6

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
Higher 2

CHEMISTRY **9729//01**

Paper 1 Multiple Choice 23 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 index number, name and CT group on the Answer Sheet.

There are **thirty** questions. 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 **15** printed pages and **1** blank page.

For each question there are four possible answers, **A**, **B**, **C**, and **D**. Choose the **one** you consider to be correct.

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

The ion $\mathbf{X}^{2+}$ has 53 electrons and 78 neutrons.

Which of the following statements are **incorrect**?

1 **X** atom is isoelectronic with Xe.

2 The fluoride of **X** is expected to have a higher melting point than RbF.

3 The first ionisation energy of element **X** is lower than that of Fr.

4 In an electric field, the ion $\mathbf{X}^{2+}$ will be deflected at a smaller angle than that of Na^+.

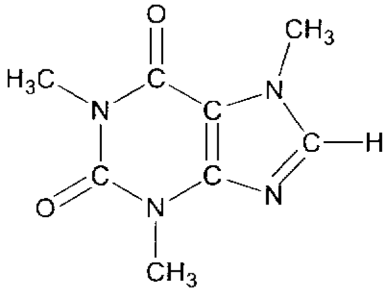
A **1**, **2** and **3**

B **1** and **4** only

C **2** and **4** only

D **3** only

2 To produce decaffeinated coffee, the ethanol–CO_2 mixture is used to extract caffeine from coffee beans.



caffeine

Which statement about caffeine is **incorrect**?

A Caffeine is more soluble in the ethanol–CO_2 mixture due to the hydrogen bond formed between ethanol and caffeine.

B Caffeine molecule has a planar structure.

C There are altogether 25 sigma bonds and 4 pi bonds in a caffeine molecule.

D There are 5 carbon atoms which are sp^2 hybridised.

3 In which pair does compound **X** have a higher boiling point than compound **Y**?

	compound **X**	compound **Y**
A	$CH_3CO_2NH_4$	$CH_3CH_2NH_2$
B	$SiCl_4$	SiO_2
C	PH_3	$SiCl_3H$
D	$Ni(OH)_2$	$NiSO_4$

4 A vessel is made of an air-filled plastic and has a volume of 40.0 cm^3.

At 27 °C and 52.8 kPa, a slightly dented vessel of volume 38.5 cm^3 is filled with air. To restore its original shape, the air inside the dented vessel is heated to a temperature of 60 °C. The pressure of air inside the vessel increases and creates a uniform outward force.

Assuming that the air inside the vessel behaves ideally, what is the pressure of air inside the vessel at 60 °C when the shape is restored?

A 56.4 kPa

B 113 kPa

C 226 kPa

D 244 kPa

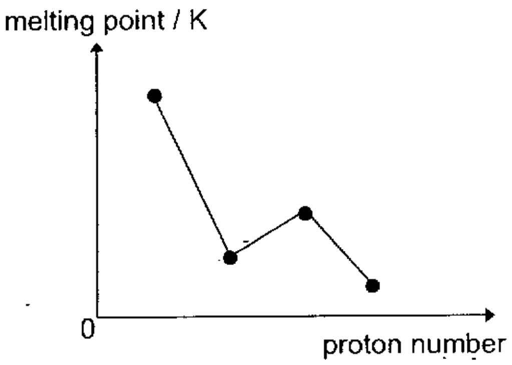
5 Elements **Y** and **Z** can be found in the third period of the Periodic Table.

Two solutions were prepared by dissolving a chloride of **Y** and an oxide of **Z** in separate portions of water. Both solutions prepared can be used to dissolve Al_2O_3 but only one can be used to dissolve SiO_2.

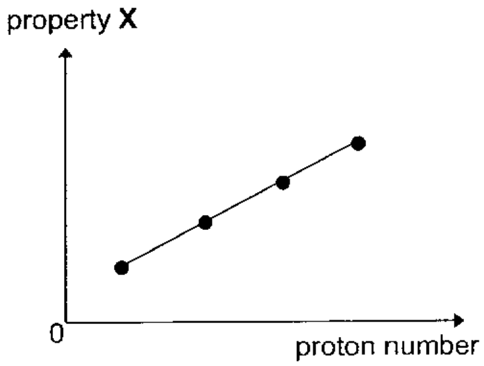
What could **Y** and **Z** be?

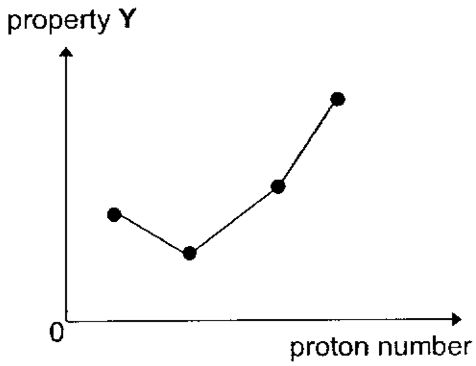
	Y	**Z**
A	silicon	phosphorus
B	phosphorus	sodium
C	magnesium	phosphorus
D	sodium	sulfur

6 The diagram represents the melting points of four consecutive elements in the third period of the Periodic Table.



The sketches below represent another two properties of the elements.





What could properties **X** and **Y** be?

	property **X**	property **Y**
A	ionic radius	effective nucleus charge
B	atomic radius	electrical conductivity
C	number of valence electrons	boiling point
D	electronegativity	third ionisation energy

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

Which statement about Group 2 elements and their compounds is correct?

A $BaCl_2$ solution has a lower pH than that of $MgCl_2$ solution.

B The volume of gases formed per gram of carbonate decomposed increases down the group.

C Strontium reacts more vigorously with cold water than magnesium since the standard reduction potential of strontium is more negative than that of magnesium.

D Barium sulfate occurs naturally as a solid ore while magnesium sulfate occurs mainly in solution since barium sulfate has a strong crystalline lattice.

8 $\mathbf{X}_2$, $\mathbf{Y}_2$ and $\mathbf{Z}_2$ are Cl_2, Br_2 and I_2 but not necessarily in the given order.

The table below recorded observations when these halogens are separately added to aqueous solutions containing the halide ions followed by the addition of an organic solvent, CCl_4.

experiment	reactants	observation after shaking with CCl_4
1	$\mathbf{X}_2$(aq) + $\mathbf{Y}^-$(aq)	Violet organic layer seen.
2	$\mathbf{Z}_2$(aq) + $\mathbf{X}^-$(aq)	Orange-red organic layer seen.
3	$\mathbf{Z}_2$(aq) + $\mathbf{Y}^-$(aq)	Violet organic layer seen.
4	$\mathbf{Y}_2$(aq) + $\mathbf{X}^-$(aq)	*(Observations not recorded)*

Which information could be deduced from the above experiments?

A H**Y** has a lower boiling point that H**X**.

B Ag**Y**(s) is soluble in excess dilute aqueous ammonia.

C K_a value of H**Z** is larger than that of H**Y**.

D The colour of the organic layer in experiments **3** and **4** is the same.

9 Sodium percarbonate, $(Na_2CO_3)_x.y(H_2O_2)$ is a compound with both reducing and oxidising properties. It is present in some home and laundry cleaning products.

10.0 cm^3 of 0.100 mol dm^{-3} sodium percarbonate releases 48.0 cm^3 of carbon dioxide at room conditions on reaction with excess aqueous sulfuric acid.

An identical sample, on titration with 0.0500 mol dm^{-3} $KMnO_4$ in acidic medium, required 24.0 cm^3 before the first pink colour appears.

What is the ratio $\frac{y}{x}$?

A $\frac{1}{3}$

B $\frac{2}{3}$

C $\frac{3}{2}$

D $\frac{3}{1}$

10 A flammable compound, with the formula CS_z, burns in oxygen to give CO_2 and SO_2 as the only products.

In a particular experiment, 20 cm^3 of CS_z vapour was completely reacted with 80 cm^3 of oxygen. The volume of the gaseous mixture obtained after combustion was treated with excess aqueous sodium hydroxide. The volume of the gaseous mixture decreased to 20 cm^3 after the treatment with sodium hydroxide.

All measurements of volume were made at the same temperature and pressure, conditions under which CS_z is a gas.

What is the value of z?

A 1

B 2

C 3

D 4

11 The enthalpy change of the following reaction between carbon and chromium(III) oxide is given:

$$3C(s) + Cr_2O_3(s) \rightarrow 2Cr(s) + 3CO(g) \qquad \Delta H_r^\ominus = +790\ \text{kJ mol}^{-1}$$

In addition to $\Delta H_r^\ominus$, one or more of the enthalpy changes listed below need to be known in order to calculate the enthalpy change of formation of Cr_2O_3.

1 enthalpy change of combustion of C

2 enthalpy change of atomisation of Cr

3 sum of the 1st, 2nd and 3rd ionisation energies of Cr

4 enthalpy change of combustion of CO

Which are the enthalpy changes that need to be known?

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

12 Instant 'cold packs' are used to relieve pain in athletes and footballers due to pulled muscles and sprained joints. They are composed of powdered ammonium nitrate and water separated by a thin plastic membrane. When the pack is squeezed, the membrane breaks and ammonium nitrate dissolves in water according to the equation below:

$$NH_4NO_3(s) + nH_2O(l) \rightarrow NH_4NO_3(aq)$$

Which statement about the above reaction is correct?

A It is spontaneous at all temperatures.

B It is not spontaneous at any temperature.

C It is more spontaneous at lower temperatures.

D It is more spontaneous at higher temperatures.

13 Hydrogen reacts with gaseous bromine to form hydrogen bromide:

$$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$$

It also reacts with gaseous iodine to form hydrogen iodide:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

For the first reaction, the rate equation is

$$\text{rate} = \frac{k_1[H_2][Br_2]^{1.5}}{[Br_2] + k_2[HBr]}$$

For the second reaction, the rate equation is

$$\text{rate} = k[H_2][I_2]$$

k_1, k_2 and k represent rate constants.

What can be deduced based on this information only?

1 The mechanism of the hydrogen / bromine reaction involves free radicals.
2 Only the hydrogen / iodine reaction could be a single-step reaction.
3 For the hydrogen / bromine reaction, the formation of HBr slows down the rate of the forward reaction.

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

14 The age of rock samples can be calculated using Uranium-Lead dating. ^{235}U is an unstable isotope which decays into ^{207}Pb. This nuclear reaction obeys first-order kinetics with a half-life of 710 million years.

The decay can be summarised by the following equation:

$$^{235}U \rightarrow {}^{207}Pb + \text{other decay products}$$

A rock sample has a ^{235}U : ^{207}Pb ratio of 1 : 15.

Assuming that all the ^{207}Pb detected is formed from the decay of ^{235}U, what is the age of the rock sample?

A 710 million years
B 1420 million years
C 2130 million years
D 2840 million years

15 Consider the equilibrium below:

$$\mathbf{P}(g) + \mathbf{Q}(g) \rightleftharpoons 2\mathbf{R}(g) \qquad K_c = 0.16 \text{ at } 700\text{ K}$$

A certain amount of **R** is placed in a sealed vessel and allowed to reach equilibrium at 700 K. The composition of the equilibrium mixture is as follows:

substance	amount / mol
P	0.50
Q	0.50
R	0.20

0.10 mol of **R** is then added to the equilibrium mixture.

What will be the amount of **R** present when the new equilibrium is established?

A 0.22

B 0.27

C 0.30

D 0.37

16 At a body temperature of 37 °C, K_w has a value of 2.4×10^{-14}.

What is the concentration of OH^- if the pH of blood is 7.4 under these conditions?

A 3.98×10^{-8} mol dm^{-3}

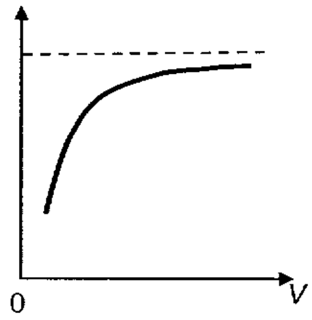
B 2.52×10^{-7} mol dm^{-3}

C 6.03×10^{-7} mol dm^{-3}

D 7.00×10^{-7} mol dm^{-3}

17 A sample of 1 mol of ethanoic acid is diluted at constant temperature to a volume V.

A graph is shown below, where the x-variable is V:



Which quantities could the y-variable be?

1 fraction of ethanoic acid that has dissociated
2 pH of ethanoic acid solution
3 K_a of ethanoic acid

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **1** only

18 The sparingly soluble salt, $Zn_3[Fe(CN)_6]_2$, consists of the cation Zn^{2+} and the anion $[Fe(CN)_6]^{3-}$.

Given that the K_{sp} value for the salt is **W**, what is the concentration of the anion when the salt dissociates to form a saturated solution at equilibrium?

A $\sqrt[3]{\frac{\mathbf{W}}{108}}$

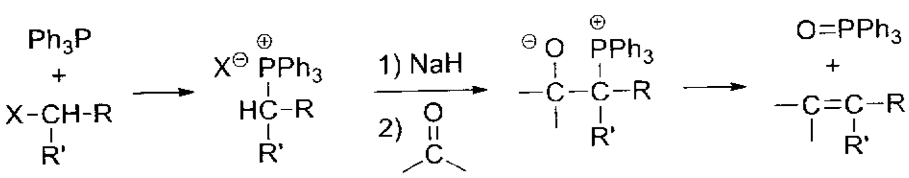
B $\sqrt[5]{\frac{\mathbf{W}}{108}}$

C $\sqrt[3]{\frac{8\mathbf{W}}{27}}$

D $\sqrt[5]{\frac{8\mathbf{W}}{27}}$

19 The Wittig reaction offers a highly versatile method to synthesise a wide variety of alkenes.

The mechanism for the reaction is summarised below.



(Ph denotes a phenyl group, $C_6H_5^-$)

Which types of reaction have occurred in the mechanism?

1 neutralisation

2 condensation

3 nucleophilic substitution

A **1**, **2** and **3**

B **1** and **2** only

C **2** and **3** only

D **3** only

20 There are six possible constitutional (structural) isomers for an organic compound with molecular formula $C_4H_8O_2$.

Which of the following is **incorrectly** named as one of the six isomers?

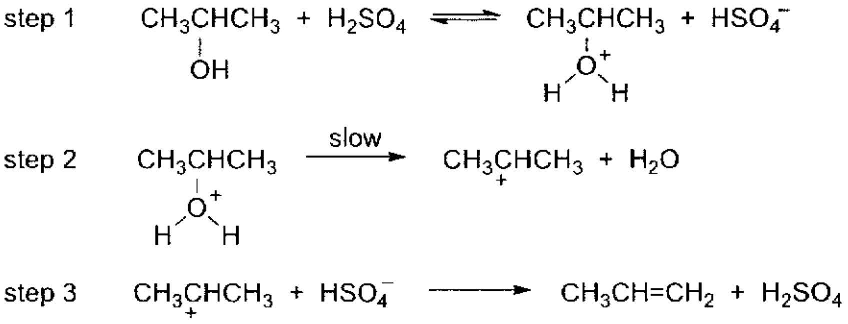
A methyl propanoate

B propyl methanoate

C 1-methylethyl methanoate

D 2-methylethyl methanoate

21 The dehydration of propan–2–ol to form propene is thought to involve the following steps.



step 1 $\underset{\overset{|}{OH}}{CH_3CHCH_3} + H_2SO_4 \rightleftharpoons \underset{H\diagup\overset{|}{O^+}\diagdown H}{CH_3CHCH_3} + HSO_4^-$

step 2 $\underset{H\diagup\overset{|}{O^+}\diagdown H}{CH_3CHCH_3} \xrightarrow{\text{slow}} CH_3\underset{+}{C}HCH_3 + H_2O$

step 3 $CH_3\underset{+}{C}HCH_3 + HSO_4^- \longrightarrow CH_3CH{=}CH_2 + H_2SO_4$

Which of the following statements are **incorrect**?

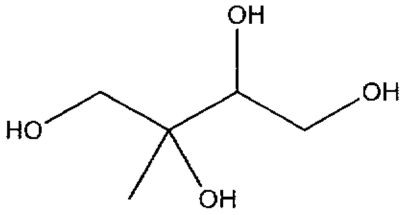
1 Aqueous H_2SO_4 is used as a reagent in this reaction.

2 It is more likely for primary alcohols to proceed via this mechanism than tertiary alcohols.

3 A possible side product of the reaction is $CH_3CH(OSO_3H)CH_3$.

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

22 The structure of 2-methylbutane-1,2,3,4-tetrol of molecular formula $C_5H_{12}O_4$ is as shown.



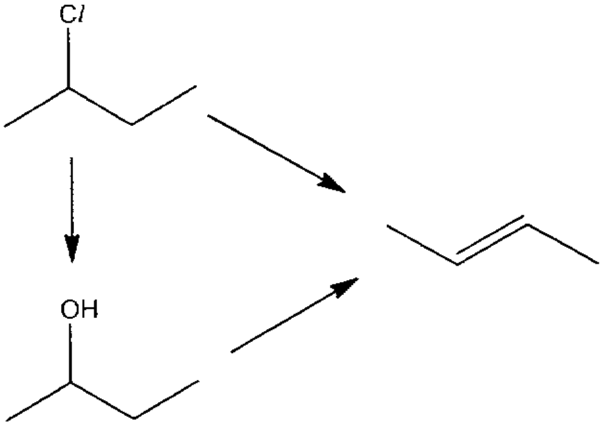
2-methylbutane-1,2,3,4-tetrol

After prolonged heating under reflux with an excess of acidified potassium dichromate(VI), it forms a compound **X** which also has five carbon atoms.

What is the molecular formula of compound **X**?

A $C_5H_{10}O_5$ **B** $C_5H_{18}O_5$ **C** $C_5H_8O_6$ **D** $C_5H_6O_6$

23 Which set of reagents and conditions **cannot** be used for the interconversion of compounds shown in the reaction scheme below?



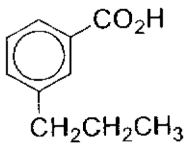
A Heat with excess concentrated H_2SO_4

B Add cold concentrated H_2SO_4, followed by water with heating

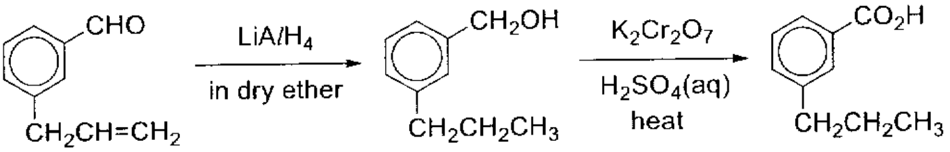
C Heat with aqueous NaOH

D Heat with alcoholic KOH

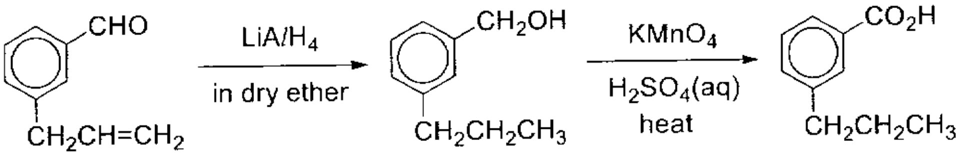
24 Which synthetic route will lead to a successful preparation of the following product?



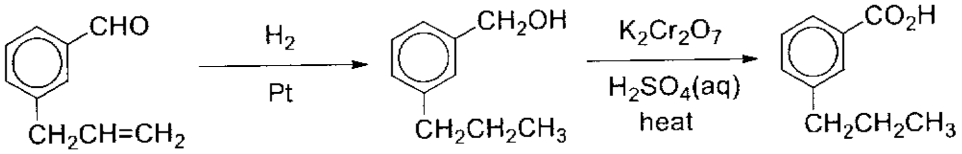
A



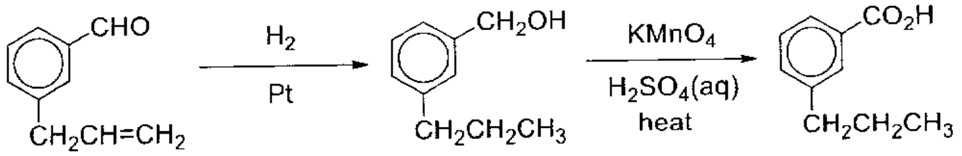
B



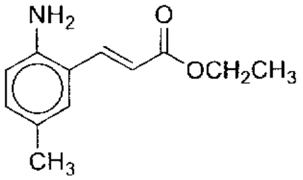
C



D



25 A student synthesised the following compound in the laboratory and wrote four statements about this compound.



Which statement is **incorrect**?

A On heating with acidified $K_2Cr_2O_7$(aq), the colour of the solution turns green.

B On warming with 2,4-dinitrophenylhydrazine, no orange crystals will be formed.

C On heating with alkaline aqueous iodine, a pale yellow precipitate will be formed.

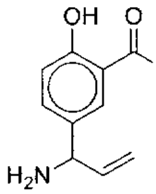
D On adding Br_2(aq), one bromine atom will be incorporated into the compound to form the major product.

26 An organic compound, $C_{10}H_{11}NO_2$ has the following physical and chemical properties:

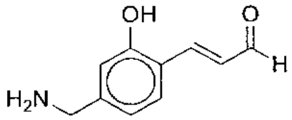
- It gives a brick red precipitate when warmed with Fehling's solution.
- It gives a purple colouration when warmed with neutral $FeCl_3$(aq).
- It is moderately soluble in water.

Which is a possible structure of this compound?

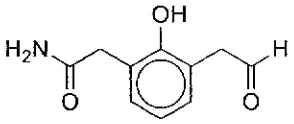
A



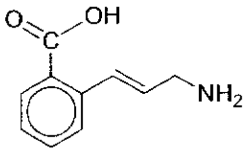
C



B



D



27 Which option shows the given ions arranged in order of increasing pK_a values?

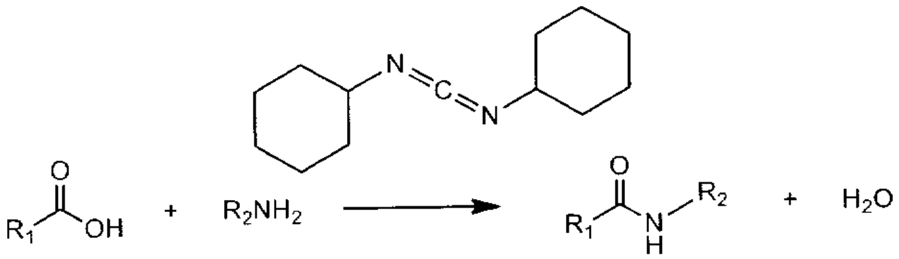
A NH_4^+, $C_6H_5NH_3^+$, $(CH_3CH_2)_2NH_2^+$

B $(CH_3CH_2)_2NH_2^+$, $C_6H_5NH_3^+$, NH_4^+

C $C_6H_5NH_3^+$, NH_4^+, $(CH_3CH_2)_2NH_2^+$

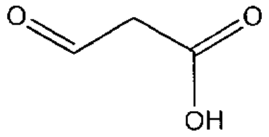
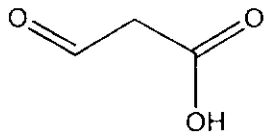
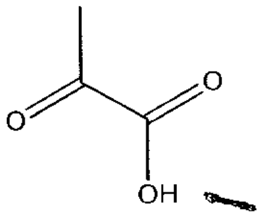
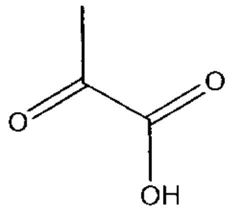
D $(CH_3CH_2)_2NH_2^+$, NH_4^+, $C_6H_5NH_3^+$

28 Amines react with carboxylic acids to form amides in the presence of the solvent dicyclohexylcarbodiimide, DCC, at room temperature.

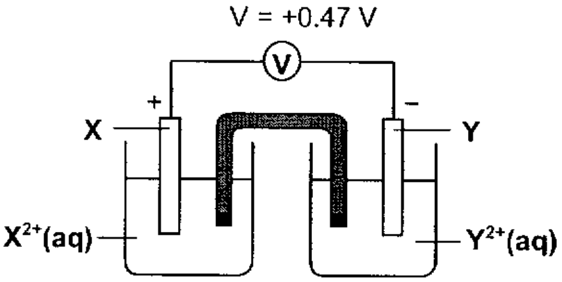


Which synthetic route converts compound **A** to compound **B** with the greatest increase in relative molecular mass?

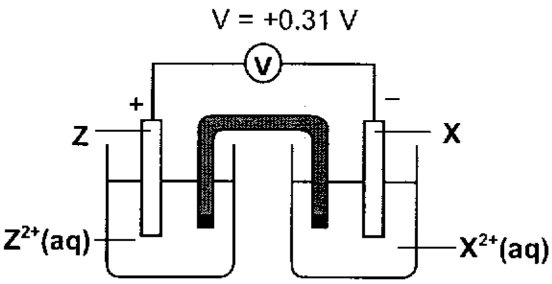
$$\text{compound } \mathbf{A} \xrightarrow{\text{I}} \xrightarrow{\text{II}} \text{compound } \mathbf{B}$$

	Compound **A**	I	II
A		Heat with $K_2Cr_2O_7$ in $H_2SO_4(aq)$	CH_3NH_2 in DCC solvent at room temperature
B		CH_3NH_2 in DCC solvent at room temperature	Heat with $K_2Cr_2O_7$ in $H_2SO_4(aq)$
C		Heat with $K_2Cr_2O_7$ in $H_2SO_4(aq)$	CH_3NH_2 in DCC solvent at room temperature
D		CH_3NH_2 in DCC solvent at room temperature	Heat with $K_2Cr_2O_7$ in $H_2SO_4(aq)$

29 Three metals **X**, **Y** and **Z**, are connected in pairs in two electrochemical cells as shown below.



electrochemical cell 1



electrochemical cell 2

Which statements are correct?

1 **Z** is the weakest reducing agent.

2 Y^{2+}(aq) can oxidise both **X** and **Z**.

3 E_{cell} is +0.78 V when the two half-cells of Y^{2+}(aq)|Y(s) and Z^{2+}(aq)|Z(s) are connected together.

4 Adding water to X^{2+}(aq)|X(s) half–cell will decrease and increase the E_{cell} of electrochemical cell 1 and 2 respectively.

A **1**, **3** and **4** only

B **1** and **4** only

C **2** and **3** only

D **2** only

30 A current of 3.0 A is used to plate a copper metal piece from 500 cm^3 aqueous $CuSO_4$. The concentration of aqueous $CuSO_4$ after 2.0 hours drops to 0.776 mol dm^{-3}.

What is the initial concentration of aqueous $CuSO_4$?

A 0.614 mol dm^{-3}

B 0.684 mol dm^{-3}

C 1.00 mol dm^{-3}

D 1.11 mol dm^{-3}

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Victoria Junior College
2021 H2 Chemistry Prelim Exam 9729/1
Suggested Answers

1	A	2	B	3	A	4	A	5	B
6	D	7	C	8	D	9	C	10	B
11	B	12	D	13	C	14	D	15	A
16	C	17	B	18	D	19	A	20	D
21	B	22	D	23	B	24	C	25	D
26	C	27	C	28	A	29	A	30	C

1 A (1, 2 and 3)

Option 1: Incorrect
X^{2+} has 53 electrons, **X** atom has 55 electrons (protons), **X** is Cs while Xe has 54 electrons (or protons). Hence, the atom of **X** is not isoelectronic with the atom of Xe.

Option 2: Incorrect
Both **XF** and RbF have giant ionic structure. Since LE α $|q^+q^-/(r^+ + r^-)|$, as size of X^+ is bigger than Rb^+, hence **XF** has a less exothermic LE and ionic bond strength in **XF** is weaker. Hence, **XF** has a lower melting point than RbF.

Option 3: Incorrect
Since Fr is below Cs, Fr should have a lower first IE as first IE decreases down the group.

Option 4: Correct
Since angle of deflection α (charge / mass)

ion	Na^+	X^{2+}
charge / mass	1/23 = 0.0435	2/133 = 0.0150

Hence, X^{2+} has a smaller angle of deflection.

2 B

Option A: Correct
Ethanol, C_2H_5OH, which has a highly electron–deficient H atom (δ+) that is covalently bonded to a highly electronegative O, can be attracted to the lone pair of a highly electronegative atom (δ–), which is O in caffeine through hydrogen bonding.

Option B: Incorrect
Caffeine does not have a planar structure since there are 3 bond pair of electrons and 1 lone pair around each N atom having three single bonds around it, it is trigonal pyramidal about each of these N atoms.

Option C: Correct
Each double bond is made up of 1 sigma and 1 pi bonds while each single bond is made up of only 1 sigma bond.

Option D: Correct
There are 5 carbon atoms having 3 bond pair of electrons around each of them, implying that they are sp^2 hybridised.

3 A

Option A: Correct
$CH_3CO_2^-NH_4^+$ has a giant ionic structure. More energy is required to break the stronger electrostatic forces of attraction between oppositely charged ions. $CH_3CH_2NH_2$ has a simple molecular structure with weaker hydrogen bonds between molecules. Hence, $CH_3CO_2^-NH_4^+$ has a higher bp.

Option B: Incorrect
SiO_2 has a giant molecular structure while $SiCl_4$ a simple molecular structure. More energy is required to break the stronger and extensive covalent bonds between atoms in SiO_2 than the id-id interactions between non-polar $SiCl_4$ molecules. Hence SiO_2 has a higher bp.

Option C: Incorrect
Both PH_3 and $SiCl_3H$ exist as simple molecules. $SiCl_3H$ has a larger electron number, hence its electron cloud is more polarisable resulting in stronger id-id interactions between $SiCl_3H$ molecules. Thus $SiCl_3H$ has a higher bp.

Option D: Incorrect
Both $Ni(OH)_2$ and $NiSO_4$ exist as giant ionic structures. Since SO_4^{2-} has a higher charge than OH^- and LE α $|q^+q^-/(r^++r^-)|$, LE of $NiSO_4$ is more exothermic and more energy is required to break the stronger ionic bonds in $NiSO_4$. Hence, $NiSO_4$ has a higher bp.

4 A
When the vessel is dented,
$pV = nRT$
$n = pV/RT$
$= (52.8 \times 10^3 \times 38.5 \times 10^{-6}) / [8.31 \times (27 + 273)]$
$= 8.15 \times 10^{-4}$ mol
Amount of gas remained unchanged when the shape of the vessel is restored. Hence, when the shape of the vessel is restored to 40.0 cm^3 at 60 °C,
$p = nRT/V$
$= [8.15 \times 10^{-4} \times 8.31 \times (60 + 273)] / (40.0 \times 10^{-6})$
$= 56.4$ kPa

5 B
Al_2O_3 is an amphoteric oxide while SiO_2 is an acidic oxide. Since both solutions prepared can dissolve Al_2O_3, but only one can dissolve SiO_2, **one solution must be basic while the other solution must be acidic**.

		Y (chloride of Y)	Z (oxide of Z)
x	A	silicon ($SiCl_4$: acidic)	phosphorus (P_4O_{10}: acidic)
✓	B	phosphorus (PCl_5 : acidic)	sodium (Na_2O: basic)
x	C	magnesium ($MgCl_2$: acidic)	phosphorus (P_4O_{10}: acidic)
x	D	sodium ($NaCl$: neutral)	sulfur (SO_3: acidic)

Hence, **Y** is **P** while **Z** is **Na**.

Chloride of **Y**: $PCl_5 + 4H_2O \rightarrow \underline{\mathbf{H_3PO_4}} + 5HCl$
Oxide of **Z**: $Na_2O + H_2O \rightarrow 2\underline{\mathbf{NaOH}}$

For reaction with Al_2O_3:
$2\underline{\mathbf{H_3PO_4}} + Al_2O_3 \rightarrow 2AlPO_4 + 3H_2O$
$2\underline{\mathbf{NaOH}} + Al_2O_3 + 3H_2O \rightarrow 2NaAl(OH)_4$

For reaction with SiO_2:
$\underline{\mathbf{H_3PO_4}} + SiO_2 \rightarrow$ no reaction
$2\underline{\mathbf{NaOH}}$(conc.) $+ SiO_2 \rightarrow Na_2SiO_3 + H_2O$

6 D
Based on the melting point data, the four elements are Si (Group 14) (high melting point due to giant molecular structure), P_4 (Group 15), S_8 (Group 16) and Cl_2 (Group 17).
Property **X** is electronegativity since electronegativity increases across the period. Property **Y** is 3rd IE since there is an anomaly at Group 15 element.

$Si^{2+} \rightarrow Si^{3+} + e$
$3s^2 \quad\quad 3s^1$

$P^{2+} \rightarrow P^{3+} + e$
$3s^2\,3p^1 \quad 3s^2$
For P^{2+}, an electron is removed from the 3p subshell which is further away from the nucleus. Thus, the 3p subshell is of a higher energy and its electron is less strongly attracted to the nucleus and hence less energy is required to remove it.

7 C
Option A: Incorrect
Ba^{2+} has a lower charge density than Mg^{2+} due to its smaller ionic radius, hence, $BaCl_2$ undergoes smaller extent of hydrolysis than $MgCl_2$, which results in a higher pH.

Option B: Incorrect
$MCO_3 \rightarrow MO + CO_2$
1 mol of MCO_3 will decompose to form 1 mol of CO_2. As M_r of MCO_3 increases down the group, amount of 1 g of MCO_3 will decrease down the group. Hence, smaller amount and volume of CO_2 gas will be produced.

Option C: Correct
Mg reacts less vigorously with cold water than strontium as the $E^\ominus(Sr^{2+}|Sr)$ is less positive / more negative than that of $E^\ominus(Mg^{2+}|Mg)$. Hence, Sr tends to be oxidised to $Sr(OH)_2$ more readily than Mg.

Option D: Incorrect
Group 2 sulfates become less soluble down the group since $|\Delta H_{hyd}|$ decreases as cations become larger in size, while $|\Delta H_{LE}|$ remains relatively constant due to large size of sulfate. Indeed, barium sulfate has a weaker ionic bond strength. It has less exothermic lattice energy since ionic radius of Ba^{2+} is larger than that of Mg^{2+}.

8 D
From expt 1, $\mathbf{Y}^-$ is oxidised to $\mathbf{Y_2}$ by $\mathbf{X_2}$. With $\mathbf{Y_2}$ appearing as violet in organic layer, $\mathbf{Y_2 = I_2}$ and **oxidising strength:** $\mathbf{X_2 > Y_2}$.

From expt 2, $\mathbf{X}^-$ is oxidised to $\mathbf{X_2}$ by $\mathbf{Z_2}$. With $\mathbf{X_2}$ appearing as orange-red in organic layer, $\mathbf{X_2 = Br_2}$ and **oxidising strength:** $\mathbf{Z_2 > X_2}$.

From expt 3, $\mathbf{Y}^-$ is oxidised to $\mathbf{Y_2}$ by $\mathbf{Z_2}$. With $\mathbf{Y_2}$ appearing as violet in organic layer, $\mathbf{Y_2 = I_2}$ and **oxidising strength:** $\mathbf{Z_2 > Y_2}$.

Hence, oxidising strength: $\mathbf{Z_2 > X_2 > Y_2}$
$\Rightarrow \mathbf{Z_2 = Cl_2, X_2 = Br_2, Y_2 = I_2}$

Option A: Incorrect
H**Y** (HI) has the highest boing point among three hydrogen halides due to its strongest instantaneous dipole–induced dipole interactions between molecules since H**Y** (HI) has the largest number of electrons.

Option B: Incorrect
K_{sp} of Ag**Y** (AgI) is so low that even at high concentration of NH_3, the ionic product of Ag**Y** is still greater than its K_{sp} value. Hence, Ag**Y** (AgI) does not dissolve in both dilute and concentrated NH_3.

Option C: Incorrect
H**Y** (HI) is a stronger acid than H**Z** (HCl), hence H**Y** has a larger K_a value. Since atomic radius of Y is larger than than of **Z**, H–**Y** bond is weaker than H–**Z** bond and less energy is needed to overcome H–**Y** bond to dissociate H**Y** into H^+ and $\mathbf{Y}^-$.

Option D: Correct
For expt 4, since $\mathbf{Y_2}$ is a weaker oxidising agent than $\mathbf{X_2}$, $\mathbf{Y_2}$ will not be able to oxidise $\mathbf{X}^-$ to $\mathbf{X_2}$. Hence, no redox reaction occurs and $\mathbf{Y_2}$ (I_2) will appear as violet in organic layer, which is the same as expt 3.

9 C
CO_3^{2-} in sodium percarbonate reacts with sulfuric acid to form CO_2 gas:
$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$
$n(CO_3^{2-}) = n(CO_2)$
$= 48 / 24000 = 2.00 \times 10^{-3}$ mol

H_2O_2 is oxidised by MnO_4^-:
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
$2\,MnO_4^- : 5\,H_2O_2$
$n(H_2O_2) = \frac{5}{2} \times n(MnO_4^-)$
$= \frac{5}{2} \times \frac{24}{1000} \times 0.0500 = 3.00 \times 10^{-3}$
$\frac{y}{x} = n(H_2O_2) / n(CO_3^{2-})$
$= (3.00 \times 10^{-3}) / (2.00 \times 10^{-3})$
$= \frac{3}{2}$

10 B

	CS_z +	$(1 + z)O_2$	$\rightarrow$	CO_2 +	zSO_2
Initial / cm^3	20	80		0	0
Change / cm^3	–20	$-20(1 + z)$		+20	+20z
End / cm^3	0	$80 - 20(1 + z)$		20	20z

Gas mixture after combustion contains unreacted O_2, CO_2 and SO_2. Upon treatment with NaOH(aq), the acidic gases, CO_2 and SO_2, are removed. Hence,
volume after treatment with NaOH(aq)
= volume of unreacted O_2
= 20

$80 - 20(1 + z) = 20$
$60 - 20z = 20$
$z = 2$

11 B (1 and 4 only)
$\Delta H_r^\ominus = 790$
$= \Sigma(\Delta H_f)_{products} - \Sigma(\Delta H_f)_{reactants}$
$= 3x\Delta H_f(CO) - \Delta H_f(Cr_2O_3)$
$\Delta H_f(Cr_2O_3) = 3x\Delta H_f(CO) - 790$
Hence, to find $\Delta H_f(Cr_2O_3)$, the value of $\Delta H_f(CO)$, enthalpy change of formation of CO, needs to be known, which, however, is not one of the options.

Now consider the definition of $\Delta H_f(CO)$:
$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta H_f(CO)$
$\Delta H_f(CO) = \Sigma(\Delta H_c)_{reactants} - \Sigma(\Delta H_c)_{products}$
$= \Delta H_c(C) - \Delta H_c(CO)$
Since $\Delta H_f(CO)$ can, in turn, be found from $\Delta H_c(C)$ and $\Delta H_c(CO)$, the enthalpy changes of combustion of C and CO, answer is options **(1)** and **(4)**.

12 D
Since ammonium nitrate functions as a 'cold pack', this suggests that the temperature decreases when it dissolves. Hence, the dissolution process is endothermic, i.e. ΔH is positive.

The dissolution process involves mixing of particles, which leads to more ways of arranging them. Hence, amount of disorder increases, i.e. ΔS is positive.

$\Delta G = \Delta H - T\Delta S$
$= |\Delta H| - T|\Delta S|$ for positive ΔH and ΔS.
For reaction to be spontaneous, ΔG has to be negative. In this case, ΔG is negative only when temperature is high enough for $T|\Delta S|$ to exceed $|\Delta H|$, i.e. reaction is more spontaneous at higher temperatures.

13 C (2 and 3 only)
Option 1: Wrong
Whether the reaction proceeds via free radicals cannot be determined just from the rate equation.

Option 2: Correct
If the reaction is a single–step reaction, the overall equation will also be the rate-determining step of the mechanism. Hence, the stoichiometry coefficient in the overall equation will coincide with the order shown in the rate equation. This is seen in the hydrogen / iodine reaction but not in the hydrogen / bromine reaction.

Option 3: Correct
From the given rate equation for the hydrogen / bromine reaction, rate decreases as [HBr] increases.

14 D
Since reaction is first order, half life is constant.
When the ratio of U : Pb is 1:15, it suggests that only 1/16 of U is left.
$(\frac{1}{2})^4 = 1/16$
This constitutes 4 half-lives and hence the rock sample is 2840 million years old.

15 A
When 0.10 mol of R is added to the old equilibrium mixture, the system is no longer at equilibrium. The new initial amounts are now:
R = 0.2 + 0.1 = 0.3 mol
P = **Q** = 0.5

By Le Chatelier's Principle, the system will try to remove the additional amount of **R** added by shifting the equilibrium backwards.

	P(g) +	Q(g)	$\rightleftharpoons$	2R(g)
Initial / mol	0.5	0.5		0.3
Change / mol	+x/2	+x/2		–x
Eqm / mol	0.5 + (x/2)	0.5 + (x/2)		0.3 – x

K_c remains the same since temperature is unchanged.

$$K_c = 0.16 = \frac{[R]^2}{[P][Q]} = \frac{[(0.3 - x)/V]^2}{[(0.5 + x/2)/V]^2}$$ where V = vol. of the sealed vessel

$\Rightarrow \sqrt{0.16} = 0.4 = \frac{(0.3 - x)}{(0.5 + x/2)}$
$\Rightarrow 0.2 + 0.2x = 0.3 - x$
$\Rightarrow x = 0.0833$
Amount of **R** in the new equilibrium
$= 0.3 - x = 0.3 - 0.0833 = 0.22$ mol

16 C
$K_w = [H^+][OH^-] = 2.4 \times 10^{-14}$
$pH = 7.4 \Rightarrow [H^+] = 10^{-7.4}$
Substituting into K_w expression:
$10^{-7.4}[OH^-] = 2.4 \times 10^{-14}$
$[OH^-] = 6.03 \times 10^{-7}$ mol dm^{-3}

17 B (1 and 2 only)
$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$ ---- (1)

Option 1: Correct
When solution is diluted, $[CH_3CO_2H]$, $[CH_3CO_2^-]$ and $[H^+]$ decrease.
The ratio $[CH_3CO_2^-][H^+]$ / $[CH_3CO_2H]$ becomes smaller than K_a. Hence, equilibrium (1) shifts right so that $[CH_3CO_2^-]$ $[H^+]$ / $[CH_3CO_2H]$ = K_a again.

As solution is diluted to an increasing extent, equilibrium (1) shifts more to the right, leading to a higher fraction of CH_3CO_2H dissociated. The fraction of CH_3CO_2H will increase to a maximum value of 1 at infinite dilution.

Option 2: Correct
$[H^+] = \sqrt{K_a[HA]}$
As solution is diluted to an increasing extent, [HA] decreases, leading to lower $[H^+]$ and higher pH. pH will increase to a maximum value of 7 at infinite dilution, when the solution is almost like pure water.

Option 3: Wrong
K_a is only dependent on temperature and is hence unaffected by dilution.

18 D
$Zn_3[Fe(CN)_6]_2(s) \rightleftharpoons 3Zn^{2+}(aq) + 2[Fe(CN)_6]^{3-}(aq)$
Let concentration of the anion be x mol dm^{-3}.
Hence, $[Zn^{2+}] = \frac{3}{2}x$

$K_{sp} = [Zn^{2+}]^3\,[\text{anion}]^2$
$W = (\frac{3}{2}x)^3\,x^2 = \frac{27}{8}x^5$
$\Rightarrow x = (\frac{8}{27}W)^{1/5}$

19 A
First step:
P has lone pair electrons which acts as a nucleophile by attacking electron deficient C bonded directly to X via **nucleophilic substitution**.

Second step:
1) **Neutralisation** occurs between basic H^- and $CHR(R')(^+PPh_3)$, in which $CHR(R')(^+PPh_3)$ acts as an acid by donating H^+ to form carbanion $^-CR(R')(PPh_3)$.
2) $^-CR(R')(PPh_3)$ then acts as a nucleophile by attacking electron deficient C bonded directly to O in propanone via **nucleophilic addition**.

Third step:
Condensation has occurred via nucleophilic addition (second step) followed by elimination of $O{=}PPh_3$ (third step).

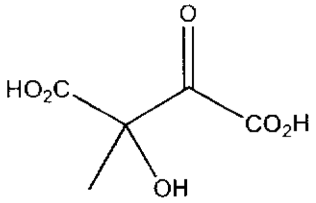
20 D
$CH(CH_3)_2COOH$: 2-methylpropanoic acid
$CH_3CH_2CH_2COOH$: butanoic acid
$CH_3CH_2COOCH_3$: methyl propanoate
$HCOOCH_2CH_2CH_3$: propyl methanoate
$CH_3COOCH_2CH_3$: ethyl ethanoate
$HCOOCH(CH_3)_2$: 1-methylethyl methanoate

21 B
Option 1: Incorrect
Conc. H_2SO_4 is used instead as a dehydrating agent while aqueous H_2SO_4 is completely dissociated into ions.

Option 2: Incorrect
The formation of carbocation in step 2 is not likely for primary alcohols as compared to tertiary alcohols since primary carbocation is less stable than tertiary carbocation.

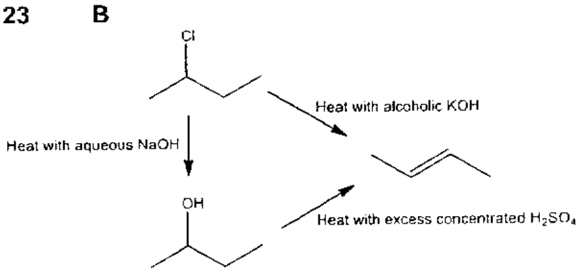
Option 3: Correct
The reactants in step 3 can undergo addition reaction to give $CH_3CH(OSO_3H)CH_3$.

22 D
Primary alcohol will be oxidised to carboxylic acid, secondary alcohol to ketone and no oxidation for tertiary alcohol.
Hence the compound **X** is



Molecular formula is $C_5H_6O_6$

23 B



24 C
Options A and B: Incorrect
$LiAlH_4$ in dry ether is unable to reduce alkene.

Option C: Correct
Both aldehyde and alkene functional groups will be reduced by H_2, Pt. Only the primary alcohol will be oxidised by $K_2Cr_2O_7$ with $H_2SO_4(aq)$, heat to form $-CO_2H$.

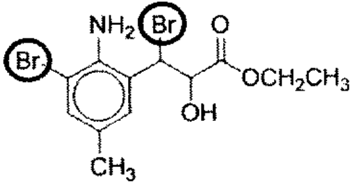
Option D: Incorrect
$KMnO_4$ with $H_2SO_4(aq)$, heat will cause both $-CH_2OH$ and $-CH_2CH_2CH_3$ side chains on the benzene ring to be oxidised to $-CO_2H$ as both side chains have a benzylic hydrogen.

25 D
Option A: Correct
Acid hydrolysis of the ester can occur first to form CH_3CH_2OH as one product. This will be oxidised by acidified $K_2Cr_2O_7$ to CH_3CO_2H, hence colour of the solution turns green.

Option B: Correct
2,4-DNPH only forms orange crystals with carbonyl compounds. Ester is **not** a carbonyl compound.

Option C: Correct
Alkaline hydrolysis of the ester can occur first to form CH_3CH_2OH as one product. This will give a positive triiodomethane test as it contains $CH_3CH(OH)$– unit.

Option D: Incorrect
Both electrophilic addition of alkene and electrophilic substitution of phenylamine can occur. Thus 2 Br atoms will be incorporated into a molecule of the major product. Major product is as follows:



26 C

Option A: Incorrect
It contains an aromatic aldehyde (benzaldehyde), and has no reaction with Fehling's solution.

Option B: Incorrect
It does not tally with the molecular formula. There are 3 oxygen atoms in the compound, but the question wants only 2 oxygen atoms.

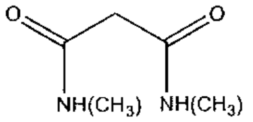
Option C: Correct
It is moderately soluble in water as it can exist as a zwitterion, comprising NH_3^+ and phenoxide group. It contains aliphatic aldehyde which gives a brick red ppt when warmed with Fehling's solution. It has phenol which gives a purple colouration when warmed with neutral $FeCl_3$.

Option D: Incorrect
Carboxylic acid does not give purple colouration with $FeCl_3$(aq) nor react with Fehling's solution.

27 C
The conjugate acid of the weakest base is the strongest acid with the highest K_a and lowest pK_a. Phenylamine, $C_6H_5NH_2$, is the weakest base as the N lone pair is delocalized into the aromatic ring making it least available for donation to an acid. Diethylamine, $(CH_3CH_2)NH$ is a stronger base than ammonia as it contains alkyl groups which exert electron-donating inductive effect making the lone pair on its N more available for donation to an acid.

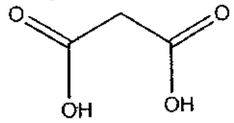
28 A

Option A: Correct
Compound **A** undergoes oxidation in reaction I and then condensation in reaction **II** to form



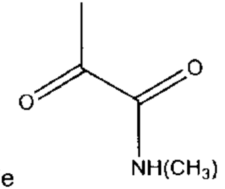
Molecular formula changes from $C_3H_4O_3$ to $C_5H_{10}O_2N_2$. There is an increase of M_r by 42.0.

Option B: Incorrect
Compound **A** undergoes condensation in reaction **I** to form $(CHO)CH_2CONH(CH_3)$ which then undergoes hydrolysis (amide to carboxylic acid) and oxidation (aldehyde to carboxylic acid) in reaction **II** to form



Molecular formula changes from $C_3H_4O_3$ to $C_3H_4O_4$. There is an increase of M_r by 16.0.

Option C: Incorrect
There is no oxidation of compound **A** in reaction **I**. It undergoes condensation in reaction **II** to form amide



Molecular formula changes from $C_3H_4O_3$ to $C_4H_7O_2N$. There is an increase of M_r by 13.0.

Option D: Incorrect
Although compound **A** forms an amide $CH_3COCONH(CH_3)$ in reaction **I**, it undergoes acid hydrolysis in reaction **II** to give back the same compound **A**. There is no oxidation of ketone functional group. There is no change in M_r.

29 A (1, 3 and 4 only)
For cell 1, Y is anode (–) while X is cathode (+).
⇒ Oxidation occurs at electrode Y; reduction at electrode X.

$E_{cell} = E_{reduced} - E_{oxidised}$
$= E(X^{2+}|X) - E(Y^{2+}|Y) = +0.47\ V$ --(1)
⇒ $\mathbf{E(X^{2+}|X) > E(Y^{2+}|Y)}$

For cell 2, X is anode (–) while Z is cathode (+).
⇒ Oxidation occurs at electrode X; reduction at electrode Z.

$E_{cell} = E_{reduced} - E_{oxidised}$
$= E(Z^{2+}|Z) - E(X^{2+}|X) = +0.31\ V$ --(1)
⇒ $\mathbf{E(Z^{2+}|Z) > E(X^{2+}|X)}$
Hence, $\mathbf{E(Z^{2+}|Z) > E(X^{2+}|X) > E(Y^{2+}|Y)}$

Option 1: Correct
Since $E(Z^{2+}|Z)$ is the most positive, Z is the least easily oxidised, hence Z is the weakest RA.

Option 2: Incorrect
Similarly, since $E(Y^{2+}|Y)$ is the least positive, Y^{2+} is the least easily reduced, hence Y^{2+} is the weakest OA and hence cannot oxidise both X and Z.

Option 3: Correct
Since
$E(X^{2+}|X) - E(Y^{2+}|Y) = +0.47\ V$ --(1)
$E(Z^{2+}|Z) - E(X^{2+}|X) = +0.31\ V$ --(2)

When the two half-cells of $Y^{2+}(aq)|Y(s)$ and $Z^{2+}(aq)|Z(s)$ are connected together, since $E(Z^{2+}|Z) > E(Y^{2+}|Y)$, reduction will take place at Z electrode while oxidation will take place at Y electrode.
$\Rightarrow E_{reduced} = E(Z^{2+}|Z)$ and $E_{oxidised} = E(Y^{2+}|Y)$
By (1) + (2)
$E_{cell} = E(Z^{2+}|Z) - E(Y^{2+}|Y) = 0.31 + 0.47 = +0.78$ V

Option 4: Correct
$X^{2+} + 2e \rightleftharpoons X$
By Le Chatelier's Principle, adding water to $X^{2+}|X$ will decrease $[X^{2+}]$, causing the position of above equilibrium to shift to the left to increase the concentration of X^{2+}. $E(X^{2+}|X)$ becomes less positive.

Hence,
For electrochemical cell 1:
$E_{cell} = E(X^{2+}|X) - E(Y^{2+}|Y)$ will decrease
For electrochemical cell 2:
$E_{cell} = E(Z^{2+}|Z) - E(X^{2+}|X)$ will increase

30 C
Quantity of charge transferred, Q
= It
= 3 x 2 x 3600
= 21600 C
No, of electrons transferred, n_{e-}
= Q / 96500
= 21600 / 96500
= 0.224 mol

$Cu^{2+} + 2e \rightarrow Cu$
$n_{Cu2+} = 0.224 / 2$
$= 0.112$ mol
Hence, $[Cu^{2+}] \times 0.500 = 0.112$
$[Cu^{2+}] = 0.224$ mol dm^{-3}

Since change in $[Cu^{2+}]$ is 0.224 mol dm^{-3},
$[Cu^{2+}]_{left} = [Cu^{2+}]_{initial} -$ Change in $[Cu^{2+}]$
$0.776 = [Cu^{2+}]_{initial} - 0.224$
$[Cu^{2+}]_{initial} = 1.00$ mol dm^{-3}

VICTORIA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATIONS
Higher 2

CANDIDATE NAME ....

CT GROUP ....

CHEMISTRY **9729//02**

Paper 2 Structured Questions **15 September 2021**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number, name and CT group in the spaces at the top of this page.
Write in dark blue or black pen.
You may use a 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.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	/10
2	/15
3	/10
4	/15
5	/12
6	/13
Total	/75

This document consists of **22** printed pages and **2** blank pages.

1 The table below shows the fifth to eighth ionisation energies of two consecutive elements, **X** and **Y** in the second period of the Periodic Table.

successive ionisation energies / kJ mol^{-1}	5th	6th	7th	8th
X	10990	13330	71330	84080
Y	11020	15160	17870	92040

(a) **(i)** With the aid of an equation, define the term *first ionisation energy* with reference to **X**.

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.... [2]

(ii) State and explain the group number of **X**.

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.... [1]

(b) **(i)** Write down the full electronic configurations of **X**$^+$ and **Y**$^+$.

X$^+$: ....

Y$^+$: .... [1]

(ii) Hence, explain which element has a less endothermic second ionisation energy.

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[2]

(c) Boron is another Period 2 element which reacts vigorously with fluorine to form boron trifluoride, BF_3, an important reactant in organic syntheses.

Boron trifluoride is a very reactive gas and it is hard to handle at room temperature. It can be converted to a liquid compound which is easily stored by reacting it with diethyl ether in the mole ratio of 1:1.

Diethyl ether can be represented by the formula ROR, where –R represents the ethyl group.

(i) Explain why boron trifluoride can form a compound with diethyl ether.

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[2]

(ii) Draw the structure of the compound formed, indicating clearly the shape and bond angle around each central atom.

[2]

[Total: 10]

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

Xenon hexafluoride, XeF_6 was one of the first noble gas compounds synthesised. XeF_6 reacts with the silicon dioxide, SiO_2, in glass to form liquid xenon oxytetrafluoride, $XeOF_4$ and gaseous silicon tetrafluoride, SiF_4 as shown by the equation below:

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

(i) An unknown amount of XeF_6 was allowed to react with silicon dioxide in a 2 m^3 closed vessel at 25 °C. When all the XeF_6 has reacted, a pressure of 0.505 kPa was measured in the vessel.

Assuming that the gas inside the vessel behaves ideally, calculate the amount of XeF_6 reacted in the vessel.

[2]

Hence, calculate the mass of XeF_6 reacted.

(b) a given vessel of a fixed volume, N_2O_5 gas decomposed to NO_2 and O_2 as sho
low at 50 °C.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

e rate equation for this thermal decomposition is as follows.

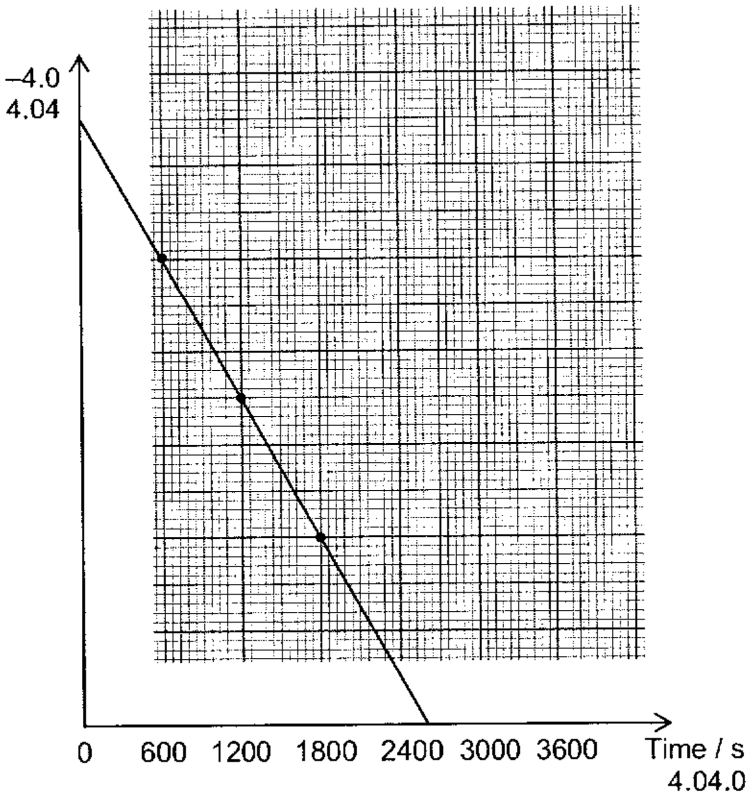
$$\text{Rate} = k[N_2O_5]$$

eory shows that under the conditions of the experiment, the following relations
tween the concentration of N_2O_5 and time is as follows.

equation 1 $\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_{\text{initial}}$

ere $[N_2O_5]_t$ = concentration of N_2O_5 present at time t

The following graph of $\ln[N_2O_5]_t$ against t is plotted with the data obtained fr
the experiment.



With the help of equation 1 and the graph above, determine

I. the initial concentration of N_2O_5

II. rate constant, *k*, including its units

[2]

(ii) It is known that the rate of the reaction doubles with every 10 °C rise in temperature.

Calculate the initial rate of the thermal decomposition of N_2O_5 when the volume of vessel is halved at 70 °C.

[2]

(c) In another experiment, O_2 reacts with NO as follows.

$$O_2 + 2NO \rightarrow 2NO_2$$

(i) Using the following data, determine the order of reaction with respect to O_2 and NO. Hence, write down the rate equation for the reaction.

experiment	$[O_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}

[2]

(ii) The following relationship can be used to calculate the activation energy of the reaction between O_2 and NO:

$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k = rate constant at the respective temperature in Kelvins.

Calculate the activation energy of the reaction if the values of the rate constants are 7.00×10^{-3} and 9.21×10^{-3} at 25 °C and 60 °C respectively. Include the correct units in your answer.

[2]

(iii) With an appropriate sketch of the Boltzmann distribution, explain why a rise in temperature increases the value of rate constant, *k*.

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.... [2]

(iv) NO_2 produced in the reaction in **(c)** reacts with CO as follows:

$NO_2 + CO \rightleftharpoons NO + CO_2 \qquad \Delta H = -225\ \text{kJ mol}^{-1}$

Given that the activation energy for the forward reaction is +116 kJ mol^{-1}, sketch a **fully labelled** energy profile diagram for this reaction. Indicate clearly on the diagram the value of the activation energy for the reverse reaction.

[2]

[Total: 15]

3 The following data refer to the Haber Process for the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

The table below shows the percentage of ammonia by volume in equilibrium mixtures at various temperatures and pressures. In all cases, N_2 and H_2 were mixed in a 1:3 molar ratio.

pressure / atm	temperature		
	300 °C	400 °C	500 °C
1	2.18	0.44	0.13
10	14.7	3.85	1.21
100	51.2	25.1	10.4

(a) With reference to the data above, explain how changes in temperature and pressure affect the percentage of NH_3 in the equilibrium mixture.

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....
[2]

(b) Calculate the partial pressure of each gas present in the equilibrium mixture at 100 atm and 400°C.

Hence determine K_p at 400°C.

[2]

(c) Hydrogen halides show clear trends in the H–X bond energy where X = C*l*, Br and I.

(i) With reference to the *Data Booklet*, predict and explain the trend in thermal stability of the hydrogen halides from HC*l* to HI.

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.... [2]

(ii) Hydrogen halides behave as weak acids in liquid ethanoic acid, dissociating to different extents.

Write an equation to show how a hydrogen halide dissociates in ethanoic acid. Use HX to represent the hydrogen halide.

.... [1]

(iii) Rank the pK_a values of the three hydrogen halides in ethanoic acid in decreasing order. Explain your answer.

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....

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.... [2]

(iv) Using the common ion effect principle, suggest why the hydrogen halides are weaker acids in ethanoic acid than in water.

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.... [1]

[Total: 10]

4 Petroleum or crude oil is a complex mixture of organic compounds consisting of mainly hydrocarbons, with small quantities of other organic compounds containing nitrogen, oxygen or sulfur.

In the refining of crude oil, this mixture is partly separated by fractional distillation. Long chain alkanes obtained from the fractional distillation of crude oil can be converted to the more useful shorter chain alkanes and alkenes via a process called cracking.

The information below is related to the thermal cracking of 1 mole of the alkane $C_{15}H_{32}$.

- Four products **P**, **Q**, **R** and **S** in the molar ratio 2:1:1:1 were obtained.
- **P** is ethene.
- **Q** has a relative molecular mass of 42.0.
- **R** has a relative molecular mass of 56.0 and exists as a pair of cis-trans isomers.

(a) (i) Suggest the structural formulae of **Q**, **R** and **S**.

Q	**R**
S	

[3]

(ii) Explain, with reference to its structure, why **R** can exist as a pair of cis–trans isomers.

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[1]

(b) The process of thermal cracking proceeds via a free radical mechanism. The following are reactions involved when propane undergoes thermal cracking.

reaction	equation
1	$CH_3CH_2CH_3 \rightarrow \bullet CH_3 + \bullet CH_2CH_3$
2	$CH_3CH_2CH_3 \rightarrow \bullet H + \bullet CH_2CH_2CH_3$
3	$\bullet CH_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \bullet CH_2CH_2CH_3$
4	$\bullet CH_2CH_3 \rightarrow \bullet H + CH_2{=}CH_2$
5	$\bullet CH_3 + CH_2{=}CH_2 \rightarrow \bullet CH_2CH_2CH_3$
6	$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$
7	$2\,\bullet CH_2CH_3 \rightarrow CH_3CH_3 + CH_2{=}CH_2$

(i) Reactions 1 and 2 are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

....

....

....

....
[1]

(ii) From reactions 3 to 7, identify those which may be termed propagation steps in the mechanism.

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[1]

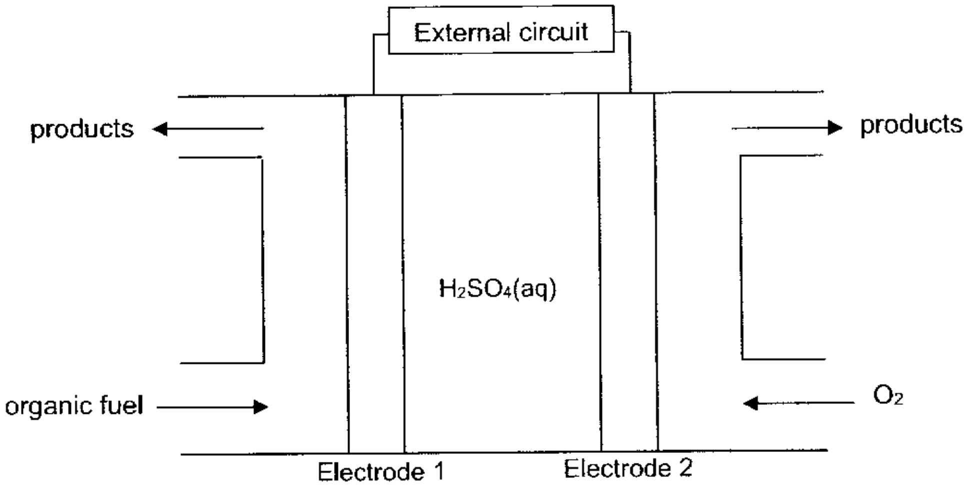
(iii) Which gas, if detected in the product mixture, would offer support for the occurrence of both reactions 2 and 4?

....
[1]

(c) Alternative energy sources that are renewable and contribute less to global warming are rapidly gaining in popularity as natural gas and crude oil are depleting at a fast rate.

As an alternative energy source, direct liquid fuel cell (DLFC) is one of the leading fuel cell types due to their great features of superior energy density, modest configuration and small size in fuel container. Commercially used liquid fuel types are prepared using alcohols, such as methanol or ethanol, glycol, and acids.

The following diagram illustrates the parts of a typical DLFC. Organic fuel is supplied to electrode 1 and oxygen is supplied to electrode 2 simultaneously. The electrons produced at electrode 1 pass around the external circuit to electrode 2. The protons formed from the oxidation move through the conducting polymer electrolyte to electrode 2, where they react with oxygen to produce water.



While fuel cells which use organic fuel such as liquid alcohols pose no storage problem, they emit carbon dioxide, thus countering the move to reduce carbon footprint. Research was done to assess the viability of the oxidation of propan-2-ol to propanone as a potential organic fuel cell reaction.

(i) Construct ion-electron equations for the reactions at electrode 1 and electrode 2 respectively.

Electrode 1

....

electrode 2

....

[2]

(ii) Hence construct the equation for the overall reaction.

....

[1]

(iii) The $E^\ominus$ of the $CH_3COCH_3/CH_3CH(OH)CH_3$ electrode reaction is –0.03 V. By using suitable data from the *Data Booklet,* calculate the $E^\ominus_{cell}$ for the reaction.

[2]

(iv) State how $E^\ominus_{cell}$ and $\Delta G^\ominus_{cell}$ will change when twice the amount of the reactants as given in the overall reaction in **(c)(ii)** is used for the reaction.

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.... [1]

(v) Pyrogallol solution is an organic compound that absorbs oxygen efficiently.

Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

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.... [2]

[Total: 15]

5 **(a)** Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure. It is formed from S_8 and Cl_2.

(i) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps. The first step involves the formation of disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write an equation to represent the second step.

.... [1]

Some chemists speculate that the intermediate is not S_2Cl_2 but **K**. **K** shares the same elemental mass percentages as sulfur dichloride, SCl_2 but it has a molar mass of 206.2 g mol^{-1} instead.

(ii) State the molecular formula of **K**.

.... [1]

(iii) The following is known about the structure of **K**:

- There is more than one central atom present.
- All the central atoms are sulfur atoms and possess at least one lone pair
- The shape about each central atom is different.

Draw a dot-and-cross diagram for **K**.

[1]

(b) Compounds **C** and **D** are chlorides of Period 3 elements. Both **C** and **D** exist in the solid state at room temperature.

When excess water was added to a sample containing 0.100 mol of **C**, an acidic solution was obtained. The resulting solution required 0.500 mol of silver nitrate for complete precipitation.

On the other hand, when excess water was added to a sample containing 0.100 mol of **D**, a neutral solution was obtained.

(i) Identify compounds **C** and **D**.

Compound **C** ....

Compound **D** ....

[2]

(ii) Explain, with the aid of equations, the difference in the pH of the solutions obtained when water is added to **C** and **D**.

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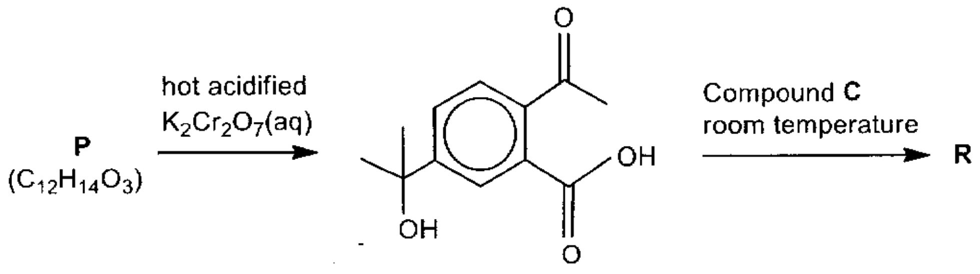
[2]

(c) Compound **C** is commonly used as a reagent in organic chemistry reactions.

(i) Consider the scheme below which involves **C** in one of the steps:



Q ($C_{12}H_{14}O_4$)

P does not react with sodium carbonate or Brady's reagent.

Suggest structures for **P** and **R**.

P

R

[2]

(ii) Write a balanced equation for the reaction between **Q** and **C** to form **R**.

[1]

(d) [Use of the *Data Booklet* is relevant to this part of the question].

Compound **Q** is a solid which can be neutralised by aqueous NaOH. An experiment was carried out to determine the enthalpy change of the reaction. 5.00 g of **Q** was added to 40.0 cm^3 of 0.800 mol dm^{-3} NaOH(aq) in a Styrofoam cup and the reaction mixture was stirred. The temperature rose from 25.0°C to 31.2°C.

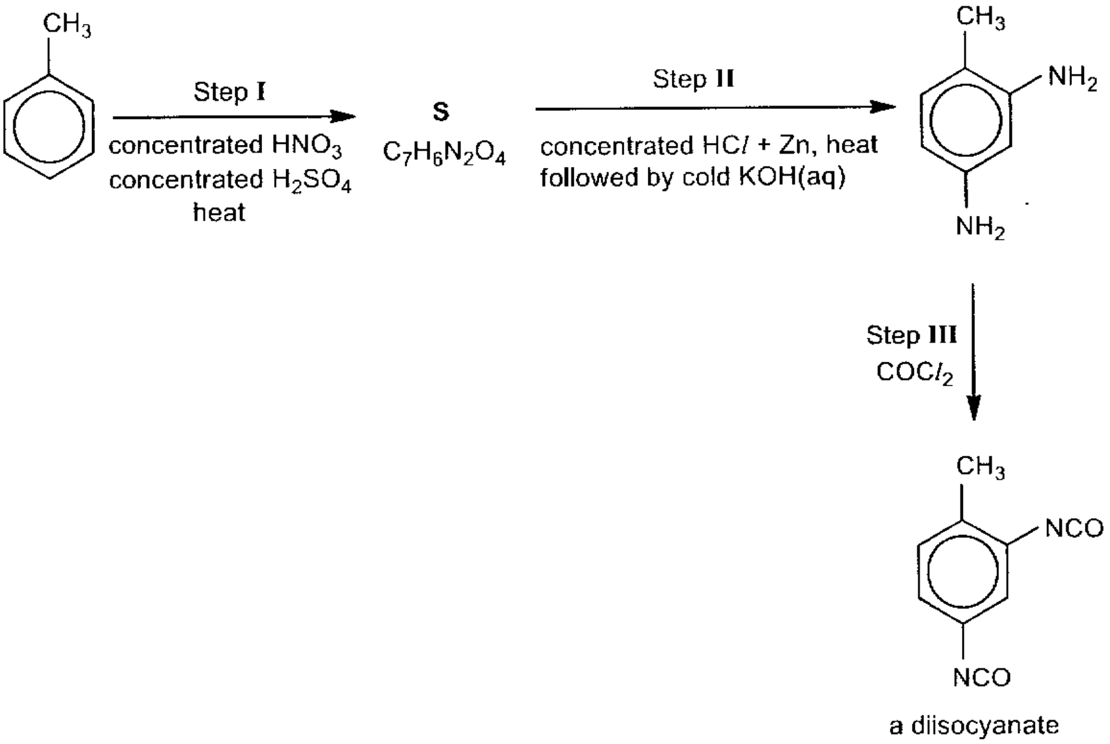
Determine the enthalpy change per mole of water formed in the reaction.

[2]

[Total: 12]

6 **(a)** Compounds containing the isocyanate functional group, –NCO, are important industrial chemicals. They react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

Shown below is the synthesis of a diisocyanate from methylbenzene:



(i) Draw the structure of **S**.

[1]

(ii) A number of isomers of **S** is formed in step **I** as side-products. Draw the structure of the side-product formed in the greatest proportion.

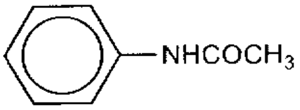
[1]

(iii) State the type of hybridisation exhibited by the carbon in the –NCO group and draw the hybrid orbitals around this carbon, showing clearly their shape and alignment.

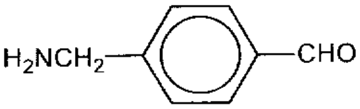
Type of hybridisation: ....

[2]

(b) The structures of two organic nitrogen compounds, **T** and **U**, are given below:



T



U

Both compounds exist as solids at room temperature and pressure. They have different basic strength, which cause them to have different solubility in an aqueous acid solution such as HC*l*(aq).

(i) Which compound, **T** or **U**, is the stronger base? Explain your answer.

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[2]

(ii) **T** and **U** are found mixed together in a sample.

By considering your answer in **(b)(i)**, outline briefly a simple method that allows you to separate the two compounds and recover them in their original solid forms. Your method should only make use of normal chemicals and apparatus found in a school laboratory.

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.... [2]

(c) In the study of the structure of a polypeptide **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

digestion using the first enzyme	digestion using the second enzyme
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

Deduce the sequence of amino acids in the polypeptide **A**.

[2]

(d) The structure of a certain tripeptide is given below:

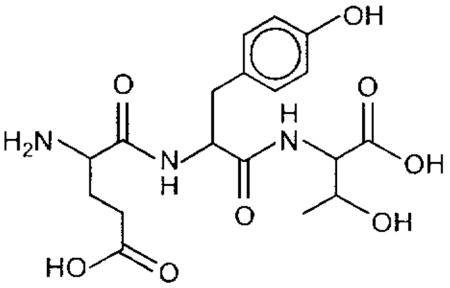

Figure 6.1

It is formed from the amino acids **W**, **X** and **Y**.

Table 6.1 shows the pK_a values of the different functional groups present in each amino acid.

Table 6.1

amino acid	pK_a of α–carboxyl group	pK_a of α–amino group	pK_a of side–chain
W	2.09	9.10	–
X	2.20	9.11	10.07
Y	2.19	9.67	4.25

W and **X** exist mainly as zwitterions at pH 7.0 but **Y** does not.
W rotates plane-polarised light and can exist as four possible stereoisomers.

(i) Circle on Figure 6.1 the part of the tripeptide that originates from **W**.

[1]

(ii) State what is meant by the term *zwitterion*.

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.... [1]

(iii) Suggest a pH at which the predominant species of **Y** is a zwitterion using the information in Table 6.1.

.... [1]

[Total: 13]

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Victoria Junior College
2021 H2 Chemistry Prelim Exam 9729/2
Suggested Answers

1 The table below shows the fifth to eighth ionisation energies of two consecutive elements, **X** and **Y** in the second period of the Periodic Table.

successive ionisation energies / kJ mol^{-1}	5th	6th	7th	8th
X	10990	13330	71330	84080
Y	11020	15160	17870	92040

(a) (i) With the aid of an equation, define the term *first ionisation energy* with reference to **X**. [2]

First ionisation energy of X is the amount of energy required to remove one mole of electrons from one mole of X gaseous atoms, producing one mole of gaseous X$^+$ ions.

$$X(g) \rightarrow X^+(g) + e^-$$

(ii) State and explain the group number of **X**. [1]

Group 16. There is a big jump from 6th to 7th IE, indicating that the 7th electron is removed from the inner principal quantum shell [OR there are 6 valence electrons].

(b) (i) Write down the full electronic configurations of **X**$^+$ and **Y**$^+$. [1]

X$^+$: $1s^2 2s^2 2p^3$
Y$^+$: $1s^2 2s^2 2p^4$

(ii) Hence, explain which element has a less endothermic second ionisation energy. [2]

Y has a less endothermic second ionisation energy. It is easier to remove a paired 2p electron in Y$^+$ due to the presence of interelectronic repulsion between electrons in the same orbital.

(c) Boron is another Period 2 element which reacts vigorously with fluorine to form boron trifluoride, BF_3, an important reactant in organic syntheses.

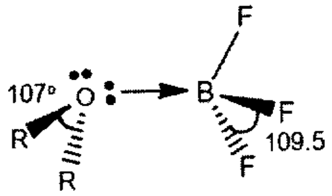
Boron trifluoride is a very reactive gas and it is hard to handle at room temperature. It can be converted to a liquid compound which is easily stored by reacting it with diethyl ether in the mole ratio of 1:1.

Diethyl ether can be represented by the formula ROR, where –R represents the ethyl group.

(i) Explain why boron trifluoride can form a compound with diethyl ether. [2]

ROR has a lone pair of electrons on O while the B in BF_3 has a vacant orbital, hence, B can accept lone pair of electrons to form a stable octet structure via dative bond formation.

(ii) Draw the structure of the compound formed, indicating clearly the shape and bond angle around each central atom. [2]



Structure should include

- **Correct structure with wedge and hash bonds**
- **Dative bond from O to B**
- **Around B: tetrahedral, 109.5°**
- **Around O: trigonal pyramidal, 107°**

[Total: 10]

S2 **(a)** *Use of the Data Booklet is relevant to this part of the question.*

Xenon hexafluoride, XeF_6 was one of the first noble gas compounds synthesised. XeF_6 reacts with the silicon dioxide, SiO_2 in glass to form liquid xenon oxytetrafluoride, $XeOF_4$ and gaseous silicon tetrafluoride, SiF_4 as shown by the equation below:

$$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$$

(i) An unknown amount of XeF_6 was allowed to react with SiO_2 in a 2 m^3 closed vessel at 25 °C. When all the XeF_6 has reacted, a pressure of 0.505 kPa was measured in the vessel.

Assuming that the gas inside the vessel behaves ideally, calculate the amount of XeF_6 reacted in the vessel. [2]

Only gaseous SiF_4 exerts a pressure of 0.505 kPa at the end of the reaction.

$PV = nRT$
$0.505 \times 10^3(2) = n(8.31)(25 + 273)$
$n = 0.408$ mol

Hence, amount of XeF_6 reacted = 2×0.408
= 0.816 mol

(ii) Hence, calculate the mass of XeF_6 reacted. [1]

Mass of XeF_6 reacted
= 0.816 (131.3 + 19.0(6))
= 200 g

(b) In a given vessel of a fixed volume, N_2O_5 gas decomposed to NO_2 and O_2 as shown below at 50 °C.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

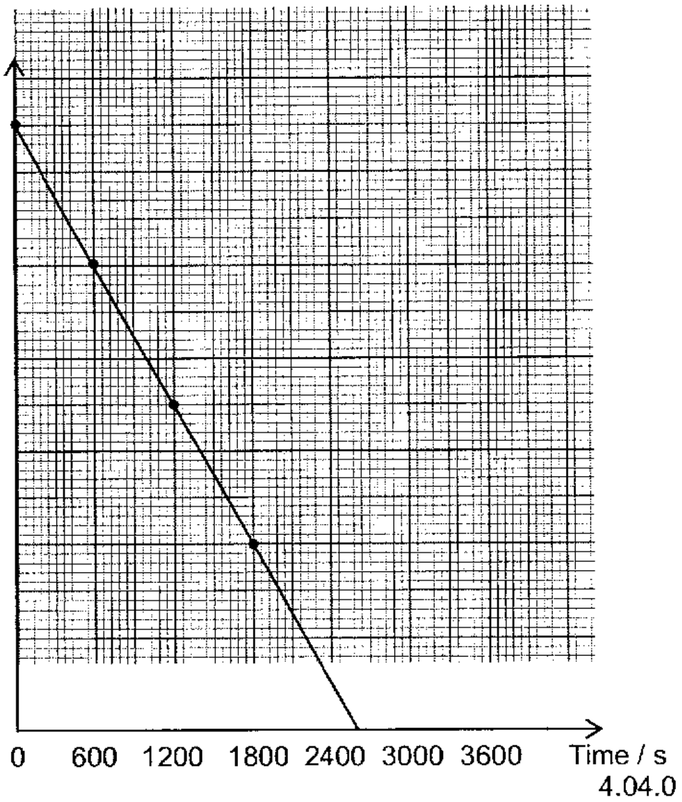
The rate equation for this thermal decomposition is as follows.

$$\text{Rate} = k[N_2O_5]$$

ieory shows that under the conditions of the experiment, the following relations
tween the concentration of N_2O_5 and time is as follows.

equation 1 $\ln[N_2O_5]_t = -kt + \ln[N_2O_5]_{initial}$

iere $[N_2O_5]_t$ = concentration of N_2O_5 present at time t
k = rate constant



With the k

I. the initial concentration of N_2O_5

From the graph, $\ln[N_2O_5]_{initial} = -4.1$
$[N_2O_5]_{initial} = 1.66 \times 10^{-2}$ mol dm^{-3}

II. rate constant, k, including its units

k = –gradient = –(–5.0 + 4.1) / 1800
= 5.00×10^{-4} s^{-1}

It is known that the rate of the reaction doubles with every 10 °C rise
temperature.

Calculate the initial rate of the thermal decomposition of N_2O_5 when the volu
of vessel is halved at 70 °C.

Rate = $k[N_2O_5]$ = $5.00 \times 10^{-4} \times 4\ (1.66 \times 10^{-2} \times 2)$
= 6.64×10^{-5} mol dm^{-3} s^{-1}

(c) In another experiment, O_2 reacts with NO as follows.

$$O_2 + 2NO \rightarrow 2NO_2$$

(i) Using the following data, determine the order of reaction with respect to O_2 and NO. Hence, write down the rate equation for the reaction.

experiment	$[O_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}

[2]

Comparing 1 and 2, when $[O_2]$ is doubled, initial rate is doubled. Hence, first order wrt O_2.
Comparing 1 and 3, when [NO] is doubled, initial rate is increased by four times. Hence, second order wrt NO.
Rate = $k[O_2][NO]^2$

(ii) The following relationship can be used to calculate the activation energy of the reaction between O_2 and NO:

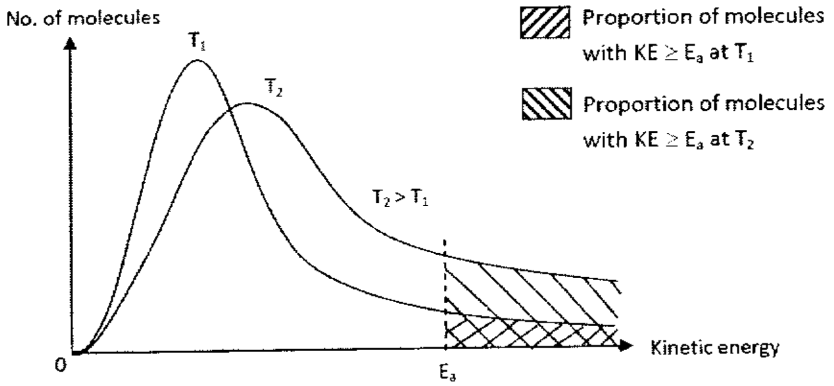
$$\ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where k = rate constant at the respective temperature in Kelvins.

Calculate the activation energy of the reaction if the values of the rate constants are 7.00×10^{-3} and 9.21×10^{-3} at 25 °C and 60 °C respectively. Include the correct units in your answer. [2]

$\ln(9.21 \times 10^{-3} / 7.00 \times 10^{-3}) = (-E_a/8.31)(1/333 - 1/298)$
$E_a = 6460$ J mol^{-1} = 6.46 kJ mol^{-1}

(iii) With an appropriate sketch of the Boltzmann distribution, explain why a rise in temperature increases the value of rate constant, k. [2]



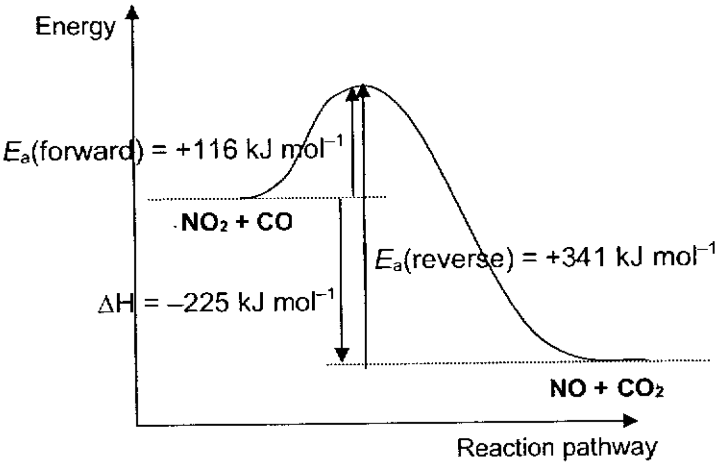
At higher temperatures, the proportion of molecules with kinetic energy greater than or equal to activation energy increases. Thus, frequency of effective collision increases, rate of reaction increases and hence rate constant increases.

(iv) NO_2 produced in the reaction in **(c)** reacts with CO as follows:

$$NO_2 + CO \rightleftharpoons NO + CO_2 \quad ; \quad \Delta H = -225 \text{ kJ mol}^{-1}$$

Given that the activation energy for the forward reaction is +116 kJ mol^{-1}, sketch a **fully labelled** energy profile diagram for this reaction. Indicate clearly on the diagram the value of the activation energy for the reverse reaction.

[2]



- **Correct labelling of axes**
- **Correct shape showing negative ΔH**
- **Correct labelling of reactants and products**
- **Correct labelling of E_a(reverse) with its value indicated**

[15 marks]

3 The following data refer to the Haber Process for the manufacture of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H < 0$$

The table below shows the percentage of ammonia by volume in equilibrium mixtures at various temperatures and pressures. In all cases, N_2 and H_2 were mixed in a 1:3 molar ratio.

pressure / atm	temperature		
	300 °C	400 °C	500 °C
1	2.18	0.44	0.13
10	14.7	3.85	1.21
100	51.2	25.1	10.4

(a) With reference to the data above, explain how changes in temperature and pressure affect the percentage of NH_3 in the equilibrium mixture.

Increase in temperature favour endothermic reaction.
Backward reaction is endothermic hence an increase in temperature results in a decrease in the % of NH_3.
An increase in pressure favours the reaction that produces less number of moles of gas.
Forward reaction produces less number of moles of gas and hence an increase in pressure results in an increase in the % of NH_3.

[2]

(b) Calculate the partial pressure of each gas present in the equilibrium mixture at 100 atm and 400°C.

Hence determine K_p at 400°C.

At 100 atm and 400°C, % NH_3 = 25.1

$$P_{NH_3} = 0.251 \times 100 = 25.1 \text{ atm}$$
$$P_{N_2} = \tfrac{1}{4}(1 - 0.251) \times 100 = 18.7 \text{ atm}$$
$$P_{H_2} = \tfrac{3}{4}(1 - 0.251) \times 100 = 56.2 \text{ atm}$$

$$K_p = (P_{NH3})^2 / (P_{H2})^3(P_{N2})$$
$$= 25.1^2 / (18.7 \times 56.2^3)$$
$$= 1.90 \times 10^{-4} \text{ atm}^{-2}$$

[2]

(c) Hydrogen halides show clear trends in the H–X bond energy where X = C*l*, Br and I.

(i) With reference to the *Data Booklet*, predict and explain the trend in thermal stability of the hydrogen halides from HC*l* to HI.

Down the group, H–X bond energy decreases from 431 to 299 kJ mol^{-1}.

This is due to the increasing radius of the halogen atom, which causes a poorer extent of overlap of orbitals between H and X. This leads to the H–X bond becoming longer and weaker, and hence less energy is required to break the H–X bond. Hence, thermal stability decreases from HC*l* to HI.

[2]

(ii) Hydrogen halides behave as weak acids in liquid ethanoic acid, dissociating to different extents. Write an equation to show how HX dissociates in ethanoic acid.

$$HX + CH_3CO_2H \rightleftharpoons CH_3CO_2H_2^+ + X^-$$

[1]

(iii) Rank the pK_a values of the three hydrogen halides in ethanoic acid in decreasing order. Explain your answer.

It becomes easier to dissociate HX down the group as H–X bond energy decreases. Hence HI is the strongest acid.
K_a of acids: HC*l* < HBr < HI
pK_a of acids: HC*l* > HBr > HI

[2]

(iv) Using common ion effect principle, suggest why the hydrogen halides are weaker acids in ethanoic acid than in water.

Since ethanoic acid is a stronger acid than water, it will partially dissociate into H^+ ion in aqueous state, hence, causing the position of equilibrium of $HX \rightleftharpoons H^+ + X^-$ to shift left (or suppress the dissociation of HX) by common ion effect.

[1]

[Total: 10]

S4 Petroleum or crude oil is a complex mixture of organic compounds consisting of mainly hydrocarbons, with small quantities of other organic compounds containing nitrogen, oxygen or sulfur.

In the refining of crude oil, this mixture is partly separated by fractional distillation. Long chain alkanes obtained from the fractional distillation of crude oil can be converted to the more useful shorter chain alkanes and alkenes via a process called cracking.

The information below is related to the thermal cracking of 1 mole of the alkane $C_{15}H_{32}$.

- Four products **P**, **Q**, **R** and **S** in the molar ratio 2:1:1:1 were obtained.
- **P** is ethene.
- **Q** has a relative molecular mass of 42.0.
- **R** has a relative molecular mass of 56.0 and exists as a pair of cis-trans isomers.

(a) **(i)** Suggest the structural formulae of **Q**, **R** and **S**.

Q: $CH_2=CHCH_3$
R: $CH_3CH=CHCH_3$
Number of carbon for S = 4
S: $CH_3CH_2CH_2CH_3$ or $CH(CH_3)_3$

[3]

(ii) Explain, with reference to its structure, why **R** can exist as a pair of cis–trans isomers.

R has a <u>C=C bond which resists rotation</u> and <u>two different groups attached to each alkene C</u>.

[1]

(b) The process of thermal cracking proceeds via a free radical mechanism. The following are reactions involved when propane undergoes thermal cracking.

reaction	equation
1	$CH_3CH_2CH_3 \rightarrow \bullet CH_3 + \bullet CH_2CH_3$
2	$CH_3CH_2CH_3 \rightarrow \bullet H + \bullet CH_2CH_2CH_3$
3	$\bullet CH_3 + CH_3CH_2CH_3 \rightarrow CH_4 + \bullet CH_2CH_2CH_3$
4	$\bullet CH_2CH_3 \rightarrow \bullet H + CH_2=CH_2$
5	$\bullet CH_3 + CH_2=CH_2 \rightarrow \bullet CH_2CH_2CH_3$
6	$\bullet CH_3 + \bullet CH_3 \rightarrow CH_3CH_3$
7	$2\,\bullet CH_2CH_3 \rightarrow CH_3CH_3 + CH_2=CH_2$

(i) Reactions 1 and 2 are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

Reaction 1 is more likely to occur as it is easier to break a C-C bond (350 kJ mol^{-1}) compared to a C-H bond (410 kJ mol^{-1})

[1]

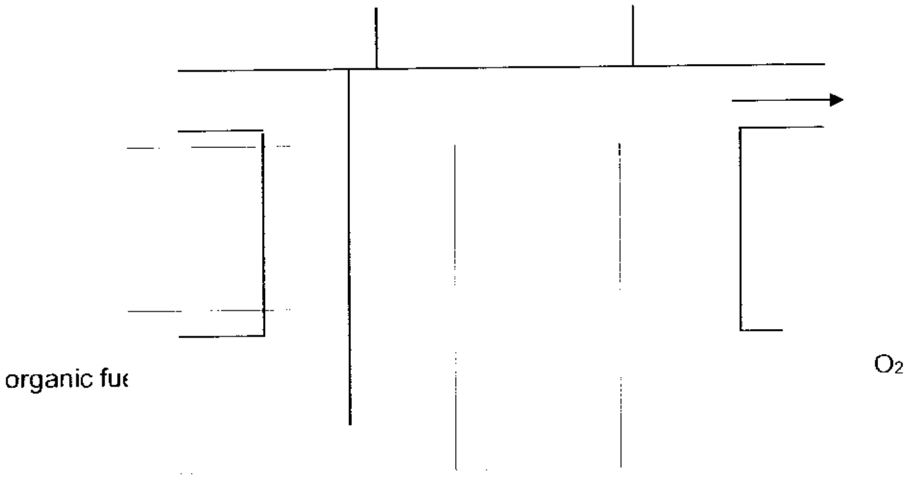
From reactions 3 to 7, identify those which may be termed propagation step the mechanism.

Which gas, if detected in the product mixture, would offer support for occurrence of both reactions (2) and (4)?

(c) rnative energy sources that are renewable and contribute less to global warr rapidly gaining in popularity as natural gas and crude oil are depleting at a fast r

an alternative energy source, direct liquid fuel cell (DLFC) is one of the leading types due to their great features of superior energy density, modest configura small size in fuel container. Commercially used liquid fuel types are prepared us hols, such as methanol or ethanol, glycol, and acids.

following diagram illustrates the parts of a typical DLFC. Organic fuel is supplie trode 1 and oxygen is supplied to electrode 2 simultaneously. The electr duced at electrode 1 pass around the external circuit to electrode 2. The prot ned from the oxidation move through the conducting polymer electrolyte trode 2, where they react with oxygen to produce water.



ile fuel cells which use organic fuel such as liquid alcohols pose no storage probl y emit carbon dioxide, thus countering the move to reduce carbon footp search was done to assess the viability of the oxidation of propan-2-ol to propan a potential organic fuel cell reaction.

Construct ion-electron equations for the reactions at electrode 1 and electrod respectively.

(ii) Hence construct the equation for the overall reaction.

$2CH_3CH(OH)CH_3 + O_2 \rightarrow 2CH_3COCH_3 + 2H_2O$

[1]

(iii) The $E^\ominus$ of the $CH_3COCH_3/CH_3CH(OH)CH_3$ electrode reaction is –0.03 V. By using suitable data from the *Data Booklet*, calculate the $E^\ominus_{cell}$ for the reaction.

$$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{ox}$$
$$= 1.23 - (-0.03)$$
$$= 1.26 \text{ V}$$

[2]

(iv) State how $E^\ominus_{cell}$ and $\Delta G^\ominus_{cell}$ will change when twice the amount of the reactants as given in the overall reaction in **(c)(ii)** is used for the reaction.

No change to $E^\ominus_{cell}$
$\Delta G^\ominus_{cell}$ is doubled

[1]

(v) Pyrogallol solution is an organic compound that absorbs oxygen efficiently.

Explain qualitatively the change in the overall E_{cell} value measured when the electrodes are contaminated with pyrogallol solution.

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$
When a small amount of pyrogallol solution is added, it decreases the partial pressure of O_2. Hence equilibrium above will shift to the left to increase partial pressure of O_2.
$E^\ominus_{red}$ will be less positive and hence overall $E^\ominus_{cell}$ value will be less positive.

[2]

[Total: 15]

5 (a) Sulfur dichloride, SCl_2, is a cherry-red liquid at room temperature and pressure. It is formed from S_8 and Cl_2.

(i) The formation of SCl_2 from S_8 and Cl_2 takes place in two steps. The first step involves the formation of disulfur dichloride, S_2Cl_2, as an intermediate.

$$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$$

Write an equation to represent the second step.

$S_2Cl_2 + Cl_2 \rightarrow 2SCl_2$

[1]

Some chemists speculate that the intermediate is not S_2Cl_2 but **K**. **K** shares the same elemental mass percentages as sulfur dichloride, SCl_2 but it has a molar mass of 206.2 g mol^{-1} instead.

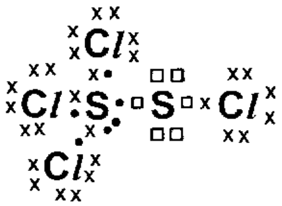
(ii) State the molecular formula of **K**.

S_2Cl_4

[1]

(iii) The following is known about the structure of **K**:
- There is more than one central atom present.
- All the central atoms are sulfur atoms and possess at least one lone pair
- The shape about each central atom is different.

Draw a dot-and-cross diagram for **K**.



[1]

(b) Compounds **C** and **D** are chlorides of Period 3 elements. Both **C** and **D** exist in the solid state at room temperature.

When excess water was added to a sample containing 0.100 mol of **C**, an acidic solution was obtained. The resulting solution required 0.500 mol of silver nitrate for complete precipitation.

On the other hand, when excess water was added to a sample containing 0.100 mol of **D**, a neutral solution was obtained.

(i) Identify compounds **C** and **D**.

C is PCl_5 and D is NaC*l*

[2]

(ii) Explain, with the aid of equations, the difference in the pH of the solutions obtained when water is added to **C** and **D**.

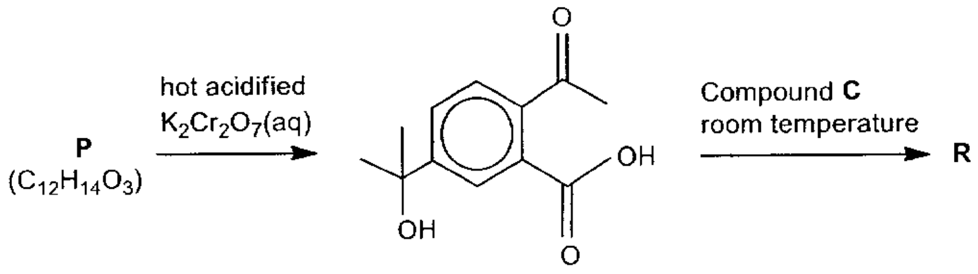
C (PCl_5) has vacant 3d orbitals on phosphorus. Hence, it undergoes hydrolysis when water is added:
$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$
H_3PO_4 and HC*l* formed cause the solution to be acidic.

D (NaC*l*) undergoes only hydration [OR $NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$]
This is due to Na^+ having low charge density.
Since there is no hydrolysis, the solution remains neutral.

[2]

(c) Compound **C** is commonly used as a reagent in organic chemistry reactions.

(i) Consider the scheme below which involves **C** in one of the steps:

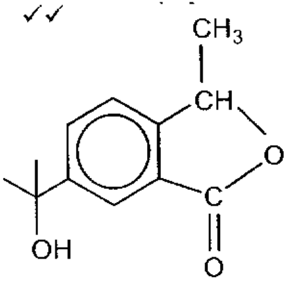


Q ($C_{12}H_{14}O_4$)

P does not react with sodium carbonate or Brady's reagent.

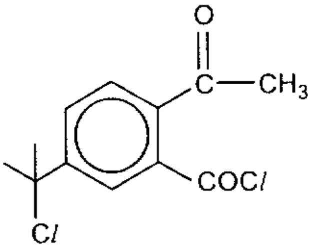
Suggest structures for **P** and **R**.

✓✓



P

✓✓

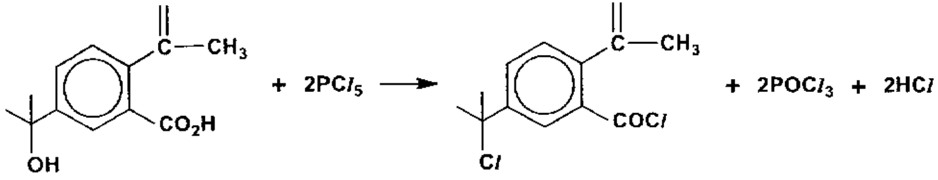


R

[2]

(ii) Write a balanced equation for the reaction between **Q** and **C** to form **R**.

✓✓



[1]

(d) [Use of the *Data Booklet* is relevant to this part of the question].

Compound **Q** is a solid which can be neutralised by aqueous NaOH. An experiment was carried out to determine the enthalpy change of the reaction. 5.00 g of **Q** was added to 40.0 cm^3 of 0.800 mol dm^{-3} NaOH(aq) in a Styrofoam cup and the reaction mixture was stirred. The temperature rose from 25.0°C to 31.2°C.

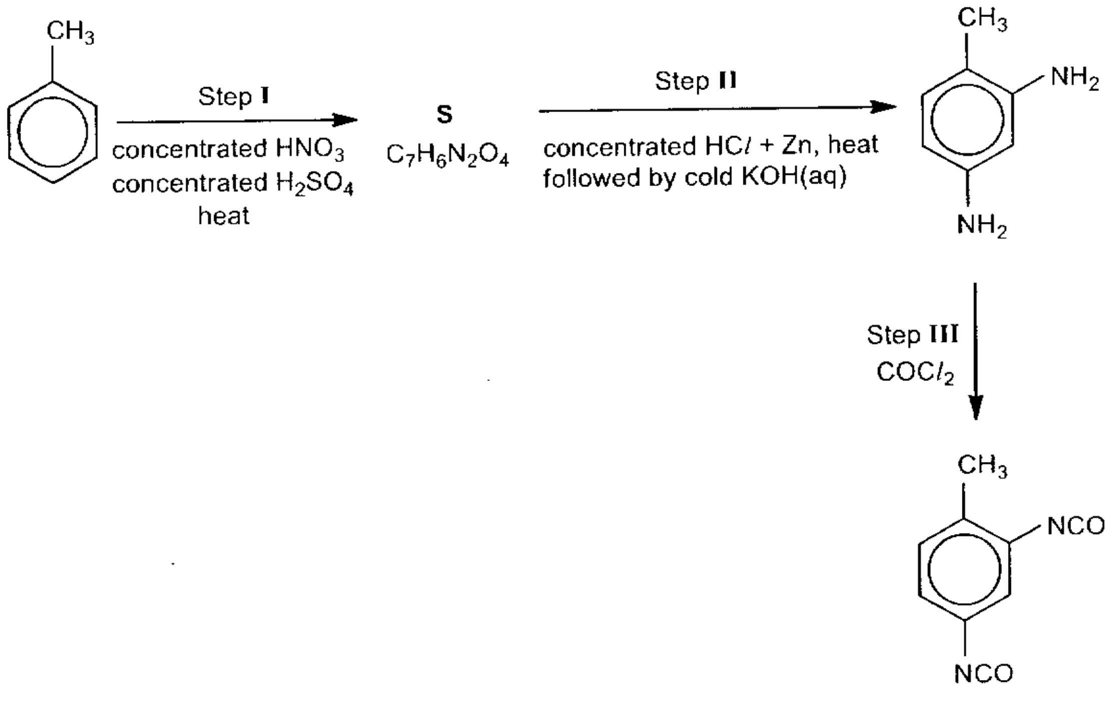
Determine the enthalpy change per mole of water formed in the reaction.

Heat evolved = $40.0 \times (31.2 - 25.0) \times 4.18 = 1036$ J = 1.036 kJ
$RCO_2H(s) + NaOH(aq) \rightarrow RCO_2^-Na^+(aq) + H_2O(l)$
Initial $n_Q = 5 / 222.0 = 0.02252$ mol
Initial $n_{NaOH} = (40.0 / 1000) \times 0.800 = 0.0320$ mol
Hence, Q is the limiting reagent.
$n_{water} = 0.02252$ mol
$\Delta H_{reaction} = -1.036 / 0.02252 = -46.0$ kJ mol^{-1}

[2]
[Total: 12]

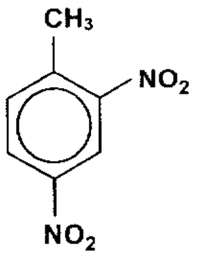
6 **(a)** Compounds containing the isocyanate functional group, –NCO, are important industrial chemicals. They react with alcohols to produce polyurethane polymers, which are components of polyurethane foams, thermoplastic elastomers and polyurethane paints.

Shown below is the synthesis of a diisocyanate from methylbenzene:



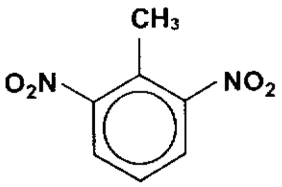
a diisocyanate

(i) Draw the structure of **S**.



[1]

(ii) A number of isomers of **S** is formed in step **I** as side-products. Draw the structure of the side-product formed in the greatest proportion.



[1]

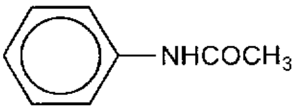
(iii) State the type of hybridisation exhibited by the carbon in the –NCO group and draw the hybrid orbitals around this carbon, showing clearly their shape and alignment.

sp hybridisation

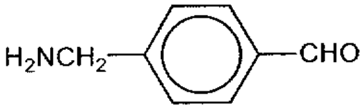
correct shape of orbital
orbitals linearly aligned

[2]

(b) The structures of two organic nitrogen compounds, **T** and **U**, are given below:



T



U

Both compounds exist as solids at room temperature and pressure. They have different basic strengths, which cause them to have different solubility in an aqueous acid solution such as HC*l*(aq).

(i) Which compound, **T** or **U**, is the stronger base? Explain your answer.

U is the stronger base. In T, the lone pair on N is delocalised into the –CO– group (OR into the benzene ring). Hence, lone pair on T is less available for donation to a proton.

[2]

(ii) **T** and **U** are found mixed together in a sample.

By considering your answer in **(b)(i)**, outline briefly a simple method that allows you to separate the two compounds and recover them in their original solid forms. Your method should only make use of normal chemicals and apparatus found in a school laboratory.

Dissolve the mixture completely in aqueous HC*l* (OR H_2SO_4 OR HNO_3).
Filter the mixture. Solid T is found in the residue while U is found in the filtrate in the protonated form.
Add excess aq NaOH to the filtrate to reform U in the solid state.
Filter the mixture to recover U as the residue.

[2]

(c) In the study of the structure of a polypeptide **A**, it was digested using two different enzymes. The fragments obtained were separated using electrophoresis. Analysis of the fragments from each digestion gave the following results:

digestion using the first enzyme	digestion using the second enzyme
his-phe-gly ser-pro-glu asp-gly thr-phe-leu	gly-asp-gly-thr pro-glu phe-leu-ser his-phe

Deduce the sequence of amino acids in the polypeptide **A**.

Overlapping the fragments, we have:
his-phe-gly
his-phe gly-asp-gly-thr
asp-gly thr-phe-leu
phe-leu-ser
ser-pro-glu
pro-glu

Complete sequence is his–phe–gly–asp–gly–thr–phe–leu–ser–pro–glu

[2]

(d) The structure of a certain tripeptide is given below:

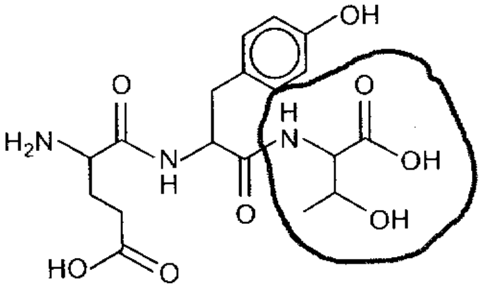


Figure 6.1

It is formed from the amino acids **W**, **X** and **Y**.

Table 6.1 shows the pK_a values of the different functional groups present in each amino acid.

Table 6.1

amino acid	pK_a of α–carboxyl group	pK_a of α–amino group	pK_a of side–chain
W	2.09	9.10	–
X	2.20	9.11	10.07
Y	2.19	9.67	4.25

W and **X** exist mainly as zwitterions at pH 7.0 but **Y** does not.
W rotates plane-polarised light and can exist as four possible stereoisomers.

(i) Circle on Figure 6.1 the part of the tripeptide that originates from **W**.

See Figure 6.1

[Reason: The amino acid that corresponds to the circled part has two chiral centres, hence giving rise to 4 stereoisomers.
It also has a neutral side-chain, which hence does not have a pK_a value.]

[1]

(ii) State what is meant by the term *zwitterion*.

Zwitterion has both positively and negatively charged groups within the same molecule and is electrically neutral.

[1]

(iii) Suggest a pH at which the predominant species of **Y** is a zwitterion using the information in Table 6.1.

3.0 (accept any value between 2.19 and 4.25)

[1]

[Total: 13]