F_2
A	2	0	1
B	2	1	1
C	1	1	2
D	3	0	2

2 Aluminium chloride is a covalent compound that forms a dimer with the formula Al_2Cl_6. A compound of gold and chlorine has a similar molecular formula of Au_2Cl_6 and has the following structure:



The three statements below are properties of the gold compound, Au_2Cl_6.

1 The oxidation state of the metal is +3.
2 The dimer exists in the vapour phase.
3 The Cl-Au-Cl bond angle is 90°.

Which property described is **different** from that of the aluminium compound, Al_2Cl_6?

A 1 and 2 only
B 1, 2 and 3
C 3 only
D 2 and 3 only

3 The table below lists three compounds:

compound	boiling point / °C
CH_3CH_2–S–H	35
CH_3–S–CH_3	37
CH_3CH_2–O–H	78

Which of the following statements about the compounds is true?

A The C–S–H bond angle is larger than the C–O–H bond angle because S is larger than O.

B CH_3CH_2–S–H has weaker intermolecular hydrogen bonding than CH_3CH_2–O–H.

C CH_3CH_2–S–H and CH_3–S–CH_3 have similar boiling points because they have intermolecular permanent dipole – permanent dipole forces of attraction of similar strengths.

D CH_3CH_2–O–H has the highest boiling point because the O–H bond energy is higher than the S–H bond energy.

4 *Use of the Data Booklet is relevant to this question.*

An isotope of a metal, **Z**, undergoes radioactive decay to form helium and an element hafnium, Hf, according to the following equation.

$$Z \longrightarrow {}^{4}_{2}He + Hf$$

Given that Hf has a nucleon number of 176, which row correctly shows the identity and composition of **Z**?

	identity of **Z**	number of nucleons in **Z**
A	tungsten	180
B	tungsten	178
C	osmium	180
D	osmium	178

5 *Use of the Data Booklet is relevant to this question.*

The first six ionisation energies of an element, **Y**, in kJ mol^{-1} are shown.

738; 1451; 7733; 10543; 13630; 18020

Y forms an oxide by heating **Y** with oxygen gas.
What is the *spdf* electronic configuration of **Y** in its oxide form?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
B $1s^2\ 2s^2\ 2p^6$
C $1s^2\ 2s^2\ 2p^6\ 3s^2$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

6 What is the element that has a **second** ionisation energy lower than that of each of the elements either side of it in the Periodic Table?

A boron **B** nitrogen **C** oxygen **D** fluorine

7 Analysis of a mixture of two sulfur-containing gases show that hydrogen sulfide, H_2S, and carbon sulfide, CS_2, are present in a 3 : 1 mole ratio.

This mixture is burned in excess oxygen.
What will be the CO_2 : SO_2 mole ratio in the mixture obtained after complete combustion?

A 1 : 2 **B** 1 : 3 **C** 1 : 4 **D** 1 : 5

8 *Use of the Data Booklet is relevant to this question.*

A mordant is a soluble salt which forms an acidic aqueous solution and improves the binding of the molecules of a dyestuff to a material.

Which solution is least likely to be used as a mordant in the dyeing process?

A sodium sulfate
B magnesium sulfate
C aluminium sulfate
D iron(II) sulfate

9 Element **X** is in Period 3 of the Periodic Table. The following four statements describe the properties of element **X** or its compounds.

Three statements are correct descriptions. One of the statements is not correct because it does not fit with the other three.

Which statement is **not** correct?

A Element **X** is a solid at room temperature which conducts electricity.

B The chloride of element **X** reacts with water to give an acidic solution.

C The oxide of element **X** reacts in water to give an acidic solution.

D Adding NaOH(aq) to the solution resulting from the reaction of $\mathbf{X}Cl_3$ with water produces a white precipitate which is soluble in an excess of NaOH(aq).

10 Which property generally increases down Group 2?

A charge density of M^{2+} ion
B electronegativity
C melting point
D thermal stability of the carbonate

11 A comproportionation reaction is a chemical reaction where two reactants, each containing the same element but with a different oxidation number, form a product in which the elements involved reach the same oxidation number.

2 mol of hydrogen sulfide, H_2S, react with 1 mol of another sulfur-containing compound to form 3 mol of elemental sulfur, S, in a comproportionation reaction.

What is a possible identity of the sulfur-containing compound?

A SO_2 **B** SO_3 **C** H_2SO_4 **D** SCl_2

12 *Use of the Data Booklet is relevant to this question.*

Dinitrogen oxide, N=N=O, burns in ethyne, C_2H_2, to produce water vapour, carbon dioxide and nitrogen gas according to the following equation.

$$5N_2O(g) + C_2H_2(g) \rightarrow H_2O(g) + 2CO_2(g) + 5N_2(g)$$

The enthalpy change for this reaction is -1668 kJ mol^{-1} and in dinitrogen oxide, the N=N bond energy has a value of +418 kJ mol^{-1}. With reference to other appropriate bond energy data from the *Data Booklet*, what is the N=O bond energy in dinitrogen oxide?

A 344 kJ mol^{-1}
B 688 kJ mol^{-1}
C 1354 kJ mol^{-1}
D 3442 kJ mol^{-1}

13 Which of the following is an endothermic process?

1 The combustion of methane
2 The condensation of steam
3 The electrolysis of water
4 The sublimation of iodine

A 1 and 2 only
B 2 and 3 only
C 3 and 4 only
D 1 and 4 only

14 At 1200 K, in the presence of gold catalyst, dinitrogen oxide, N_2O, decomposes according to the equation below.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The following data is obtained in an experiment.

time, t / s	0	1030	2360	4230	7430
partial pressure of N_2O / kPa	25.0	20.0	15.0	10.0	5.0

Which of the following statements is correct?

1 The partial pressure of N_2O at any given time is not affected by temperature.
2 The reaction is first order with respect to N_2O.
3 The value of the rate constant remains unchanged in the absence of gold.
4 The total pressure at the completion of the reaction can be determined from the above data.

A 1 and 2 only
B 1 and 3 only
C 2 and 4 only
D 3 and 4 only

15 The reaction shown below takes place via a one-step mechanism.

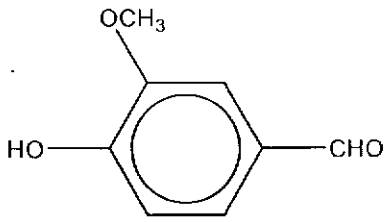
$$A(g) + 2B(g) \rightleftharpoons C(g)$$

Which of the following statements is most likely to be correct?

1 The yield of C increases at lower pressure.
2 The yield of C decreases when the volume of the reaction vessel is halved.
3 The equilibrium concentration of C is given by the expression: $[C] = K_C[A][B]^2$
4 The rate of the forward reaction is given by the expression: rate = $k[A][B]^2$

A 1 and 2 only
B 1 and 3 only
C 2 and 4 only
D 3 and 4 only

16 Vanillin is the key flavour compound in vanilla, and its structure is shown.



vanillin

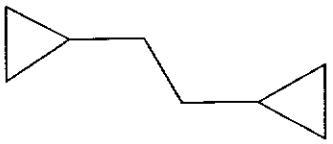
How many sp^2 hybridised carbons are there in a molecule of vanillin?

A 5 **B** 6 **C** 7 **D** 8

17 A non-cyclic organic compound has the molecular formula $C_3H_4O_2$.
Which combination of functional groups **cannot** be present in this molecule?

A one alkene and one carboxylic acid group
B one alkene and one ester group
C one alkene and two alcohol groups
D one aldehyde and one ketone group

18 Compound **W**, C_8H_{14}, reacts with chlorine gas in the presence of *uv* light.



W

Which of the following statements about this reaction is correct?

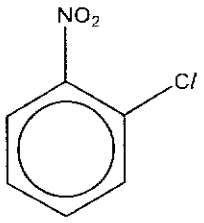
1 The maximum number of mono-chlorinated constitutional isomers with formula $C_8H_{13}Cl$ is 3.
2 $C_{16}H_{28}$ is present in small quantities in the product.
3 Homolytic fission only occurs in the initiation step.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

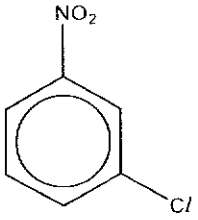
19 When nitrobenzene is heated with $BrCl$ and $AlBr_3$, a mono-halogenated product is formed.

Which product is most likely to be formed?

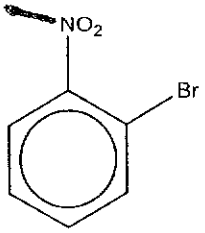
A



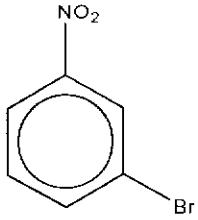
B



C

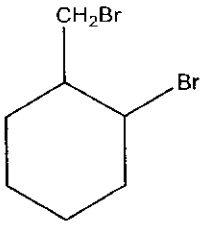


D

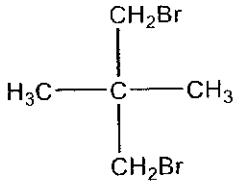


20 1 mol of organic compound **V** reacts with ethanolic sodium hydroxide to form 2 mol of HBr. What could **V** be?

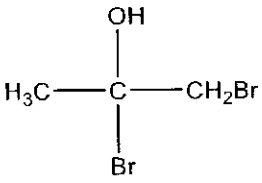
A



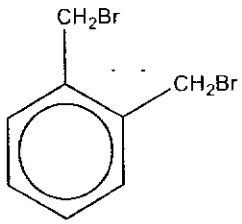
B



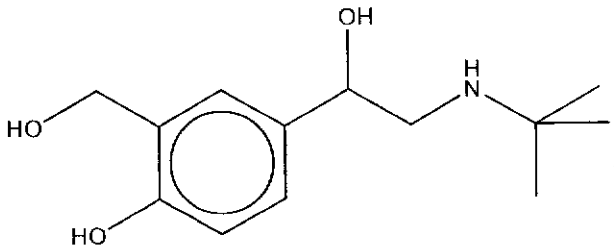
C



D



21 Salbutamol is a common medicine used to alleviate asthma attacks.



salbutamol

Which statement about 1 mol of salbutamol is **incorrect**?

A It reacts with 4 mol of ethanoyl chloride, CH_3COCl, to form 3 ester and 1 amide group.

B It reacts with excess acidified $K_2Cr_2O_7$(aq) to form 1 carboxylic acid and 1 ketone group.

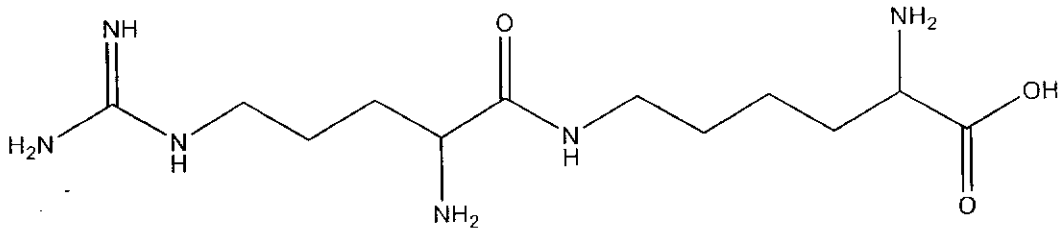
C It reacts with 3 mol of sodium metal.

D It reacts with 2 mol of NaOH(aq).

22 Which of the following shows the correct order of decreasing pK_a?

A	C_6H_5OH	>	CH_3CH_2OCOH	>	$CH_3CH_2CO_2H$	> CH_3CHFCO_2H
B	CH_3CH_2OCOH	>	C_6H_5OH	>	$CH_3CH_2CO_2H$	> CH_3CHFCO_2H
C	CH_3CHFCO_2H	>	$CH_3CH_2CO_2H$	>	C_6H_5OH	> CH_3CH_2OCOH
D	CH_3CH_2OCOH	>	CH_3CHFCO_2H	>	$CH_3CH_2CO_2H$	> C_6H_5OH

23 Compound **U** is a by-product formed in the body to counteract the effect of the drug administered to treat herpes.



compound **U**

Which one of the following statements about compound **U** is correct?

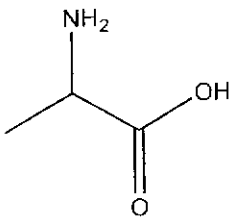
A **U** undergoes nucleophilic addition with chloroethane.
B 1 mol of **U** can be hydrolysed to produce 2 mol of amino acids.
C 1 mol of **U** can react with 6 mol of hydrochloric acid at room temperature.
D When an aqueous solution of **U** at pH 3 is analysed by electrophoresis, it is found near the anode.

24 A compound **T** is boiled with aqueous sodium hydroxide and the resulting mixture cooled and acidified. The final product includes a compound $C_3H_6O_2$ and an alcohol that gives a positive iodoform test.

Which formula could represent compound T?

A $CH_3CH_2CO_2CH_2CH_2Cl$
B $CH_3CH_2OCOCH_3$
C $CH_3OCOCH_2COCH_3$
D $CH_3CH_2CO_2CH_2CHClCH_3$

25 Which of the following is **not** a correct statement about *alanine* extracted from silkworm?



alanine

A *Alanine* is able to rotate plane-polarised light.
B *Alanine* has a higher solubility in water than in ether.
C *Alanine* can react with ethanoic acid to give an amide.
D An aqueous solution of *alanine* has a buffering capacity.

26 The equation below shows a ligand exchange reaction.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

Which is a possible reason to explain why NH_3 ligands displace H_2O ligands?

A ΔS is positive for the displacement reaction.
B NH_3 is more tightly bound to Cu^{2+} ions than H_2O.
C The energy difference for d→d transition in $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is greater than that in $[Cu(H_2O)_6]^{2+}(aq)$.
D The pH of NH_3 is higher than the pH of $H_2O(l)$

27 *Use of the Data Booklet is relevant to this question.*

The table below gives data about some physical properties of the elements calcium and copper.
Which row gives the correct properties under the correct element?

		calcium	copper
A	melting point / K	1358	1112
B	density / g cm^{-3}	1.54	8.92
C	first ionisation energy / kJ mol^{-1}	745	590
D	atomic radius (metallic) / nm	0.128	0.197

28 *Use of the Data Booklet is relevant to this question.*

The silver chloride electrode is a type of reference electrode commonly used in electrochemical measurements. It can be represented as below.

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

The reduction potential of Cr^{3+}/Cr^{2+} half-cell is −0.61 V when it is measured using the AgCl /Ag reference electrode at standard conditions.

What is the reduction potential of AgCl /Ag electrode when it is measured against the standard hydrogen electrode as reference?

A +0.80 V **B** +0.41 V **C** +0.20 V **D** –0.41V

29 A voltaic cell is set up using the Mg^{2+}/Mg and Fe^{3+}/Fe^{2+} half-cells.

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^{\ominus}_{Mg^{2+}/Mg} = -2.38\ V$

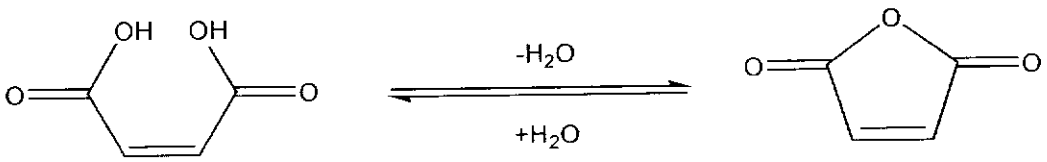
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

Under standard conditions, the cell e.m.f. would be 3.15 V. However, the voltmeter recorded a reading of 3.05 V.

What is the best explanation for this lower e.m.f.?

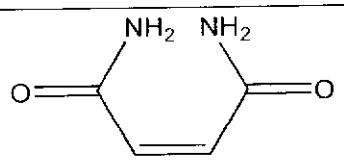
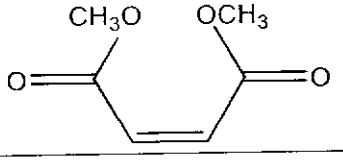
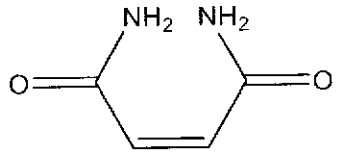
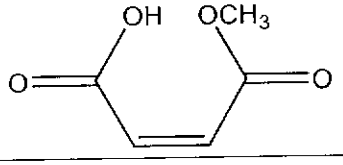
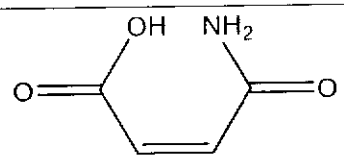
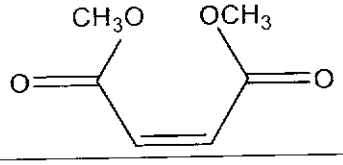
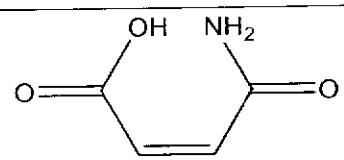
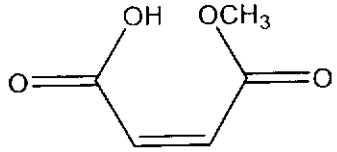
A a smaller magnesium electrode was used
B a higher concentration of Fe^{3+} was used
C a higher concentration of Mg^{2+} was used
D water evaporated from the Fe^{3+}/Fe^{2+} half-cell

30 Maleic acid loses water on strong heating to form compound **S**. On addition of water to compound **S**, it reforms maleic acid.



maleic acid compound **S**

Which of the following shows the correct compounds formed when ammonia and methanol are added to compound **S** separately?

	Addition of NH_3	Addition of CH_3OH
A		
B		
C		
D		

Catholic Junior College

JC 2 Preliminary Examinations

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

Paper 1 Multiple Choice

9729/01

September 2021

1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

WORKED SOLUTIONS

General comments

Students found questions **2, 3, 14, 18, 19, 20, 22, 23, 24, 25, and 30** to be the **most challenging**.

(You should revisit and fully understand these even you got it correct)

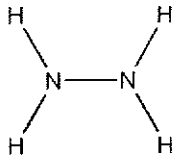
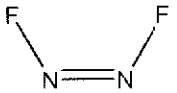
This document consists of **12** printed pages.

1 Nitrogen exists as a diatomic molecule, N_2. Hydrazine, N_2H_4, and dinitrogen difluoride, N_2F_2, are compounds of nitrogen.

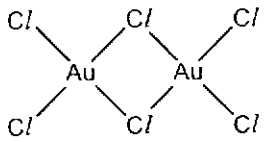
Which of the following gives the correct number of π bonds in N_2, N_2H_4 and N_2F_2?

	number of π bonds in N_2	number of π bonds in N_2H_4	number of π bonds in N_2F_2
A	2	0	1
B	2	1	1
C	1	1	2
D	3	0	2

(Inspired by H1 2020 MCQ6)
Concept: Chemical Bonding, σ and π bonds
Answer: A

	number of π bonds in N_2 	number of π bonds in N_2H_4 	number of π bonds in N_2F_2  (either cis or trans)
A	(1σ), 2π	(5σ), no π	(3σ), 1π

2 Aluminium chloride is a covalent compound that forms a dimer with the formula Al_2Cl_6. A compound of gold and chlorine has a similar molecular formula of Au_2Cl_6 and has the following structure:



The three statements below are properties of the gold compound, Au_2Cl_6.

1 The oxidation state of the metal is +3.
2 The dimer exists in the vapour phase.
3 The *Cl*-Au-*Cl* bond angle is 90°.

Which property described is **different** from that of the aluminium compound, Al_2Cl_6?

A 1 and 2 only
B 1, 2 and 3
C 3 only
D 2 and 3 only

(Inspired by H2 2018 MCQ2)
Concept: Chemical Bonding, Al_2Cl_6.
Answer: C

1. This is a similar property to Al_2Cl_6. Chlorine is more electronegative than Al. Each Al also has an oxidation state of +3 as each Cl has an oxidation state of -1.
2. This is a similar property to Al_2Cl_6. Al_2Cl_6 dimer exists in the gas phase.
3. Not similar. The Cl-Al-Cl bond angle is 109.5°.

3 The table below lists three compounds:

compound	boiling point / °C
CH_3CH_2–S–H	35
CH_3–S–CH_3	37
CH_3CH_2–O–H	78

Which of the following statements about the compounds is true?

A The C–S–H bond angle is larger than the C–O–H bond angle because S is larger than O.
B CH_3CH_2–S–H has weaker intermolecular hydrogen bonding than CH_3CH_2–O–H.
C CH_3CH_2–S–H and CH_3–S–CH_3 have similar boiling points because they have intermolecular permanent dipole – permanent dipole forces of attraction of similar strengths.
D CH_3CH_2–O–H has the highest boiling point because the O–H bond energy is higher than the S–H bond energy.

(Inspired from 2019 H2 A level P3 Q2(f)(i))
Concept: Chemical Bonding, Bond angle and IMF
Answer: C

A The C–S–H bond angles are <u>smaller</u> than the C–O–H bond angle because S is <u>less electronegative</u> than O. The valence electrons around S will be further away compared to the valence electrons in O. As a result, there is weaker bond pair – bond pair repulsion around S than around O, giving rise to a smaller bond angle.
B CH_3CH_2–S–H does not have intermolecular hydrogen bonding as the H present in the molecule is not bonded to F, O or N.
C True. Both are isomers of each other (same number of electrons) and both are polar molecules.
D CH_3CH_2–O–H has the highest boiling point due to stronger intermolecular hydrogen bonding which is absent in the other two compounds. The strength of covalent bonds is not relevant to the boiling point for simple molecules.

4 *Use of the Data Booklet is relevant to this question.*

An isotope of a metal, **Z**, undergoes radioactive decay to form helium and an element hafnium, Hf, according to the following equation.

$$Z \longrightarrow {}^{4}_{2}He + Hf$$

Given that Hf has a nucleon number of 176, which row correctly shows the identity and composition of **Z**?

	identity of **Z**	number of nucleons in **Z**
A	tungsten	180
B	tungsten	178
C	osmium	180
D	osmium	178

Concept: Atomic Structure, sub-atomic particles.
Answer: A
From *Data Booklet*, the atomic number of hafnium is 72. Given that the nucleon number is 176, this will be a more detailed equation of the decay:

$$Z \longrightarrow {}^{4}_{2}He + {}^{176}_{72}Hf$$

Hence, proton number of Z is 72 + 2 = 74. This correlates to tungsten.
The nucleon number of Z is 176 + 4 = 180

5 *Use of the Data Booklet is relevant to this question.*

The first six ionisation energies of an element, Y, in kJ mol^{-1} are shown.

738; 1451; 7733; 10543; 13630; 18020

Y forms an oxide by heating Y with oxygen gas.
What is the *spdf* electronic configuration of Y in its oxide form?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
B $1s^2\ 2s^2\ 2p^6$
C $1s^2\ 2s^2\ 2p^6\ 3s^2$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

Concept: Atomic Structure, ionisation energy.
Answer: B
The significant increase from the second to the third ionisation energy indicates that Y is from Group 2.
From Data Booklet, the ionisation energies match Mg ($1s^2\ 2s^2\ 2p^6\ 3s^2$) most closely.

When Mg forms MgO, it loses its two valence electrons and hence its electronic configuration is $1s^2\ 2s^2\ 2p^6$.

6 What is the element that has a **second** ionisation energy lower than that of each of the elements either side of it in the Periodic Table?

A boron **B** nitrogen **C** oxygen **D** fluorine

(Inspired from 2010 H1 A level MCQ3)
Concept: Atomic Structure. Second Ionisation energy
Answer: D

Second IE is $F^+ \rightarrow F^{2+} + e^-$

Element before F: O		Element after F: Ne
O^+: $1s^2 2s^2\ 2p_x^1 2p_y^1 2p_z^1$	F^+: $1s^2\ 2s^2\ 2p_x^2 2p_y^1 2p_z^1$	Ne^+: $1s^2 2s^2\ 2p_x^2 2p_y^2 2p_z^1$

Comparing F and O:
Less energy is required to remove a paired $2p_x$ electron from F^+ due to interelectronic repulsion. Hence second IE of F is less than O.

Comparing F and Ne:
Less energy is required to remove the electron from F^+ because it has a lower nuclear charge than Ne and a smaller ionic size than Ne^+.

Alternatively, check the Data Booklet:
Second IE values in kJ mol^{-1}:

O	F	Ne
3390	3370	3950

7 Analysis of a mixture of two sulfur-containing gases show that hydrogen sulfide, H_2S, and carbon sulfide, CS_2, are present in a 3 : 1 mole ratio.

This mixture is burned in excess oxygen.
What will be the CO_2 : SO_2 mole ratio in the mixture obtained after complete combustion?

A 1 : 2 **B** 1 : 3 **C** 1 : 4 **D** 1 : 5

2016 P1 Q2 modified
Concept: Mole concept & stoichiometry
Ans: D

Let amount of H_2S be $3x$ mol and CS_2 be x mol,

$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O$

Amount of SO_2 produced by H_2S = $3x$ mol

$CS_2 + 3O_2 \rightarrow 2SO_2 + CO_2$

Amount of SO_2 produced by CS_2 = $2x$ mol, Amount of CO_2 produced = x mol

Hence, mole ratio of CO_2 : SO_2 in the mixture after complete combustion will be $x : (3x + 2x)$ = **1 : 5**

8 *Use of the Data Booklet is relevant to this question.*

A mordant is a soluble salt which forms an acidic aqueous solution and improves the binding of the molecules of a dyestuff to a material.

Which solution is least likely to be used as a mordant in the dyeing process?

A sodium sulfate
B magnesium sulfate
C aluminium sulfate
D iron(II) sulfate

2018 A-level P1 Q13 modified
Concept: Periodic Table; extension of reaction of Period 3 chlorides with water
Ans: A

Recall from Periodic Table, pH of $Al^{3+}(aq)$ = 3, pH of $Mg^{2+}(aq)$ = 6.5

Al^{3+}, Mg^{2+} and Fe^{2+} can undergo hydrolysis to give H^+ due to their high charge densities, polarising an O-H bond in H_2O.

Charge density of Al^{3+} ($\propto \frac{+3}{0.050}$) is the highest among all the cations in the question.

Charge density of Fe^{2+} ($\propto \frac{+2}{0.061}$) is similar to the charge density of Mg^{2+} ($\propto \frac{+2}{0.065}$) hence it can also undergo hydrolysis.

Na^+ is not able to undergo hydrolysis due to its low charge density ($\propto \frac{+1}{0.095}$), hence sodium sulfate is a neutral solution and is unlikely to be used as a mordant.

9 Element **X** is in Period 3 of the Periodic Table. The following four statements describe the properties of element **X** or its compounds.

Three statements are correct descriptions. One of the statements is not correct because it does not fit with the other three.

Which statement is **not** correct?

A Element **X** is a solid at room temperature which conducts electricity.

B The chloride of element **X** reacts with water to give an acidic solution.

C The oxide of element **X** reacts in water to give an acidic solution.

D Adding NaOH(aq) to the solution resulting from the reaction of **X**Cl_3 with water produces a white precipitate which is soluble in an excess of NaOH (aq).

2017 P1 Q15 modified
Concept: Periodic Table, trends and variation in chemical and physical properties
Ans: C

Element **X** is Al.

Al_2O_3 in insoluble in water hence it will not react with water to give an alkaline solution.

Al^{3+} reacts with OH^- to form white ppt of $Al(OH)_3$. In the presence of excess OH^-, the $Al(OH)_3$ ppt will react further to form soluble complex $Al(OH)_4^-$ which explains the solubility of the white ppt in excess NaOH(aq).

10 Which property generally increases down Group 2?

A charge density of M^{2+} ion
B electronegativity
C melting point
D thermal stability of the carbonate

2015 P1 Q15 modifed
Concept: Periodic Table; Group 2 properties
Ans: D

A Charge density of M^{2+} ion decreases since +2 charge remains constant but cationic radius increases.
B Electronegativity decreases down the group as the distance between valence electron shell and the nucleus increases.
C Melting point decreases down the group as the cationic radius of M^{2+} ions increases, hence the strength of electrostatic attractions between the sea of delocalised electrons and M^{2+} ions decreases, resulting in less energy needed to overcome the metallic bonds.
D Thermal stability of the carbonate increases down Group 2, as the polarising power of M^{2+} ion decreases down the group, resulting in the decreasing ability of M^{2+} ion to distort the electron cloud of the CO_3^{2-} anion.

11 A comproportionation reaction is a chemical reaction where two reactants, each containing the same element but with a different oxidation number, form a product in which the elements involved reach the same oxidation number.

2 mol of hydrogen sulfide, H_2S, react with 1 mol of another sulfur-containing compound to form 3 mol of elemental sulfur, S, in a comproportionation reaction.

What is a possible identity of the sulfur-containing compound?

A SO_2 **B** SO_3 **C** H_2SO_4 **D** SCl_2

2018 P1 Q10 modified
Concept: Mole concept & stoichiometry, redox
Ans: A

	H_2S +	S^x	→ S
Mole ratio	2	1	3

$\therefore 2H_2S + S^x \rightarrow 3S$ (not balanced)

By figuring out the changes in the oxidation states of S during the redox reaction,

$2H_2S$ +	S^x	→ 3S
2(–2)	(+x)	3(0)
–4	+4	0

Since $2H_2S \equiv 4\ e^- \equiv 1S^x$
1 mole of S would have gained 4 moles of electrons to form 1 mole of S

Thus, oxidation number of S in the sulfur-containing compound = +4
Hence the sulfur-containing compound is SO_2.

O.N. of S in SO_2 = +4
O.N. of S in SO_3 = +6
O.N of S in H_2SO_4 = +6
O.N. of S in SCl_2 = +2

12 *Use of the Data Booklet is relevant to this question.*

Dinitrogen oxide, N=N=O, burns in ethyne, C_2H_2, to produce water vapour, carbon dioxide and nitrogen gas according to the following equation.

$$5N_2O(g) + C_2H_2(g) \rightarrow H_2O(g) + 2CO_2(g) + 5N_2(g)$$

The enthalpy change for this reaction is –1668 kJ mol^{-1} and in dinitrogen oxide, the N=N bond energy has a value of +418 kJ mol^{-1}. With reference to other appropriate bond energy data from the *Data Booklet*, what is the N=O bond energy in dinitrogen oxide?

A 344 kJ mol^{-1}
B 688 kJ mol^{-1}
C 1354 kJ mol^{-1}
D 3442 kJ mol^{-1}

Concept: Chemical Energetics (Bond Energy)
Answer: B

5(N=N=O) + H–C≡C–H → H–O–H + 2O=C=O + 5N≡N
H_{rxn} = ∑BE(reactants) – ∑BE(products)
–1668 = [(5 x 418) + 5BE(N=O) + (2 x 410) + 840] – [(2 x 460) + (4 x 805) + (5 x 944)]
BE(N=O) = 688.4 kJ mol^{-1}

13 Which of the following is an endothermic process?

1 The combustion of methane
2 The condensation of steam
3 The electrolysis of water
4 The sublimation of iodine

A 1 and 2 only
B 2 and 3 only
C 3 and 4 only
D 1 and 4 only

Concept: Chemical Energetics, Endothermic reactions

Answer: C (3 and 4 only)

1: Combustion is always exothermic as it releases heat energy to the surroundings when it forms more stable compounds relative to the reactants after combustion.
2: Bond formation due to formation of water in liquid state (hydrogen bonds between water molecules) has occurred, thus condensation is an exothermic process.
3: The electrolysis of water is an endothermic reaction (electrical energy supplied) with the following equation: $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$
4: $I_2(s)$ is converted to I_2 vapour when the intermolecular instantaneous diploe – induced dipole forces of attraction holding the I_2 molecules in a crystal lattice are broken. Thus, it is an endothermic process.

14 At 1200 K, in the presence of gold catalyst, dinitrogen oxide, N_2O, decomposes according to the equation below.

$$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$$

The following data is obtained in an experiment.

time, t / s	0	1030	2360	4230	7430
partial pressure of N_2O / kPa	25.0	20.0	15.0	10.0	5.0

Which of the following statements is correct?

1 The partial pressure of N_2O at any given time is not affected by temperature.
2 The reaction is first order with respect to N_2O.
3 The value of the rate constant remains unchanged in the absence of gold.
4 The total pressure at the completion of the reaction can be determined from the above data.

A 1 and 2 only
B 1 and 3 only
C 2 and 4 only
D 3 and 4 only

Concept: Reaction Kinetics

Answer: C (2 and 4 only)

1: pV = nRT, partial pressure is affected by temperature
2: The time taken for partial pressure of N_2O to decrease from 20.0 to 10.0 kPa (4230 – 1030 = 3200 s) is same as time taken for partial pressure of N_2O to decrease from 10.0 to 5.0 kPa (4230 – 7430 = 3200 s), implying constant half life and hence 1st order wrt N_2O.
3: From Arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$, k is affected by activation energy, which in turn is lowered by catalyst.
4: From stoichiometric equation, the total pressure of all the products at completion of reaction = 3/2 x pressure of N_2O at the start of reaction.

15 The reaction shown below takes place via a one-step mechanism.

$$A(g) + 2B(g) \rightleftharpoons C(g)$$

Which of the following statements is most likely to be correct?

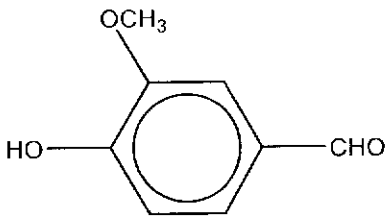
1 The yield of C increases at lower pressure.
2 The yield of C decreases when the volume of the reaction vessel is halved.
3 The equilibrium concentration of C is given by the expression: $[C] = K_c[A][B]^2$
4 The rate of the forward reaction is given by the expression: rate = $k[A][B]^2$

A 1 and 2 only
B 1 and 3 only
C 2 and 4 only
D 3 and 4 only

Concept: Reaction Kinetics, Chemical Equilibria
Answer: D

1: At lower pressure, POE shifts LHS to favour the side with more moles of gas according to LCP. Hence, yield of C decreases.
2: pV = nRT. When volume of reaction vessel is halved, pressure doubles resulting in POE shifting RHS to decrease pressure. Hence, yield of C increases.
3: $K_c = [C] / [A] [B]^2$. Hence, $[C] = K_c[A][B]^2$
4: If reaction takes place via one-step mechanism, rate = $k[A][B]^2$

16 Vanillin is the key flavour compound in vanilla, and its structure is shown.



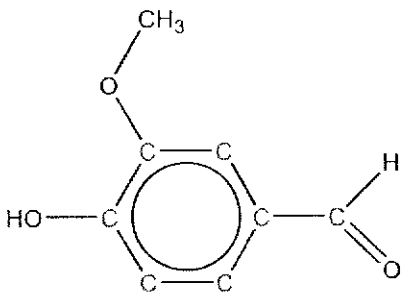
vanillin

How many sp^2 hybridised carbons are there in a molecule of vanillin?

A 5 **B** 6 **C** 7 **D** 8

Concept: Introduction to Organic Chemistry – hybridisation
Ans: C

The 7 sp^2 hybridised carbons are shown in red, each with 3 σ bonds and 1 π bond.

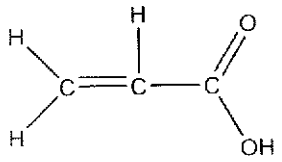


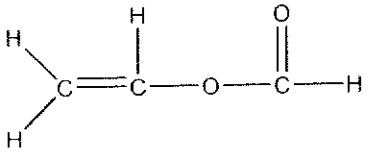
17 A non-cyclic organic compound has the molecular formula $C_3H_4O_2$.
Which combination of functional groups **cannot** be present in this molecule?

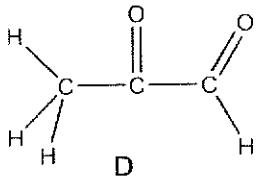
A one alkene and one carboxylic acid group
B one alkene and one ester group
C one alkene and two alcohol groups
D one aldehyde and one ketone group

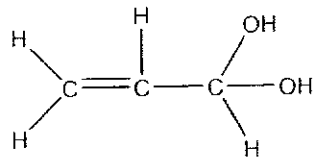
(inspired by 2013/P1/39)
Concept: Introduction to Organic Chemistry
Ans: C

As shown A, B and D are possible, but a molecule with an alkene and two alcohol groups would need 2 more H atoms, hence molecular formula $C_3H_6O_2$ (one more degree of saturation)

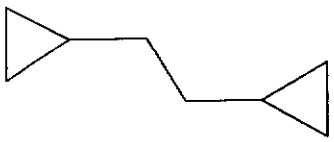

A


B


D


C - $C_3H_6O_2$

18 Compound **W**, C_8H_{14}, reacts with chlorine gas in the presence of *uv* light.

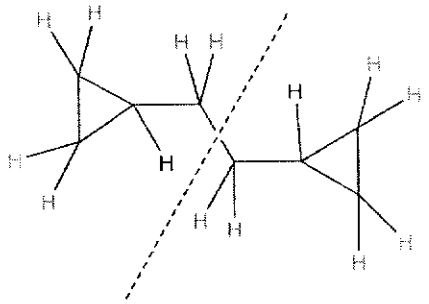

W

Which of the following statements about this reaction is correct?
1 The maximum number of mono-chlorinated constitutional isomers with formula $C_8H_{13}Cl$ is 3.
2 $C_{16}H_{28}$ is present in small quantities in the product.
3 Homolytic fission only occurs in the initiation step.

A 1, 2 and 3 **B** 1 and 2 only **C** 2 and 3 only **D** 1 only

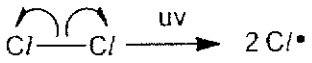
Concept: Alkanes
Ans: D

Statement **1** is correct as there are 3 types of equivalent H atoms, as shown.

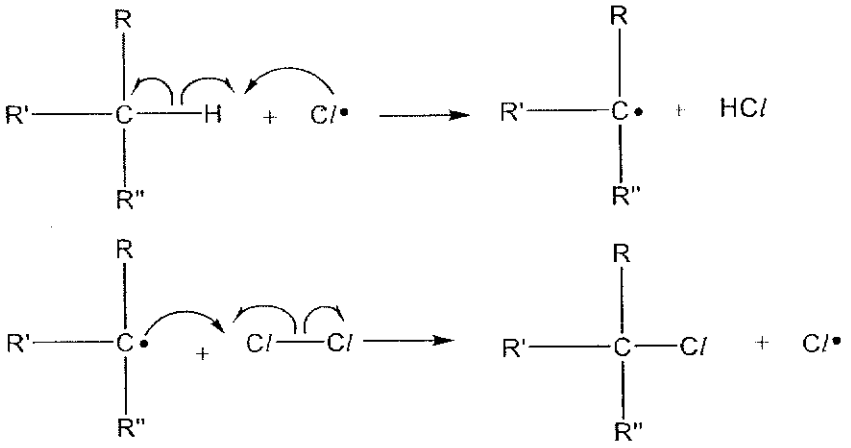


Statement **2** is wrong, $C_{16}H_{26}$ is formed in small quantities in the reaction.
Statement **3** is wrong, homolytic fission occurs in the propagation step too.
Mechanism:

Stage I: Initiation



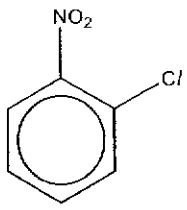
Stage II: Propagation



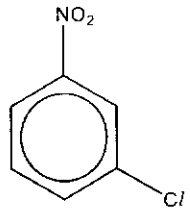
19 When nitrobenzene is heated with BrCl and $AlBr_3$, a mono-halogenated product is formed.

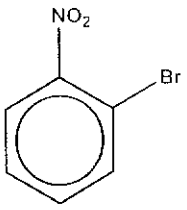
Which product is most likely to be formed?

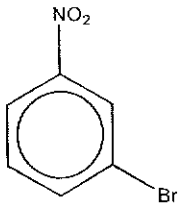
A



B



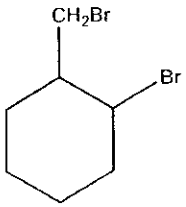
C 

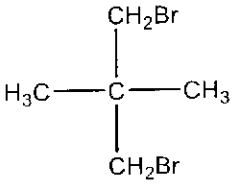
D 

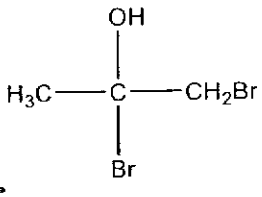
(inspired by 2017 P3 Q1d)
Concept: Arenes, electrophilic substitution
Ans: D

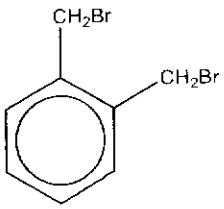
In the presence of $AlBr_3$ catalyst, electrophilic substitution occurs.
In the first step, Br^+ is formed as the electrophile as it is less electronegative than *Cl*.
Also, $-NO_2$ is 3-directing so Br will be substituted in the 3rd position, not the 2nd position.

20 1 mol of organic compound **V** reacts with ethanolic sodium hydroxide to form 2 mol of HBr. What could **V** be?

A 

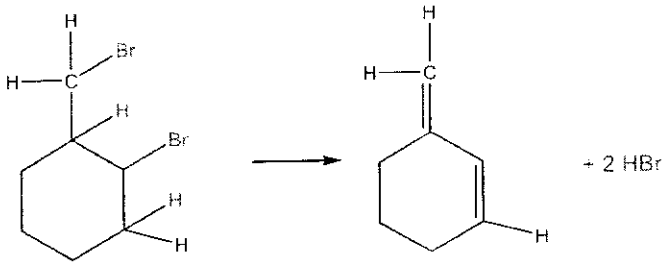
B 

C 

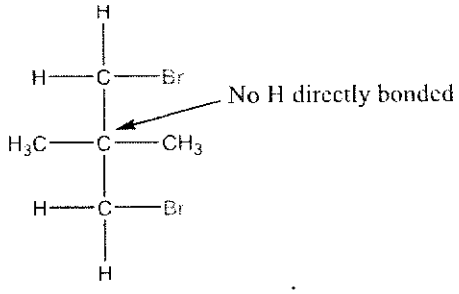
D 

Concept: Halogen derivatives, elimination
Ans: A

Option **A** can undergo elimination as shown. (note that this is a cyclohexane ring, not benzene)

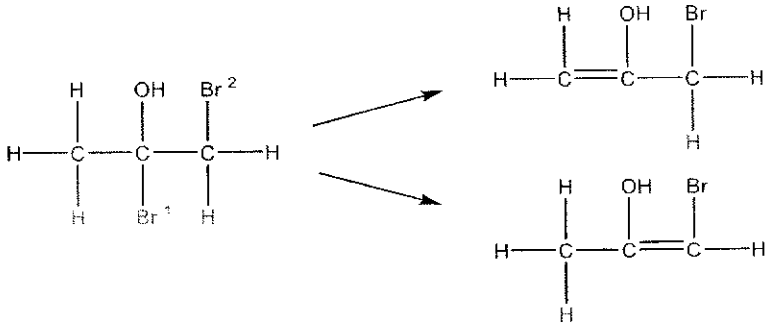
A 

For option **B**, the carbons with Br attached do not have an adjacent carbon with H to be eliminated.



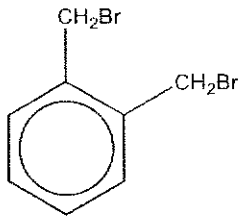
B

For option **C**, only 1 mole of HBr can be eliminated from Br ^{1} but not Br ^{2}.



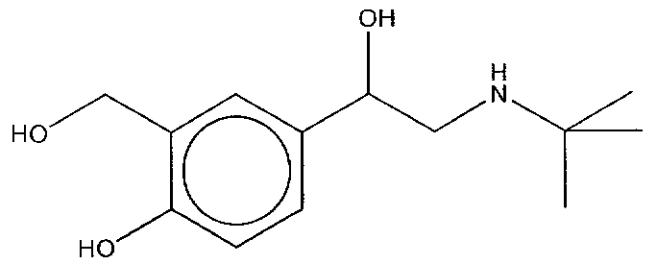
C

For option **D**, the adjacent carbons (on the benzene ring) to the carbons with Br do not have any H to undergo elimination.



D

21 Salbutamol is a common medicine used to alleviate asthma attacks.



salbutamol

Which statement about 1 mol of salbutamol is **incorrect**?

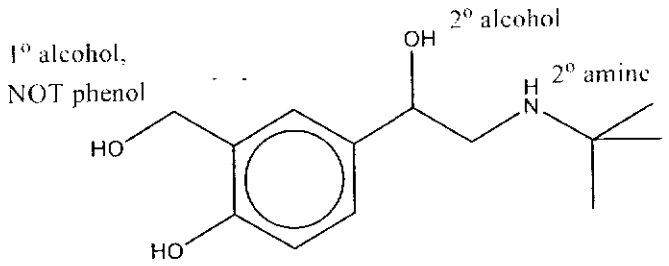
A It reacts with 4 mol of ethanoyl chloride, CH_3COCl, to form 3 ester and 1 amide group.

B It reacts with excess acidified $K_2Cr_2O_7$(aq) to form 1 carboxylic acid and 1 ketone group.

C It reacts with 3 mol of sodium metal.

D It reacts with 2 mol of NaOH(aq).

(inspired by 2013 P1 Q26)
Concept: ROH + RCO_2H + derivatives
Ans: D



phenol salbutamol - $C_{13}H_{21}O_3N$

A – alcohols and the phenol react with acyl chlorides to form esters, while the amine reacts to form an amide.
B – the 1° and 2° alcohol can be oxidized to form a carboxylic acid and ketone respectively.
C – both alcohols and phenol react with Na(s)
D – only phenol reacts with NaOH(aq)

ROH + RCO_2H + derivatives

22 Which of the following shows the correct order of decreasing pK_a?

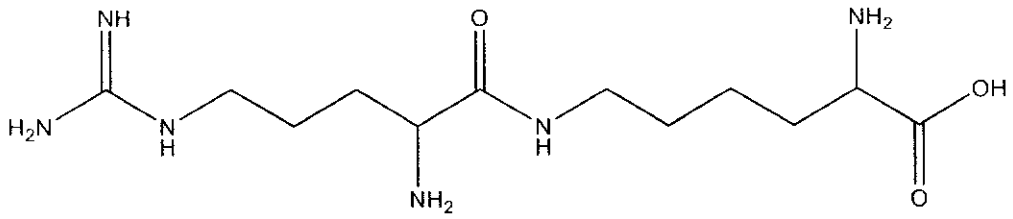
A	C_6H_5OH	>	CH_3CH_2OCOH	>	$CH_3CH_2CO_2H$	>	CH_3CHFCO_2H
B	CH_3CH_2OCOH	>	C_6H_5OH	>	$CH_3CH_2CO_2H$	>	CH_3CHFCO_2H
C	CH_3CHFCO_2H	>	$CH_3CH_2CO_2H$	>	C_6H_5OH	>	CH_3CH_2OCOH
D	CH_3CH_2OCOH	>	CH_3CHFCO_2H	>	$CH_3CH_2CO_2H$	>	C_6H_5OH

Answer: B
Decreasing pK_a ⇒ increasing K_a ⇒ increasing acidity.

CH_3CH_2OCOH (ester) is neutral; carboxylic acid ($CH_3CH_2CO_2H$) is more acidic than phenol (C_6H_5OH) and electron-withdrawing group (F) in CH_3CHFCO_2H will further stabilise the carboxylate ion, making CH_3CHFCO_2H the strongest acid.

Nitrogen compound

23 Compound **U** is a by-product formed in the body to counteract the effect of the drug administered to treat herpes.



Compound **U**

Which one of the following statements about compound **U** is correct?

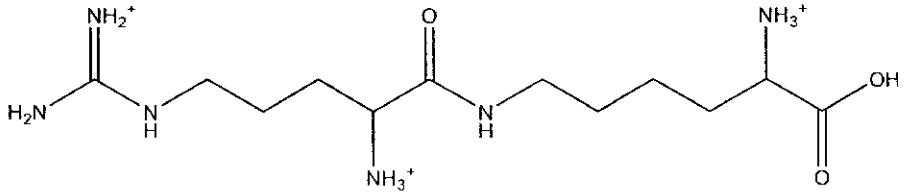
A **U** undergoes nucleophilic addition with chloroethane.
B 1 mol of **U** can be hydrolysed to produce 2 mol of amino acids.
C 1 mol of **U** can react with 6 mol of hydrochloric acid at room temperature.
D When an aqueous solution of **U** at pH 3 is analysed by electrophoresis, it is found near the anode.

Answer: B

A Incorrect – amine groups in **U** undergo nucleophilic substitution with chloroethane

B Correct – amide group (peptide linkage) hydrolysed to give two amino acids.

C Incorrect – only 3 amino groups react with hydrochloric acid and get protonated as shown below; the amide group (neutral) does not react with hydrochloric acid at r.t.



D Incorrect – At pH 3, amine groups are protonated and **U** is likely to have a net positive charge and so, is likely to be found near the cathode.

Simple elucidation

24 A compound **T** is boiled with aqueous sodium hydroxide and the resulting mixture cooled and acidified. The final product includes a compound $C_3H_6O_2$ and an alcohol that gives a positive iodoform test.

Which formula could represent compound **T**?

A $CH_3CH_2CO_2CH_2CH_2Cl$
B $CH_3CH_2OCOCH_3$
C $CH_3OCOCH_2COCH_3$
D $CH_3CH_2CO_2CH_2CHClCH_3$

Answer: D

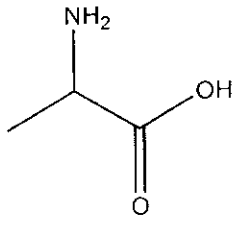
- When boiled with aq. NaOH, hydrolysis of ester and nucleophilic substitution of chloroalkane occurred.

$$CH_3CH_2CO_2CH_2\mathbf{CHCl}CH_3 \rightarrow CH_3CH_2CO_2H + HOCH_2\mathbf{CH(OH)}CH_3$$
$$(C_3H_6O_2)$$

- The alcohol formed has $CH_3CH(OH)$– group and so, gives a positive iodoform test (yellow precipitate of CHI_3 formed).

Nitrogen compound

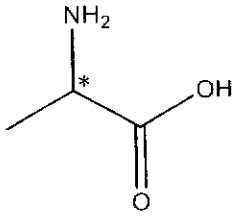
25 Which of the following is **not** a correct statement about *alanine* extracted from silkworm?



alanine

A *Alanine* is able to rotate plane-polarised light.
B *Alanine* has a higher solubility in water than in ether.
C *Alanine* can react with ethanoic acid to give an amide.
D An aqueous solution of *alanine* has a buffering capacity.

Answer: C



A Correct – *alanine* has chiral C (marked *) and is able to rotate plane polarised light.

B Correct – *alanine* exists as zwitterions and so, is more soluble in water.

C Incorrect – with ethanoic acid, *alanine* undergoes acid-base reaction instead of condensation reaction.

D Correct – *alanine*, an amino acid, can act as a buffer.

Transition Element

26 The equation below shows a ligand exchange reaction.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$$

Which is a possible reason to explain why NH_3 ligands displace H_2O ligands?

A ΔS is positive for the displacement reaction.
B NH_3 is more tightly bound to Cu^{2+} ions than H_2O.
C The energy difference for d→d transition in $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$ is greater than that in $[Cu(H_2O)_6]^{2+}(aq)$.
D The pH of NH_3 is higher than the pH of $H_2O(l)$

Answer: B
NH_3 is a stronger base (Lewis base) than H_2O and so, forms stronger dative covalent bond with the central Cu^{2+} ion (Lewis acid).

27 *Use of the Data Booklet is relevant to this question.*
The table below gives data about some physical properties of the elements calcium and copper.
Which row gives the correct properties under the correct element?

		calcium	copper
A	melting point / K	1358	1112
B	density / g cm^{-3}	1.54	8.92
C	first ionisation energy / kJ mol^{-1}	745	590
D	atomic radius (metallic) / nm	0.128	0.197

Answer: B
Copper, as a transition metal, has higher melting point and density compared to a typical S block element, calcium. Answer is B.

Values of ionisation energy and atomic radius can be found from the Data Booklet.

28 *Use of the Data Booklet is relevant to this question.*
The silver chloride electrode is a type of reference electrode commonly used in electrochemical measurements. It can be represented as below.

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

The reduction potential of Cr^{3+}/Cr^{2+} half-cell is −0.61 V when it is measured using the AgCl /Ag reference electrode at standard conditions.

What is the reduction potential of AgCl /Ag electrode when it is measured against the standard hydrogen electrode as reference?

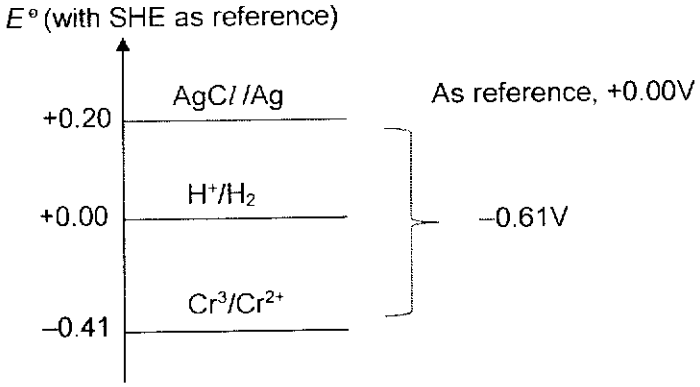
A +0.80 V B +0.41 V C +0.20 V D –0.41V

Answer: C
As it is the reduction potential measured, the following formula can be applied:

$E^\circ_{cell} = E^\circ_{Cr3+/Cr2+} - E^\circ_{AgCl/Ag} = -0.61$ V
$-0.41 - E^\circ_{AgCl/Ag} = -0.61$ V

$E^{\ominus}_{AgCl/Ag} = -0.41 + 0.61$
$= +0.20\ V$

Or pictorially,



29 A voltaic cell is set up using the Mg^{2+}/Mg and Fe^{3+}/Fe^{2+} half-cells.

$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ $\quad E^{\ominus}_{Mg^{2+}/Mg} = -2.38\ V$
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $\quad E^{\ominus}_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

Under standard conditions, the cell e.m.f. would be 3.15 V. However, the voltmeter recorded a reading of 3.05 V.

What is the best explanation for this lower e.m.f.?

A a smaller magnesium electrode was used
B a higher concentration of Fe^{3+} was used
C a higher concentration of Mg^{2+} was used
D water evaporated from the Fe^{3+}/Fe^{2+} half-cell

Answer: C

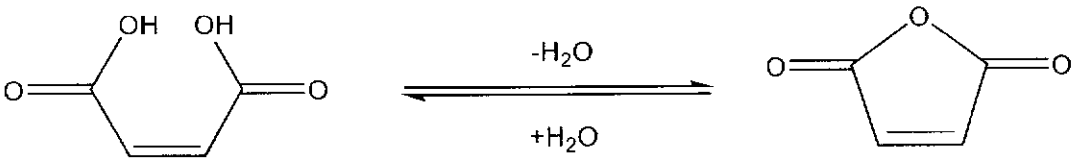
A incorrect – changing the size of a solid does not shift the position of equilibrium

B incorrect – a higher concentration of Fe^{3+} would result in an even greater tendency for reduction, so $E_{Fe^{3+}/Fe^{2+}}$ becomes more positive, and cell e.m.f. becomes more positive as well.

C correct – a higher concentration of Mg^{2+} shifts the position of equilibrium of Mg^{2+}/Mg to the right. $E_{Mg^{2+}/Mg}$ becomes less negative and cell e.m.f. becomes less positive.

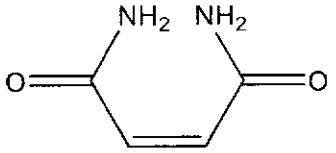
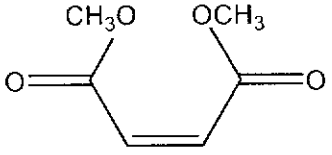
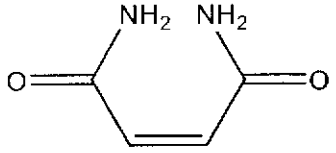
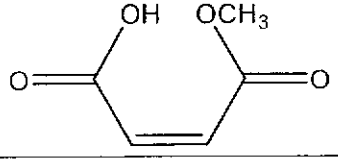
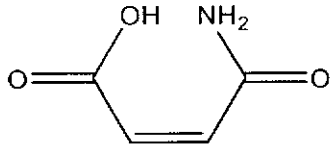
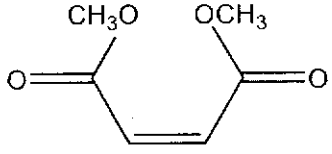
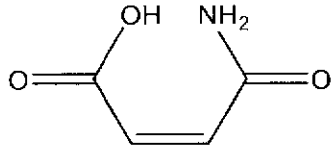
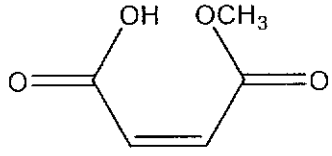
D incorrect – concentration of both $Fe^{3+}$and Fe^{2+} increases by the same extent. Hence, there is no shift in position of equilibrium.

30 Maleic acid loses water on strong heating to form compound **S**. On addition of water to compound **S**, it reforms maleic acid.

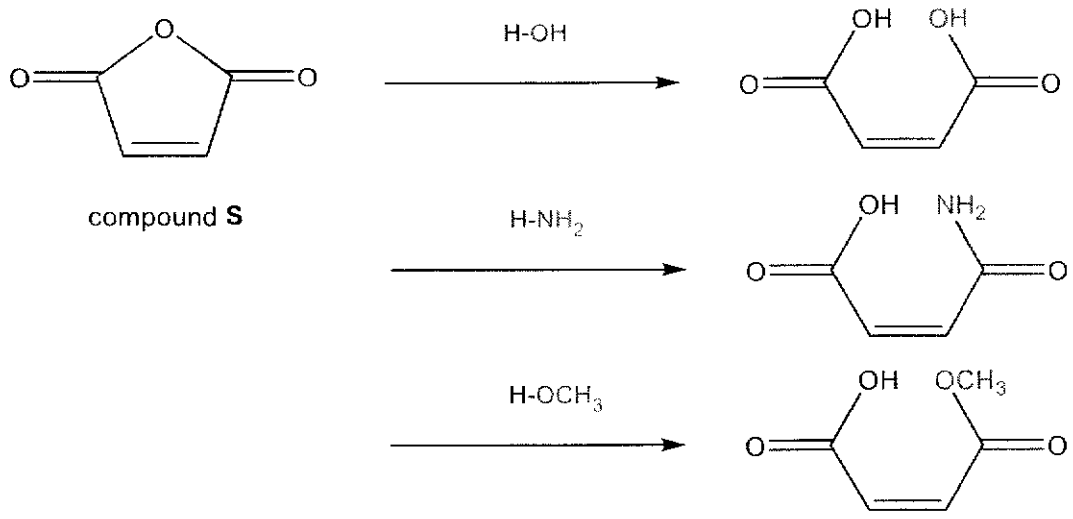


maleic acid compound **S**

Which of the following shows the correct compounds formed when ammonia and methanol are added to compound **S** separately?

	Addition of NH_3	Addition of CH_3OH
A		
B		
C		
D		

Answer: D



Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE NAME	
CLASS	2T

CHEMISTRY

9729/02

Paper 2 Structured Questions

August 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.

Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Paper 1		/30
Paper 2	Q1	/14
	Q2	/8
	Q3	/12
	Q4	/9
	Q5	/15
	Q6	/17
		/75
Paper 3		/80
Paper 4		/55
OVERALL (100%)		
Grade		

This document consists of **19** printed pages and **1** blank page.

1 **(a)** Calcium is a Group 2 element. Table below shows the radius of the calcium atom and the radius of the calcium ion.

Element	Radius / pm
Ca	197
Ca^{2+}	100

Explain the difference in size between calcium atom and calcium ion.

.....

.....[1]

(b) Describe and explain the trend in ionic radii down Group 2.

.....

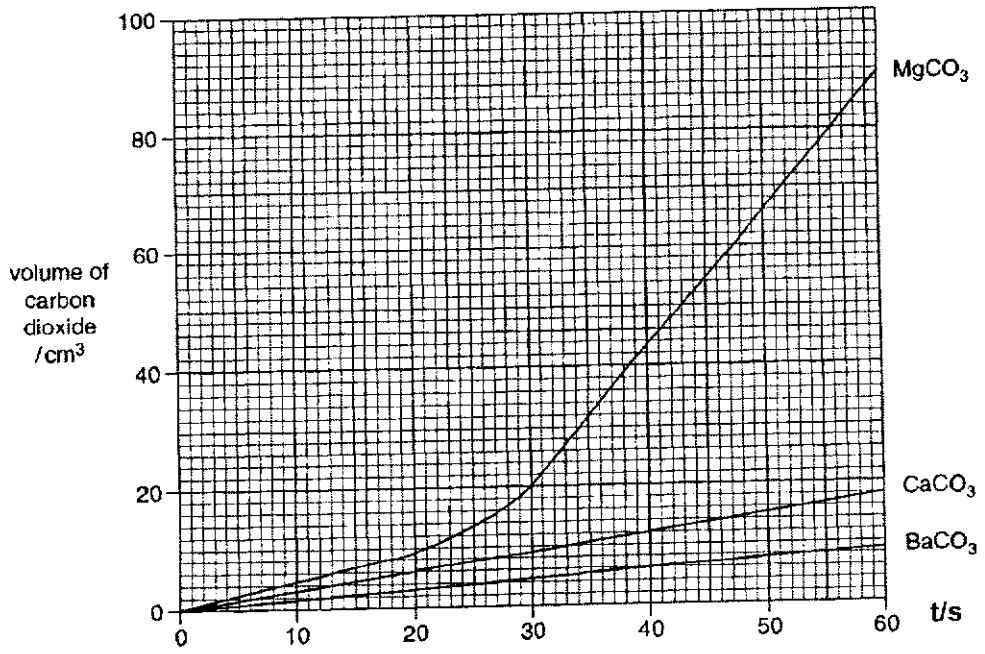
.....

.....

.....[2]

(c) A student investigates the thermal decomposition of the carbonates of Group 2 elements. He separately heats the carbonates of magnesium, calcium and barium and records the total volume of carbon dioxide collected every 10 seconds. In each experiment, he uses the same amount, in moles, of each carbonate and uses the hottest flame of a Bunsen burner.

The graph of his experimental results is given below.



(i) Write an equation to represent the thermal decomposition of barium carbonate, indicating clearly the state symbols.

..... [1]

(ii) Identify the least thermally stable carbonate and explain how the graph supports your answer.

.....

.....

.....

.....

.....[2]

(d) The student wanted to perform the same investigation on the carbonates of the elements in Group 13 but found that $Al_2(CO_3)_3$ does not exist at room temperature. Suggest a reason for this.

.....

.....

.....

.....

.....[2]

(e) Compare and explain the difference between the lattice energy of barium carbonate and magnesium carbonate.

.....

.....

.....

.....

.....

.....[2]

(f) The first ionisation energies of Group 2 elements are given below:

Group 2 Elements	1st I.E/ kJ mol^{-1}
Be	900
Mg	736
Ca	590
Sr	548

Explain why the first ionisation energies decrease in magnitude down Group 2.

.....

.....

.....

.....

.....

.....

.....

.....

.....[2]

(g) Lithium nitrate is the only Group 1 nitrate that decomposes on heating, in the same way as Group 2 nitrates. Suggest a reason for why its behaviour is similar to Group 2 nitrates, and give an equation for its decomposition.

.....

.....

.....

.....

.....

.....[2]

[Total: 14]

2 **(a) (i)** Calculate the average oxidation number of sulfur in sodium thiosulfate, $Na_2S_2O_3$.

[1]

(ii) Draw the structure of a thiosulfate anion, $S_2O_3^{2-}$, with a single central S atom, and clearly label the actual oxidation number of each S atom.

[2]

(b) Thiosulfate anions undergo disproportionation as shown.

$$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + HS^- + H^+$$

By considering the change in oxidation states in all the sulfur-containing species, deduce the number of moles of electrons involved in this reaction.

[2]

(c) The values of standard reduction potentials are given for the following redox systems.

$S_4O_6^{2-}$ / $S_2O_3^{2-}$ $\quad E^{\ominus} = +0.09$ V

MnO_4^- / Mn^{2+} $\quad E^{\ominus} = +1.52$ V

(i) Among the species above, identify the strongest oxidising agent and the strongest reducing agent.

Strongest oxidising agent: .....[1]

Strongest reducing agent: .....[1]

(ii) With reference to the *Data Booklet*, write a balanced ionic equation for the most spontaneous reaction involving the four species above.

.....[1]

[Total: 8]

3 (a) *Use of the Data Booklet is relevant to this question.*

The reaction between peroxodisulfate(VII) ions, $S_2O_8^{2-}$, and iodide ions, I^-, is represented by the following equation:

$$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

This reaction is catalysed by adding a suitable transition metal species which acts as a homogeneous catalyst for the reaction.

(i) Suggest why the above reaction requires the addition of a catalyst.

.....

.....[1]

(ii) Explain why the transition metal can be used as a homogeneous catalyst.

.....

.....

.....[1]

(iii) By considering suitable $E^{\ominus}$ values from the *Data Booklet*, suggest a catalyst for the reaction between $S_2O_8^{2-}$ and I^- ions, and write equations to show how the homogeneous catalysis occurs.

.....

.....

.....

.....

.....[3]

(b) The rate of reaction between $S_2O_8^{2-}$ and I^- ions may be studied using the iodine clock reaction, which make use of the property that iodine forms an intense blue complex with starch.

In the iodine clock reaction, the following set of reactions take place and a colour change involving the starch-iodine complex happens after a fixed amount of iodine is produced, allowing the kinetics of the reaction to be determined.

Reaction 1: $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Reaction 2: $I_2 + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

During an experiment to determine the rate equation, different concentrations of KI, and $Na_2S_2O_8$ are mixed according to the following table. The rates for the colour change in each solution are shown below.

flask	$[I^-]$ / mol dm^{-3}	$[S_2O_8^{2-}]$ / mol dm^{-3}	rate / s^{-1}
1	0.10	0.10	0.0222
2	0.10	0.20	0.0434
3	0.10	0.30	0.0665
4	0.15	0.05	0.0167
5	0.20	0.15	0.0675

(i) Suggest what was done in the experiment to ensure a fixed amount of iodine is produced.

.....

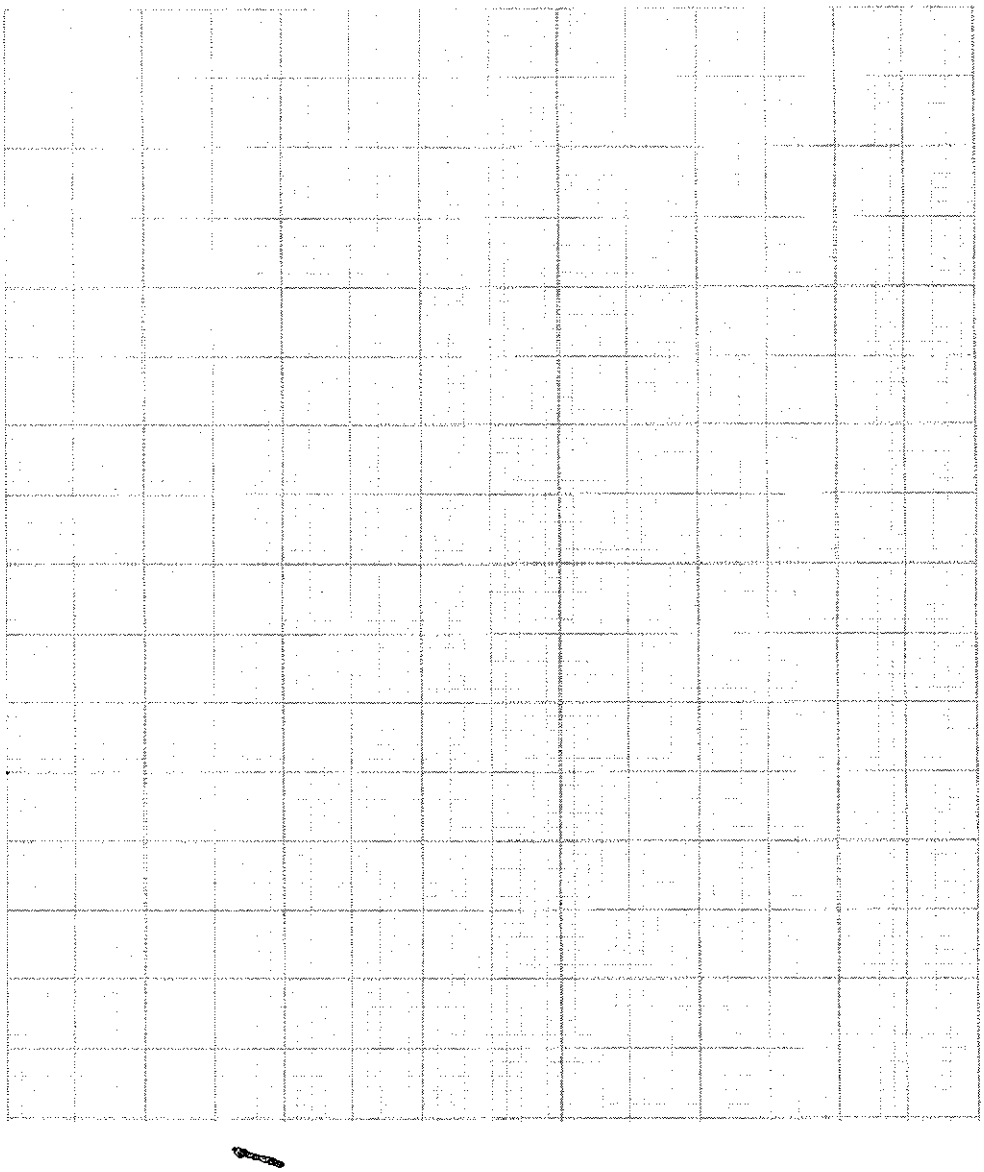
.....[1]

(ii) Deduce two sets of variables from the table whose values can be plotted to obtain the order of reaction with respect to $S_2O_8^{2-}$.

plot: .....

against: ..... [1]

(iii) On the grid provided, plot a graph using the variables in **(b)(ii)** to determine the order of reaction with respect to $S_2O_8^{2-}$. Label the axes clearly.



Order of reaction with respect to $S_2O_8^{2-}$: ..... [2]

(iv) By using a non-graphical method, deduce the order of reaction with respect to I^-.

[1]

(v) Hence or otherwise, write the rate equation and calculate a value for the rate constant, k, stating clearly the units.

[2]

[Total: 12]

4 Ethers have the general formula, R-O-R' (where R and R' are alkyl or aryl groups). The most useful method of preparing ethers is by the Williamson ether synthesis, in which an alkoxide ion (RO^-) reacts with a primary alkyl halide (R'X) in an S_N2 mechanism.

(a) A reaction scheme is shown below:

$$ROH \xrightarrow[\text{step 1}]{NaH} RO^-Na^+ \xrightarrow[\text{step 2}]{R'X \text{ (alkyl halide)}} ROR'$$

(i) State the type of reaction for step **1**.

..... [1]

(ii) Suggest why step **1** is necessary in the Williamson ether synthesis.

..... [1]

(iii) Using 1-chloropropane as the alkyl halide and $CH_3CH_2O^-$ as the alkoxide ion, describe the mechanism for step **2** of the Williamson ether synthesis.

Show all charges and relevant lone pairs of electrons and show the movement of electron pairs by using curly arrows.

[3]

(iv) The same reaction in **(a)(iii)** was repeated using iodopropane instead of chloropropane. State and explain the effect on the rate of reaction.

.....

..... [1]

(b) Epoxides are cyclic ethers commonly used in organic reactions. Epoxyethane is the simplest epoxide and has the structure as shown:

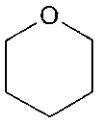
(i) Epoxyethane can be synthesised via an intramolecular Willamson ether synthesis with a low yield because it is unstable. Suggest why epoxyethane is unstable.

.....

..... [1]

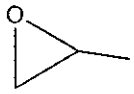
(ii) In the boxes below, suggest the structure of the organic reagent used to synthesise each of the following ethers via intramolecular Williamson ether synthesis.

I



Organic reagent:

II



Organic reagent:

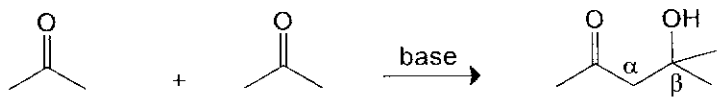
[2]

[Total: 9]

5 (a) The Aldol Addition reaction is important in organic synthesis as it provides a method for linking two smaller molecules by introducing a carbon–carbon bond between them.

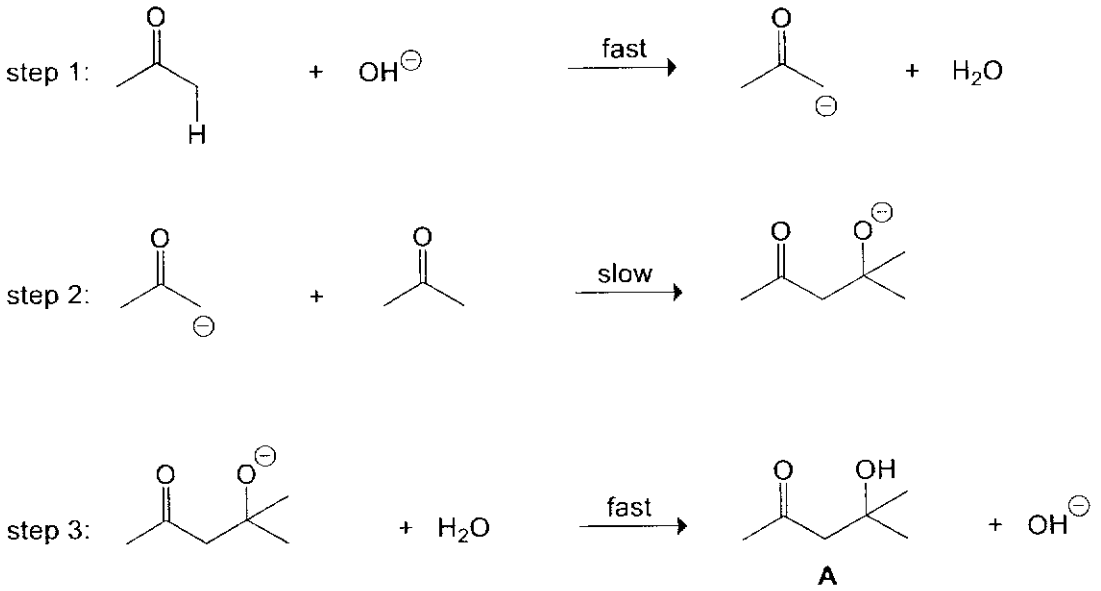
The reaction combines two carbonyl compounds to form a new β–hydroxy carbonyl compound, also known as *aldols*, which are commonly found in many important molecules, whether naturally occurring or synthetic.

One example of Aldol Addition reaction between two propanone molecules to form an aldol **A** is shown in the equation below.



Aldol **A**

The following shows the mechanism for the Aldol Addition reaction involving two propanone molecules.



(i) State the type of reaction that has occurred in step 2 of the mechanism.

..... [1]

(ii) Complete the mechanism for steps 1 and 2 by showing the movement of electron pairs using curly arrows on the diagram shown above. Indicate all partial charges and relevant lone pairs. [2]

(iii) When this reaction is carried out using a mixture of propanone and ethanal, three other compounds are formed in addition to compound **A.** Compound **B** has M_r value of 88, while compounds **C** and **D** have M_r value of 102. Draw the structures of these three products labelled as **B**, **C** and **D**. [3]

B (M_r = 88.0)	**C** (M_r = 102)	**D** (M_r = 102)

(iv) Suggest two chemical tests that could be used to distinguish the three products from each other. You should state clearly the observations for each test.

.....

.....

.....

.....

.....

.....[2]

(b) At a higher temperature, the carbonyl compounds can undergo Aldol Condensation reaction, which involves the loss of a water molecule from the aldol product obtained earlier and results in the formation of an alkene functional group between the α and β carbons.

Draw the displayed formula of the product formed from the Aldol Condensation involving two propanone molecules. [1]

(c) Intramolecular Aldol Condensation reaction can also occur to give a cyclic unsaturated carbonyl compound when a dicarbonyl compound with a sufficiently long carbon chain is used. An example of such a reaction is given below.

Q

(i) State the hybridisation of the carbon atom in C=C and draw the hybrid orbitals of this carbon atom.

[2]

(ii) What type(s) of stereoisomerism can compound **Q** exhibit, and how many stereoisomers of each type(s) are there?

.....

.....[2]

(iii) Draw the structures of the stereoisomers of compound **Q**.

[2]

[Total: 15]

6 Among the typical ingredients in vaccine are four ionic salts, which makes up the phosphate-buffered saline (PBS).

A student found incomplete instructions for preparing 1 dm^3 of PBS with some missing quantities.

Step 1: Add 8.00 g of NaCl, 0.200 g of KCl, certain amount of KH_2PO_4 and Na_2HPO_4. The initial pH will be at 7.94

Step 2: Add a certain amount of HCl to the solution to reach the pH that is similar to the pH of blood in human body.

The resultant buffer solution also has ion concentrations similar to that in human body, with 0.157 mol dm^{-3} of Na^+ and 0.1423 mol dm^{-3} of Cl^-.

The ions $H_2PO_4^-$ and HPO_4^{2-} are related by the following equilibrium.

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \qquad pK_a = 7.20$$

With the above information and further calculations from **(a)(ii)** to **(v)**, the student managed to prepare the desired PBS solution.

(a) **(i)** Explain what the term buffer means, and write two equations to describe how the PBS can act as a buffer.

.....

.....

.....

.....

.....[3]

(ii) Calculate the ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ at the initial pH.

[2]

(iii) Calculate, to **four** significant figures, the amount of NaCl and KCl (in moles) separately present in 1 dm^3 of PBS.

[2]

(iv) Hence, using your answers in **(a)(iii)** and taking into account the total amount of Na^+ ions, calculate the initial amount of Na_2HPO_4 and subsequently the initial amount of KH_2PO_4 that should be added at step 1.

[2]

(v) Using your answers in **(a)(iii)** and taking into account the total amount of Cl^- ions, calculate the amount of HCl added.

[1]

(vi) Hence, show with calculation, that the final ratio of $[HPO_4^{2-}]/[H_2PO_4^-]$ is 1.56 after HCl is added in step 2.

[1]

(vii) Maximum buffer capacity of a phosphate buffer is when $[HPO_4^{2-}] = [H_2PO_4^-]$. Compare and comment on the buffer capacity of the phosphate solution at the end of step 1 and at the end of step 2.

.....

.....

..... [1]

(b) Mohr's method is a type of titration to determine the concentration of Cl^- in a sample. The same student carried out this titration with 0.100 mol dm^{-3} $AgNO_3$ as titrant and 1.50 mol dm^{-3} K_2CrO_4 as indicator.

He conducted the titration by pipetting 10.0 cm^3 of the phosphate–buffered saline (PBS) into a conical flask and added K_2CrO_4 indicator. Upon adding $AgNO_3$, white precipitate is immediately formed and the end-point is indicated by the first appearance of a red precipitate of Ag_2CrO_4. At the end-point, a saturated solution of $AgCl$ is present. Based on his calculation, it will take 14.25 cm^3 of $AgNO_3$ to reach the end-point.

This titration works on the nature of sparingly soluble silver salt, and the relevant K_{sp} values are below:

compound	K_{sp}
$AgCl$	1.77×10^{-10}
Ag_2CrO_4	1.12×10^{-12}

(i) Calculate the concentration of $Cl^-(aq)$ ions that remains in the solution at the end-point of the titration, assuming that $[Ag^+(aq)] = [Cl^-(aq)]$.

[1]

(ii) If 1.00 cm^3 of K_2CrO_4 was added at the start of titration, calculate the concentration of CrO_4^{2-}(aq) ions at the end-point and determine if Ag_2CrO_4 precipitate will form at the end-point.

[3]

(iii) The sample's pH range must be between 6.5 and 9 for Mohr's method titration to be conducted. Suggest a reason why it should not be conducted at a higher pH.

.....

.....

..... [1]

[Total: 17]

BLANK PAGE