NATIONAL JUNIOR COLLEGE
SH2 PRELIMINARY EXAMINATION
Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

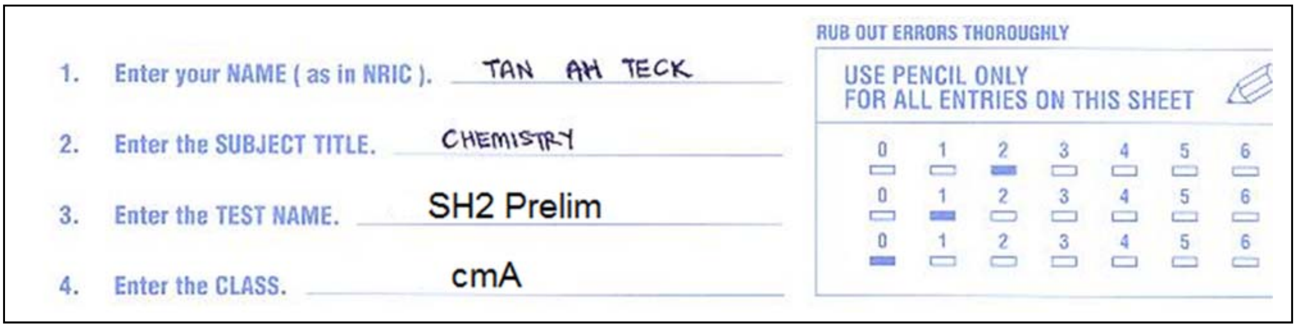
CHEMISTRY
Paper 1 Multiple Choice
Additional Materials: Optical Answer Sheet
Data Booklet

9729/01
Thur 13 September 2018
1 hour

READ THESE INSTRUCTIONS FIRST
Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name, subject class and registration number on the Answer Sheet in the spaces provided unless this has been done for you.
There are **30** 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 paper consists of **17** printed pages

Instructions on how to fill in the Optical Mark Sheet



1. Enter your NAME (as in NRIC). TAN AH TECK
2. Enter the SUBJECT TITLE. CHEMISTRY
3. Enter the TEST NAME. SH2 Prelim
4. Enter the CLASS. cmA

RUB OUT ERRORS THOROUGHLY

USE PENCIL ONLY
FOR ALL ENTRIES ON THIS SHEET

0 ☐	1 ☐	2 ●	3 ☐	4 ☐	5 ☐	6 ☐
0 ☐	1 ●	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐
0 ●	1 ☐	2 ☐	3 ☐	4 ☐	5 ☐	6 ☐

Student	Examples of Registration No.	Shade:
	1705648	75648

Example:

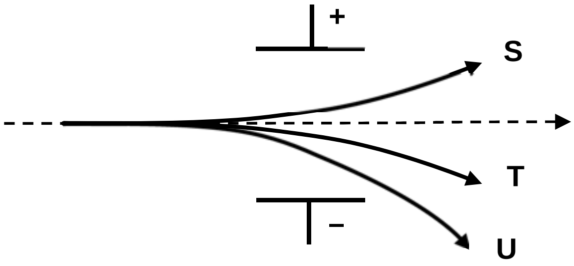
Shade the index number in a 5 digit format on the optical mark sheet:

2nd digit and the last 4 digits of the Registration Number.

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 following are flight paths of charged particles when accelerated in an electric field.



Which correctly identifies **S**, **T** and **U**?

	S	T	U
A	$^{15}O^{+}$	$^{14}C^{+}$	$^{14}N^{+}$
B	$^{15}O^{-}$	$^{15}O^{+}$	$^{28}Si^{+}$
C	$^{14}N^{-}$	$^{28}Si^{2+}$	$^{14}C^{2+}$
D	$^{14}N^{-}$	$^{14}C^{+}$	$^{28}Si^{2+}$

2 In which sequence is the molecules listed in the order of increasing dipole moment?

A SO_3, CO_2, $AlCl_3$

B H_2O, H_2S, HBr

C CF_4, CO, HF

D NH_3, HF, $BeCl_2$

3 In which row are the molecules arranged in order of increasing bond angle?

1 CH_4, $AlCl_3$, XeF_2

2 H_2S, PH_3, NH_3,

3 NF_3 , NCl_3, SO_3

A 1, 2 and 3

B 1 and 2

C 2 and 3

D 1 only

4 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$\underset{\text{propadiene}}{H_2C{=}C{=}CH_2} \rightleftharpoons \underset{\text{propyne}}{CH_3C{\equiv}CH}$$

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by s – sp overlap

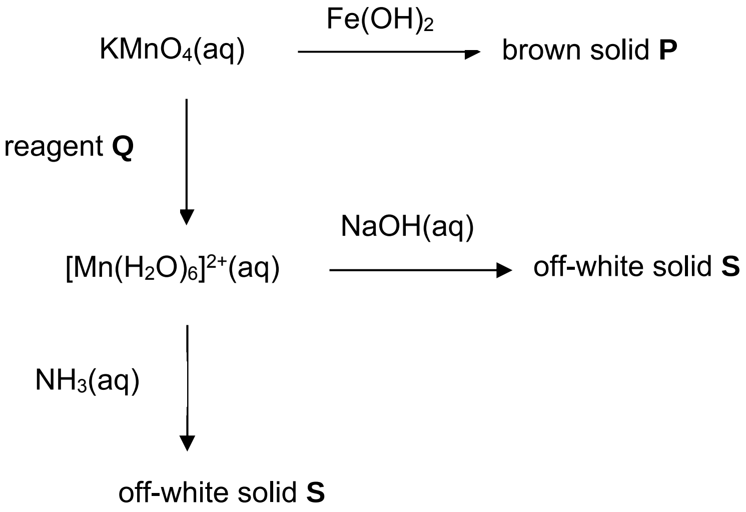
B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap

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

A reaction scheme regarding manganese compounds is shown below.



Which statements are true?

1 Off-white solid **S** is able to dissolve in excess of $NH_3(aq)$.
2 Manganese in brown solid **P** has an oxidation state of +4.
3 Reagent **Q** can be acidified $[V(H_2O)_6]^{3+}(aq)$.
4 Off white solid **S** turns brown upon standing.

A	1, 2 and 4	**B**	2, 3 and 4
C	2 and 3	**D**	All correct

6 In which chemical reaction does the transition metal compound or element behave as the described catalyst?

	Reaction	Catalyst
1	Formation of ethanal from ethanol, using acidified potassium dichromate	Homogeneous
2	Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide	Heterogeneous
3	Chlorination of benzene, using chlorine and iron(III) chloride	Homogeneous
4	Removal of air pollutants in exhaust systems of cars, using nickel	Heterogeneous

A 1, 2 and 4

B 2 and 3

C 3 and 4

D 2, 3 and 4

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

Given the following standard enthalpy changes,

	ΔH /kJ mol^{-1}
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	−75

What is the standard enthalpy change of atomisation of graphite?

A +693 kJ mol^{-1}

B +1129 kJ mol^{-1}

C −2151 kJ mol^{-1}

D −2587 kJ mol^{-1}

8 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta H^{\ominus} = -176 \text{ kJ mol}^{-1}$$

The magnitude of standard entropy change of this reaction is 284 J K^{-1} mol^{-1}.

Which statements are correct?

1 $\Delta G^{\ominus} = -261$ kJ mol^{-1}.

2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

3 There is an increase in order as strong hydrogen bonding between NH_3 and HCl hold the particles in NH_4Cl in fixed positions and close to each other.

A 1 only

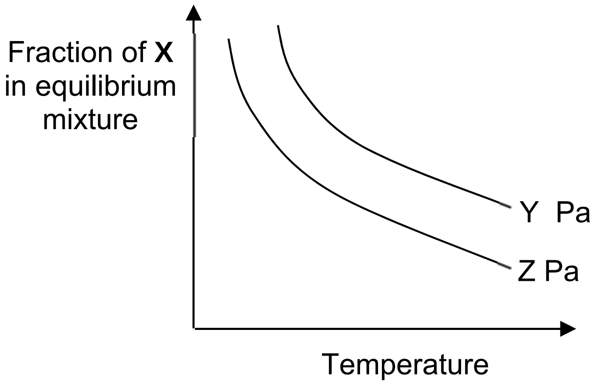
B 1 and 2

C 2 only

D 2 and 3

9 The graph below shows how the fraction of **X**, which represents one of the following compounds in the given equilibrium mixture, varies with temperature at pressures of Y Pa and Z Pa.

$$4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g) \qquad \Delta H = -1267 \text{ kJ mol}^{-1}$$



Identify **X** and the correct relative magnitudes of Y and Z.

	X	**Pressure**
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

10 One of the key production stages in the Contact Process is the production of sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

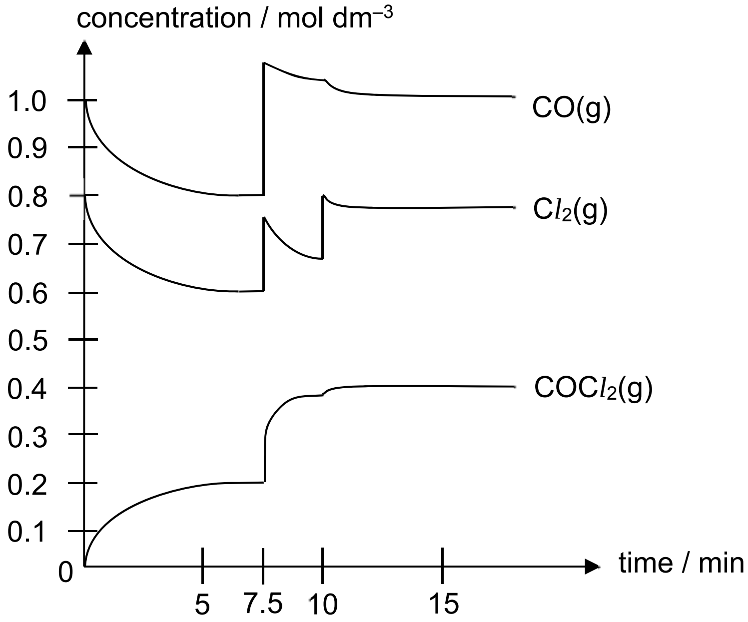
The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to k_1, k_{-1} and K_c if the temperature of the reaction is increased?

	k_1	k_{-1}	K_c
A	increase	increase	increase
B	increase	decrease	increase
C	decrease	increase	decrease
D	increase	increase	decrease

11 The reaction between carbon monoxide and chlorine was studied in an experiment by mixing the two gases and changing the reaction conditions inside the reaction vessel at different times during the experiment. The concentrations of the gases in the vessel were followed with time, and the following graph is obtained.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H^{\ominus} = -113.4\ \text{kJ mol}^{-1}$$



Which conclusion deduced from the graph is **incorrect**?

A The rate of forward reaction equals the rate of backward reaction at 7 min.

B The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.

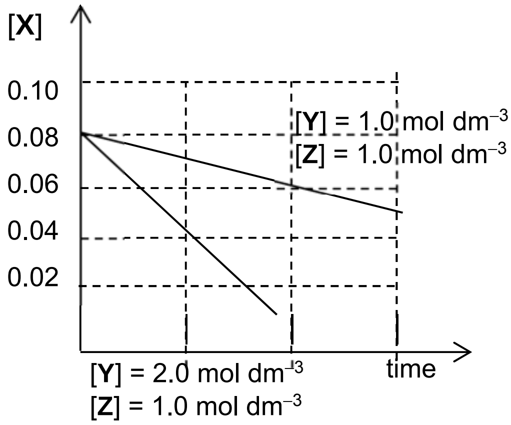
C The equilibrium constant, K_c, for the system when determined at 7 min is 0.417 mol^{-1} dm^3.

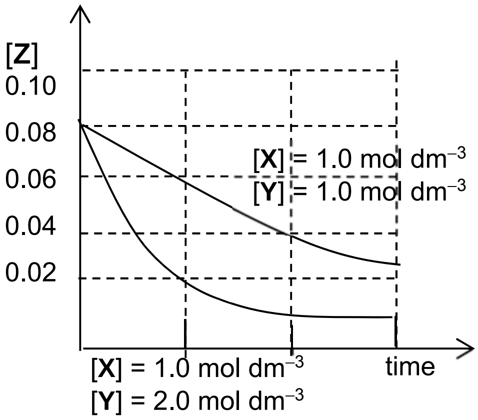
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

12 Substances **X**, **Y** and **Z** react according to the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) + \mathbf{Z}(aq) \rightarrow 2\mathbf{W}(aq) + \mathbf{U}(aq)$$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied while the other two were kept constant. The results are shown below.





Which rate equations represent the experimental results?

A rate = k[**Y**]^2

B rate = k[**Y**][**Z**]

C rate = k[**Y**]^2[**Z**]

D rate = k[**X**][**Y**][**Z**]

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

The reaction of acidified aqueous potassium iodide with hydrogen peroxide is represented by the following equation.

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Which statements about the reaction are true?

1 E^θ_{cell} = +1.23 V.

2 E_{cell} becomes more negative when Br_2(aq) is added to the anode.

3 E_{cell} becomes more positive when a few drops of $AgNO_3$(aq) is added to the anode.

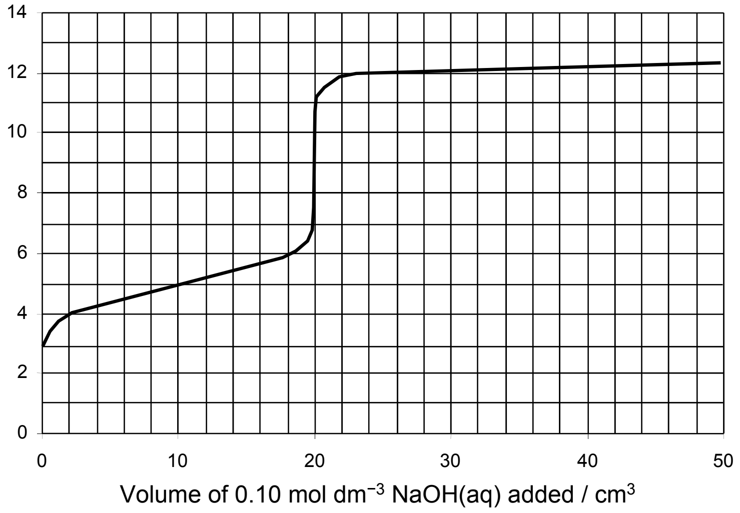
A 1 only

B 1 and 2

C 2 and 3

D 1, 2 and 3

14 The titration curve below shows the reaction between a monoprotic acid, **HX**, and aqueous sodium hydroxide.



Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Methyl red	red to yellow	4.2 – 6.3
Bromothylmol blue	yellow to blue	6.0 – 7.6
Thymolpthalein	colourless to blue	8.3 – 10.5

What statements are correct?

1 Methyl red will indicate an endpoint at a value lower than 20.0 cm^3.

2 K_a value of HX is 1.0×10^{-5}

3 Buffer at maximum buffer capacity is formed at 25.0 cm^3 since the pH change in that region is relatively constant.

4 Alkaline hydrolysis of salt takes place after the equivalence point accounting for the alkaline pH value of the reaction mixture.

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

15 Given the following data,

K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Reaction mixture **X**:
25.0 cm^3 of 2.0×10^{-5} mol dm^{-3} CH_3COOH and 25.0 cm^3 water

Reaction mixture **Y**:
25.0 cm^3 of 0.02 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.01 mol dm^{-3} NaOH

Reaction mixture **Z**:
25.0 cm^3 of 0.01 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.02 mol dm^{-3} NaOH

Which is the correct order of pH values of the above reaction mixture?

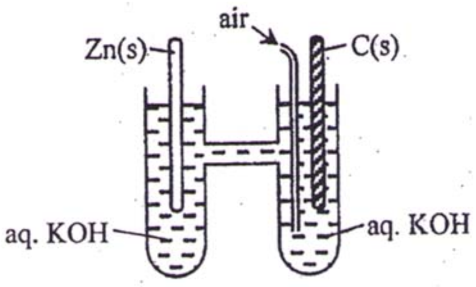
A **Z** > **Y** > **X**

B **Z** > **X** > **Y**

C **Y** > **X** > **Z**

D **X** > **Y** > **Z**

16 A cell is constructed with zinc and carbon electrodes, each weighing 50 g, partly immersed in aqueous KOH.



When connected in a circuit, some zinc passes into solution as zincate(II) ions, $ZnO_2^{2-}(aq)$. The cell delivers a current of 1.68×10^{-2} A. The zinc electrode is replaced once 60% of it is used up.

What is the time taken, in seconds, before replacement of zinc electrode becomes necessary?

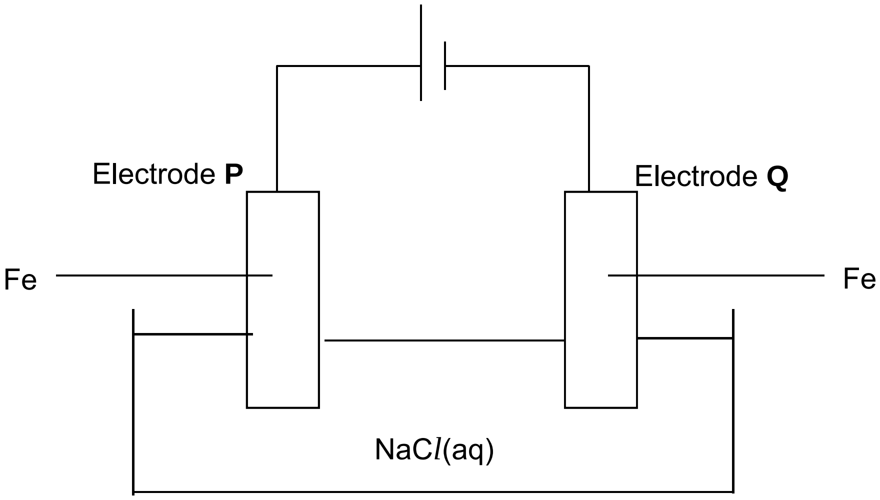
A 2.63×10^6

B 4.39×10^6

C 5.27×10^6

D 8.78×10^6

17 An experiment is set up as shown below to study the corrosion of iron.



What will occur at electrodes **P** and **Q**?

	Electrode **P**	Electrode **Q**
A	No corrosion of Fe	Corrosion of Fe ; H_2 gas evolved
B	No corrosion of Fe	Corrosion of Fe ; O_2 gas evolved
C	Corrosion of Fe	No corrosion of Fe ; Na deposited
D	Corrosion of Fe	No corrosion of Fe ; H_2 gas evolved

18 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been replaced by safer options such as the standard hydrogen electrode (S.H.E.).

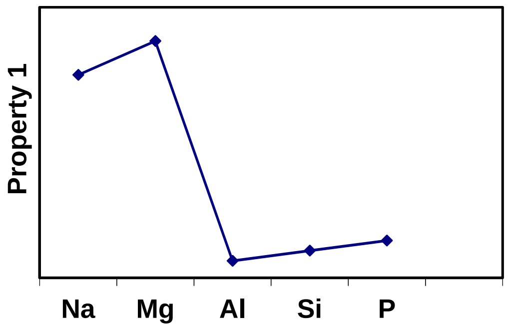
Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

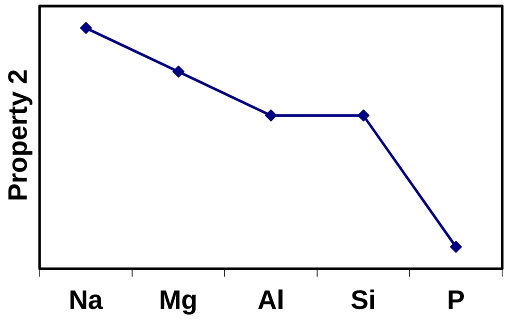
When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V **B** +1.30 V **C** –1.79 V **D** –2.82 V

19 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.





Which correctly describes properties 1 and 2?

	Property 1	**Property 2**
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the chlorides at the highest oxidation states	pH of the oxides when added to water
C	melting point of the oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the chlorides at the highest oxidation states when added to water

20 What mass of sodium ethanedioate, $Na_2C_2O_4$, should be added to 250 cm^3 of a 2.2×10^{-3} mol dm^{-3} solution of calcium nitrate before a precipitate is formed?
[K_{sp} of $CaC_2O_4 = 2.27 \times 10^{-9}$ mol^2 dm^{-6}]

A 3.5×10^{-5} g

B 1.0×10^{-6} g

C 2.5×10^{-7} g

D 2.3×10^{-9} g

21 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

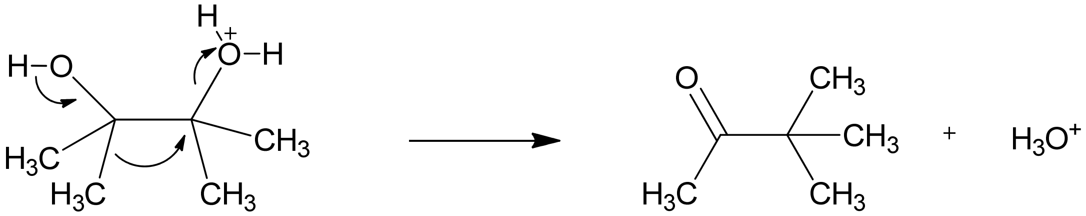
A It can be formed by the reduction of $C_6H_5CH_2CN$.

B It reacts with CH_3CO_2H to form $C_6H_5CH_2NHCOCH_3$.

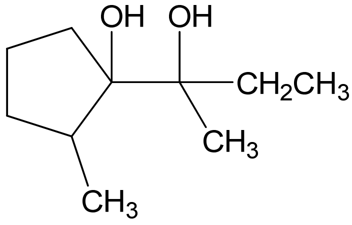
C It is formed by the reaction between $C_6H_5NO_2$ and tin in concentrated HCl, followed by NaOH.

D It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

22 When a 1,2–diol is treated with a dilute acid, the protonated diol undergoes the following pinacol rearrangement.

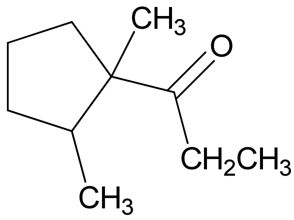


Which structure is **not** formed when diol **Z** undergoes pinacol rearrangement?

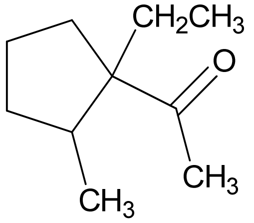


diol **Z**

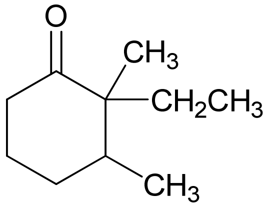
A



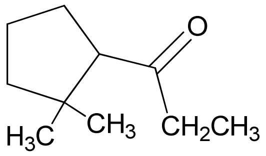
B



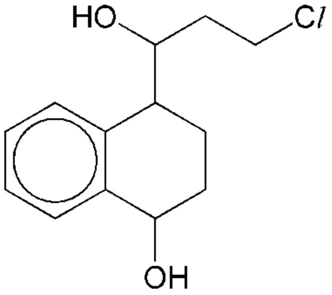
C



D



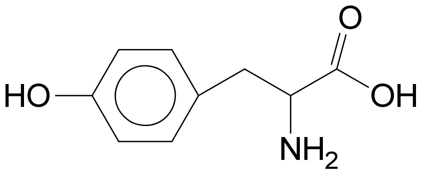
23 What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H_2SO_4?



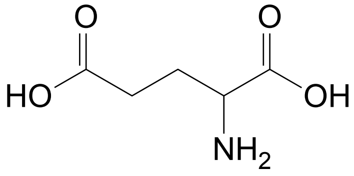
A 2 **B** 4 **C** 6 **D** 8

24 Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species move towards the anode.

With a buffer at pH 4, which statement is true?



Tyrosine (pI = 5.7)



Glutamic acid (pI = 3.2)

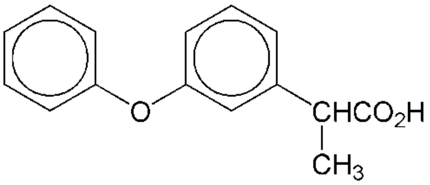
A Both species move towards the anode

B Both species move towards the cathode.

C Tyrosine moves towards the anode, glutamic acid moves towards the cathode.

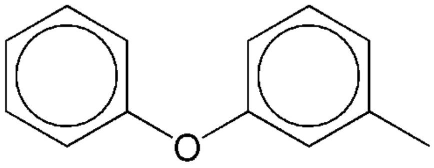
D Tyrosine moves towards the cathode, glutamic acid moves towards the anode.

25 *Fenoprofen* is an anti-arthritic agent.



Which of the following could be part of a reaction sequence for synthesising *Fenoprofen*?

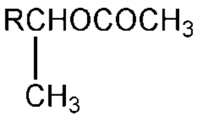
In the sequences below, R =



A $RCHBrCH_3 \xrightarrow[\text{heat}]{\text{NaCN(ethanolic)}} \text{Intermediate} \xrightarrow[\text{heat}]{H^+(aq)}$ *Fenoprofen*

B $RCH(CH_3)_2 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

C



$RCH(CH_3)OCOCH_3 \xrightarrow[\text{warm}]{I_2,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

D $RCH(OH)CH_3 \xrightarrow[\text{heat}]{KMnO_4,\ OH^-(aq)} \text{Intermediate} \xrightarrow{H^+(aq)}$ *Fenoprofen*

26 Chlorofluorocarbons (CFCs) are commonly used as aerosols, propellants and refrigerants. However in the stratosphere, CFCs can damage the ozone layer through a radical chain reaction.

In which sequence are the following compounds listed in increasing order of their ability to destroy ozone?

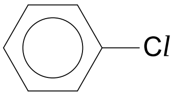
A $CHClFCClF_2 < CCl_2FCCl_2F < CHClF_2$

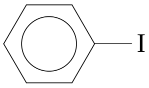
B $CCl_2FCCl_2F < CHClF_2 < CHClFCClF_2$

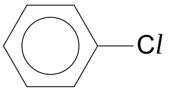
C $CHClF_2 < CCl_2FCCl_2F < CHClFCClF_2$

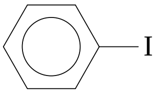
D $CHClF_2 < CHClFCClF_2 < CCl_2FCCl_2F$

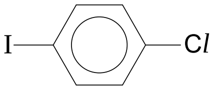
27 Which is the product formed when benzene reacts with iodine chloride, ICl in the presence of a suitable catalyst?

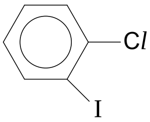
A 

B 

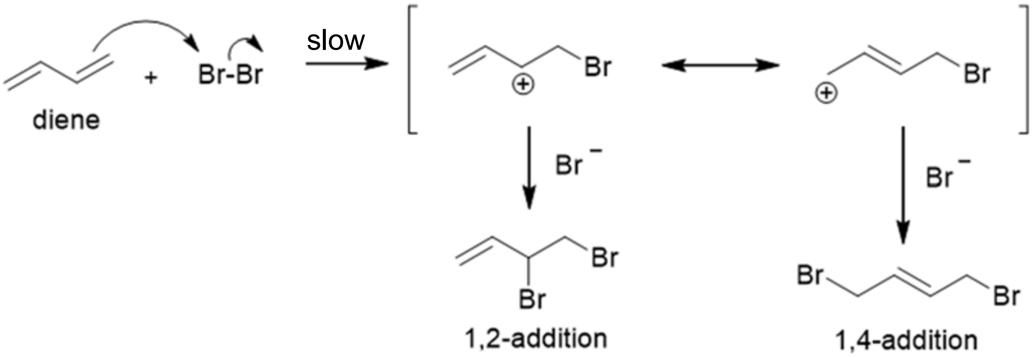
C a mixture of 

and 

D a mixture of 

and 

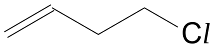
28 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.



Which statement is **not** correct?

A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HCl is used is 

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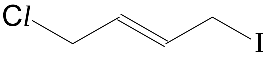
D The 1,4–addition product formed when ICl is used is 

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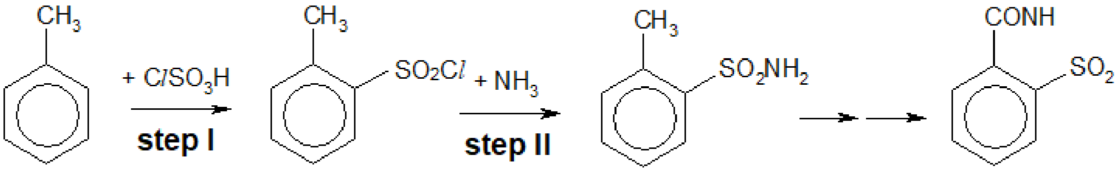
29 Saccharin is an artificial sweetening agent used in some soft drinks and is manufactured from methylbenzene through a four-step synthesis. Part of the reaction scheme is shown below.



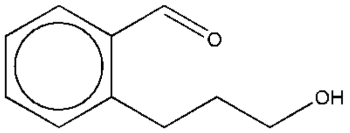
What type of reaction do steps **I** and **II** illustrate?

	Step I	**Step II**
A	Electrophilic addition	Nucleophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

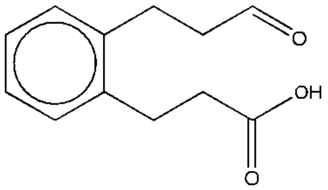
30 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 respectively but a negative result when treated with alkaline Cu(II) complex.

What could **X** be?

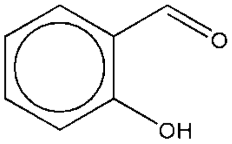
A



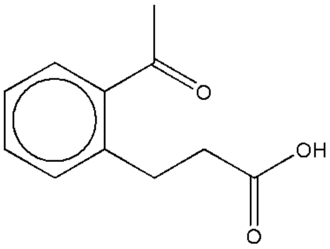
B



C



D

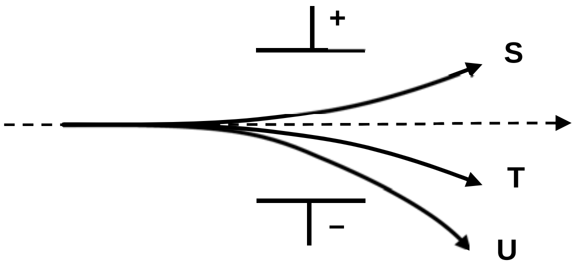


END of PAPER

NJC 2018 SH2 H2 Chemistry Paper 1 Solutions:

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

The following are flight paths of charged particles when accelerated in an electric field.



Which correctly identifies **S**, **T** and **U**?

	S	T	U
A	$^{15}O^+$	$^{14}C^+$	$^{14}N^+$
B	$^{15}O^-$	$^{15}O^+$	$^{28}Si^+$
C	$^{14}N^-$	$^{28}Si^{2+}$	$^{14}C^{2+}$
D	$^{14}N^-$	$^{14}C^+$	$^{28}Si^{2+}$

C: Negatively charged ions attracted to positive plate, positive ions to negative plate.

particles	$^{14}N^-$	$^{14}C^{2+}$	$^{14}C^+$	$^{28}Si^{2+}$
Charge /mass	1/14	2/14 = 1/7	1/14	2/28 = 1/14

Since angle of deflection is charge/mass ratio, **S** and **T** have roughly the same angle of deflection but different polarity, while **U** has almost double the angle of deflection as **T**.

2 In which sequence is the molecules listed in the order of increasing dipole m

A SO_3, CO_2, $AlCl_3$

All non-polar. Dipole moments cancel out due to shape of molecule.

B H_2O, H_2S, HBr

H_2O and H_2S have bent shape. **H_2O is more polar than H_2S** as O is more electronegative than S.

C CF_4, CO, HF

CF_4 is non-polar, dipole moments cancel out due to tetrahedral shape of molecule.

CO and HF are linear. HF is more polar than CO, as electronegativity difference is greater between H and F than between C and O.

D NH_3, HF, $BeCl_2$

NH_3 and HF are polar but $BeCl_2$ is non-polar, dipole moments cancel out due to linear shape of molecule.

3 In which row are the molecules arranged in order of increasing bond angle?

1 CH_4, $AlCl_3$, XeF_2

CH_4 (tetrahedral, 109 degrees)
$AlCl_3$ (trigonal planar, 120 degrees)
XeF_2 (linear, 180 degrees)

2 H_2S, PH_3, NH_3,

H_2S (tetrahedral, 109 degrees)
PH_3 and NH_3 (trigonal pyramidal, around 107 degrees)
NH_3 has a larger bond angle than PH_3 as

1) N is more electronegative than P, N pulls electron density of bond pairs more towards itself, leading to greater bond-pair bond-pair repulsion.
2) N has a smaller lone pair region than P (N is above P in group 15). Lone-pair bond-pair repulsion is smaller, leading to a larger bond angle.

3 NF_3 , NCl_3, SO_3

NF_3 , NCl_3 (trigonal pyramidal, around 107 degrees)
NF_3 has a smaller bond angle than NCl_3. F is more electronegative than N and N is more electronegative than Cl). F pulls electron density of bond pairs more towards itself/ away from central N atom, leading to smaller bond-pair bond-pair repulsion.
SO_3 (trigonal planar, 120 degrees)

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

4 Propadiene and propyne both have the same molecular formula, C_3H_4. They exist in equilibrium as shown:

$$\underset{\text{propadiene}}{H_2C{=}C{=}CH_2} \rightleftharpoons \underset{\text{propyne}}{CH_3C{\equiv}CH}$$

Which bond is present in propadiene but **not** present in propyne?

A a σ bond formed by s – sp overlap

B a π bond formed by p – p overlap

C a σ bond formed by sp – sp^2 overlap

D a σ bond formed by sp^2 – sp^2 overlap

propadiene hybridisation: $H_2C{=}C{=}CH_2$
sp^2 sp sp^2

propyne hybridisation: $CH_3C{\equiv}CH$
sp^3 sp sp

A a σ bond formed by s – sp overlap: in propyne **$CH_3C\equiv C–H$**, not in propadiene

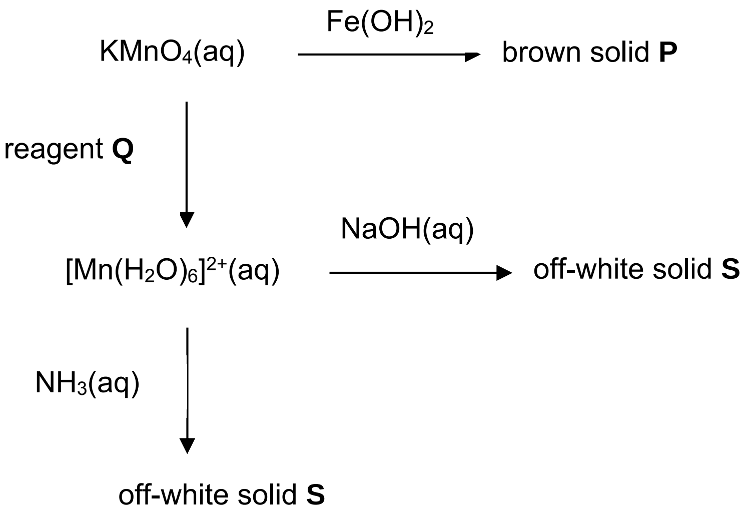
B a π bond formed by p – p overlap: present in both molecules

C a σ bond formed by sp – sp^2 overlap: in propadiene H_2**C=C**$=CH_2$, not in propyne

D a σ bond formed by sp^2 – sp^2 overlap :absent in both

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

A reaction scheme regarding manganese compounds is shown below.



Which statements are true?

1 Off-white solid **S** is able to dissolve in excess of NH_3(aq).
2 Manganese in brown solid **P** has an oxidation state of +4.
3 Reagent **Q** can be acidified $[V(H_2O)_6]^{3+}$(aq).
4 Off white solid **S** turns brown upon standing.

A 1, 2 and 4
B 2, 3 and 4
C 2 and 3
D All correct

1 off-white solid S is $Mn(OH)_2$. It is insoluble in excess of NH_3(aq). *Check Data Booklet.*

2 Brown solid P is MnO_2. Oxidation state of Mn in MnO_2 is +4. $KMnO_4$(aq) oxidises $Fe(OH)_2$, itself is reduced to MnO_2.
3 Reagent Q can be acidified $[V(H_2O)_6]^{3+}$ as the $E_{cell} > 0$.

(E_{cell} = (+1.52) + (- 0.34) = +1.18V)

4 off-white solid S turns brown upon standing. *Check Data Booklet.* $Mn(OH)_2$ is further oxidised by air.

6 In which chemical reaction does the transition metal compound or element behave as the described catalyst?

	Reaction	Catalyst
1	Formation of ethanal from ethanol, using acidified potassium dichromate $K_2Cr_2O_7$ is an oxidising agent, not a catalyst.	Homogeneous
2	Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide $Fe(OH)_3$ is a solid catalyst used in the decomposition of hydrogen peroxide, due to the slow rate of reaction.	Heterogeneous
3	Chlorination of benzene, using chlorine and iron(III) chloride $FeCl_3$ is a catalyst as well as a halogen carrier, is regenerated in the last step of the electrophilic substitution.	Homogeneous
4	Removal of air pollutants in exhaust systems of cars, using nickel Nickel is a catalyst in the catalytic converter and is in solid phase, a different phase from the gaseous reactant	Heterogeneous

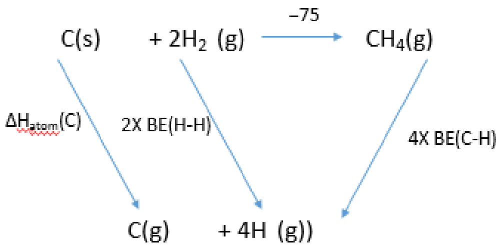
A 1, 2 and 4 **B** 2 and 3

C 3 and 4 **D** 2, 3 and 4

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

Given the following standard enthalpy changes,

	ΔH /kJ mol^{-1}
$C(graphite) + 2H_2(g) \rightarrow CH_4(g)$	−75



a + (2 x436) − (4x 410) = −75

a = +693 kJ mol^{-1}

What is the standard enthalpy change of atomisation of graphite?

A +693 kJ mol^{-1}

B +1129 kJ mol^{-1}

C −2151 kJ mol^{-1}

D −2587 kJ mol^{-1}

8 Ammonia gas and hydrogen chloride gas react to form ammonium chloride as shown in the equation below:

$$NH_3(g) \quad + \quad HCl(g) \quad \rightarrow \quad NH_4Cl(s) \qquad\qquad \Delta H^{\ominus} = -176 \text{ kJ mol}^{-1}$$

The magnitude of standard entropy change of this reaction is 284 J K^{-1} mol^{-1}.

Which statements are correct?

1 $\Delta G^{\ominus} = -261$ kJ mol^{-1}.

No of mol of gas decreases => $\Delta S^{\ominus} = -284$ J K^{-1} mol^{-1}
$\Delta G^{\ominus} = -176 - 298\,(-0.284) = -91.4$ kJ mol^{-1}.

2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

Crossover temperature occurs when $\Delta G^{\ominus} = 0$
$\Delta H^{\ominus} = T\Delta S^{\ominus}$
T = -176000/ -284 = 620K

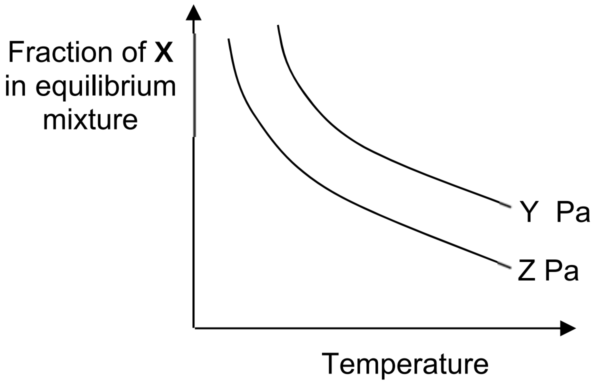
3 There is an increase in order as strong hydrogen bonding between NH_3 and HC*l* hold the particles in NH_4Cl in fixed positions and close to each other.

NH_4Cl is ionic lattice with strong ionic bonds between NH_4^+ and Cl^-, not strong H bonding between the NH_3 and HC*l* molecules.

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

9 The graph below shows how the fraction of X, which represents one of the following compounds in the given equilibrium mixture, varies with temperature at pressures of Y Pa and Z Pa.

$$4NH3(g) + 3O2(g) \rightleftharpoons 2N2(g) + 6H2O(g) \qquad \Delta H = -1267 \text{ kJ mol}-1$$



Identify X and the correct relative magnitudes of Y and Z.

	X	Pressure
A	N_2	Z > Y
B	O_2	Y > Z
C	H_2O	Y > Z
D	NH_3	Z > Y

Shape of graph:

(i) As temperature increase, fraction of X decrease.

(ii) As temperature increase, as forward reaction is exothermic, fraction of product should decrease.

Matching (i) and (ii): X should be the product of the reaction => either N_2 or H_2O.

Comparison of the two graphs:

(i) 7 mol of gaseous reactants vs 8 mol of gaseous products => decrease pressure will favour the forward reaction, to partially increase pressure.

(ii) Decrease pressure increase the fraction of X (since X is the product)

Matching (i) and (ii): Fraction of X is higher for Y Pa than Z Pa (Y Pa < Z Pa)

10 One of the key production stages in the Contact Process is the production of sulfur trioxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H < 0$$

The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

What happens to k_1, k_{-1} and K_c if the temperature of the reaction is increased?

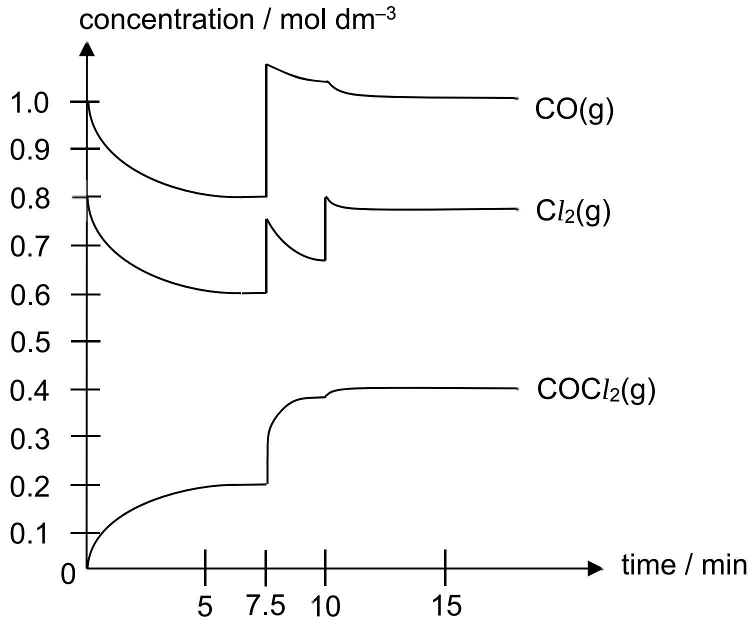
	k_1	k_{-1}	K_c
A	increase	increase	increase
B	increase	decrease	increase
C	decrease	increase	decrease
D	increase	increase	decrease

When temperature increased, no of molecules with energy greater than activation energy increases, frequency of effective collision increased, rate of reaction increases as rate constant increased. k_1 and k_{-1} increase.

As reaction is exothermic, as temperature increase, equilibrium shift backward to partially absorb the excess heat. Hence, K_c decrease as [product]/[reactant] decrease.

11 The reaction between carbon monoxide and chlorine was studied in an experiment by mixing the two gases and changing the reaction conditions inside the reaction vessel at different times during the experiment. The concentrations of the gases in the vessel were followed with time, and the following graph is obtained.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g) \qquad \Delta H^\ominus = -113.4 \text{ kJ mol}^{-1}$$



Which conclusion deduced from the graph is **incorrect**?

A The rate of forward reaction equals the rate of backward reaction at 7 min.

Correct: At 7 min, the system is in dynamic equilibrium and hence the rate of forward reaction is equal to the rate of backward reaction.

B The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.

Incorrect: Increase in volume at constant temperature will cause the concentration to decrease.

C The equilibrium constant, K_c, for the system when determined at 7 min is 0.417 $\text{mol}^{-1}\,\text{dm}^3$.

Correct: Using $K_c = \frac{[COCl_2]}{[CO][Cl_2]}$ and calculate

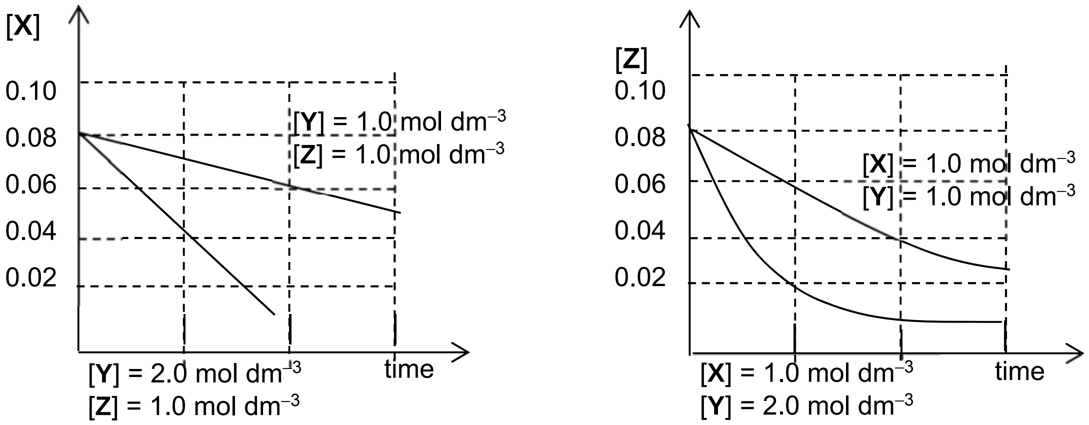
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

Correct: When chlorine is added, the concentration of chlorine will increase instantaneously as shown in the graph.

12 Substances **X**, **Y** and **Z** react according to the following equation:

$$\mathbf{X}(aq) + 2\mathbf{Y}(aq) + \mathbf{Z}(aq) \rightarrow 2\mathbf{W}(aq) + \mathbf{U}(aq)$$

To find the rate equation for the above reaction, two sets of separate experiments were performed, in which the initial concentrations of each of the reactants **X**, **Y** and **Z** were varied while the other two were kept constant. The results are shown below.



Which rate equations represent the experimental results?

A rate = k[**Y**]^2

B rate = k[**Y**][**Z**]

C rate = k[**Y**]^2[**Z**]

D rate = k[**X**][**Y**][**Z**]

From the [X] versus time graph, a straight line indicates that the rate is constant with respect to any changes in [X]. Therefore order of reaction with respect to X is zero.

From the [Z] versus time graph, a constant half-time is obtained which indicates that the reaction is first order with respect to Z.

From the [Z] versus time graph, the time taken when [Y] is 2.0 mol dm^{-3} is $\frac{1}{4}$ of the time taken when [Y] is 1.0 mol dm^{-3} for [Z] to drop from 0.08 mol dm^{-3} to 0.04 mol dm^{-3} . Therefore order of reaction with respect to Y is 2.

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

The reaction of acidified aqueous potassium iodide with hydrogen peroxide is represented by the following equation.

$$2I^-(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Which statements about the reaction are true?

1 E^θ_{cell} = +1.23 V.
True: E^θ_{cell} = (-0.54) + (+1.77) = +1.23 V

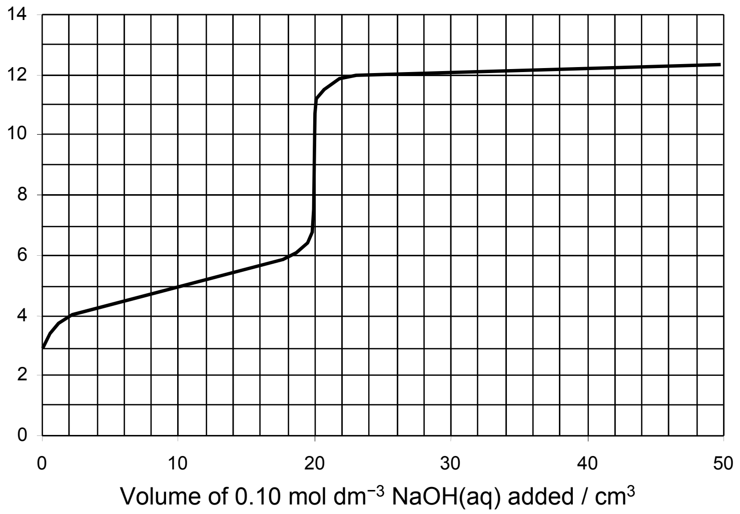
2 E^θ_{cell} becomes more negative when $Br_2(aq)$ is added to the anode.
True: $Br_2(aq)$ added will remove I^- causing $E^\theta_{oxidation}$ of I^- to be more negative when will cause E^θ_{cell} becomes more negative

3 E^θ_{cell} becomes more positive when a few drops of $AgNO_3(aq)$ is added to the anode.
False: $AgNO_3(aq)$ added with remove I^- causing $E^\theta_{oxidation}$ of I^- to be more negative when will cause E^θ_{cell} becomes more negative

A 1 only **B** 1 and 2

C 2 and 3 **D** 1, 2 and 3

14 The titration curve below shows the reaction between a monoprotic acid, **HX**, and aqueous sodium hydroxide.



Given the following data:

Indicator	Colour change (acidic to basic medium)	pH range in which colour change occurs
Methyl red	red to yellow	4.2 – 6.3
Bromothylmol blue	yellow to blue	6.0 – 7.6
Thymolpthalein	colourless to blue	8.3 – 10.5

What statements are correct?

1 Methyl red will indicate an endpoint at a value lower than 20.0 cm^3.

Correct: At a value lower than 20.0 cm^3, the pH is less than 6.5 which coincide with the working range of methyl red.

2 K_a value of HX is 1.0×10^{-5}

Correct: At max buffer capacity, pH= $pK_a = 5$

$K_a = 1.0 \times 10^{-5}$

3 Buffer at maximum buffer capacity is formed at 25.0 cm^3 since the pH change in that region is relatively constant.

Incorrect: Maximium buffer capacity is formed at 10.0 cm^3 where [HX] = [NaX]

4 Alkaline hydrolysis of salt takes place after the equivalence point accounting for the alkaline pH value of the reaction mixture.

Incorrect: Alkaline hydrolysis of salt takes place **AT** equivalence point accounting for the alkaline pH value of the reaction mixture.

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

15 Given the following data,

K_a of $CH_3COOH = 1.8 \times 10^{-5}$

Reaction mixture **X**:
25.0 cm^3 of 2.0×10^{-5} mol dm^{-3} CH_3COOH and 25.0 cm^3 water

Reaction mixture **Y**:
25.0 cm^3 of 0.02 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.01 mol dm^{-3} NaOH

Reaction mixture **Z**:
25.0 cm^3 of 0.01 mol dm^{-3} CH_3COOH and 25.0 cm^3 of 0.02 mol dm^{-3} NaOH

Which is the correct order of pH values of the above reaction mixture?

A **Z > Y > X**

B **Z > X > Y**

C **Y > X > Z**

D **X > Y > Z**

For reaction mixture X, $[CH_3COOH]_{new} = 0.5 \times 2.0 \times 10^{-5} = 1.0 \times 10^{-5}$ mol dm^{-3}

$[H^+] = \sqrt{(1.0 \times 10^{-5} \times 1.8 \times 10^{-5})} = 1.3416 \times 10^{-5}$ mol dm^{-3}

$pH = -lg(1.3416 \times 10^{-5}) = 4.87$

For reaction mixture Y,

	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.0005		0.00025		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0.00025		0		0.00025		-

An acidic buffer is formed.

$pH = pK_a$ since $[CH_3COOH]_{new} = [CH_3COONa]_{new}$

$pH = -lg(1.8 \times 10^{-5}) = 4.74$

For reaction mixture Z,

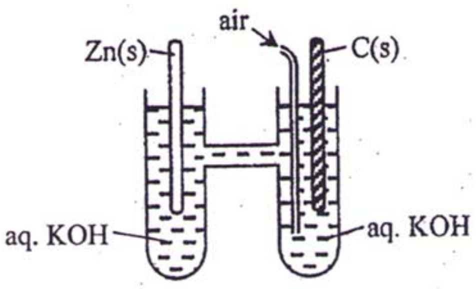
	CH_3COOH	+	NaOH	→	CH_3COONa	+	H_2O
Initial / mol	0.00025		0.0005		0		-
Change / mol	– 0.00025		– 0.00025		+ 0.00025		-
Final / mol	0		0.00025		0.00025		-

Salt hydrolysis is not considered as presence of strong base will suppress the salt's dissociation

$pH = 14 - pOH = 14 + lg(0.00025 / \frac{25.0+25.0}{1000}) = 11.70$

Answer is B

16 A cell is constructed with zinc and carbon electrodes, each weighing 50 g, partly immersed in aqueous KOH.



When connected in a circuit, some zinc passes into solution as zincate(II) ions, ZnO_2^{2-}(aq). The cell delivers a current of 1.68×10^{-2} A. The zinc electrode is replaced once 60% of it is used up.

What is the time taken, in seconds, before replacement of zinc electrode becomes necessary?

A	2.63×10^6	**B**	4.39×10^6
C	5.27×10^6	**D**	8.78×10^6

Oxidation state of Zn in ZnO_2^{2-} is +2, hence 2 moles of electrons are transferred per mole of Zn.

Amount of Zn used up = $\frac{60}{100} \times \frac{50}{65.4}$ = 0.4587 mol

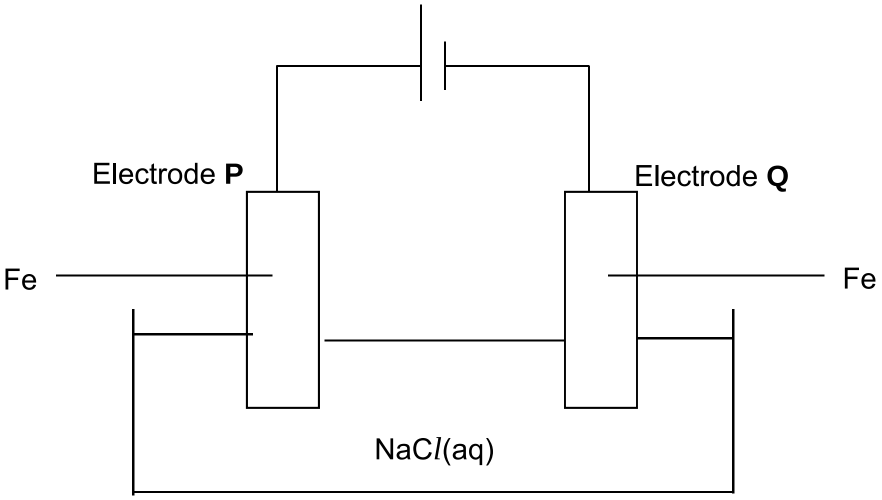
n_e = 0.4587 × 2 = 0.9174 mol and since $Q = It = n_eF$

$(1.68 \times 10^{-2})t = 0.9174 \times 96500$

$= 5.27 \times 10^6$ s

Answer is C

17 An experiment is set up as shown below to study the corrosion of iron.



What will occur at electrodes **P** and **Q**?

	Electrode **P**	Electrode **Q**
A	No corrosion of Fe	Corrosion of Fe ; H_2 gas evolved
B	No corrosion of Fe	Corrosion of Fe ; O_2 gas evolved
C	Corrosion of Fe	No corrosion of Fe ; Na deposited
D	Corrosion of Fe	No corrosion of Fe ; H_2 gas evolved

Electrode P is the positive anode, while electrode Q is the negative cathode

Since oxidation occurs at the anode, while reduction occurs at the cathode,

At the anode:

$Fe \rightleftharpoons Fe^{2+} + 2e^-$	$E^\theta_{ox} = +0.44$ V
$Cl^- \rightleftharpoons Cl_2 + 2e^-$	$E^\theta_{ox} = -1.36$ V
$2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^-$	$E^\theta_{ox} = -1.23$ V

Corrosion of Fe will occur at electrode P since first E^θ_{ox} is the most positive

At the cathode:

$Na^+ + e^- \rightleftharpoons Na$	$E^\theta = -2.71$ V
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	$E^\theta = -0.83$ V

No corrosion of Fe will occur, since Fe cannot be reduced. H_2 gas will be evolved since second E^θ is the most positive

Answer is D

18 *Use of Data Booklet is relevant to this question.*

The calomel electrode was used extensively a reference electrode in the past. However, it has since been replaced by safer options such as the standard hydrogen electrode (S.H.E.).

Calomel electrode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$

When measured with reference to the calomel electrode, a half–cell containing Zn^{2+}/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn^{2+}.

What is the standard electrode potential of the calomel electrode?

A +0.27 V **B** +1.30 V **C** –1.79 V **D** –2.82 V

A change in Gibbs' free energy of +199 kJ per mole of Zn^{2+} being reduced is equivalent to a change in Gibbs' free energy of –199 kJ per mole of Zn being oxidised

$\Delta G^{\theta} = -nFE^{\theta}_{cell}$

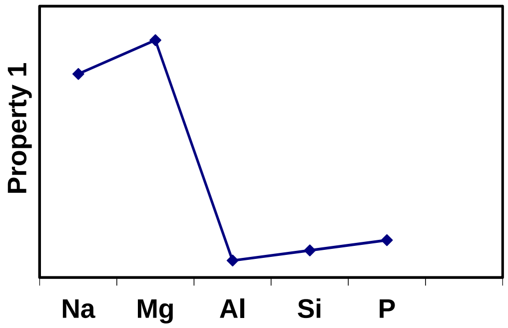
$-199 \times 1000 = -(2)(96500)E^{\theta}_{cell}$

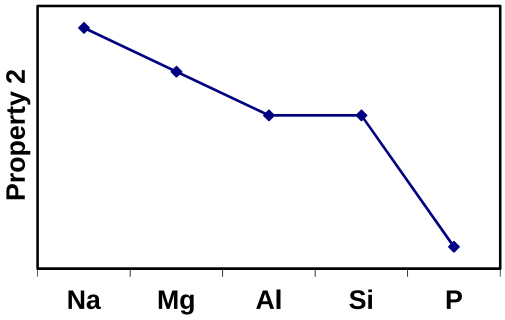
$E^{\theta}_{cell} = +1.03\ V = E^{\theta} + E^{\theta}_{ox\ (Zn\ /\ Zn2+)} = E^{\theta} + 0.76\ V$

$E^{\theta} = +0.27\ V$

Answer is A

19 The graphs below show the variation of two properties of some period 3 elements and/or their compounds.





Which correctly describes properties 1 and 2?

	Property 1	Property 2
A	atomic radius of the elements	electrical conductivity of the elements
B	boiling point of the highest oxidation state chlorides	pH of the oxides when added to water
C	melting point of oxides	first ionisation energies of the elements
D	electrical conductivity of elements	pH of the highest oxidation state chlorides when added to water

For option A Property 1 cannot be atomic radii as it should be a continuous decrease across the period due to increase in nuclear attraction for the outermost electron. This is because of increase in nuclear charge but constant shielding caused by the same number of inner electrons.	Property 2: Electrical conductivity should increase from Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.
For option B Boiling point of chloride compounds decreases from NaCl to $AlCl_3$ as $AlCl_3$ is a simple covalent molecule therefore easier to overcome the intermolecular temporary dipole induced dipole than ionic bonds in giant ionic lattice of NaCl and $MgCl_2$. From $AlCl_3$ to PCl_5, they have the structure of simple covalent molecules with Mr of $AlCl_3$ (133.5) < $SiCl_4$ (170.1) < PCl_5 (208.5). B.pt increases with increasing ease of distortion of the electron cloud of the chloride compound. Hence property1 shows the correct trend in the b.pt of chlorides across period 3 element.	Property 2: **acid base property of oxide** depends on the **nature of bonds present in the oxide** compound. While ionic oxide tends to be basic and covalent oxide is acidic; ionic oxides with significant covalent character will be amphoteric, this is usually observed when cation has high charge/size ratio. **pH of oxides in aqueous medium** not only depends on the nature of the bonds, **solubility** also matters. Na_2O is **basic and fully soluble** in water, therefore pH very high (highly alkaline). Solubility of MgO less than Na_2O but more than Al_2O_3, hence pH of MgO > Al_2O_3. **pH of Al_2O_3 and SiO_2 are both equal to 7 because both are insoluble in water** but Al_2O_3 is an amphoteric oxide while SiO_2 is an acidic oxide. Oxides of P dissolves in water to give phosphoric acid therefore pH is very low. Hence property 2 shows the correct trend for pH of aqueous oxides across period 3.
For option C Melting points of oxides across the period should peak at SiO_2 since it has a very strong giant covalent lattice. Phosphoric oxide is a simple covalent molecule, therefore there should be a drastic drop of m.pt from SiO_2 to P_4O_{10}. Hence property 1 cannot be m.pt of oxides across period 3 elements.	First ionisation energy of elements across period should exhibit a general increasing trend due to increasing nuclear attraction for the most loosely held electron. This is due to increase in nuclear charge but constant shielding effect by the same number of inner shell electrons. Hence property 2 cannot be first ionisation energy.
For option D Electrical conductivity should increase from Na to Mg to Al due to increase in number of mobile charged carriers (more electrons in the sea of delocalised electrons). Electrical conductivity should be very low for Si while P exhibit zero	For chlorides across period 3 element, they are all soluble in aqueous medium. For chlorides that dissociates into ions in aq medium, cation hydrolysis gives rise to acidic solution. Extent of cation hydrolysis increases with charge/size ratio of the cation. Hence $AlCl_3$ (aq) more acidic than $MgCl_2$(aq) while NaCl is neutral (pH =7)

electrical conductivity. Hence graph shows a wrong trend for electrical conductivity.	On the other hand, covalent chlorides react with water to form HCl therefore the pH value should be low for both $SiCl_4$ and PCl_5. Hence graph of property 2 do not agree with the pH trend of aqueous chlorides across the period.

20 What mass of sodium ethanedioate, $Na_2C_2O_4$, should be added to 250 cm^3 of a 2.2×10^{-3} mol dm^{-3} solution of calcium nitrate before a precipitate is formed?
[K_{sp} of CaC_2O_4 = 2.27×10^{-9} mol^2 dm^{-6}]

In order for precipitate to take place, ionic product > Ksp.
Expression for ionic product and K_{sp} is the same.

$$K_{sp} = [Ca^{2+}][C_2O_4^{2-}]$$

Magnitude of Ionic product = K_{sp} when solution is saturated with $Na_2C_2O_4$.

$$\left(\frac{mass}{(23.0 \times 2 + 24.0 + 64.0)} \times \frac{1000}{250}\right)(2.2 \times 10^{-3}) = 2.27 \times 10^{-9}$$

Min mass of $Na_2C_2O_4$ = 3.46×10^{-5} g

A	3.5×10^{-5} g	**B**	1.0×10^{-6} g
C	2.5×10^{-7} g	**D**	2.3×10^{-9} g

21 Benzylamine has the formula $C_6H_5CH_2NH_2$ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

A It can be formed by the reduction of $C_6H_5CH_2CN$.

B It reacts with CH_3CO_2H to form $C_6H_5CH_2NHCOCH_3$.

C It is formed by the reaction between $C_6H_5NO_2$ and tin in concentrated HC*l* followed by NaOH.

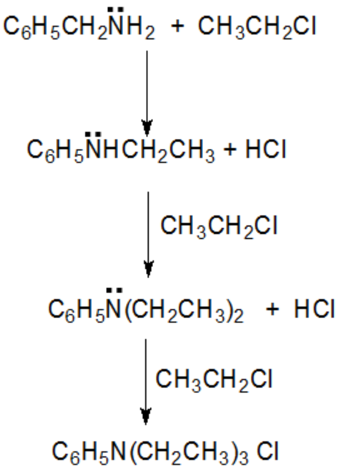
D It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

Option A: reduction of $C_6H_5CH_2CN$ gives $C_6H_5CH_2CH_2NH_2$ with 1 C more than $C_6H_5CH_2NH_2$. Hence it is not the correct answer.

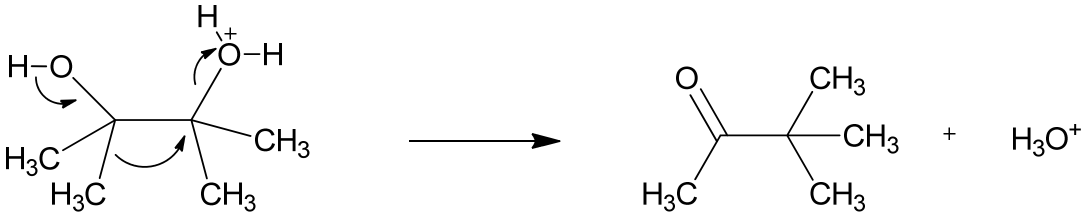
Option B: N in $C_6H_5CH_2NH_2$ uses its lone pair to accept H^+ from CH_3COOH (acid base reaction instead of nucleophilic acyl substitution (condensation)). Hence $(CH_3COO^-)(C_6H_5CH_2NH_3)^+$ is formed instead of $C_6H_5CH_2NHCOCH_3$.

Option C: $C_6H_5NO_2$ will be reduced to $C_6H_5NH_2$ which is isolated as $C_6H_5NH_3Cl$ due to acidic medium. $C_6H_5NO_2$ has 1 less C than $C_6H_5CH_2NH_2$ after reduction, hence not the answer.

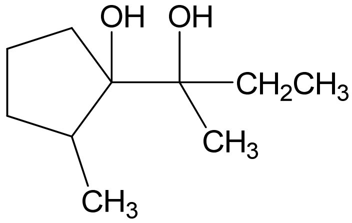
Option D: Correct answer. A quaternary ammonium salt is formed when $C_6H_5CH_2NH_2$ reacts with excess CH_3CH_2Cl.



22 When a 1,2–diol is treated with a dilute acid, the protonated diol undergoes the following pinacol rearrangement.

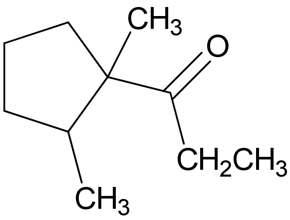


Which structure is **not** formed when diol **Z** undergoes pinacol rearrangement?

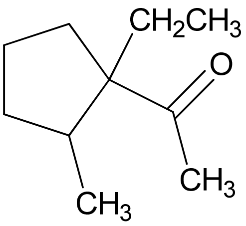


diol **Z**

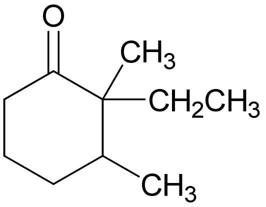
A



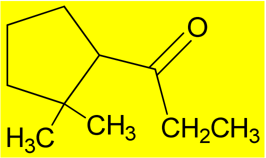
B

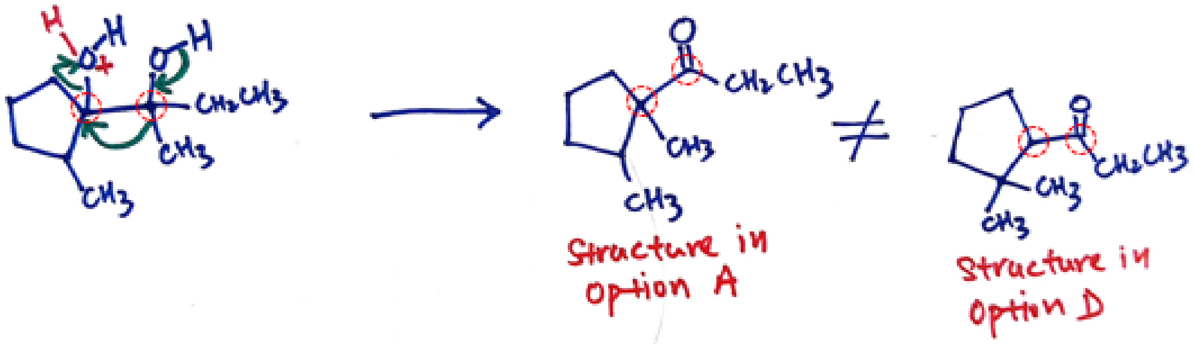


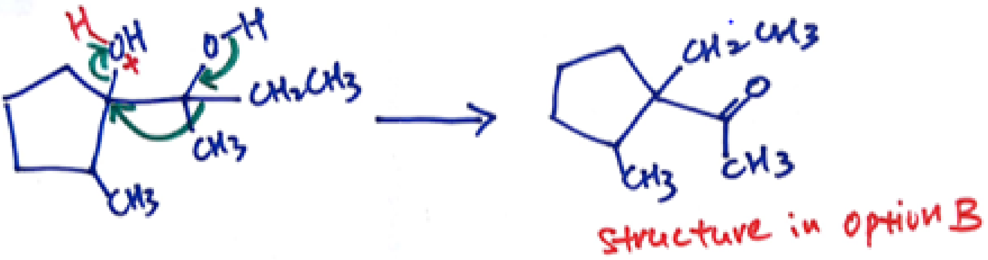
C

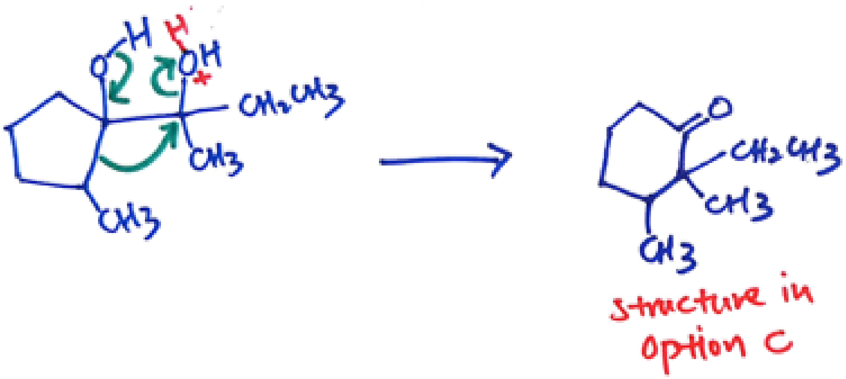


D

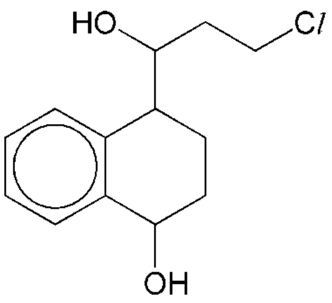






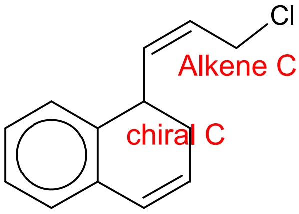


23 What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H_2SO_4?



A 2 **B** 4 **C** 6 **D** 8

The molecule undergoes elimination of H_2O with excess concentrated H_2SO_4 to give alkene. The product is



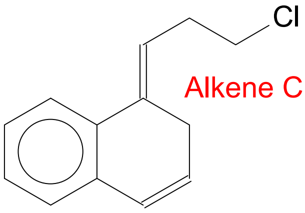
Alkene C that can exhibit cis-trans isomerism

chiral C

Using the formula,

No of stereoisomers = 2^{n+m} where n = no of chiral C and m= no of alkene C that can exhibit cis-trans isomerism, this alkene has $2^{1+1} = 4$ isomers.

Another possible products of elimination:



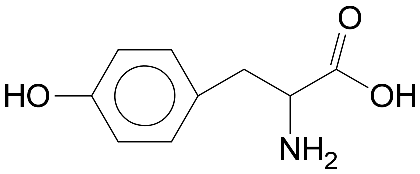
Alkene C that can exhibit cis-trans isomerism

No of stereoisomers: $2^1=2$ isomers

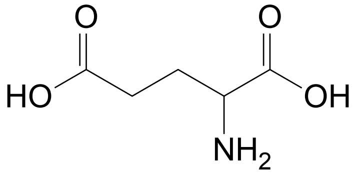
Total no of stereoisomers = $2^2 + 2 = 6$

24 Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species move towards the anode.

With a buffer at pH 4, which statement is true?



Tyrosine (pI = 5.7)



Glutamic acid (pI = 3.2)

A Both species move towards the anode

B Both species move towards the cathode.

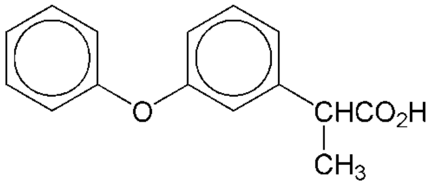
C Tyrosine moves towards the anode, glutamic acid moves towards the cathode.

D Tyrosine moves towards the cathode, glutamic acid moves towards the anode.

Since pH < pI of Tyrosine, the –NH_2 grp will get protonated => Overall positively charged, hence move towards cathode.

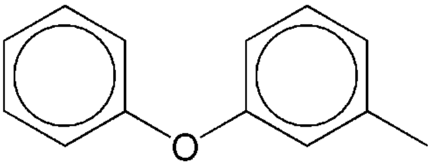
Since pH > pI of Glutamic acid, both the –COOH grps will get deprotonated => Overall negatively charged, hence move towards anode. Answer is (D).

25 *Fenoprofen* is an anti-arthritic agent.



Which of the following could be part of a reaction sequence for synthesising *Fenoprofen*?

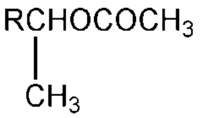
In the sequences below, R =



A $\mathrm{RCHBrCH_3} \xrightarrow[\text{heat}]{\text{NaCN(ethanolic)}} \text{Intermediate} \xrightarrow[\text{heat}]{\mathrm{H^+(aq)}} \textit{Fenoprofen}$

B $\mathrm{RCH(CH_3)_2} \xrightarrow[\text{heat}]{\mathrm{KMnO_4,\ OH^-(aq)}} \text{Intermediate} \xrightarrow{\mathrm{H^+(aq)}} \textit{Fenoprofen}$

C



$\mathrm{RCH(CH_3)OCOCH_3} \xrightarrow[\text{warm}]{\mathrm{I_2,\ OH^-(aq)}} \text{Intermediate} \xrightarrow{\mathrm{H^+(aq)}} \textit{Fenoprofen}$

D $\mathrm{RCH(OH)CH_3} \xrightarrow[\text{heat}]{\mathrm{KMnO_4,\ OH^-(aq)}} \text{Intermediate} \xrightarrow{\mathrm{H^+(aq)}} \textit{Fenoprofen}$

For option (A), the halogenoalkane $\mathrm{RCHBrCH_3}$ undergoes nucleophilic substitution when heated with ethanolic NaCN, forming $\mathrm{RCH(CN)CH_3}$ as the intermediate, which then undergoes acidic hydrolysis of the –CN group to form –COOH.

For option (B), $\mathrm{RCH(CH_3)_2}$ does not undergo oxidation when heated with alkaline $\mathrm{KMnO_4}$.

For option (C), $\mathrm{RCHO(CH_3)COCH_3}$ has methyl carbonyl which is part of the ester functional grp, hence does not undergo iodoform reaction when warmed with alkaline iodine.

For option (D), secondary alcohol $\mathrm{RCH(OH)CH_3}$ undergoes oxidation to form ketone intermediate, $\mathrm{RCOCH_3}$, which does not react with $\mathrm{H^+}$.

26 Chlorofluorocarbons (CFCs) are commonly used as aerosols, propellants and refrigerants. However in the stratosphere, CFCs can damage the ozone layer through a radical chain reaction.

In which sequence are the following compounds listed in increasing order of their ability to destroy ozone?

A $CHClFCClF_2$ < CCl_2FCCl_2F < $CHClF_2$

B CCl_2FCCl_2F < $CHClF_2$ < $CHClFCClF_2$

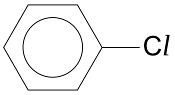
C $CHClF_2$ < CCl_2FCCl_2F < $CHClFCClF_2$

D $CHClF_2$ < $CHClFCClF_2$ < CCl_2FCCl_2F

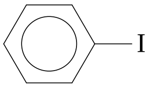
C-F bond is much stronger than C-Cl, it does not break easily to form F radicals => does not damage ozone layer.
All four options (A), (B), (C) and (D) comprise of molecules containing C-F and C-Cl bonds. The molecule with more C-Cl bonds will have higher ability to destroy ozone due to more Cl radicals it is able to produce. Hence, answer is (D).

27 Which is the product formed when benzene reacts with iodine chloride, ICl in the presence of a suitable catalyst?

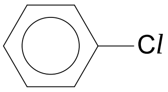
A



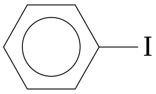
B



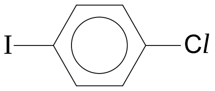
C a mixture of



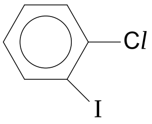
and



D a mixture of



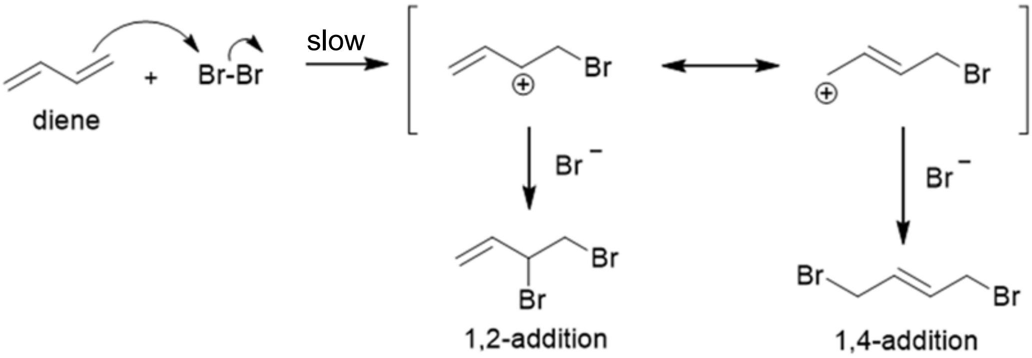
and



Answer:

Cl is more electronegative than I, hence only I^+ electrophile forms for reaction.
$AlCl_3 + ICl \rightarrow AlCl_4^- + I^+$
Hence only 1 electrophilic substitution product is possible.

28 When a conjugated diene undergoes electrophilic addition with Br_2, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.



Which statement is **not** correct?

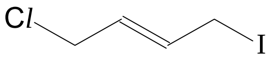
A The overall rate law is second order.

B The carbocation intermediates are resonance stabilised.

C The 1,2–addition product formed when HC*l* is used is

.

D The 1,4–addition product formed when IC*l* is used is



.

Answer:

A is correct.

Step 1 can be determined to be the slow step as bond breaking occurs. 1 mole of diene and 1 mole of bromine are involved and hence the overall order is 2.

B is correct.

The presence of the pi bond stabilises the positive charge on the cations.

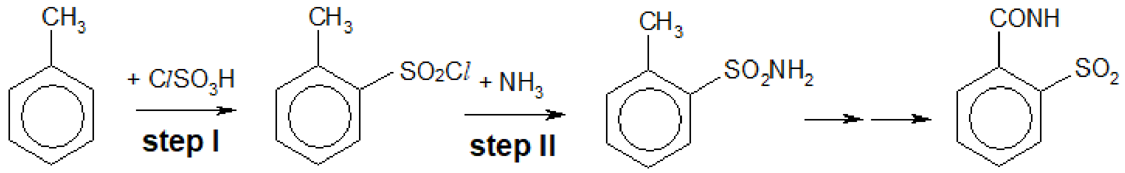
C is incorrect.

For the 1,2-addition product, the positive charge is on the 2nd carbon and hence C*l* should be on the 2nd carbon instead.

D is correct.

C*l* is more electronegative than I, hence in step 1, the I which is δ+ will function as the electrophile and Cl^- is generated which then attacks the carbocation.

29 Saccharin is an artificial sweetening agent used in some soft drinks and is manufactured from methylbenzene through a four-step synthesis. Part of the reaction scheme is shown below.



What type of reaction do steps **I** and **II** illustrate?

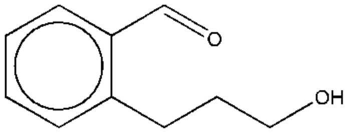
	Step I	**Step II**
A	Electrophilic addition	Nucleophilic addition
B	Electrophilic substitution	Nucleophilic substitution
C	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

Answer:
Step 1: Benzene ring is electron rich: Electrophilic Substitution
Step 2: S is δ+ due to the electronegative atoms attached to it; -C*l* replaced by $-NH_2$: Nucleophilic Substitution

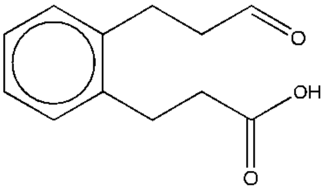
30 Compound **X** gives a positive result when treated with $[Ag(NH_3)_2]^+$ and PCl_5 respectively but a negative result when treated with alkaline Cu(II) complex.

What could **X** be?

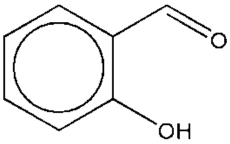
A



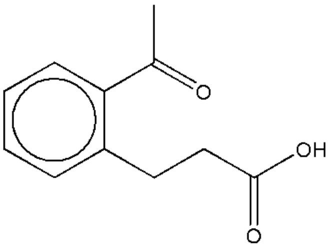
B



C



D



Reacts with $[Ag(NH_3)_2]^+$ (Tollen's)	Aldehyde
Reacts with PCl_5	-OH which can undergo substitution present (not phenol)
No reaction with alkaline Cu(II) complex (Fehlings)	Aromatic aldehyde

END of PAPER

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

NATIONAL JUNIOR COLLEGE
SH 2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME

SUBJECT CLASS

REGISTRATION NUMBER

CHEMISTRY

9729/02

Paper 2 Structured Questions

Tues 21 Aug 2018
2 hours

Candidates answer **all** questions on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams, graphs.
Do not use staples, paper clips, glue or correction fluid/tape.

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

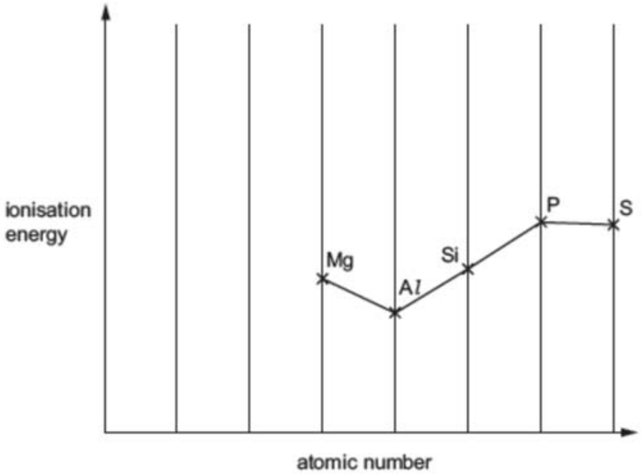
At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use			
1	/8		
2	/14		
3	/13		
4	/11		
5	/14		
6	/15		
Penalty units			
Penalty sf			
Paper 2	/75		

Answer <u>ALL</u> questions on the space provided.
This paper consists of **18** printed pages.

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*: ....

....

....

P and S: ....

....

....

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.
L is a chloride of an element in Period 3. A students investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

(i) Identify **L** and **M.**

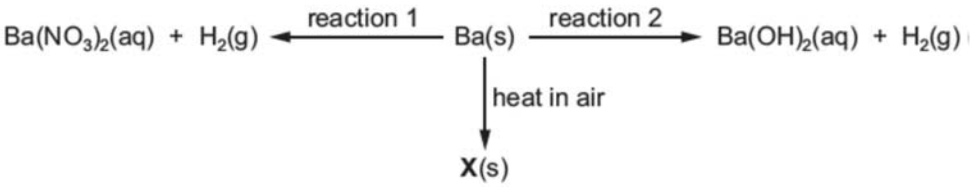
L: ………………………………………… **M:** ………………………………………

[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

……………………………………………………………………………………… [1]

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



$$\begin{tikzcd} Ba(NO_3)_2(aq) + H_2(g) & Ba(s) \arrow[l, "\text{reaction 1}"'] \arrow[r, "\text{reaction 2}"] \arrow[d, "\text{heat in air}"] & Ba(OH)_2(aq) + H_2(g) \\ & \mathbf{X}(s) & \end{tikzcd}$$

(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1 ………………………………………………………………………………..

Reaction 2 ………………………………………………………………………………..

[2]

(ii) Write an equation for the formation of **X**.

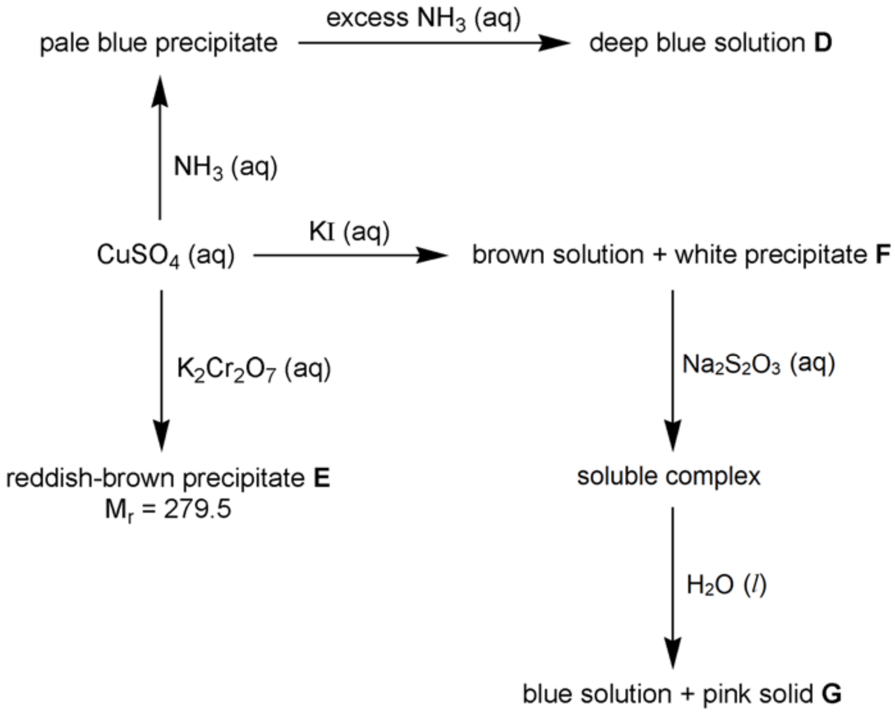
………………………………………………………………………………………………

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: ……………………………….. **E**: ………………………………..

F: ……………………………….. **G**: ………………………………..

[4]

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

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……………………………………………………………………………………………

[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

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……………………………………………………………………………………………

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

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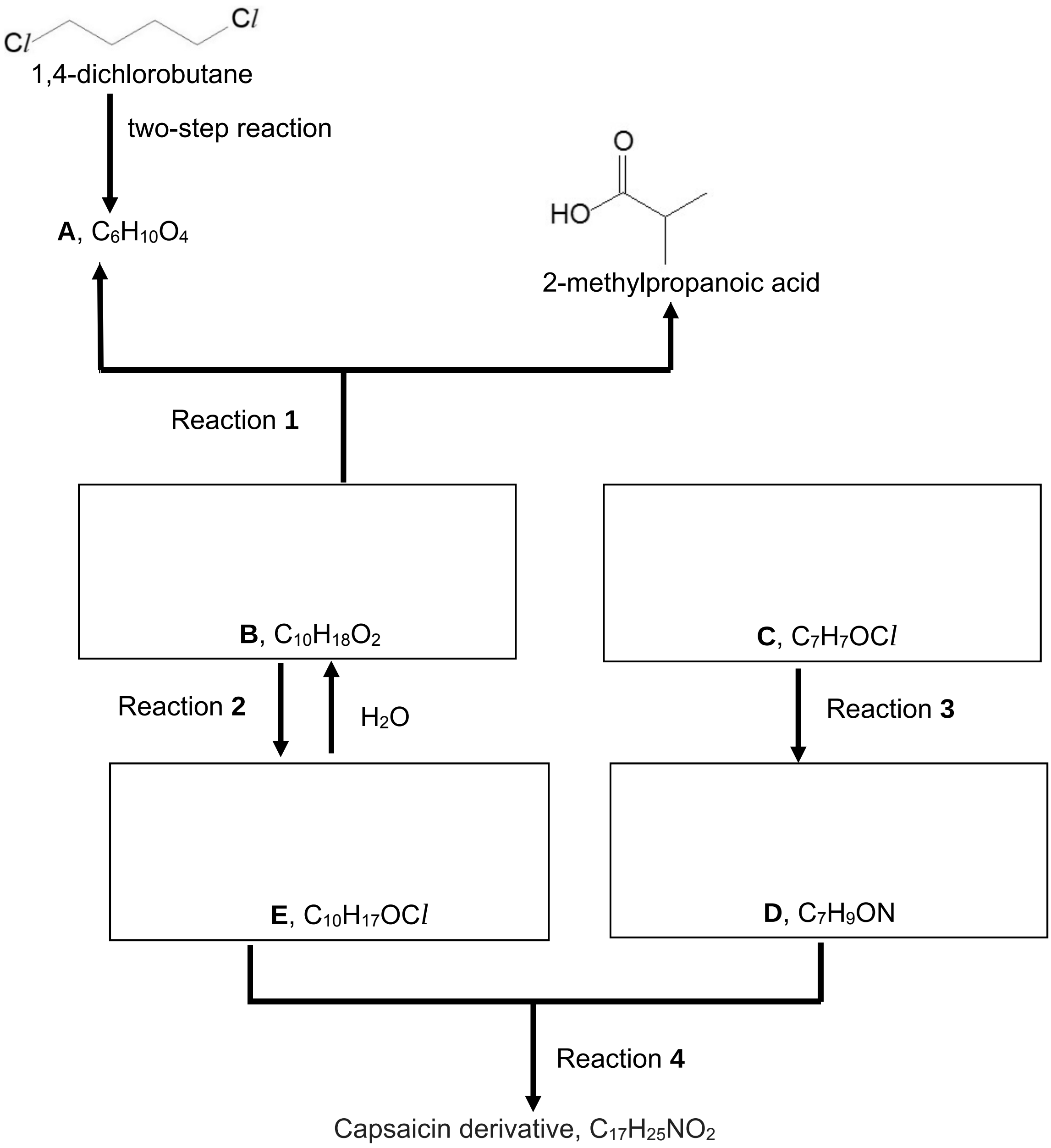
[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

……………………………………………………………………………………………… [1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps.
Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: ………………………………………………………..

Step 2: ………………………………………………………..

Intermediate product:

[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: ……………….……………….

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: …………………………………………………..

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt.
Draw the structure of Compounds **C** and **D** in the box on pg 6.
Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: ………………………………………………………….

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: …………………………………………………..

[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.

[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	**Volume Percentage**
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	Rapidly increasing
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HC*l*	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume}$$

However, percentages are only additive for ideal gases.

(a) **(i)** State **two** assumptions of the kinetic theory of gases.

……………………………………………………………………………………………..

……………………………………………………………………………………………..

……………………………………………………………………………………………..

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

……………………………………………………………………………………………..

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

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……………………………………………………………………………………………...

……………………………………………………………………………………………...

[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.
Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43°C and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Volume percentage of carbon dioxide = …………………

……………………………………………………………………………………………...

……………………………………………………………………………………………...

[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\ H_2S(g) \rightleftharpoons CS_2(g) + H_2(g)$$

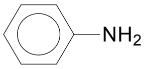
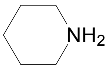
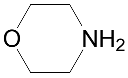
1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960°C and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

Examiners Comments:
Most students are able to identify that O is electronegative and hence able to exert electron withdrawing effect. There are a handful who thought that the lone pair will delocalise into O. This is impossible as the 2 atoms are not adjacent to each other and no orbital overlap exists.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

Examiners Comments:
Most students are able to recognise that the lone pair on N can delocalise into the ring and hence a reduction in availability of lone pair for donation to a proton. Do use the correct key word "delocalisation" as some students will use terms like "dissociate" or "diffuse" into the ring which is not very accurate.

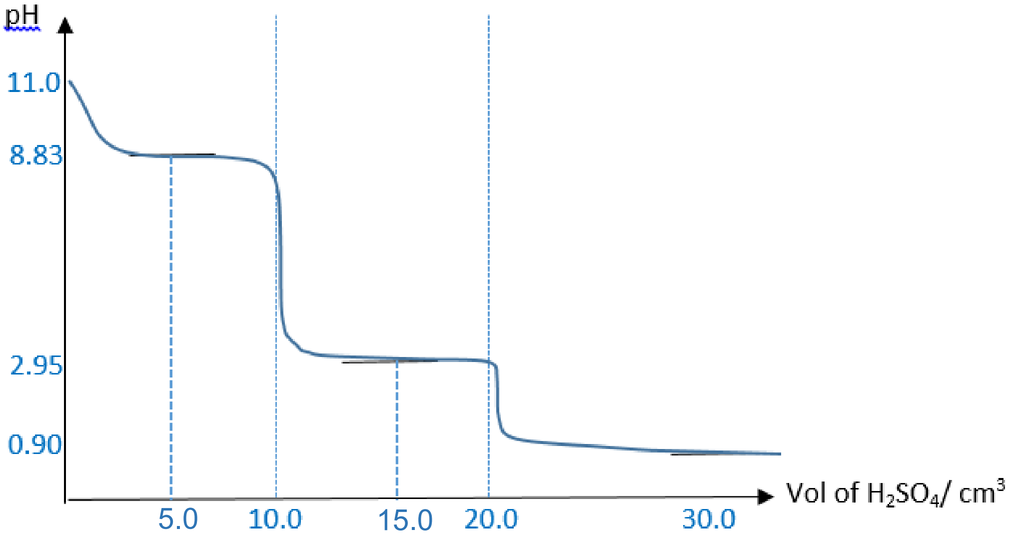
[2]

(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the pH–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- pH of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.
- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
pOH = pK$_b$ at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
$[H^+]$ = 0.005 x 1000/ 40 = 0.125 moldm^{-3}
pH = 0.90

Examiners Comments:
Students did badly for this question.
Most students did not manage to recognise two equivalence point (represented by 2 steep slope).
To identify how many equivalence point(s) there is, students need to **focus on the analyte**. If the analyte is (1) weak **and** (2) multi-protic, then it will have multiple equivalence points.

Most students also could not calculate the volume of H_2SO_4 used correctly. To do so, since both acid and base are diprotic,

$N_2H_4 + H_2A \rightarrow N_2H_6^{2+} + A^{2-}$
Mol ratio is 1:1

Hence **total volume** of acid required is 20 cm^3

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

$$\underset{\textbf{A}}{C_4H_{10}} \xrightarrow{\text{step 1}} \underset{\textbf{B}}{C_4H_9Cl} \xrightarrow{\text{step 2}} C_4H_{11}N$$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

Step 1: limited Cl_2, UV. light

Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

(ii) Outline the mechanism for step 1.

			[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **c(ii).**

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[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

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

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

....
[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH^-, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

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[3]

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	[$C_6H_5CHClCH_3$] / mol dm^{-3}	[OH^-] / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Order with respect to $C_6H_5CHClCH_3$ = ...

Order with respect to OH^- = ...

[2]

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

rate = ... mol dm^{-3} s^{-1}

units of *k* = ...

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

[3]

(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers.
Explain your answer.

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....

....

[2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

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....

....

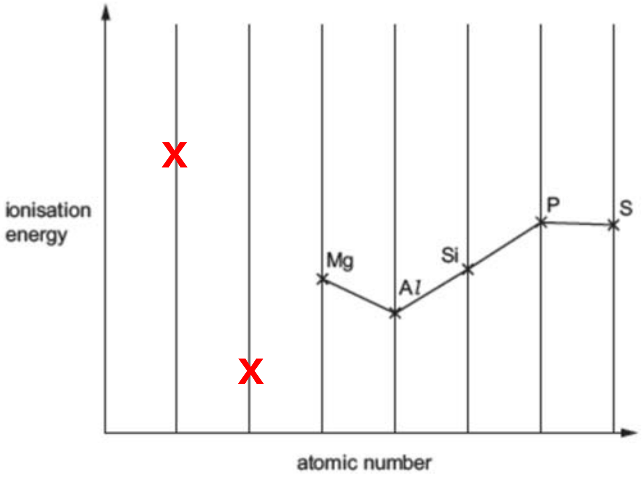
[2]

[Total: 15]

NJC SH2 H2 Chemistry P2 Solutions

1 The properties of elements and their compounds show similarities, differences and trends depending on the positions of the elements.

(a) The elements in the third period, and their compounds, show trends in their physical and chemical properties.
A sketch graph of the first ionisation energies of five successive elements in the third period is shown.



(i) Sketch on the graph, the position of the ionisation energy of the two elements that come before Mg in this sequence.

Cross shown on first vertical line from the y-axis (group 0/Ne) is clearly higher than all shown.
Cross shown on second vertical line from the y-axis (group 1/Na) is clearly lower than all shown.

[1]

(ii) Explain, with reference to electronic arrangements, the decreases in first ionisation energy between Mg and A*l* and between P and S.

Mg and A*l*:
The most loosely held electron in A*l* is in the **higher energy 3p subshell** while that of Mg is in the **lower energy 3s subshell.**
This **outweighs the effect of the increase in nuclear charge** from Mg to A*l*.
Hence **nuclear attraction for the most loosely held electron in A*l* is weaker**, i.e. A*l* has a lower 1st IE. [1]

P and S:
The most loosely held electron in S is one of the **paired electrons in 3p** orbital while that of P is in the **singly filled 3p** orbital.
Inter-electronic repulsion between the paired electrons in the same p orbital **outweighs the effect of an increase in nuclear charge**.
Hence, **nuclear attraction for the most loosely held electrons is weaker in S**, i.e. S has a lower first IE. [1]

[2]

(b) The chlorides of the elements in the third period behave in different ways when added to water, depending on their structure and bonding.

L is a chloride of an element in Period 3. A student investigated **L** and the results are as given below.

- **L** is a white crystalline solid with a melting point of 987 K.
- **L** dissolves in water to form a weakly acidic solution.
- Addition of NaOH(aq) to an aqueous solution of **L** produces a white precipitate, **M** .

(i) Identify **L** and **M.**

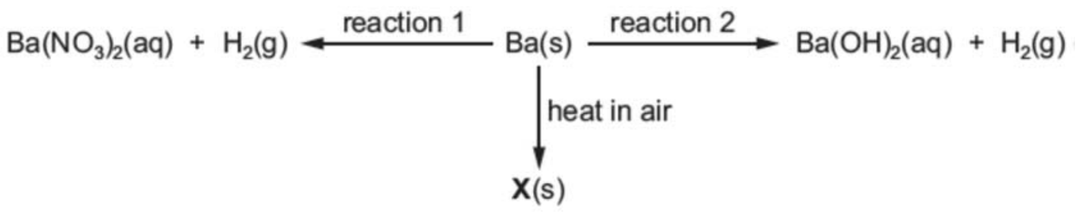
L: $MgCl_2$ **M:** $Mg(OH)_2$

[1]

(ii) Write an equation to illustrate the formation of the weakly acidic solution.

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^{+}(aq) + H_3O^{+}(aq)$ [1]
(state symbols not necessary)

(c) Some reactions based on the Group 2 metal barium, Ba, are shown below.



(i) State the reagent needed for each of reactions 1 and 2.

Reaction 1: HNO_3 [1]

Reaction 2: H_2O [1]

(ii) Write an equation for the formation of **X**.

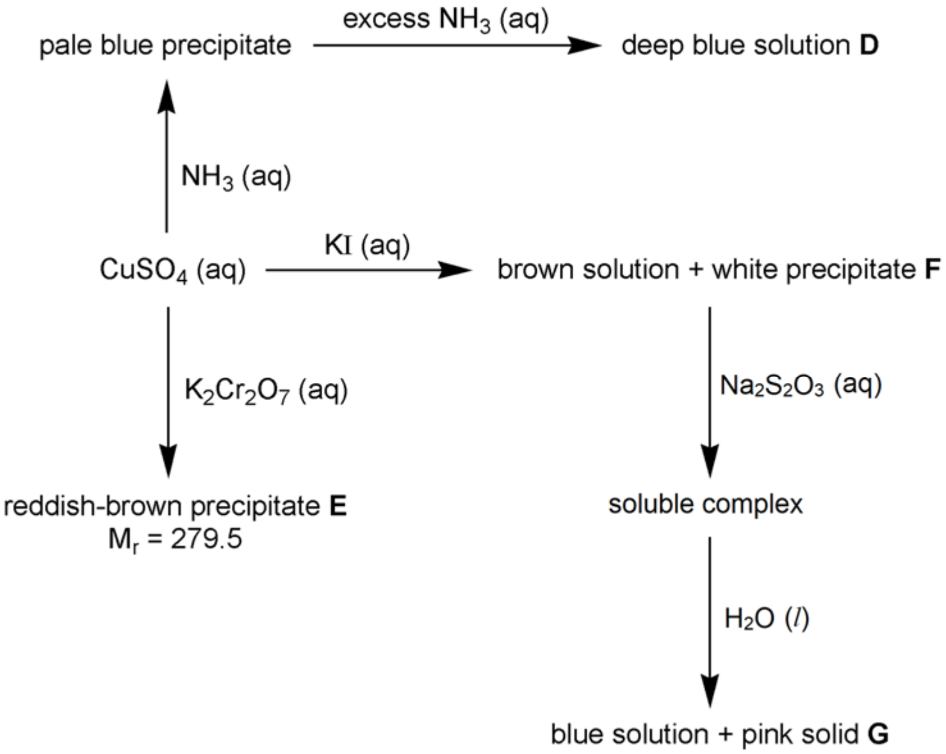
$2Ba + O_2 \rightarrow 2BaO$

[1]

[Total: 8]

2 The use of *Data Booklet* is relevant to this question.

(a) Copper(II) sulfate, an inorganic compound that has wide uses in organic syntheses and in engraving of zinc plates for intaglio printmaking, can undergo a series of reactions as shown below.



(i) Identify **D**, **E**, **F** and **G**.

D: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ or $[Cu(NH_3)_4]^{2+}$

E: $CuCr_2O_7$

F: CuI

G: Cu

(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l)$ ---(1)

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^{-}(aq)$ ---(2)

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. This causes the ionic product of $Cu(OH)_2$ to become less than K_{sp} of $Cu(OH)_2$, and hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

OR

Formation of $[Cu(NH_3)_4]^{2+}$ complex lowers $[Cu^{2+}]$. By Le Chatelier's Principle, the position of equilibrium (2) shifts to the right to partially increase $[Cu^{2+}]$. Hence the pale blue $Cu(OH)_2$ precipitate dissolves to form the deep blue solution.

[2]

(b) **(i)** By quoting relevant data, account for the trend in the thermal stabilities from HC*l* to HI.

BE(H–C*l*) = 431 kJ mol^{-1} BE(H–Br) = 366 kJ mol^{-1}
BE(H–I) = 299 kJ mol^{-1}

Down the group, less energy is needed to break the weaker H–X bond, resulting in decreasing thermal stability of HX.

[2]

(ii) Identify a transition metal cation that can be used to differentiate the oxidising abilities of Br_2 and I_2. Explain your answer with appropriate workings.

[3]

The transition metal cation is Fe^{2+}.

From Data Booklet	$E^\ominus$ / V
$Br_2 + 2e \rightleftharpoons 2Br^-$	+1.07
$I_2 + 2e \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	+0.77

$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$ $E^\ominus_{cell} = +0.30 \text{ V} > 0$

Br_2 can oxidise Fe^{2+} to Fe^{3+} since the reaction is spontaneous.

$I_2 + 2Fe^{2+} \rightarrow 2I^- + 2Fe^{3+}$ $E^\ominus_{cell} = -0.23 \text{ V} < 0$

I_2 cannot oxidise Fe^{2+} to Fe^{3+} since the reaction is non-spontaneous.

(iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:

- Aqueous silver nitrate
- Aqueous ammonia
- Aqueous nitric acid
- Filter paper
- Filter funnel

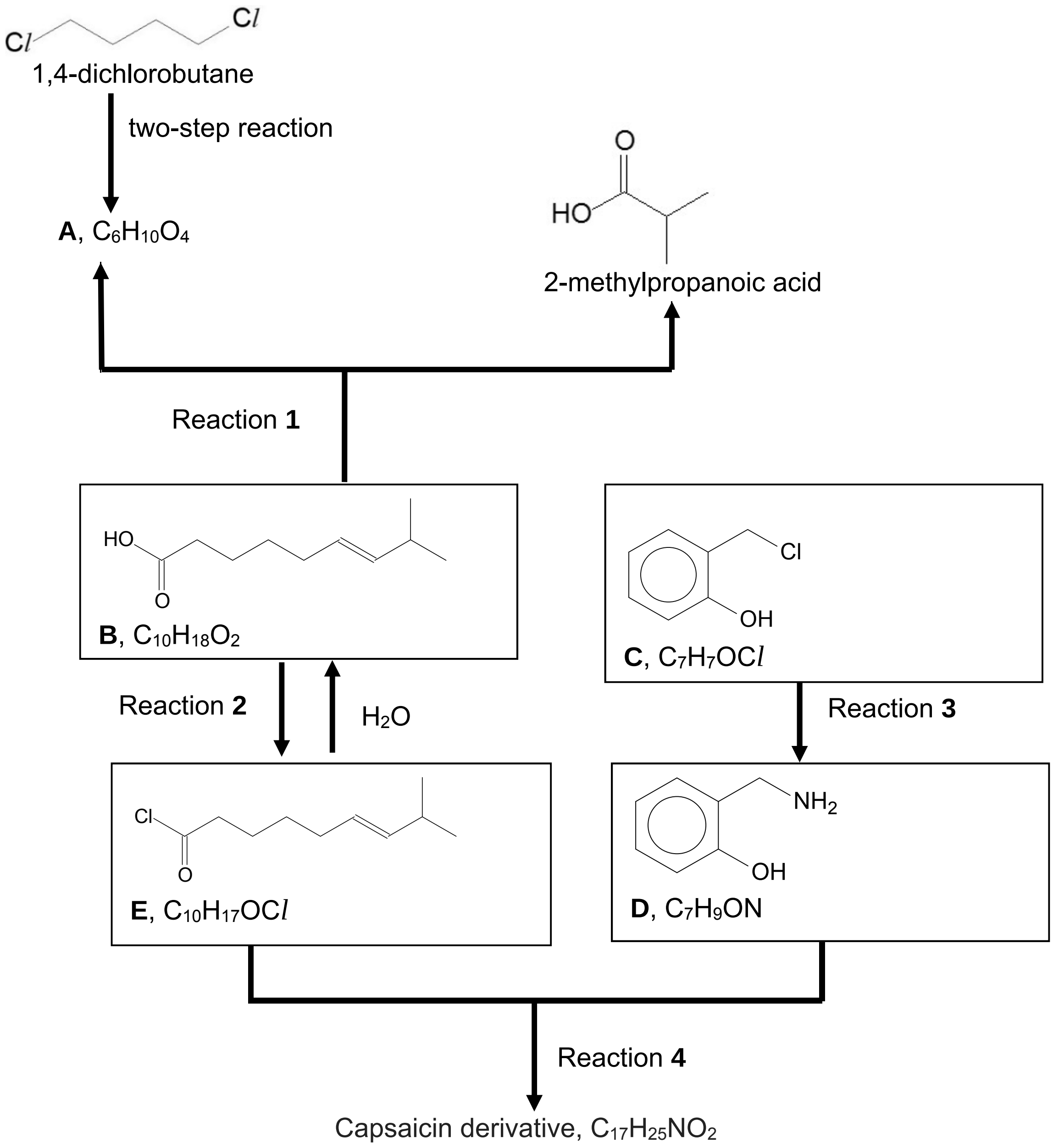
1. Add excess aqueous silver nitrate to the mixture. Yellowish-white precipitate is formed.
2. Next, add excess aqueous ammonia. Some of the precipitate will dissolve and only a yellow precipitate remains.
3. Filter the mixture with filter paper and filter funnel. Yellow residue indicates the presence of iodide ions.
4. To the colourless filtrate, add excess aqueous nitric acid. White precipitate formed indicates the presence of chloride ions.

[3]

[Total: 14]

3 Capsaicin is an active component of chili peppers. The reaction scheme involving the formation of a derivative of Capsaicin, $C_{17}H_{25}NO_2$, is shown below.

Information on compounds **A** to **D** are given on pages 6 and 7.



Compounds **A** to **D** react with sodium metal.
Compounds **A** and **B** react with aqueous sodium carbonate.
Compound **C**, Compound **D** and the capsaicin derivative reacts with aqueous sodium hydroxide but does not react with aqueous sodium carbonate.
Compounds **B** and **E** also react with cold acidified $KMnO_4$.

(a) Name the functional group common to compounds **A** and **B**.

Carboxylic acid

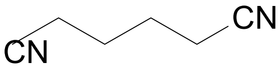
[1]

(b) Compound **A** can be synthesised from 1,4-dichlorobutane in two steps. Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.

Step 1: ethanolic NaCN, heat

Step 2: dil H_2SO_4, heat

Intermediate product:



[3]

(c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified $KMnO_4$.

Functional group that reacts with cold acidified $KMnO_4$: alkene

[1]

(d) Hence, draw the structure of compound **B** in the box on pg 6 and state the reagents and conditions for reaction **1**.

Reagents and conditions for reaction **1**: $KMnO_4$, dil H_2SO_4, heat

[2]

(e) Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt. Draw the structure of Compounds **C** and **D** in the box on pg 6. Name the type of reaction for reaction **3**.

Type of reaction for reaction **3**: nucleophilic substitution

[3]

(f) Compound **E** readily hydrolyses in water to produce Compound **B**.

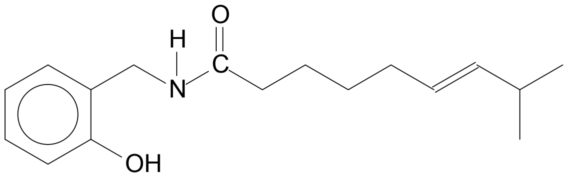
Draw the structure of compound **E** in the box on pg 6, and hence state the reagents and conditions for reaction **2**.

Reagents and conditions for reaction **2**: PCl_5 (s), anhydrous

[2]

(g) Compounds **D** and **E** react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.



[1]

[Total: 13]

4 On 11 May 2018, Mount Merapi on Central Java, Indonesia erupted, causing the local airport to be closed. The eruption was reported to be caused by accumulation of volcanic gases. The volcanic ash and gases spewed can be dangerous to planes passing through the plume. The most abundant volcanic gas is harmless water vapour. However, significant amounts of carbon dioxide, sulfur dioxide, hydrogen sulfide and hydrogen halides are also emitted.

When carbon dioxide is emitted from volcanoes, it typically becomes diluted to low concentrations very quickly and is not life threatening. However, cold carbon dioxide gas can flow into low-lying areas where it can reach much higher concentrations. Breathing air with more than 3% CO_2 can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Table 1.1: Volcanic gas composition in area **A**

Gas	Volume Percentage
Water vapour, H_2O	87.1
Carbon dioxide, CO_2	unknown
Sulfur dioxide, SO_2	0.5
Hydrogen, H_2	0.7
Carbon monoxide, CO	0.01
Hydrogen sulfide, H_2S	0.23
Hydrochloric acid, HCl	2.89
Hydrofluoric acid, HF	2.55

Composition of the volcanic gases are typically expressed in terms of volume percentage, which can be calculated as follows

$$volume\ percentage = \frac{volume\ of\ gas}{Total\ volume} \times 100\%$$

However, percentages are only additive for ideal gases.

(a) **(i)** State **two** assumptions of the kinetic theory of gases.

1) Negligible attractive or repulsive forces between gas particles
2) Negligible volume of gas particles compared to the volume they are moving in/ volume of the container they are in.

[2]

(ii) Under what conditions of temperature and pressure would you expect the behaviour of carbon dioxide to be most like that of an ideal gas?

Low pressure and high temperature.

[1]

(iii) Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.

At low temperatures, there is insufficient energy to overcome the strong temporary dipole induced dipole (tdid) interactions between CO_2 molecules. Hence CO_2 would aggregate together/ more CO_2 molecules in a smaller volume and have a higher density thus sink down.

[2]

(iv) People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly.

Given that 0.30 mg of CO_2 was present in 10 cm^3 of gas mixture at 43 °C and 11.2 kPa, determine the volume percentage of carbon dioxide present.

Hence comment on the possible danger if people remained in the area.

Amt of CO_2 = $\frac{0.30 \times 0.001}{44.0} = 6.818 \times 10^{-6} mol$

pV = nRT

$(11200)(V) = (6.818 \times 10^{-6})(8.31)(273 + 43)$

$V = 1.598 \times 10^{-6}$ m^3

volume percentage of $CO_2 = \frac{1.598 \times 10^{-6}}{10 \times 10^{-6}} \times 100\%$ = 16.0%

Ans: 16.0% unconsciousness and death can result quickly.

[3]

(b) Hydrogen sulfide can react with methane in the following equation.

$$CH_4(g) + 2\,H_2S(g) \rightleftharpoons CS_2(g) + \mathbf{4\,H_2(g)}$$

1 mol of CH_4, 2 mol of H_2S, 1 mol of CS_2 and 1 mol of H_2 was allowed to reach equilibrium at a constant temperature and pressure of 960°C and 2 atm.

Given that partial pressure of CS_2 was found to be 0.5 atm at equilibrium, determine the value of K_p, giving its units.

[3]

Q says to reach equilibrium at 960^{o}C and 2 atm, i.e. Total P initially and Total P at eqm is same, 2 atm.

	$CH_4(g)$	$+ 2 H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	$+ 4 H_2(g)$
Initial/ mol	1	2		1	1
Eqm/ mol	1-x	2-2x		1 + x	1 + 4 x

Total mol at eqm = 5 + 2x

partial pressure of CS_2 == $2\left(\frac{1+x}{5+2x}\right) = 0.5 \text{ atm}$

solve for x , x = 0.5

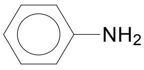
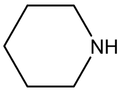
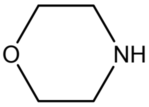
	$CH_4(g)$	$+ 2 H_2S(g)$	$\rightleftharpoons$	$CS_2(g)$	$+ 4 H_2(g)$
Eqm/ mol	0.5	1		1.5	3
	Total amt of gas at eqm = 6				
Eqm / atm	$\frac{0.5}{6} \times 2 = \frac{1}{6}$	$\frac{1}{6} \times 2 = \frac{1}{3}$		0.5	$\frac{3}{6} \times 2 = 1$

$$K_p = \frac{(P_{H2})^4 . P_{CS2}}{P_{CH4} . (P_{H2S})^2}$$

$$K_p = \frac{1^4(0.5)}{(1/6).(1/3)^2} = 27.0 \text{ atm}^2$$

[Total: 11]

5 **(a)** The following table contains the pK_b values of different nitrogen organic compounds.

Compound	pK_b
$(CH_3)_3CNH_2$ 2-amino-2-methylpropane	3.19
 phenylamine	9.38
 piperidine	2.88
 morpholine	5.17
N_2H_4 hydrazine	5.17, 11.05

(i) Suggest a reason why pK_b of morpholine is higher than piperidine.

Morpholine has an electronegative O that exert ***electron withdrawing effect***, it reduces the availability of lone pair on N to accept H^+, therefore Morpholine is a weaker base hence a higher pK_b value.

(ii) Suggest a reason why pK_b of phenylamine is so much higher than 2-amino-2-methylpropane.

Lone pair on N of phenylamine is delocalised into the benzene ring, making lone pair much less available to receive H^+ than lone pair of N in $(CH_3)_3CNH_2$, phenylamine is a weaker base hence a higher pKb value than $(CH_3)_3CNH_2$.

[2]

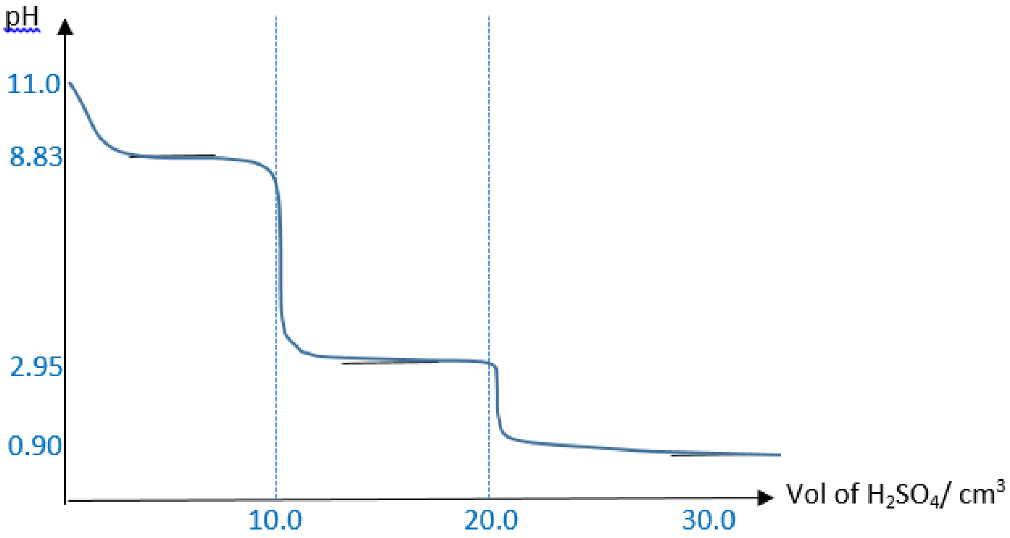
(b) 10.0 cm^3 of an aqueous mixture containing 0.5 mol dm^{-3} of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

Sketch the p*H*–volume graph on the axis provided when 10.0 cm^3 of the aqueous mixture was titrated with 0.25 mol dm^{-3} dilute sulfuric acid until a total volume of 30.0 cm^3 of dilute sulfuric acid was added.

Your sketch should include the following points

- Initial pH of hydrazine
- p*H* of the reaction mixture when 30.0 cm^3 of H_2SO_4 is added.

- Maximum buffer points (if any)



Initial pH = 11.0 given in question

volume of H_2SO_4 required for the 1st equiv point = 10.0 cm^3
total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm^3

Max buffer points occur at 5 and 15 cm^3.
$pOH = pK_b$ at max buffer pts
pH = 14- pOH
pH are 14 – 5.17 = 8.83 and 14 – 11.05 = 2.95 respectively.

Final pH
Amt of unreacted H^+ = (2 x 10/1000 x 0.25) = 0.005 mol (since H_2SO_4 is diprotic)
$[H^+]$ = 0.005 x 1000/ 40 = 0.125 $moldm^{-3}$ => pH = 0.90

[3]

(c) Student **M** suggested a 2–step process as shown, to synthesise 2-amino-2-methylpropane from a suitable alkane.

$$\underset{\textbf{A}}{C_4H_{10}} \xrightarrow{\text{step 1}} \underset{\textbf{B}}{C_4H_9Cl} \xrightarrow{\text{step 2}} C_4H_{11}N$$

(i) Identify the structures of compounds **A** and **B**, and suggest reagents and conditions for each of the two steps.

$(CH_3)_3CH$ Structure of **A**	$(CH_3)_3CCl$ Structure of **B**

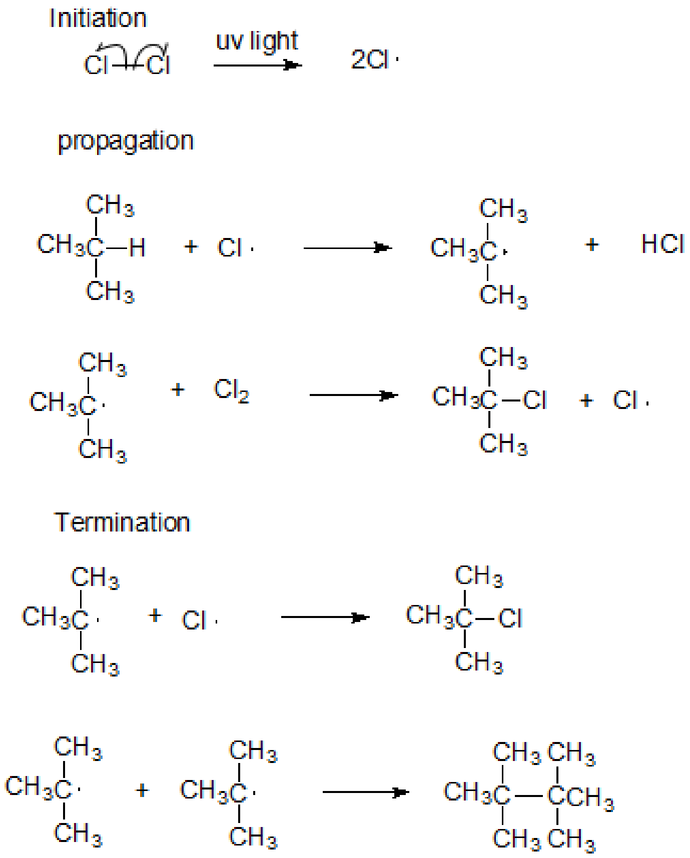
Step 1: limited Cl_2, UV. light

Step 2: excess NH_3 in ethanol, heat in sealed tube

[4]

(ii) Outline the mechanism for step 1.

Free radical substitution



[3]

(iii) A student **N** suggested an alternative synthetic route for the synthesis of 2-amino-2-methylpropane, using an alkene as a starting material.

Explain why this synthetic route will give a higher yield as compared to the suggested route in **(c) (ii).**

Electrophilic addition via alkene can only give two possible products and the tertiary carbocation is formed at a greater rate that forms the major product 2-amino-2-methylpropane, while free radical substitution of alkane gives rise to a variety of reactive intermediates that lead to multiple products being formed.

[2]

[Total: 14]

6 1–chloro–1–phenylethane undergoes hydrolysis with hydroxide ions to produce 1–phenylethanol, as shown in the equation below.

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

(a) The rate of this reaction can be studied by measuring the amount of hydroxide ions that remain in the solution at a given time after the reaction has been quenched.

(i) Suggest a suitable quenching agent that can be used to stop the reaction effectively.

cold water

[1]

(ii) Using your answer in **(i)**, describe a suitable method for determining the order of reaction with respect to OH^-, given the following.

- Solution **A**, 1.0 mol dm^{-3} 1-chloro-1-phenylethane
- Solution **B**, 0.10 mol dm^{-3} sodium hydroxide
- 0.10 mol dm^{-3} hydrochloric acid
- Quenching agent [as suggested in **(i)**]
- Stopwatch
- Standard laboratory equipment

Specific details of volumes and time is not required.

Continuous Method:

1. Mix Solution **A** & **B**, swirl the beaker and start the stopwatch.
2. At a certain time, withdraw a fixed volume of mixture into a conical flask, add fixed volume of cold water to the mixture to quench the reaction.
3. Titrate against hydrochloric acid, using phenolphthalein as indicator.
4. Titrate until colour of mixture turns from pink to colourless.
5. Repeat steps 2 - 4 at fixed time intervals (eg, 6 min, 9 min, 12 min)
6. Plot graph of volume of HCl against time.
7. If straight-line graph, it means that reaction is 0 order wrt OH^-
   If constant half-life, it means that reaction is 1st order wrt OH^-
   If increasing half-life, it means that reaction is 2nd order wrt OH^-

(b) The rate of this reaction was measured using different initial concentrations of the two reagents and the results are shown below.

Experiment	[$C_6H_5CHClCH_3$] / mol dm^{-3}	[OH^-] / mol dm^{-3}	Relative rate
1	0.05	0.10	1.0
2	0.10	0.20	2.0
3	0.15	0.10	3.0

(i) Deduce the order of reaction with respect to each of the reagents. Explain your reasoning.

Comparing experiment 1 & 3, when [OH^-] is constant, [$C_6H_5CHClCH_3$] is tripled, relative rate is tripled. Hence, reaction is 1st order with respect to $C_6H_5CHClCH_3$. [1]

Comparing experiment 1 & 2, when both [OH^-] and [$C_6H_5CHClCH_3$] are doubled, relative rate is doubled. Since reaction is 1st order with respect to $C_6H_5CHClCH_3$, the doubling of [OH^-] has no effect on rate, so reaction is zero order with respect to OH^-. [1]

* Accept if student write conc / rate <u>increases by</u> 3 times.

Order with respect to $C_6H_5CHClCH_3$ = **first order**

Order with respect to OH^- = **zero order**

(ii) Write the rate equation for this reaction, stating the units of the rate constant, *k*.

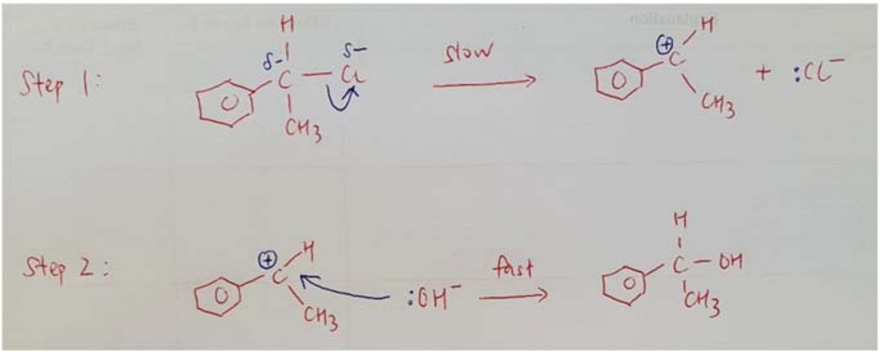
rate = $k[C_6H_5CHClCH_3]$ mol dm^{-3}s^{-1}

units of *k* = s^{-1}

[2]

(c) **(i)** By making use of your answer in **(b)(i)**, describe the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions.
In your answer, you should show relevant charges, lone pairs, dipoles and show movement of electrons by curly arrow.

<u>Nucleophilic substitution (S_N1)</u>



(ii) This reaction was carried out using a single optical isomer of 1-chloro-1-phenylethane. Use your mechanism in **(i)** to predict whether the product will be a single optical isomer or a mixture of two optical isomers. Explain your answer.

A mixture of 2 optical isomers (racemic mixture) will be formed because the nucleophile can attack the trigonal planar intermediate from top or bottom of the plane with equal probability.

If S_N2 in c(i),
A single optical isomer will be formed as the nucleophile attack the molecule from the opposite side of the leaving chloride, resulting in an inversion of configuration. [2]

(iii) 1-chloro-2-ethyl benzene, $C_6H_4ClCH_2CH_3$, is an isomer of 1-chloro-1-phenylethane, $C_6H_5CHClCH_3$. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

In 1-chloro-2-ethyl benzene, the p-orbital of C*l* overlaps with the π-electron cloud of benzene, resulting in delocalisation of electrons, strengthening the C-C*l* bond, giving it a partial double bond character.

Hence, the C-C*l* bond does not break easily and the ease of hydrolysis will be much lower than that of 1-chloro-1-phenylethane.

[Total: 15]

NATIONAL JUNIOR COLLEGE

SH2 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME	

SUBJECT CLASS		REGISTRATION NUMBER	

CHEMISTRY

9729/03

Paper 3 Free Response

Monday 10 Sep 2018
2 hours

Candidates answer on separate paper.

Additional Materials: Data Booklet
Answer Paper

READ THESE INSTRUCTIONS FIRST

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.

You may use a soft pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid/tape.

Section A
Answers **all** questions.

Section B
Answers **one** question.

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

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

Section A

Answer **all** the questions in this section.

1 **(a)** The melting points of some compounds are given

Substance	Octan-1-ol	Iodine	Fullerene	Graphite
Formula	$CH_3(CH_2)_7OH$	I_2	C_{60}	C
Melting point/ K	277	286	873	>3000

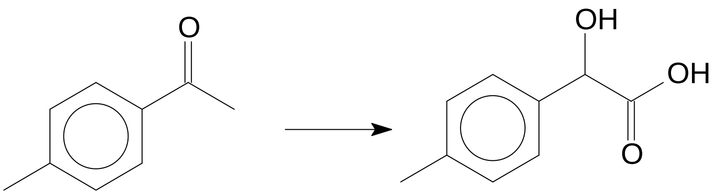
(i) Explain why the melting points of octan-1-ol and iodine are comparable. [2]

(ii) Explain why the melting point of graphite is higher than that of fullerene. [2]

(b) In 1932, Harry Lister Riley and coworkers published their findings on the use of selenium dioxide, SeO_2, in the synthesis of aldehyde and ketone functional groups. One of such reactions is shown below.

$CH_3COCH_3 + SeO_2 \xrightarrow{} CH_3COCHO + Se + H_2O$ reaction **I**

Using the synthetic method above in one of your steps, devise a three–stage synthesis of compound **B** from compound **A**.



Compound **A** Compound **B**

[5]

(c) The most common source of acidity in water is dissolved carbon dioxide.

Carbon dioxide enters the water through equilibrium with the atmosphere.

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad K_H = 3.3 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{kPa}^{-1}$$

where K_H is known as the Henry's Law constant given by the equation:

$$[CO_2(aq)] = K_H \times P_{CO2}$$

Carbon dioxide can react with water to form carbonic acid as shown in the following reaction.

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \qquad K_c = 1.3 \times 10^{-3}$$

(i) Calculate $[CO_2(aq)]$ at a pressure of 101.3 kPa, given that air contains 0.035% by volume of carbon dioxide. [2]

(ii) Using your answer from **(i)**, calculate $[H_2CO_3]$. [1]

Carbonic acid will further dissociate in the following reactions.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \quad K_{a1} = 2.5 \times 10^{-4}$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq) \quad K_{a2} = 4.7 \times 10^{-11}$$

(iii) The pH of the carbonic acid is largely contributed by K_{a1}. Explain why. [1]

(iv) Hence, calculate pH of carbonic acid. [1]

(c) Many organic compounds that occur naturally have molecules that can show stereoisomerism, that is cis-trans or optical isomerism.

Draw the structures of all the possible stereoisomers which have the following features.

- They are acyclic.
- They have molecular formula $C_4H_{10}N_2$.
- No nitrogen atom is attached to any carbon atom which is involved in a double bond.
- No carbon atom has more than one nitrogen atom joined to it.

For **each** structure you draw, state the type of stereoisomerism it shows.

[4]

[Total:18]

2 Electric or hybrid vehicles are expected to reach 27 million by 2027. Copper is used as a major component in the windings and copper rotors of electric vehicles.

Crude copper was obtained when a particular copper ore was reduced. Crude copper contains cobalt and silver as minor impurities. It contained no other metal. In order to purify it, crude copper was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

(a) Explain, with reference to relevant $E^\ominus$ values, what happens to the cobalt and silver impurities during this purification process.

[3]

An experiment was carried out to determine the percentage purity of the crude copper obtained from reduction of copper ore. A current of 2.15 A was passed through the cell described in **(a)** for 28.0 minutes, and the electrodes removed and weighed. It was found that the anode has lost 1.25 g.

After filtering it off, the deposit underneath the anode weighed 0.07 g. On adding an excess of dimethylglyoxime to the electrolyte, the highly insoluble red complex with the formula $Co(C_4H_7N_2O_2)_2$ was precipitated. Its mass was 0.55 g.

(b) **(i)** Calculate the *actual mass of copper* removed from the crude copper.

[2]

(ii) Hence determine the percentage purity of the crude copper produced in **(a),** assuming that the crude copper is of uniform mixture.

[1]

(iii) Suggest how the procedure can be improved to increase the reliability of results.

[1]

(iv) Calculate the *expected increase* in mass of the cathode.

[2]

(c) $Co(C_4H_7N_2O_2)_2$ has a solubility of 1.23×10^{-4} mol dm^{-3}.

Calculate its solubility product.

[2]

Lithium is a scavenger for hydrogen, hence it is able to prevent the reaction between hydrogen and copper during pure copper casting. Reaction with hydrogen makes the copper brittle, causing it to fall apart under very light stress.

Table 1

	Enthalpy / kJ mol^{-1}
Enthalpy change of formation of LiH(s)	–90.5
Enthalpy change of formation of $LiAlH_4(l)$	–152.5
Enthalpy change of formation of $Li_3AlH_6(s)$	–454
Enthalpy change of atomisation of Li(s)	+159.5
Electron affinity of hydrogen atoms	–73.0

(d) Heating lithium in a stream of hydrogen gas produces white, crystalline, ionic lithium hydride, LiH.

(i) With the help of a suitable energy level diagram, calculate the lattice energy of LiH using relevant data from **Table 1** and the *Data Booklet*.

[3]

(ii) By quoting relevant data from the *Data Booklet*, suggest and explain how the magnitude of the lattice energy of Li*Cl* would compare to LiH.

[2]

(e) When lithium hydride is heated with anhydrous aluminium chloride, lithium aluminium hydride, $LiAlH_4$ and lithium chloride are produced.

$$4\ LiH\ +\ AlCl_3\ \rightarrow\ LiAlH_4\ +\ 3\ LiCl$$

When 5 g each of $AlCl_3$ and LiH are reacted in a bomb calorimeter, the temperature rise is 8.4 °C. Given that the heat capacity of the bomb calorimeter is 1.24 kJ K^{-1}, determine the enthalpy change of this reaction per mole of $LiAlH_4$.

[3]

(f) Just above its melting point, $LiAlH_4$ decomposes according to the following equation.

$$3\ LiAlH_4\ (l) \rightarrow Li_3AlH_6(s) + 2Al(s) + 3H_2(g)$$

(i) Use relevant data in **Table 1**, calculate the standard enthalpy change of this reaction.

[1]

(ii) Given that $\Delta G^\ominus = -27.7$ kJ mol^{-1}, calculate $\Delta S^\ominus$ for this reaction at 298K, and comment on its sign with respect to the equation for this reaction.

[2]

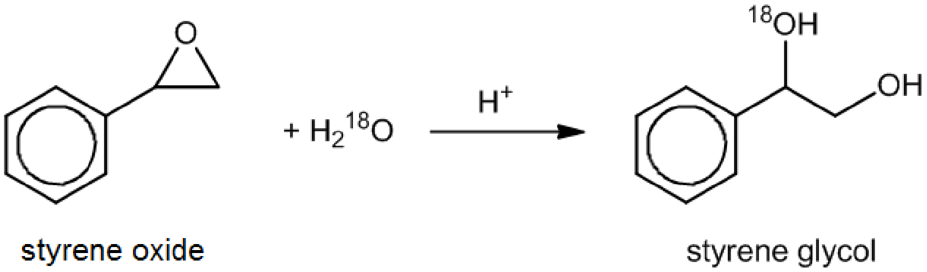
(iii) Hence calculate the melting point of $LiAlH_4$. [1]

[Total: 23]

3 **(a)** Epoxides are a class of organic compounds with a three-membered ring structure. The three-membered ring in epoxides makes them highly reactive and susceptible to "ring-opening reactions" whereby one of the C–O bonds breaks.

(i) An example of an epoxide ring-opening reaction is the hydrolysis of styrene oxide in the presence of a strong acid catalyst to form styrene glycol.

To determine the reaction mechanism, isotopic labelling was used. The hydrolysis was carried out using "heavy-oxygen water", $H_2{}^{18}O$.



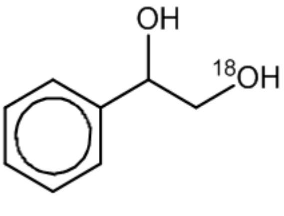
Some details of the mechanism are as given.

1. Protonation of the oxygen atom by a strong acid catalyst
2. Heterolytic fission of the C–O bond to generate a carbocation intermediate, which is a slow step
3. Attack of the carbocation by one molecule of $H_2{}^{18}O$ to form a new C–O bond
4. Loss of a proton to form styrene glycol and regenerate the acid catalyst

Describe steps 1 to 4 of the unimolecular nucleophilic substitution mechanism, showing all relevant charges, lone pairs, dipoles and movement of electrons by curly arrows. You are to label the ^{18}O atom in all necessary species.

[3]

(ii) Trace amounts of an isotopic isomer **A** are also detected upon analysis of the styrene glycol product formed from the hydrolysis.



isotopic isomer **A**

Explain why **A** was formed only in trace amounts.

[2]

(iii) Draw the structure of a side product formed if the same reaction is carried out in the presence of aqueous sodium chloride.

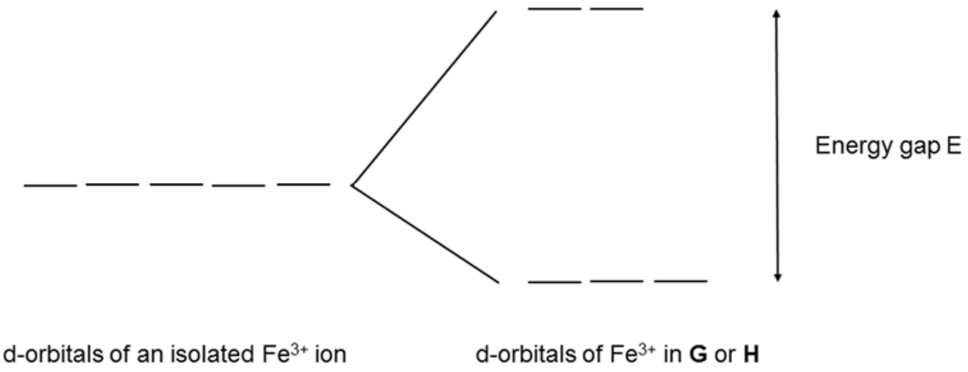
[1]

(b) In 2012, a group of scientists synthesised two ligands, N,N-diethylethylenediamine and N-ethylethylenediamine, and reacted each with Fe^{3+} to form two complexes, **G** and **H**, with different colours respectively.

(i) Explain why iron(III) complexes are usually coloured.

[3]

The following diagram shows how the d-orbitals are split in an octahedral environment.



When the ligand in **H** is substituted with N,N-diethylethylenediamine ligand to form **G**, the Fe^{3+} ion changes its electronic configuration from a 'high spin' state to a 'low spin' state.

In a 'high spin' state, the electrons occupy all the d-orbitals singly, before starting to pair up in the lower energy d-orbitals.

In a 'low spin' state, the lower energy d-orbitals are filled first, by pairing up if necessary, before the higher energy d-orbitals are used.

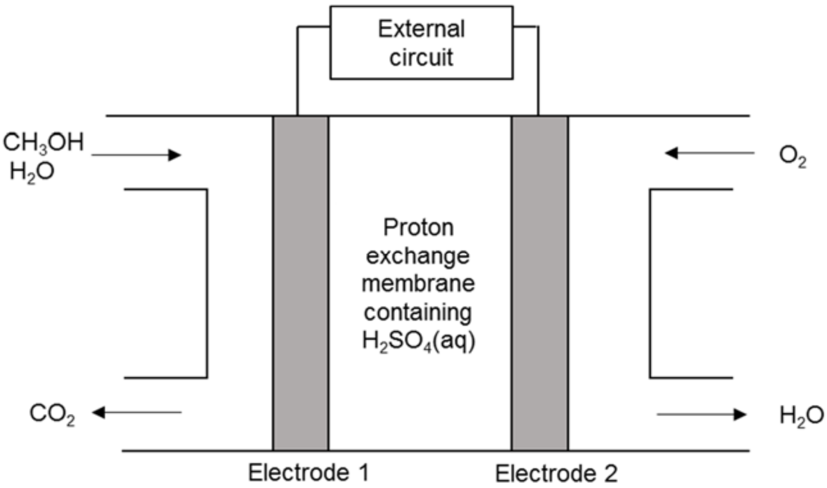
(ii) Use diagrams like the one above to show the electronic distribution of a Fe^{3+} ion in a high spin state, and in a low spin state.

[2]

(iii) By using the information provided thus far and your answer in **(ii)**, state and explain which of the two complexes will contain the larger energy gap, E, between its d-orbitals.

[2]

(c) The following diagram illustrates the parts of a type of fuel cell, Direct methanol fuel cell (DMFC). Methanol is supplied to Electrode 1 where methanol and water react to form carbon dioxide. Oxygen is supplied to Electrode 2 simultaneously and reacts with the protons at the cathode to form water.



(i) Determine the oxidation number of carbon in carbon dioxide and methanol.

[1]

(ii) Write half equations for the reactions which take place at Electrode 1 and Electrode 2. Hence, construct an equation for the overall reaction.

[2]

(iii) The cell is capable of producing an e.m.f. of 1.62 V.

Predict how the voltage of this cell would change if the concentration of methanol was reduced.

[2]

(iv) Suggest a possible advantage of using DMFC as compared to a hydrogen-oxygen fuel cell.

[1]

[Total:19]

Section B

Answer **one** question from this section.

4 **(a)** Proteins are diverse groups of polypeptides required by the human body for growth and maintenance. Human serum albumin, HSA is an important protein that transports hydrophobic molecules in the blood stream.

Four of the most common amino acids in the HSA molecule are listed below.

Amino acid	Formula of side chain (R in $RCH(NH_2)CO_2H$)
Glutamic acid	$-CH_2CH_2CO_2H$
Leucine	$-CH_2CH(CH_3)_2$
Lysine	$-CH_2CH_2CH_2CH_2NH_2$
Valine	$-CH(CH_3)_2$

(i) Use the above amino acids to draw the structural formula of a section of the polypeptide chain of HSA, consisting of 3 amino acid residues.

[2]

(ii) The ability of a protein to carry out its function lies in its unique structure that is a result of interactions within the polypeptide chain.

Given that the secondary structure occurs due to interactions between the peptide linkages, state the type of interaction in the secondary structure and illustrate it with a simple diagram.

[2]

(iii) The hydrophobic groups are transported in the inside of the spherical HSA molecule.
Which 2 amino acids from the above table are likely to be responsible for this? Explain your answer.

[2]

(b) **(i)** Amino acids exist as zwitterions. Using leucine as an example, suggest what is meant by the term *zwitterion*.

[1]

(ii) How would you expect the melting point and the solubility in water, of an unionised form of leucine to compare with the actual properties of the zwitterionic form?

[3]

(c) Compound **A**, $C_8H_{10}O_2$, reacts with aqueous bromine to form a white precipitate, compound **B** with molecular formula, $C_8H_7O_2Br_3$.

Compound **A** also reacts with dilute nitric acid to give compound **C**, $C_8H_9NO_4$. Treatment of compound **C** with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound **D**, $C_8H_{10}NO_2Na$.

Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$. 1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.

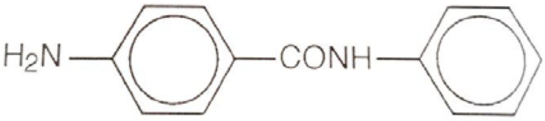
Compound **E** reacts with phosphorus pentachloride to give compound **F**, $C_8H_7NO_2$.

Deduce the structures of compounds **A, B, C, D, E and F** and explain the chemistry of the reactions described.

[10]

[Total:20]

5 **(a)** The structure of 4-amino-N-phenylbenzamide, used in the treatment of epilepsy, is given below. It forms interactions with water but has low solubility in water.



(i) State the type of interaction occurring between water molecules and 4-amino-N-phenylbenamide. Illustrate it with a simple diagram involving a water molecule.

[2]

(ii) Explain the low solubility of 4-amino-N-phenylbenzylamide in water.

[2]

(b) 4-amino-N-phenylbenzylamide is warmed with aqueous sodium hydroxide. Distillation was carried out to separate the products.

(i) Draw the structures of the products formed when 4-amino-N-phenylbenzylamide is warmed with aqueous sodium hydroxide.

[2]

(ii) Suggest and explain the identity of the distillate.

[2]

(iii) When the other product is carefully neutralised, a compound that can be used to maintain the pH of systems at a desired value is obtained.

By means of equations, show how this is achieved when small amounts of
I. dilute HC*l*,
II. dilute NaOH,
is added to a solution of the compound.

[2]

(c) **G**, $C_6H_9O_2N$, is a neutral compound with the ability to rotate plane polarized light.

On heating **G** with aqueous NaOH, a pungent gas **H** that turned moist red litmus blue was liberated. Upon acidification of the reaction mixture, **J**, $C_5H_8O_4$, was formed.

J reacts with LiA*l*H$_4$ to form **K**, $C_5H_{12}O_2$. On heating with excess concentrated H_2SO_4, **K** forms **L**, C_5H_8. **L** does not exhibit cis-trans isomerism. When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed.

M reacts with aqueous Na_2CO_3 to produce effervescence that forms a white precipitate in limewater. **M** also forms a yellow precipitate when warmed with alkaline aqueous I_2.

Deduce the structures of compounds **G, H, J, K, L** and **M,** and explain the chemistry of the reactions described.

[10]
[Total:20]

COVER PAGE

NATIONAL JUNIOR COLLEGE SENIOR HIGH 2
PRELIM EXAMINATION

NAME : ______________________________

SUBJECT CLASS : ______________________________

REGISTRATION NO : ☐☐☐☐☐☐☐

SUBJECT TITLE/PAPER NO : ______________________________

For Candidate's Use	For Examiner's Use
Question Number	Marks Obtained
1	
2	
3	
Penalty	
Sf/units	☐☐☐☐☐☐
Total for **Section A**	

Instructions to Candidates

1 Write the information required in the box above.

2 *Place this cover page on top of your answer sheets for **section A**.
*Use the string provided to tie this cover on top of your answer sheets securely.
*Do not tie the answer sheets so tightly that the examiners cannot easily turn the pages.
*Do not staple your answer sheets.

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COVER PAGE

NATIONAL JUNIOR COLLEGE SENIOR HIGH 2
PRELIM EXAMINATION

NAME : ______________________

SUBJECT CLASS : ______________________

REGISTRATION NO : ☐☐☐☐☐☐☐

SUBJECT TITLE/PAPER NO : ______________________

For Candidate's Use	For Examiner's Use
Question Number	Marks Obtained
4	
5	
Penalty	
Sf/Units	
Total for **Section B**	

<u>Instructions to Candidates</u>

1 Write the information required in the box above.

2 **Circle** the question number of the question attempted in the left hand margin of the writing paper and in the left hand column of the box on this cover page.

3
- * Place this cover page on top of your answer sheets for **section B**.
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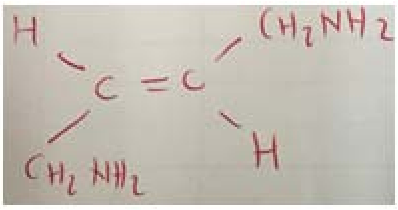
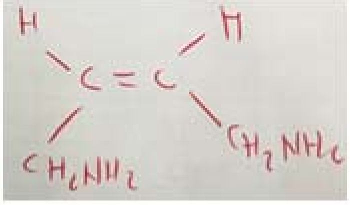
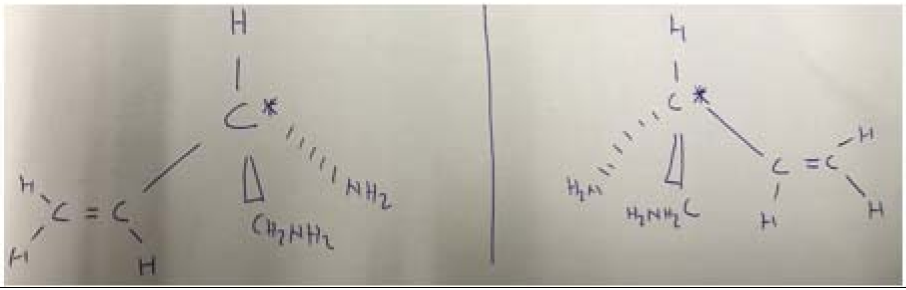
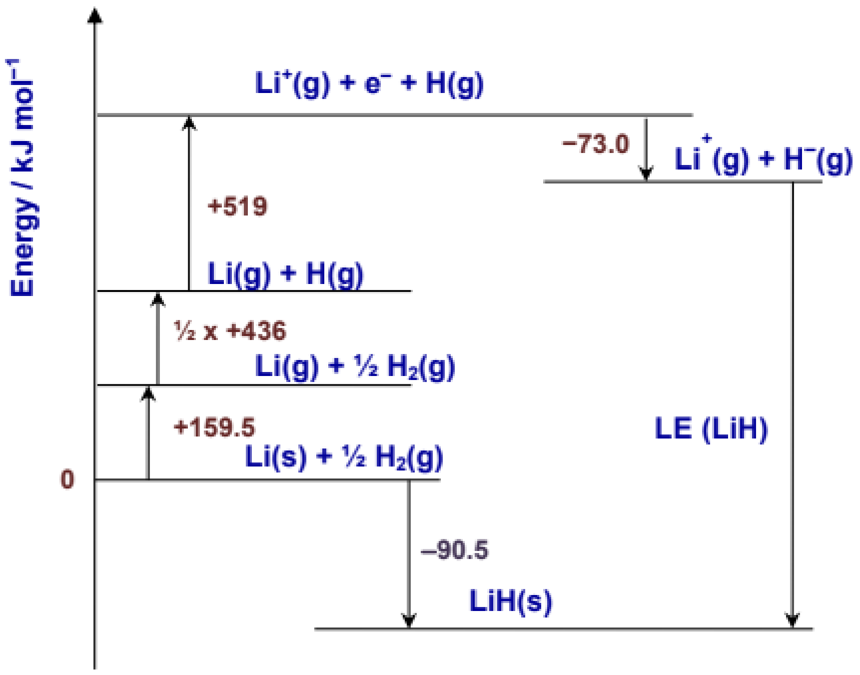
NJC 2018 SH2 H2 Chemistry Prelim Paper 3 Solutions:

Question 1	
(a)(i)	**Suggested solution** Both octan-1-ol and iodine have simple covalent structure Strength of Td-Id in iodine due to its large electron cloud size is comparable to the stronger hydrogen bonding between octan-1-ol molecules.
(ii)	**Suggested solution** Graphite has a giant molecular structure with strong covalent bonds between carbon atoms to be overcome during melting. Fullerene has a simple covalent structure with weaker td-id interactions between fullerene molecules to be overcome during melting. Hence, more energy is required to melt graphite and a higher temperature is required.
(b)	**Suggested solution** Step 1: reaction 1 ;(-COCHO) Step 2: $K_2Cr_2O_7$/$KMnO_4$ with H_2SO_4(aq) and heat; (-COCOOH) Step 3: $NaBH_4$ in ethanol or H_2 with Nickel/Pt ; (compound B)
c(i)	**Suggested solution** $P_{CO2} = \frac{0.035}{100} \times 101.3\text{kPa}$ $= 0.03546\text{kPa}$ $K_H = \frac{[CO_2(aq)]}{P_{CO2}}$ $[CO_2(aq)]$= 1.17×10^{-5} mol dm^{-3}
c(ii)	**Suggested solution** $K_c = \frac{[H_2CO_2(aq)]}{[CO_2]}$ $[H_2CO_3]$ = 1.52×10^{-8} mol dm^{-3}
(iii)	**Suggested solution** K_{a1} is larger than K_{a2}. H_2CO_3 will dissociate accordingly to eqm 1 first and $[H^+]$ from eqm 1 suppresses the dissocation of HCO_3^- in eqm 2. OR HCO_3^- from eqm 1 is low as K_{a1} is small. Hence $[H^+]$ from HCO_3^- is negligible. $[H^+]$ is largely from eqm 2.
c(iv)	**Suggested solution** $K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ $[H^+]$=1.915×10^{-6} $moldm^{-3}$ pH = 5.71
d	**Suggested solution**

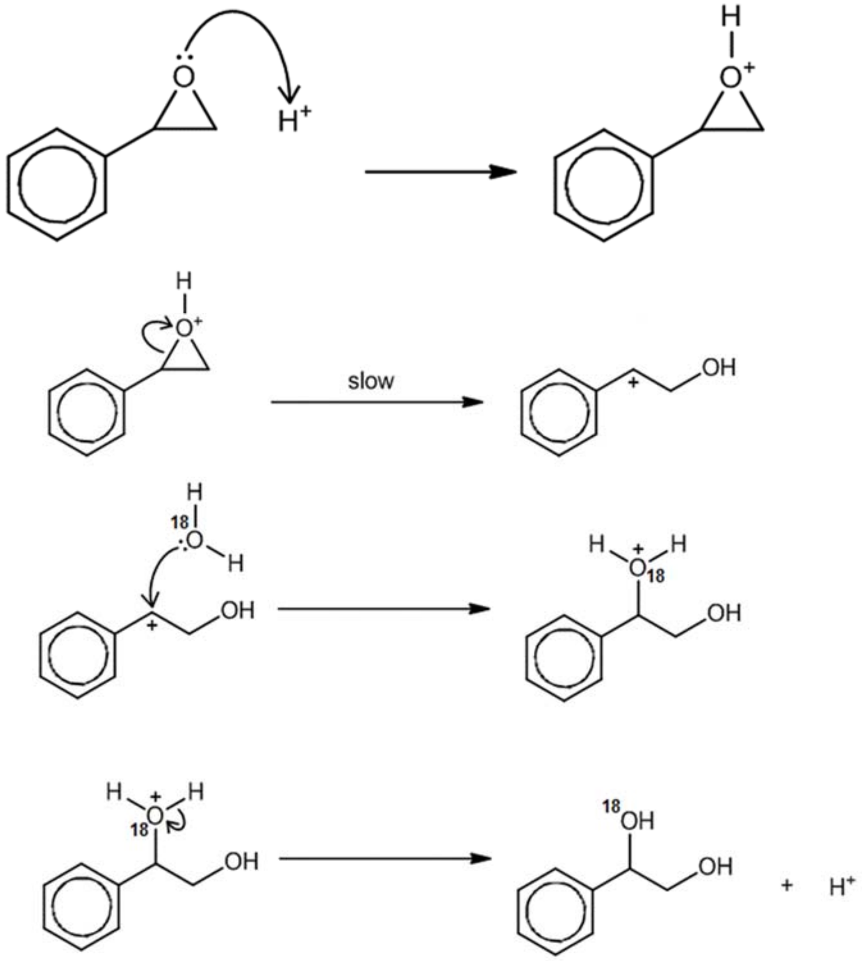
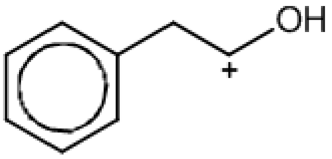
	  

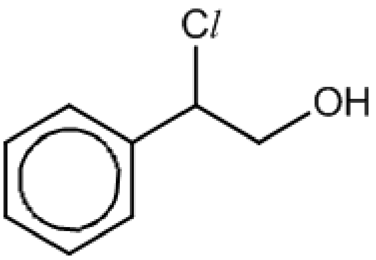
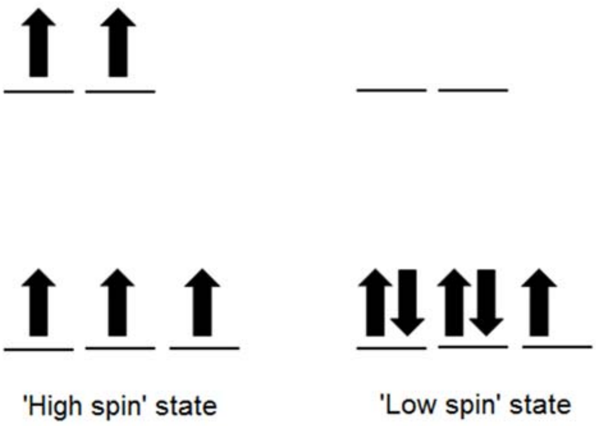
Question 2	
(a)	**Suggested solution:** At anode: Co has $E^{\ominus}_{ox}$ (Co/Co^{2+}) = +0.28V more positive that $E^{\ominus}_{ox}$ (Cu/Cu^{2+}) = –0.34V, hence Co will be oxidised together with Cu and dissolve as Co^{2+}, becoming part of the electrolyte. Ag on the other hand has more negative $E^{\ominus}_{ox}$ (Ag/Ag^{+}) of –0.80V, hence will not be oxidised. It will fall below anode as sludge. At cathode: Co^{2+} has a more negative $E^{\ominus}_{red}$(Co^{2+}/Co) = –0.28 V than $E^{\ominus}_{red}$(Cu^{2+}/Cu) = 0.34 V, hence Co^{2+} is not reduced at the cathode, remain dissolved as electrolyte.
(b) (i)	**Suggested solution** • mass of Ag = 0.07 g • No of moles of Co oxidised at anode = no of moles of Co($C_4H_7N_2O_2$)$_2$ $= \frac{0.55}{58.9+2(4\times12+7+2\times14+2\times16)}$ = 0.0019038 mol Mass of Co in alloy (anode) = 0.0019038 x 58.7 = 0.112 g Mass of Cu = 1.25 – 0.07 – 0.112 = 1.068 g
b(ii)	% purity = 1.068 /1.25 x 100 = 85.4%
b(iii)	**Suggested solution:** **Any one of the suggestion below is acceptable:** (i) Mass of Ag and Co($C_4H_7N_2O_2$)$_2$ should be heated to consistent mass to ensure all water is driven off, so that mass measured is that of dry mass of Ag and Co($C_4H_7N_2O_2$)$_2$. (ii) As mass of Ag (sludge) is rather small, use electronic balance of higher precision in order to reduce % uncertainty in mass measurement. (iii) Repeat the experiment using fresh samples so that an average of the mass measurements can be taken to reduce random error.
b(iv)	**Suggested solution:**

	Total no of moles of e used for electrolysis = 2.15 x 28.0 x 60 ÷ 96500 = 0.03743 No of moles of Cu expected to be discharged = 0.043523 ÷ 2 = 0.018715 Mass expected = 0.018715 x 63.5 = 1.19 g (3sf)
(c)	**Suggested solution:** $Co(C_4H_7N_2O_2)_2$ + aq ⇌ Co^{2+} + 2 $C_4H_7N_2O_2^-$ -1.23×10^{-4} $+1.23 \times 10^{-4}$ $+ 2 \times 1.23 \times 10^{-4}$ $K_{sp} = [Co^{2+}][C_4H_7N_2O_2]^2$ $= (1.23 \times 10^{-4})(1.23 \times 10^{-4} \times 2)^2$ $= 7.44 \times 10^{-12}$ mol^3dm^{-9}
(d)(i)	**Suggested solution**  By Hess' law: L.E. = 73.0 – 519 – (½ x 436) – 159.5 – 90.5 = <u>**– 914 kJ mol^{-1}**</u>
d(ii)	**Suggested solution:** $|LE| = \left|\frac{q^+q^-}{r^+ + r^-}\right|$ Ionic radii of Cl^- = 0.181, ionic radii of H^- = 0.208nm They have the same product but LiH has a larger interionic distance than LiC*l*, therefore LE magnitude of LiH is smaller.
(e)	**Suggested solution:** Amt of $AlCl_3$ = $\frac{5}{27+35.5\,x\,3)}$ = 0.037453 mol

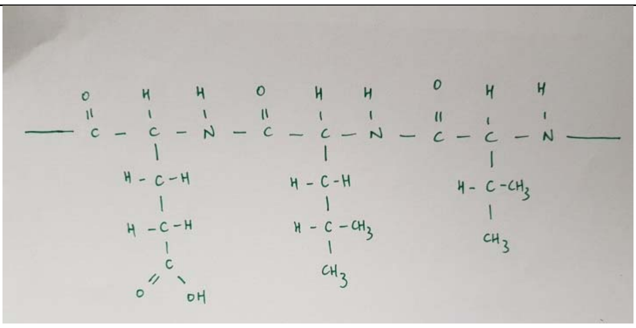
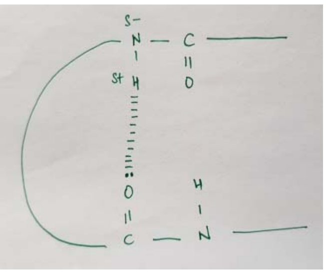
	Amt of LiH = $\frac{5}{7.9}$ = 0.6329 mol $AlCl_3$ is limiting since 0.037453 mol of $AlCl_3$ requires 0.037453 x 4 mol of LiH_4 = 0.14981 mol < 0.6329 mol. No of moles of $LiAlH_4$ formed = 0.037453 mol $0.037453 \times \Delta H_{reaction} = -1.24 \times 8.4$ $\Delta H_{reaction} = -1.24 \times 8.4 \div 0.037453$ $= -278$ kJmol^{-1}
(f)(i)	**suggested solution** $\Sigma n\Delta Hf(\text{products}) - \Sigma n\Delta Hf(\text{reactants}) = -454 - 3(-152.5)$ $= +3.5$ kJmol^{-1}
f(ii)	**Suggested solution** $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ $-27.7 = +3.5 - 298 \times \Delta S^\ominus$ $\Delta S^\ominus = +0.105$ kJmol^{-1}K^{-1} ΔS is positive as there is an increase of 3 moles of gas molecules after the reaction; there are more ways to distribute the molecules and their energies, increasing entropy level of the system at the end of reaction.
f(iii)	**Suggested solution** Temp at which decomposition becomes spontaneous is the cross over temperature. $\Delta G = 0$ $+3.5 = 0.105 \times T$ T = 33.3 K

Question 3	
(a)(i)	**Suggested solution:**

	
(ii)	**Suggested solution:** A is formed from the primary carbocation as shown.  This primary carbocation is less stable due to the positive charge not being resonance stabilised by the aromatic ring. Hence, the carbocation is formed in trace amounts, leading to trace amounts of A being formed.
(iii)	**Suggested solution:**

	
(b)(i)	**Suggested solution:** In the presence of ligands, d-orbitals of Fe^{3+} are split into two different energy levels with small energy gap. d-d transition, where the electron is promoted from a lower energy d orbital to a higher energy d orbital, is possible. Energy that corresponds to the wavelength of light in the visible region of the electromagnetic spectrum is absorbed. Colour observed is complementary to the wavelength of visible light absorbed.
(ii)	**Suggested solution:** 
(iii)	**Suggested solution:** G has a larger energy gap. Since the electronic configuration of Fe^{3+} in G is in a 'low spin' state, energy required to overcome the energy gap in adding subsequent electrons to higher energy d-orbitals is more than that required to overcome inter-electronic repulsion when electrons paired up in the lower energy d-orbitals.
(c)(i)	**Suggested solution:** Oxidation number of C in carbon dioxide: +4 Oxidation number of C in methanol: -2

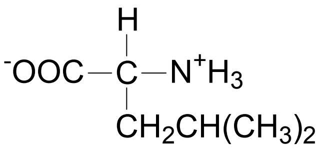
(ii)	**Suggested solution:** Electrode 1 : $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ Electrode 2 : $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ Overall: $2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$
(iii)	**Suggested solution:** When $[CH_3OH]$ is decreased, oxidation of methanol becomes less favoured OR by LCP, the position of equilibrium for $CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$ shifts to the left to partially increase $[CH_3OH]$. Thus, $E_{ox(CH3OH/CO2)}$ becomes less positive. A less positive $E_{ox(CH3OH/CO2)}$ will cause E_{cell} to be less positive since $E_{cell} = E + E_{ox}$.
(iv)	**Suggested solution:** CH_3OH is a liquid at room temperature and thus can be easily transported and stored than hydrogen gas OR CH_3OH is less explosive than H_2 gas OR CH_3OH is less expensive to maintain than H_2 gas

Question 4	
(a)(i)	
(ii)	**Suggested solution:**  Hydrogen bonding - lone pair

<table>
<tr><td></td><td>- δ+ / δ-
- dotted lined to show bond</td></tr>
<tr><td>**(iii)**</td><td>**Suggested solution:**

Leucine and Valine.

Their side chains consist of hydrocarbon chains which are able to form temporary dipole-induced dipole interactions with hydrophobic groups to transport them in the blood stream.</td></tr>
<tr><td>**(b)(i)**</td><td>**Suggested solution:**


$^{-}OOC-\overset{H}{\underset{CH_2CH(CH_3)_2}{C}}-N^{+}H_3$</td></tr>
<tr><td>**(ii)**</td><td>**Suggested solution:**

Melting point

Unionised form: Hydrogen bonding
Zwitterionic form: Ionic bonding
More energy is required to overcome the stronger ionic bonding compared to the hydrogen bonds. Hence the zwitterionic form will have a higher melting point.

Solubility:

Unionised form: Hydrogen bonds with water
Zwitterionic form: ion-dipole interactions with water
Stronger ion-dipole interactions produce more energy to overcome the hydrogen bonds between water molecules and the interactions between the solute. Hence the zwitterionic form will be more soluble in water.</td></tr>
<tr><td>**(c)**</td><td>**Suggested solution:**
<table>
<tr><td>Observation</td><td>Deductions</td></tr>
<tr><td>Compound **A**, $C_8H_{10}O_2$, reacts with $Br_2(aq)$ to form a white precipitate compound **B** with molecular formula, $C_8H_7O_2Br_3$</td><td>**A** contains phenol (reacts without halogen carrier)

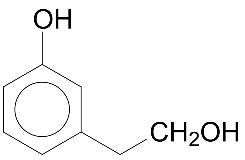
B is 2,4,6- trisubstituted</td></tr>
<tr><td>Compound **A** also reacts with dilute nitric acid to give compound **C**, $C_8H_9NO_4$</td><td>Mononitration of **A** to give **C**

Confirm presence of phenol</td></tr>
<tr><td>Compound **C** with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound **D**, $C_8H_{10}NO_2Na$.</td><td>NO_2 group in **C** is reduced to $–NH_2$

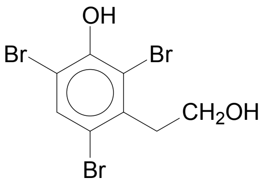
phenol in **C** is converted to sodium phenoxide in **D**</td></tr>
</table>
</td></tr>
</table>

Compound **D** turns hot acidified potassium dichromate solution green and forms compound **E,** $C_8H_9NO_3$.	**D** undergoes oxidation to form carboxylic acid primary alcohol present in **D,** phenoxide in **D** is acidified to phenol in **E**
1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.	2 acidic groups present Carboxylic acid and phenol confirmation
Compound **E** reacts with phosphorus pentachloride to give compound **F,** $C_8H_7NO_2$.	$-CO_2H$, in **E** is converted into an acyl chloride, $-COCl$,by PCl_5. Amine undergoes internal nucleophilic substitution),with loss of Cl^-, to yield the cyclic amide **F** Carboxymethyl group, $-CH_2CO_2H$, must be adjacent to amine $-NH_2$ group in **A** to enable ring formation

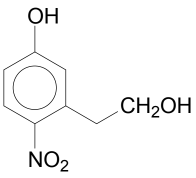
A:



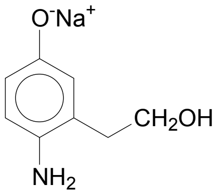
B:



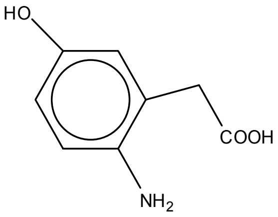
C:



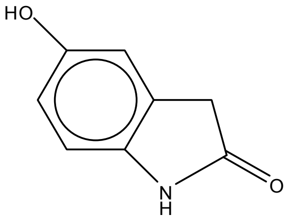
D:



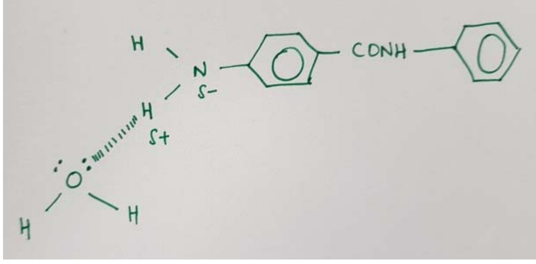
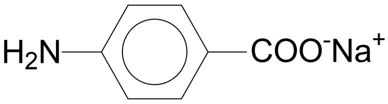
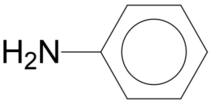
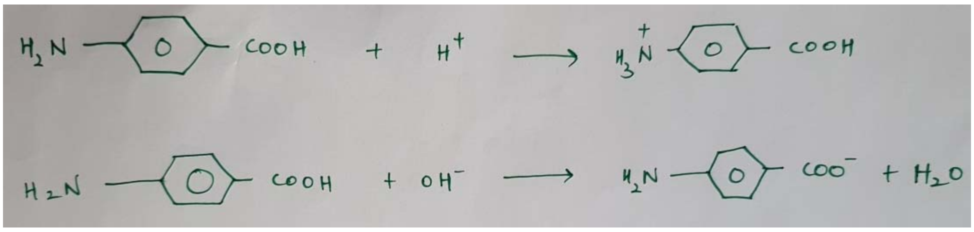
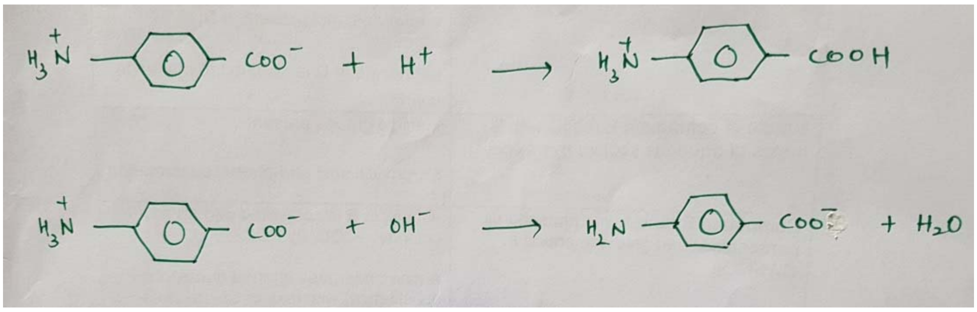
E:



F:

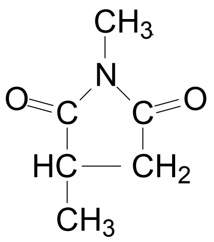
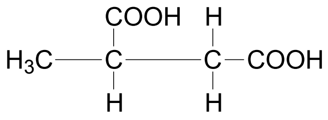


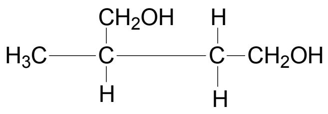
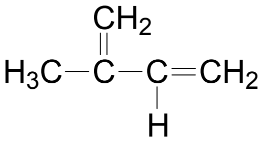
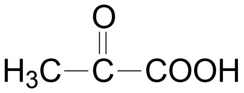
Question 5	
(a)(i)	**Suggested solution:**

	 Hydrogen bond - lone pair - $\delta+$ / $\delta-$ - dotted lined to show bond
(ii)	**Suggested solution:** Energy given out when hydrogen bonds are formed between water molecules and 4-amino-N-phenylbenzylamide is insufficient to overcome the extensive temporary dipole-induced dipole interactions between 4-amino-N-phenylbenzylamide molecules. Hence solubility is low.
(b)(i)	**Suggested solution:**  
(ii)	**Suggested solution:** Phenylamine is a simple covalent molecule with weak intermolecular attractions between them whereas the other product is an ionic compound with strong electrostatic forces of attraction between ions. Phenylamine thus has a lower boiling point of the 2 and will distil out first to be the distillate.
(iii)	**Suggested solution:**  OR 

(c) **Suggested solution:**

Information / Type of reaction	**Deductions**
Compound **G**, $C_6H_9O_2N$, is a neutral compound with the ability to rotate plane polarised light.	As **G** contains N and is neutral, **G** is likely to be an amide. **G** contains at least 1 chiral carbon.
G reacts with aqueous sodium hydroxide to form pungent gas **H** that turned moist red litmus blue. Upon acidification with aqueous hydrochloric acid, **J** $C_5H_8O_4$.	Alkaline hydrolysis Alkaline gas **H**: $CH_3NH_2(g)$. (**J** has 1 less carbon than **G**) **J** has 2 carboxylic acid groups. **G** is cyclic amide.
J reacts with LiA/H₄ to form **K**, $C_5H_{12}O_2$.	**K** has 2 is primary alcohol groups.
On heating with excess concentrated H_2SO_4, **K** forms **L**, C_5H_8. **L** does not exhibit cis-trans isomerism.	**K** undergoes elimination of H_2O to form **L**, C_5H_8, with 2 alkene groups. Most likely terminal alkenes as no cis-trans isomerism.
When **L** is heated with acidified $KMnO_4$ solution, **M,** $C_3H_4O_3$ is formed.	**L** undergoes oxidative cleavage to form **M,** $C_3H_4O_3$
M reacts with aqueous Na_2CO_3 to produce effervescence that forms a white precipitate in limewater.	acid-base reaction **M** contains a carboxylic acid**.**
M also forms a yellow precipitate when warmed with alkaline aqueous I_2.	**M** contains CH_3CO- group. (must be ketone as it is a product of oxidative cleavage of a C=C)

G	H	J
	$CH_3NH_2^-$	 $H_3C-CH(COOH)-CH_2-COOH$

K  $H_3C-\overset{CH_2OH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_2OH$	L  $H_3C-\overset{CH_2}{\overset{\|}{C}}-\underset{H}{C}=CH_2$	M  $H_3C-\overset{O}{\overset{\|}{C}}-COOH$