		UNIOR COLLEC		
CANDIDATE NAME				
SUBJECT CLASS		REGISTRATION NUMBER		
CHEMISTRY Paper 1 Multiple Cho Additional Materials:	ice Optical Ansv Data Bookle		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.

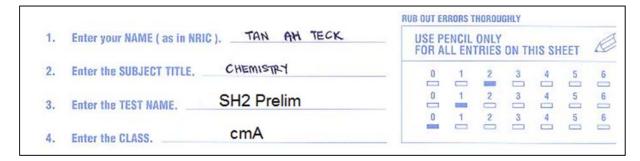
Read the instructions on the Answer Sheet very carefully.

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.

Instructions on how to fill in the Optical Mark Sheet



Student	Examples of Registration No.	Shade:
	1 <u>7</u> 0 <u>5648</u>	75648

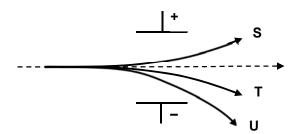
Example:

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	Т	U
Α	¹⁵ O ⁺	¹⁴ C+	¹⁴ N ⁺
В	¹⁵ O ⁻	¹⁵ O ⁺	²⁸ Si ⁺
С	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** SO₃, CO₂, A lCl_3

B H₂O, H₂S, HBr

C CF₄, CO, HF

- **D** NH₃, HF, BeC l_2
- 3 In which row are the molecules arranged in order of increasing bond angle?
 - 1 CH₄, AlCl₃, XeF₂
 - 2 H₂S, PH₃, NH₃,
 - 3 NF₃, NC l_3 , SO₃
 - **A** 1, 2 and 3

B 1 and 2

C 2 and 3

D 1 only

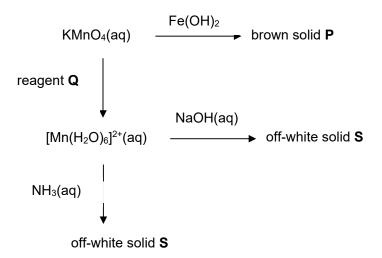
4 Propadiene and propyne both have the same molecular formula, C₃H₄. They exist in equilibrium as shown:

$$H_2C=C=CH_2 \iff CH_3C\equiv CH$$
 propadiene propyne

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 sp² 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 NH₃(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 Homogeneous dichromate 2 Heterogeneous Formation of oxygen from hydrogen peroxide, using iron(III) hydroxide 3 Chlorination of benzene, using chlorine and iron(III) chloride Homogeneous 4 Removal of air pollutants in exhaust systems of cars, using Heterogeneous nickel Α 1, 2 and 4 В 2 and 3 С 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,

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:

$$NH_3(g) + HCI(g) \rightarrow NH_4CI(s)$$
 $\Delta H^{\circ} = -176 \text{ kJ mol}^{-1}$

The magnitude of standard entropy change of this reaction is 284 J K⁻¹ mol⁻¹.

Which statements are correct?

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

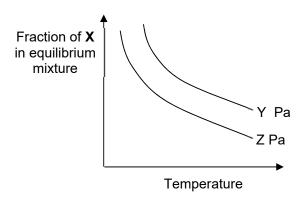
2 The reaction becomes non-spontaneous at temperatures higher than 620 K.

There is an increase in order as strong hydrogen bonding between NH₃ and HC*l* hold the particles in NH₄C*l* 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.

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



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

	X	Pressure
Α	N_2	Z > Y
В	O_2	Y > Z
С	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.

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

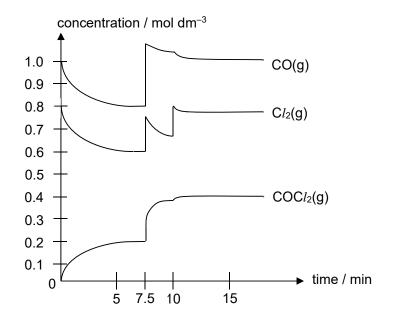
The rate constants of the forward and backward reactions are given as k_1 and k_{-1} respectively.

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

	<i>k</i> ₁	<i>k</i> −1	K _c
Α	increase	increase	increase
В	increase	decrease	increase
С	decrease	increase	decrease
D	increase	increase	decrease

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.

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



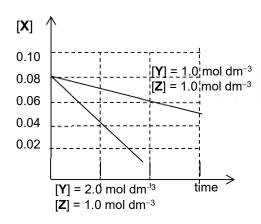
Which conclusion deduced from the graph is incorrect?

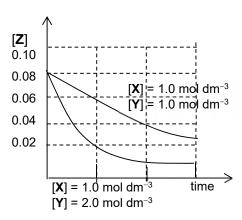
- A The rate of forward reaction equals the rate of backward reaction at 7 min.
- **B** The change in concentration from 7.5 min to 10 min was produced by an increase in volume at constant temperature.
- **C** The equilibrium constant, K_c , for the system when determined at 7 min is $0.417 \text{ mol}^{-1} \text{ dm}^3$.
- **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:

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

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 =
$$k[Y]^2$$

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 $E_{cell}^{\theta} = +1.23 \text{ V}.$
- **2** E_{cell} becomes more negative when Br₂(aq) is added to the anode.
- 3 E_{cell} becomes more positive when a few drops of AgNO₃(aq) is added to the anode.

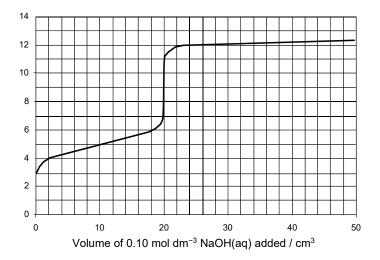
A 1 only

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	pH range in which colour
	(acidic to basic medium)	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 cm³.
- 2 K_a value of HX is 1.0×10^{-5}
- 3 Buffer at maximum buffer capacity is formed at 25.0 cm³ 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:

 $25.0 \text{ cm}^3 \text{ of } 2.0 \times 10^{-5} \text{ mol dm}^{-3} \text{ CH}_3\text{COOH and } 25.0 \text{ cm}^3 \text{ water}$

Reaction mixture Y:

 $25.0 \text{ cm}^3 \text{ of } 0.02 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH} \text{ and } 25.0 \text{ cm}^3 \text{ of } 0.01 \text{ mol dm}^{-3} \text{ NaOH}$

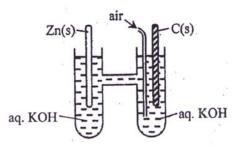
Reaction mixture Z:

 $25.0 \text{ cm}^3 \text{ of } 0.01 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ and $25.0 \text{ cm}^3 \text{ of } 0.02 \text{ mol dm}^{-3} \text{ NaOH}$

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?

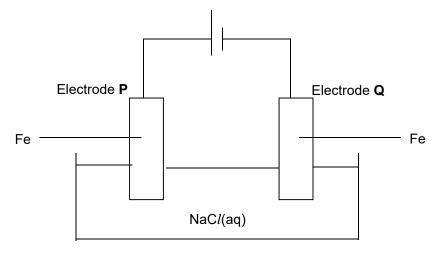
A 2.63×10^6

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
Α	No corrosion of Fe	Corrosion of Fe ; H ₂ gas evolved
В	No corrosion of Fe	Corrosion of Fe; O ₂ gas evolved
С	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.).

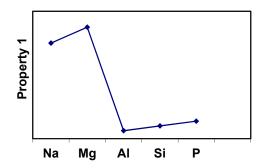
Calomel electrode: $\frac{1}{2}$ Hg₂C l_2 + e⁻ \iff Hg + C l^-

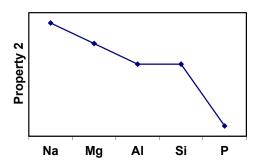
When measured with reference to the calomel electrode, a half–cell containing Zn²⁺/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn²⁺.

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

electrical conductivity of the elements pH of the oxides when added to water

Property 2

A atomic radius of the elements
 B boiling point of the chlorides at the highest oxidation states
 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 cm³ of a 2.2×10^{-3} mol dm⁻³ solution of calcium nitrate before a precipitate is formed? [K_{sp} of $CaC_2O_4 = 2.27 \times 10^{-9}$ mol² dm⁻⁶]

A
$$3.5 \times 10^{-5}$$
 g

B
$$1.0 \times 10^{-6}$$
 g

C
$$2.5 \times 10^{-7}$$
 g

D
$$2.3 \times 10^{-9} \,\mathrm{g}$$

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

Which statements about benzylamine is correct?

- $\label{eq:A} \textbf{A} \qquad \text{It can be formed by the reduction of $C_6H_5CH_2CN$.}$
- $\label{eq:Bounds} \textbf{B} \qquad \text{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 HC1, followed by NaOH.
- **D** It reacts with excess CH_3CH_2Cl under heat to form the compound, $C_{13}H_{22}NCl$.

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

$$H_3C$$
 H_3C
 CH_3
 H_3C
 CH_3
 H_3C
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

OH OH

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

What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H₂SO₄?

Α

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?

HO
$$\longrightarrow$$
 OH \longrightarrow O

- 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?

A RCHBrCH₃
$$\xrightarrow{\text{NaCN}(\text{ethanolic})}$$
 Intermediate $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen heat $\xrightarrow{\text{heat}}$ Fenoprofen heat $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen $\xrightarrow{\text{CH}(\text{CH}_3)_2}$ $\xrightarrow{\text{L}_2, \text{OH}^+(\text{aq})}$ Intermediate $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{CH}_3}$ Intermediate $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{CH$

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?

CCl₂FCCl₂F CHClFCClF2 < CHClF₂ В CCl_2FCCl_2F < CHClF₂ CHClFCClF2 C CHClF₂ CCl_2FCCl_2F < < CHClFCClF2 CHClFCClF2 < D CHC*l*F₂ < CCl₂FCCl₂F

Which is the product formed when benzene reacts with iodine chloride, IC*l* in the presence of a suitable catalyst?





$$\mathbf{D}$$
 a mixture of $\mathbf{C}l$ and $\mathbf{C}l$

When a conjugated diene undergoes electrophilic addition with Br₂, it forms two products through the 1,2–addition and the 1,4–addition, which is shown in the mechanism below.

diene
$$\begin{array}{c} & \text{slow} \\ & \oplus \\ & & \oplus \\$$

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

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	
Α	Electrophilic addition	Nucleophilic addition	
В	Electrophilic substitution	Nucleophilic substitution	
С	Nucleophilic addition	Elimination	
D	Electrophilic substitution	Neutralisation	

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.

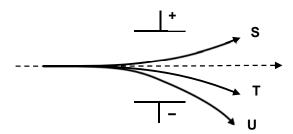
What could X be?

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	Т	U
Α	¹⁵ O ⁺	¹⁴ C ⁺	¹⁴ N ⁺
В	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 mo

A SO₃, CO₂, AlCl₃

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

C CF₄, CO, HF

CF₄ 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.

B H₂O, H₂S, HBr

H₂O and H₂S have bent shape. **H₂O is more polar than H₂S** as O is more electronegative than S.

D NH₃, HF, BeC l_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

CH₄ (tetrahedral, 109 degrees)

AlCl₃ (trigonal planar, 120 degrees)

XeF₂ (linear, 180 degrees)

2 H₂S, PH₃, NH₃,

H₂S (tetrahedral, 109 degrees)

PH₃ and NH₃ (trigonal pyramidal, around 107 degrees)

NH₃ has a larger bond angle than PH₃ 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 NF₃, NC l_3 , SO₃

NF₃, NCl₃ (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 CI). 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, C₃H₄. They exist in equilibrium as shown:

$$H_2C=C=CH_2 \iff CH_3C\equiv CH$$

propadiene propyne

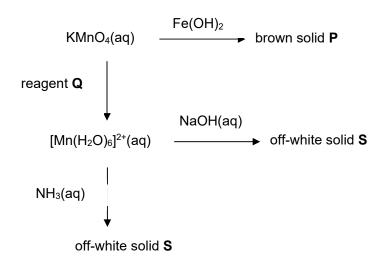
Which bond is present in propadiene but **not** present in propyne?

- **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 sp² overlap
- **D** a σ bond formed by $sp^2 sp^2$ overlap

propadiene $H_2C=C=CH_2$ hybridisation: $sp^2 sp sp^2$ propyne $CH_3C\equiv CH$ hybridisation: $sp^3 sp sp$

- A a σ bond formed by s sp overlap: in propyne $CH_3C = C-H$, not in propadiene
- **B** a π bond formed by p p overlap: present in both molecules
- \Box a \Box bond formed by sp sp² overlap: in propadiene H₂C=C=CH₂, 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 NH₃(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.
- 1 off-white solid S is Mn(OH)₂. It is insoluble in excess of NH₃(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 Homogeneous dichromate
 - K₂Cr₂O₇ is an oxidising agent, not a catalyst.
- **2** Formation of oxygen from hydrogen peroxide, using iron(III) Heterogeneous hydroxide
 - $Fe(OH)_3$ is a solid catalyst used in the decomposition of hydrogen peroxide, due to the slow rate of reaction.
- 3 Chlorination of benzene, using chlorine and iron(III) chloride Homogeneous FeCl₃ is a catalyst as well as a halogen carrier, is regenerated in the last step of the electrophilic substitution.
- 4 Removal of air pollutants in exhaust systems of cars, using Heterogeneous nickel
 - Nickel is a catalyst in the catalytic converter and is in solid phase, a different phase from the gaseous reactant
- **A** 1, 2 and 4

B 2 and 3

C 3 and 4

D 2. 3 and 4

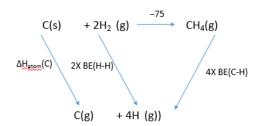
 $\Delta H/kJ \text{ mol}^{-1}$

-75

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

Given the following standard enthalpy changes,

$$C(graphite) \ + \ 2H_2(g) \ \rightarrow \ CH_4(g)$$



$$a + (2 x436) - (4x 410) = -75$$

 $a = +693 \text{ kJ mol}^{-1}$

What is the standard enthalpy change of atomisation of graphite?

- +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:

$$NH_3(g) + HCI(g) \rightarrow NH_4CI(s)$$
 $\Delta H^e = -176 \text{ kJ mol}^{-1}$

The magnitude of standard entropy change of this reaction is 284 J K⁻¹ mol⁻¹.

Which statements are correct?

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

No of mol of gas decreases =>
$$\Delta S^{\circ}$$
 = -284 J K⁻¹ mol⁻¹ ΔG° = -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
$$\Delta G^{\circ} = 0$$

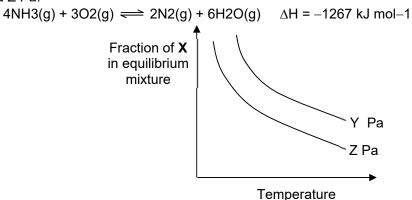
 $\Delta H^{\circ} = T \Delta S^{\circ}$

T = -176000/ -284 = 620K

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.

NH₄Cl is ionic lattice with strong ionic bonds between NH₄⁺ and Cl⁻, not strong H bonding between the NH₃ 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.



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

	X	Pressure
A	N_2	Z > Y
В	O_2	Y > Z
С	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 \Rightarrow 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.

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

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?

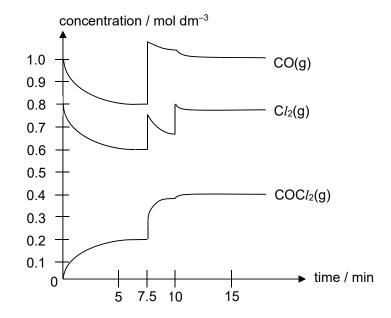
	k ₁	<i>k</i> −1	K _c	
Α	increase	increase	increase	
В	increase	decrease	increase	
С	decrease	increase	decrease	
D	increase	increase	decrease	

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_2 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.

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



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.

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

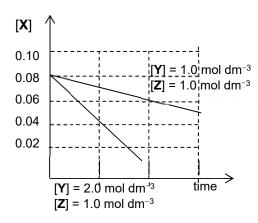
D The change in concentration from 10 min to 15 min was produced by the addition of more chlorine.

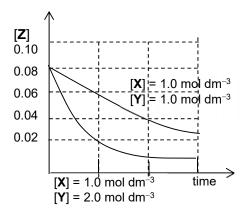
Correct: When chlorine is added, the concentration of chlorine will increase instantaneously as shown in the graph.

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

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

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 =
$$k[Y]^2$$

$$\mathbf{C} \qquad \text{rate = } \mathbf{k}[\mathbf{Y}]^2[\mathbf{Z}]$$

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_{cell}^{θ} = +1.23 V.

True: E^{θ}_{cell} = (-0.54) + (+1.77) = +1.23 V

2 E_{cell}^9 becomes more negative when $Br_2(aq)$ is added to the anode.

True: Br₂(aq) added will remove I⁻ causing $E^{\theta}_{\text{oxidation}}$ of I⁻ to be more negative when will cause E^{θ}_{cell} becomes more negative

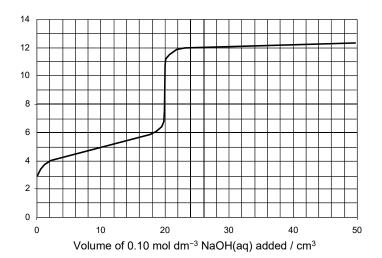
- 3 E^θ_{cell} becomes more positive when a few drops of AgNO₃(aq) is added to the anode.

 False: AgNO₃(aq) added with remove I⁻ causing E^θ_{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	pH range in which colour		
	(acidic to basic medium)	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 cm³.

Correct: At a value lower than 20.0 cm³, 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 cm³ since the pH change in that region is relatively constant.

Incorrect: Maximium buffer capacity is formed at 10.0 cm³ 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 <u>AT</u> 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 $_3$ COOH and 25.0 cm 3 water

Reaction mixture Y:

25.0 cm³ of 0.02 mol dm⁻³ CH₃COOH and 25.0 cm³ of 0.01 mol dm⁻³ NaOH

Reaction mixture **Z**:

 $25.0~\text{cm}^3$ of $0.01~\text{mol}~\text{dm}^{-3}$ CH₃COOH and $25.0~\text{cm}^3$ of $0.02~\text{mol}~\text{dm}^{-3}$ 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, [CH₃COOH]_{new} = $0.5 \times 2.0 \times 10^{-5} = 1.0 \times 10^{-5}$ mol dm⁻³

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

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

For reaction mixture Y,

	CH₃COOH	+	NaOH	\rightarrow	CH₃COONa	+	H ₂ O
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.

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

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

For reaction mixture Z,

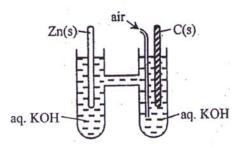
	CH ₃ COOH	+	NaOH	\rightarrow	CH₃COONa	+	H ₂ O
Initial / mol	0.00025		0.0005		0		-
Change / mol	- 0.00025		- 0.00025		+ 0.00025		-
Final / mol	0		0.00025		0.00025		-

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

 $C = 5.27 \times 10^6$

D 8.78 × 10⁶

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

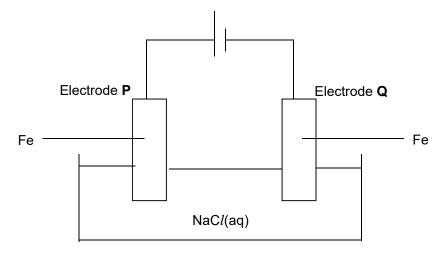
 $n_e = 0.4587 \times 2 = 0.9174$ mol and since Q = It = $n_e F$

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

$$= 5.27 \times 10^6 \,\mathrm{s}$$

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
Α	No corrosion of Fe	Corrosion of Fe ; H ₂ gas evolved
В	No corrosion of Fe	Corrosion of Fe; O ₂ gas evolved
С	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
$$\Longrightarrow$$
 Fe²⁺ + 2e⁻ E⁰_{ox} = +0.44 V
Cl⁻ \Longrightarrow Cl₂ + 2e⁻ E⁰_{ox} = -1.36 V
2H₂O \Longrightarrow O₂ + 4H⁺ + 4e⁻ E⁰_{ox} = -1.23 V

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

At the cathode:

$$Na^{+} + e^{-} \Longrightarrow Na$$
 $E^{\theta} = -2.71 \text{ V}$ $2H_{2}O + 2e^{-} \Longrightarrow H_{2} + 2OH^{-}$ $E^{\theta} = -0.83 \text{ V}$

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: $\frac{1}{2}$ Hg₂C $l_2 + e^- \iff$ Hg + C l^-

When measured with reference to the calomel electrode, a half–cell containing Zn²⁺/Zn has a change in Gibbs' free energy of +199 kJ per mole of Zn²⁺.

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 Zn²⁺ being reduced is equivalent to a change in Gibbs' free energy of –199 kJ per mole of Zn being oxidised

$$\Delta G^0 = -nFE^0_{cell}$$

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

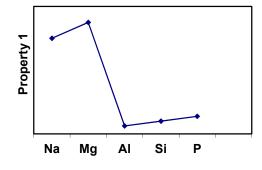
$$E_{cell}^{0} = +1.03 \text{ V} = E_{cell}^{0} + E_{ox(Zn/Zn2+)}^{0} = E_{cell}^{0} + 0.76 \text{ V}$$

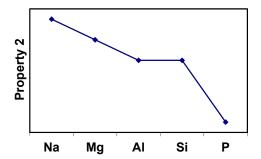
$$E^{\theta} = +0.27 \text{ V}$$

Answer is A

Α

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

- atomic radius of the elements
- boiling point of the highest oxidation state chlorides
- C melting point of oxides
- **D** electrical conductivity of elements

Property 2

electrical conductivity of the elements

pH of the oxides when added to water

first ionisation energies of the 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 AlCl₃ as AlCl₃ 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 MgCl₂.

From AlCl₃ to PCl₅, they have the structure of simple covalent molecules with Mr of AlCl₃ (133.5) < SiCl₄ (170.1) < PCl₅ (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.

Na₂O 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 SiO₂ 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)

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, Na₂C₂O₄, should be added to 250 cm³ of a 2.2×10^{-3} mol dm⁻³ solution of calcium nitrate before a precipitate is formed? $[K_{sp} \text{ of } CaC_2O_4 = 2.27 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}]$

> 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 Na₂C₂O₄.

$$\left(\frac{mass}{(23.0 \times 2 + 24.0 + 64.0)} \times \frac{1000}{250}\right) (2.2 \times 10^{-3}) = 2.27 \times 10^{-9}$$
in mass of Na₂C₂O₄ = 3.46 x 10⁻⁵ g

Α 3.5×10^{-5} g **B** 1.0×10^{-6} g **D** 2.3×10^{-9} g

 2.5×10^{-7} g

- Benzylamine has the formula C₆H₅CH₂NH₂ and is a common precursor in organic synthesis.

Which statements about benzylamine is correct?

- Α It can be formed by the reduction of C₆H₅CH₂CN.
- В It reacts with CH₃CO₂H to form C₆H₅CH₂NHCOCH₃.
- C It is formed by the reaction between C₆H₅NO₂ and tin in concentrated HC*l* followed by NaOH.
- D It reacts with excess CH₃CH₂Cl under heat to form the compound, C₁₃H₂₂NCl.

Option A: reduction of C₆H₅CH₂CN gives C₆H₅CH₂CH₂NH₂ with 1 C more than C₆H₅CH₂NH₂. Hence it is not the correct answer.

Option B: N in C₆H₅CH₂NH₂ uses its lone pair to accept H⁺ from CH₃COOH (acid base reaction instead of nucleophilic acyl substitution (condensation)). Hence (CH₃COO⁻) (C₆H₅CH₂NH₃)⁺ is formed instead of C₆H₅CH₂NHCOCH₃.

Option C: C₆H₅NO₂ will be reduced to C₆H₅NH₂ which is isolated as C₆H₅NH₃Cl due to acidic medium. C₆H₅NO₂ has 1 less C than C₆H₅CH₂NH₂ after reduction, hence not the answer.

Option D: Correct answer. A quaternary ammonium salt is formed when C₆H₅CH₂NH₂ reacts with excess CH₃CH₂C*l*.

$$\begin{array}{c|cccc} C_{6}H_{5}CH_{2} \ddot{N}H_{2} & + & CH_{3}CH_{2}CI \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\$$

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

$$H_3C$$
 H_3C
 CH_3
 H_3C
 CH_3
 H_3C
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3
 CH_3

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

CH₃

What is the total number of possible stereoisomers exhibited by the products when the following compound reacts with excess concentrated H₂SO₄?

The molecule undergoes elimination of H₂O with excess concentrated H₂SO₄ to give alkene. The product is

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:

No of stereoisomers: 21=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?

HO
$$\longrightarrow$$
 OH HO \longrightarrow OH NH₂ \longrightarrow

- 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 –NH₂ 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?

RCHBrCH₃
$$\xrightarrow{\text{NaCN}(\text{ethanolic})}$$
 Intermediate $\xrightarrow{\text{heat}}$ Fenoprofen heat

RCH(CH₃)₂ $\xrightarrow{\text{KMnO}_4, \text{ OH}^-(\text{aq})}$ Intermediate $\xrightarrow{\text{heat}}$ Fenoprofen heat

C RCHCCCH₃ $\xrightarrow{\text{I}_2, \text{ OH}^-(\text{aq})}$ Intermediate $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen $\xrightarrow{\text{Fenoprofen}}$ $\xrightarrow{\text{CH}_3}$ $\xrightarrow{\text{KMnO}_4, \text{ OH}^-(\text{aq})}$ Intermediate $\xrightarrow{\text{H}^+(\text{aq})}$ Fenoprofen $\xrightarrow{\text{Fenoprofen}}$

For option (A), the halogenoalkane RCHBrCH₃ undergoes nucleophilic substitution when heated with ethanolic NaCN, forming RCH(CN)CH₃ as the intermediate, which then undergoes acidic hydrolysis of the –CN group to form –COOH.

For option (B), RCH(CH₃)₂ does not undergo oxidation when heated with alkaline KMnO₄.

For option (C), $RCHO(CH_3)COCH_3$ 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 RCH(OH)CH₃ undergoes oxidation to form ketone intermediate, RCOCH₃, which does not react with H⁺.

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?

CHClFCClF2 < CCl₂FCCl₂F CHClF₂ В CCl₂FCCl₂F CHClF₂ CHClFCClF2 < < CHClF₂ CCl₂FCCl₂F C < CHClFCClF2 CHC/F₂ < $CHClFCClF_2 <$ CCl₂FCCl₂F

C-F bond is much stronger than C-C*l*, 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-C*l* bonds. The molecule with more C-C*l* bonds will have higher ability to destroy ozone due to more C*l* radicals it is able to produce. Hence, answer is (D).

Which is the product formed when benzene reacts with iodine chloride, IC*l* in the presence of a suitable catalyst?

Answer:

Cl is more electronegative than I, hence only I^+ electrophile forms for reaction.

 $A l C l_3 + IC l \rightarrow A l C l_4^- + I^+$

Hence only 1 electrophilic substitution product is possible.

When a conjugated diene undergoes electrophilic addition with Br₂, 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.
- The 1,2–addition product formed when HC*l* is used is
- f D The 1,4–addition product formed when ICl 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 2^{nd} carbon and hence Cl should be on the 2^{nd} carbon instead.

D is correct.

Cl 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
Α	Electrophilic addition	Nucleophilic addition
В	Electrophilic substitution	Nucleophilic substitution
С	Nucleophilic addition	Elimination
D	Electrophilic substitution	Neutralisation

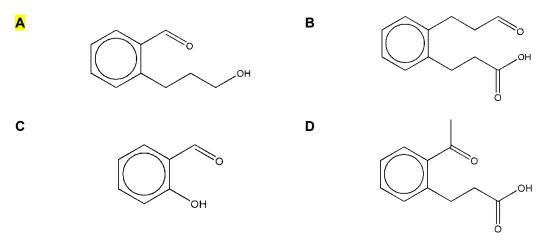
Answer:

Step 1: Benzene ring is electron rich: Electrophilic Substitution

Step 2: S is δ + due to the electronegative atoms attached to it; -Cl replaced by -NH $_2$: Nucleophilic Substitution

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?



Reacts with [Ag(NH ₃) ₂] ⁺ (Tollen's)	Aldehyde
Reacts with PCI ₅	-OH which can undergo substitution present (not phenol)
No reaction with alkaline Cu(II) complex (Fehlings)	Aromatic aldehyde

END of PAPER

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

	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 ${f all}$ 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.

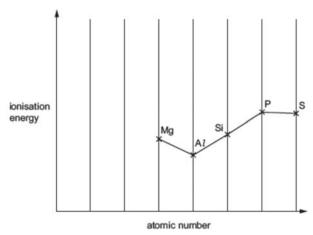
For Examiner's Use		
1	/8	
2	/14	
3	/13	
4	/11	
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Penalty		
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31		
Paper 2	/75	

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 <i>l</i> :
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.

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

$$Ba(NO_3)_2(aq) + H_2(g) \xrightarrow{reaction 1} Ba(s) \xrightarrow{reaction 2} Ba(OH)_2(aq) + H_2(g)$$
heat in air
$$X(s)$$

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

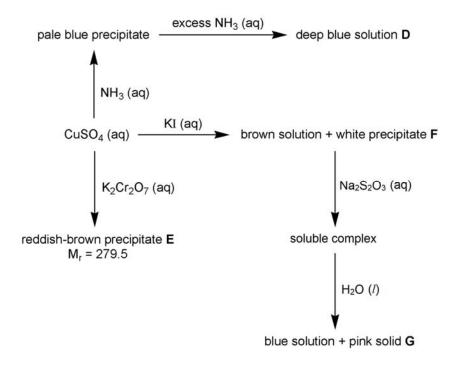
Reaction 1	
Reaction 2	
	[2]

(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)	Identif	v D	F	F	and	G
w	IUCIIIII	y D	. – .		anu	U .

D:	E:
F:	G:

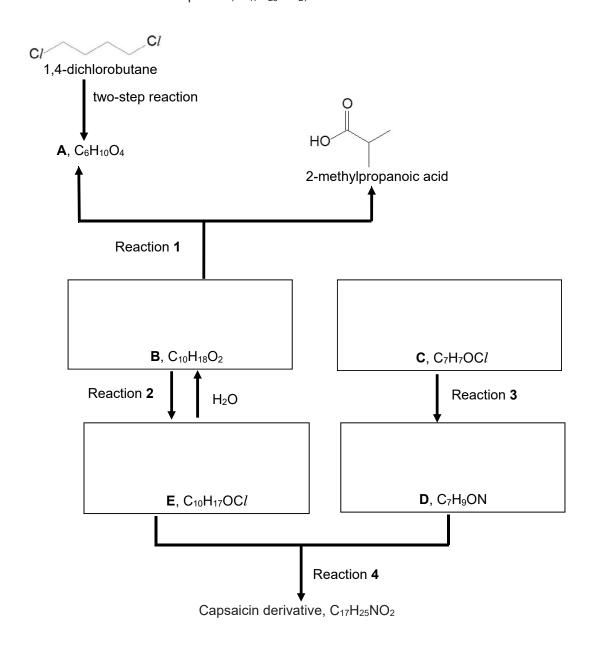
(ii) With the aid of relevant equations, account for the formation of the deep blue solution **D** from the pale blue precipitate.

[2]

[4]

(b)	(i)	By quoting relevant data, account for the trend in the thermal stabilities from to HI.			
		[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.	j		
			_		
		[3			
	(iii)	Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:	į		
		Aqueous silver nitrate Filter paper			
		Aqueous ammonia Filter funnel			
		Aqueous nitric acid			
		[3]		

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 ${\bf C}$, Compound ${\bf D}$ 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 KMnO₄.

(a)	Name the functional group common to compounds A and B .					
		[1]				

(D)	Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction.
	Step 1:
	Step 2:
	Intermediate product:
	101
	[3]
(c)	There are two functional groups in compound ${\bf B}$. Suggest the identity of the functional group in ${\bf B}$ 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 ${\bf D}$ and ${\bf E}$ react to produce the Capsaicin derivative.

Draw the structure of the Capsaicin derivative.

[1]

[Total: 13]

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% CO₂ can quickly lead to headaches, dizziness, increased heart rate and difficulty breathing. At about 15%, unconsciousness and death can result quickly.

Gas **Volume Percentage** Water vapour, H₂O 87.1 Carbon dioxide, CO₂ Rapidly increasing Sulfur dioxide, SO₂ 0.5 Hydrogen, H₂ 0.7 Carbon monoxide, CO 0.01 Hydrogen sulfide, H₂S 0.23 Hydrochloric acid, HCl 2.89 Hydrofluoric acid, HF 2.55

Table 1.1: Volcanic gas composition in area A

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.		
	(ii)		[2]	
		Under what conditions of temperature and pressure would you expect behaviour of carbon dioxide to be most like that of an ideal gas?	the	
			[1]	

(iii)	Suggest a reason why at low temperature, carbon dioxide would sink rapidly and accumulate to high concentrations.
	[2]
(iv)	People living in area A were evacuated as the level of carbon dioxide and temperature of surroundings were increasing rapidly. Given that $0.30~\text{mg}$ of CO_2 was present in $10~\text{cm}^3$ of gas mixture at 43°C and $11.2~\text{kPa}$, 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.

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

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]

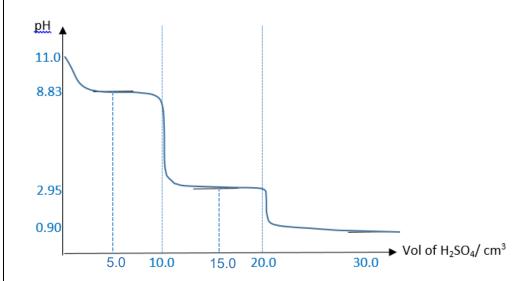
5	(a)	The following table contains the pK _b values of different nitrogen organic compounds.					
		Compound pK _b]		
				(CH ₃) ₃ CNH ₂	3.19	_	
				2-amino-2-methylpropane	55		
				NH ₂	9.38		
				phenylamine			
				NH ₂	2.88		
				piperidine			
				ONH ₂	5.17		
				morpholine			
				N₂H₄ hydrazine	5.17, 11.05		
			1			_	
		(i)	Suggest a reason why pK _b of morpholine is higher than piperidine.			peridine.	
			Morpholine has an electronegative O that exert <i>electron withdrawing effect</i> , it reduces the availability of lone pair on N to accept H ⁺ , therefore Morpholine is a weaker base hence a higher pK _b value.				
			Most students exert electron v pair will deloca	aminers Comments: ost students are able to identify that O is electronegative and hence able to ert electron withdrawing effect. There are a handful who thought that the lone ir will delocalise into O. This is impossible as the 2 atoms are not adjacent to ch other and no orbital overlap exists.			
		(ii)	Suggest a re 2-amino-2-met	reason why pK _b of phenylamine is so much higher than nethylpropane.			
			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) ₃ CNH ₂ , phenylamine is a weaker base hence a higher pKb value than (CH ₃) ₃ CNH 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 cm³ 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 cm³ of the aqueous mixture was titrated with 0.25 mol dm⁻³ dilute sulfuric acid until a total volume of 30.0 cm³ 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 cm³ of H₂SO₄ 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 cm³ total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm³

Max buffer points occur at 5 and 15 cm³.

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⁺ = $(2 \times 10/1000 \times 0.25) = 0.005$ mol (since H₂SO₄ is diprotic) [H⁺] = $0.005 \times 1000/40 = 0.125$ 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 ₂ SO ₄ used correctly. To do so, since both acid and base are diprotic,					
		$_{2}H_{4} + H_{2}A \rightarrow N_{2}H_{6}^{2+} + A^{2-}$ Iol ratio is 1:1					
		e total volume of acid required is 20 cm ³					
(c)	Stude	ent M suggested a 2–step process as shown, to synthesise					
		ino-2-methylpropane from a suitable alkane.					
		$C_4H_{10} \xrightarrow{\text{step 1}} C_4H_9CI \xrightarrow{\text{step 2}} C_4H_{11}N$ A B					
	(i)	Identify the structures of compounds A and B , and suggest reagents and conditions for each of the two steps.					
		(CH ₃) ₃ CH (CH ₃) ₃ CCI					
		Structure of A 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 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) .
		[2]

[Total: 14]

6			1–phenylethane undergoes hydrolysis with hydroxide ions to produce thanol, as shown in the equation below.
			$C_6H_5CHC\mathit{I}CH_3 + OH^- \rightarrow C_6H_5CH(OH)CH_3 + C\mathit{I}^-$ 1-chloro-1-phenylethane 1-phenylethanol
	(a)		rate of this reaction can be studied by measuring the amount of hydroxide ions 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.

[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 ₆ H ₅ CHC <i>l</i> CH 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 $C_6H_5CHC\mathit{l}CH$	3 =	
---	-----	--

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

$$rate = \dots mol dm^{-3} s^{-1}$$

[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.

(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.
[2]
(iii) 1-chloro-2-ethyl benzene, C₆H₄ClCH₂CH₃, is an isomer of 1-chloro-1-phenylethane, C₆H₅CHClCH₃. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

[3]

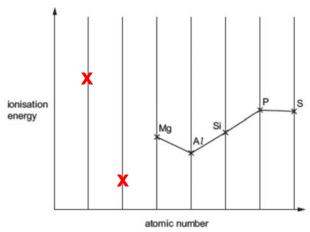
[2]

[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 <u>higher energy 3p</u> 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.

<u>Inter-electronic repulsion</u> 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 <u>weaker in</u> 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.

$$[Mg(H2O)6]2+(aq) + H2O(I) \rightleftharpoons [Mg(H2O)5(OH)]+(aq) + H3O+(aq)$$
 [1] (state symbols not necessary)

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

$$Ba(NO_3)_2(aq) + H_2(g) \xrightarrow{reaction 1} Ba(s) \xrightarrow{reaction 2} Ba(OH)_2(aq) + H_2(g)$$
heat in air
$$X(s)$$

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

Reaction 1: HNO₃ [1]

Reaction 2: H₂O [1]

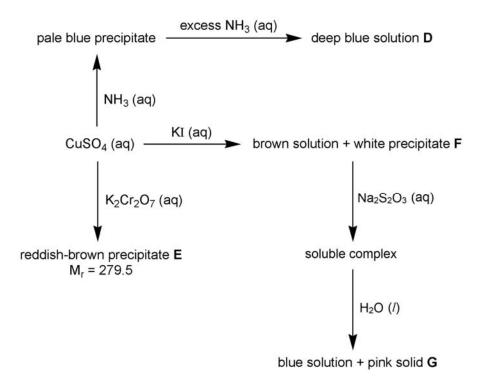
(ii) Write an equation for the formation of **X**.

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.

$$\begin{split} [Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) &\rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O(l) ---(1) \\ Cu(OH)_2(s) &\rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq) ---(2) \end{split}$$

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.

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

 $BE(H-Cl) = 431 \text{ kJ mol}^{-1}$ $BE(H-Br) = 366 \text{ kJ mol}^{-1}$ $BE(H-I) = 299 \text{ kJ mol}^{-1}$

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 Fe²⁺.

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

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

Br₂ can oxidise Fe²⁺ to Fe³⁺ since the reaction is spontaneous.

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

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

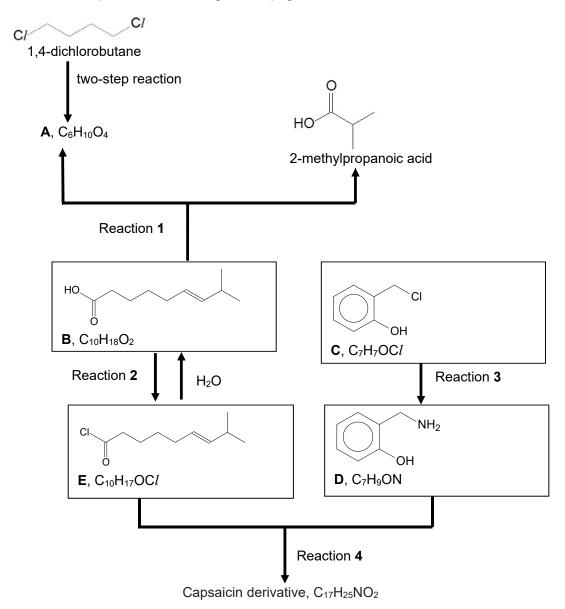
- (iii) Suggest a series of steps to verify the presence of chloride and iodide ions in a mixture, given the following reagents:
 - Aqueous silver nitrate
- Filter paper
- Aqueous ammonia
- Filter funnel
- Aqueous nitric acid
- 1. Add excess aqueous silver nitrate to the mixture. Yellowish-white precipitate 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 ${\bf C}$, Compound ${\bf D}$ 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 KMnO₄.

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

Carboxylic acid

Compound **A** can be synthesised from 1,4-dichlorobutane in two steps. (b) Suggest reagents and conditions for the synthesis, and the intermediate product for the reaction. Step 1: ethanolic NaCN, heat Step 2: dil H₂SO₄, heat Intermediate product: CN [3] (c) There are two functional groups in compound **B**. Suggest the identity of the functional group in **B** that reacts with cold acidified KMnO₄. Functional group that reacts with cold acidified KMnO₄: 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: KMnO₄, dil H₂SO₄, heat [2] Compound **C** reacts with hot ethanolic silver nitrate to produce a white ppt. (e) 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**. and conditions for reaction 2.

Draw the structure of compound E in the box on pg 6, and hence state the reagents

Reagents and conditions for reaction 2: PCl₅ (s), anhydrous

[2]

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

Draw the structure of the Capsaicin derivative.

[1]

[Total: 13]

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, H₂O	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 ₂ S	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]

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 CO₂ molecules. Hence CO₂ would aggregate together/ more CO₂ 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 CO₂ was present in 10 cm³ 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 CO₂ =
$$\frac{0.30\times0.001}{44.0}$$
 = $6.818\times10^{-6}mol$

pV = nRT

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

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

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.

$$CH_4(g) + 2 H_2S(g) \longrightarrow CS_2(g) + 4 H_2(g)$$

1 mol of CH₄, 2 mol of H₂S, 1 mol of CS₂ and 1 mol of H₂ 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°C and 2 atm, i.e. Total P initially and Total P at eqm is same, 2 atm.

	CH ₄ (g)	+ 2 H ₂ S(g)	 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
$$CS_2 == 2\left(\frac{1+x}{5+2x}\right) = 0.5$$
 atm solve for x , x = 0.5

	CH ₄ (g)	+ 2 H ₂ S(g)	 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	$\frac{3}{6} \times 2 = 1$

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

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

[Total: 11]

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

Compound	p <i>K</i> ₀
(CH ₃) ₃ CNH ₂ 2-amino-2-methylpropane	3.19
phenylamine	9.38
NH	2.88
O NH morpholine	5.17
N₂H₄ hydrazine	5.17, 11.05

(i) Suggest a reason why p K_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]

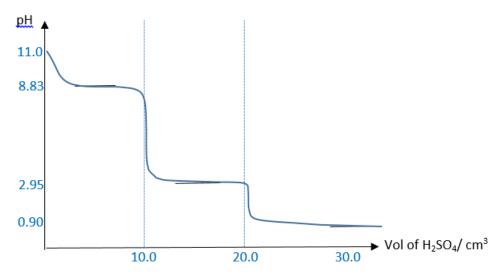
(b) 10.0 cm³ of an aqueous mixture containing 0.5 mol dm⁻³ of hydrazine was placed in a conical flask and the initial pH was found to be 11.0.

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
- pH of the reaction mixture when 30.0 cm³ of H₂SO₄ 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 cm³ total vol of H_2SO_4 required for 2nd equiv point = 20.0 cm³

Max buffer points occur at 5 and 15 cm³. **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.

$$C_4H_{10}$$
 $\xrightarrow{\text{step 1}}$ C_4H_9CI $\xrightarrow{\text{step 2}}$ $C_4H_{11}N$
B

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



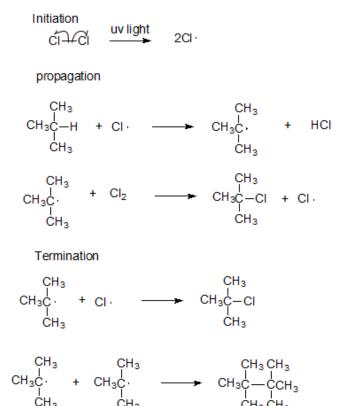
Step 1: limited Cl₂, UV. light

Step 2: excess NH₃ 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.

$$C_6H_5CHC\mathit{l}CH_3+OH^- \rightarrow C_6H_5CH(OH)CH_3+C\mathit{l}^-$$
 1-chloro-1-phenylethane 1-phenylethanol

- (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 ₆ H ₅ CHC <i>l</i> CH 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, $[C_6H_5CHC/CH_3]$ is tripled, relative rate is tripled. Hence, reaction is 1st order with respect to C_6H_5CHC/CH_3 . [1]

Comparing experiment 1 & 2, when both $[OH^-]$ and $[C_6H_5CHC/CH_3]$ are doubled, relative rate is doubled. Since reaction is 1st order with respect to C_6H_5CHC/CH_3 , the doubling of $[OH^-]$ has no effect on rate, so reaction is zero order with respect to OH^- .

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

Order with respect to $C_6H_5CHClCH_3$ = first order

Order with respect to OH⁻ = zero order

[2]

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

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

S⁻¹

(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.

Nucleophilic substitution (S_N1)

(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 $S_N 2$ 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, C₆H₄C*l*CH₂CH₃, is an isomer of 1-chloro-1-phenylethane, C₆H₅CHC*l*CH₃. The ease of hydrolysis for each of the 2 compounds is different. Explain why.

In 1-chloro-2-ethyl benzene, the p-orbital of Cl overlaps with the π -electron cloud of benzene, resulting in delocalisation of electrons, strengthening the C-Cl 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 JUNIO SH2 PRELIMINAR Higher 2		ON
CANDIDATE NAME			
SUBJECT CLASS		REGISTRATION NUMBER	
CHEMISTR	Υ		9729/03
Paper 3 Free Re	sponse		Monday 10 Sep 2018 2 hours
Candidates ansv	ver 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	lodine	Fullerene	Graphite
Formula	CH ₃ (CH ₂) ₇ OH	I_2	C ₆₀	С
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, SeO₂, in the synthesis of aldehyde and ketone functional groups. One of such reactions is shown below.

$$CH_3COCH_3 + SeO_2 \longrightarrow CH_3COCHO + Se + H_2O$$
 reaction I

Using the synthetic method above in one of your steps, devise a three–stage synthesis of compound ${\bf B}$ from compound ${\bf A}$.

[5]

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

Carbon dioxide enters the water through equilibrium with the atmosphere.

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

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.

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

- (i) Calculate [CO₂(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 [H₂CO₃]. [1]

Carbonic acid will further dissociate in the following reactions.

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

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

- (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 C₄H₁₀N₂.
- 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 CuSO₄ as electrolyte.

(a) Explain, with reference to relevant E° 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 LiA/H ₄ (l)	-152.5
Enthalpy change of formation of Li ₃ A/H 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 LiC*l* would compare to LiH.

[2]

(e) When lithium hydride is heated with anhydrous aluminium chloride, lithium aluminium hydride, LiA/H₄ and lithium chloride are produced.

$$4 \text{ LiH} + AlCl_3 \rightarrow \text{LiA}lH_4 + 3 \text{LiC}l$$

When 5 g each of A/Cl₃ 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 LiA/H₄.

[3]

(f) Just above its melting point, LiA/H₄ decomposes according to the following equation.

$$3 \text{ LiA}/H_4(I) \rightarrow \text{Li}_3A/H_6(s) + 2A/(s) + 3H_2(g)$$

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

[1]

(ii) Given that $\Delta G^{e} = -27.7$ kJ mol⁻¹, calculate ΔS^{e} 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 LiA*l*H₄.

[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", H₂¹⁸O.

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 H₂¹⁸O 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 ¹⁸O 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]

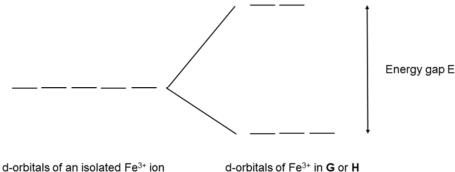
(iii) Draw the structure of a side product formed if the same reaction is carried out in the presence of aqueous sodium chloride.

[1]

- In 2012, a group of scientists synthesised two ligands, N,N-diethylethylenediamine and N-ethylethylenediamine, and reacted each with Fe³⁺ to form two complexes, G and **H**, with different colours respectively.
 - Explain why iron(III) complexes are usually coloured. (i)

[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-diethylenediamine ligand to form **G**, the Fe³⁺ 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.

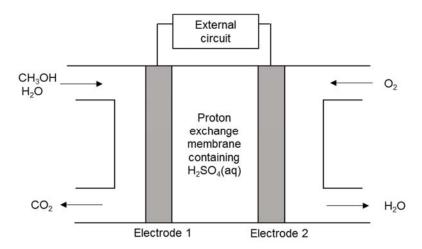
Use diagrams like the one above to show the electronic distribution of a Fe³⁺ ion in a high spin state, and in a low spin state.

[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 hydrogenoxygen 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 ₂ H)
Glutamic acid	-CH ₂ CH ₂ CO ₂ H
Leucine	-CH ₂ CH(CH ₃) ₂
Lysine	-CH ₂ CH ₂ CH ₂ CH ₂ NH 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**, C₈H₉NO₃. 1 mole of compound **E** reacts with 2 moles of aqueous sodium hydroxide.

Compound **E** reacts with phosphorus pentachloride to give compound **F**, C₈H₇NO₂.

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.

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

- **(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.

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

(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 HCl,

(ii)

II. dilute NaOH,

is added to a solution of the compound.

[2]

[2]

[2]

[2]

[2]

(c) G, C₆H₉O₂N, 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**, C₅H₈O₄, was formed.

J reacts with LiA/ 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 KMnO₄ solution, **M**, $C_3H_4O_3$ is formed.

 ${f M}$ reacts with aqueous Na₂CO₃ to produce effervescence that forms a white precipitate in limewater. ${f M}$ also forms a yellow precipitate when warmed with alkaline aqueous I₂.

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

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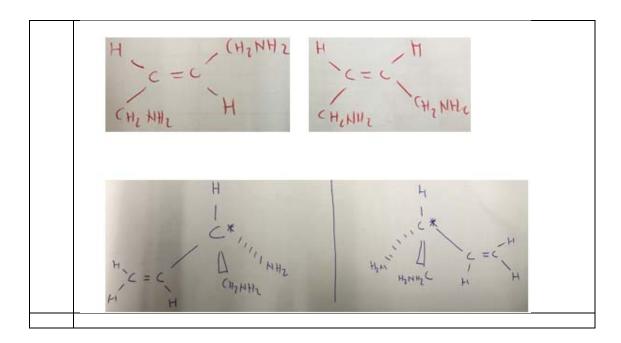
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NJC 2018 SH2 H2 Chemistry Prelim Paper 3 Solutions:

	estion 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 ₂ Cr ₂ O ₇ /KMnO ₄ with H ₂ SO ₄ (aq) and heat; (-COCOOH) Step 3: NaBH ₄ in ethanol or H ₂ with Nickel/Pt; (compound B)					
c(i)	Suggested solution					
	$P_{CO2} = \frac{0.035}{100} \times 101.3 \text{kPa}$ $= 0.03546 \text{kPa}$ $K_{H} = \frac{[CO_{2}(aq)]}{P_{CO2}}$ $[CO_{2}(aq)] = 1.17 \times 10^{-5} \text{ mol dm}^{-3}$					
c(ii)	Suggested solution					
	$K_c = \frac{[H_2CO_2(aq)]}{[CO_2]}$ [H ₂ CO ₃] = 1.52x 10 ⁻⁸ mol dm ⁻³					
(iii)	Suggested solution					
	It is more difficult to remove a proton from a negatively charged ion as attractive forces have to be overcome.					
c(iv)	Suggested solution					
	$K_{a1} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$ $[H^+]=1.915 \times 10^{-6} \text{ moldm}^{-3}$ $pH = 5.71$					
d	Suggested solution					



(a) Suggested solution:

Question 2

(i)

At anode: Co has E_{ox}^{θ} (Co/Co²⁺) = +0.28V more positive that E_{ox}^{θ} (Cu/Cu²⁺) = -0.34V, hence Co will be oxidised together with Cu and dissolve as Co²⁺, becoming part of the electrolyte. Ag on the other hand has more negative E_{ox}^{θ} (Ag/Ag⁺) of -0.80V, hence will not be oxidised. It will fall below anode as sludge.

<u>At cathode</u>: Co^{2+} has a more negative $E^{\theta}_{red}(Co^{2+}/Co) = -0.28$ V than $E^{\theta}_{red}(Cu^{2+}/Cu) = 0.34$ V, hence Co^{2+} is not reduced at the cathode, remain dissolved as electrolyte.

(b) Suggested solution

- mass of Ag = 0.07 g
- No of moles of Co oxidised at anode = no of moles of Co(C₄H₇N₂O₂)₂

$$= \frac{0.55}{58.9 + 2(4 \times 12 + 7 + 2 \times 14 + 2 \times 16)}$$

= 0.0019038 mol

Mass of Co in alloy (anode) = $0.0019038 \times 58.7 = 0.112 \text{ g}$ 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 \overline{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 = 0.03743No of moles of Cu expected to be discharged = $0.043523 \div 2$ = 0.018715Mass expected = 0.018715×63.5 = 1.19 g (3sf)Suggested solution: (c) $Co(C_4H_7N_2O_2)_2 + aq \rightleftharpoons Co^{2+} + 2 C_4H_7N_2O_2^{-}$ -1.23×10^{-4} +1.23 x 10⁻⁴ + 2 x 1.23 x 10⁻⁴ $Ksp = [Co^{2+}][C_4H_7N_2O_2]^2$ = $(1.23 \times 10^{-4})(1.23 \times 10^{-4} \times 2)^2$ $= 7.44 \times 10^{-12} \, \text{mol}^3 \text{dm}^{-9}$ Suggested solution (d)(i) Energy / kJ mol⁻¹ $Li^{+}(g) + e^{-} + H(g)$ -73.0 Li⁺(g) + H⁻(g) +519 Li(g) + H(g) ½ x +436 $Li(g) + \frac{1}{2} H_2(g)$ +159.5 LE (LiH) $Li(s) + \frac{1}{2} H_2(g)$ 0 -90.5 LiH(s) By Hess' law: L.E. = $73.0 - 519 - (\frac{1}{2} \times 436) - 159.5 - 90.5 = -914 \text{ kJ mol}^{-1}$ Suggested solution: d(ii) $|LE| = \left| \frac{q^+ q^-}{r^+ + r^-} \right|$ Ionic radii of $C\Gamma = 0.181$, ionic radii of $H^- = 0.208$ nm They have the same product but LiH has a larger interionic distance than LiCI, therefore LE magnitude of LiH is smaller.

Suggested solution:

Amt of AlCl₃ = $\frac{5}{27+35.5 \times 3)}$ = 0.037453 mol

(e)

	Amt of LiH = $\frac{5}{7.9}$ = 0.6329 mol
	AlCl ₃ is limiting since 0.037453 mol of AlCl ₃ requires 0.037453×4 mol of LiH ₄ = 0.14981 mol < 0.6329 mol.
	No of moles of LiAlH ₄ formed = 0.037453 mol 0.037453 x Δ H _{reaction} = -1.24 x 8.4
	$\Delta H_{\text{reaction}} = -1.24 \times 8.4 \div 0.037453$ = -278 kJmol ⁻¹
(f)(i)	suggested solution
	Σ n \triangle Hf(products) - Σ n \triangle Hf(reactants) = $-454 - 3(-152.5)$ = $+3.5$ kJmol ⁻¹
f(ii)	Suggested solution
	ACO - ALIO TACO
	$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$ -27.7 = +3.5 - 298 x ΔS°
	$\Delta S^{e} = +0.105 \text{ kJmol}^{-1} \text{K}^{-1}$
	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.

Questi	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:

OH OH

(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:





11111

'High spin' state

'Low spin' state

(iii) Suggested solution:

G has a larger energy gap. Since the electronic configuration of Fe³⁺ 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 [CH₃OH] is decreased, oxidation of methanol becomes less favoured OR by LCP, the position of equilibrium for CH₃OH + H₂O \rightleftharpoons CO₂ + 6H⁺ + 6e⁻ shifts to the left to partially increase [CH₃OH]. 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:

CH₃OH 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

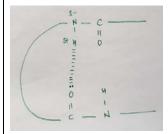
OR

 CH_3OH is less expensive to maintain than H_2 gas

Question 4

(a)(i)

(ii) Suggested solution:



Hydrogen bonding

- lone pair

- dotted lined to show bond

(iii) 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.

(b)(i) Suggested solution:

$$^{\text{H}}_{^{-}\text{OOC}} - ^{\text{H}}_{\text{C}} + ^{\text{H}}_{3}$$
 $^{\text{CH}_{2}\text{CH}(\text{CH}_{3})_{2}}$

(ii) 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

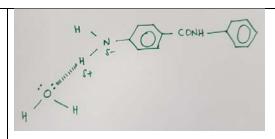
Stronger ion-dipole interactions produce more energy to overcome the hydrogen bonds between water molecules and the interactions between the solute. Hence the zwitterionic form will be more soluble in water.

(c) Suggested solution:

Observation	Deductions
Compound $\bf A$, $C_8H_{10}O_2$, reacts with $Br_2(aq)$ to form a white precipitate compound $\bf B$ with molecular formula, $C_8H_7O_2Br_3$	A contains phenol (reacts without halogen carrier)
	B is 2,4,6- trisubstituted
Compound A also reacts with dilute nitric acid to give compound C , C ₈ H ₉ NO ₄	Mononitration of A to give C Confirm presence of phenol
Compound ${\bf C}$ with tin in concentrated hydrochloric acid, followed by hot aqueous sodium hydroxide gives compound ${\bf D}$, $C_8H_{10}NO_2Na$.	NO ₂ group in C is reduced to –NH ₂ phenol in C is converted to sodium phenoxide in D

Compound D turns hot acidified potassium	D undergoes oxidation to form carboxylic
dichromate solution green and forms compound E, C ₈ H ₉ NO ₃ .	acid
Compound L, Carigino3.	and the second second second second second
	primary alcohol present in D ,
	phenoxide in D is acidified to phenol in E
1 mole of compound E reacts with 2 moles	2 acidic groups present
of aqueous sodium hydroxide.	a second 8. carpo p. cacano
	Carboxylic acid and phenol confirmation
Compound E reacts with phosphorus	-CO ₂ H, in E is converted into an acyl
pentachloride to give compound F ,	chloride, –COC <i>I</i> ,by PC <i>I</i> ₅ .
$C_8H_7NO_2$.	Amine undergoes internal nucleophilic
	substitution), with loss of C/–, to yield the
	cyclic amide F
	Carboxymethyl group, –CH ₂ CO ₂ H, must be
	adjacent to amine – NH ₂ group in A to
	enable ring formation
ОН	ОН
	ОН
OH Br CH2OH	Br CH ₂ OH CH ₂ OH
OH Br	Br CH₂OH CH₂OH
OH Br CH2OH	Br CH ₂ OH CH ₂ OH
A: CH ₂ OH B: Br	Br CH ₂ OH CH ₂ OH
A: CH ₂ OH B: Br	Br CH ₂ OH CH ₂ OH
A: CH ₂ OH B: Br	Br CH ₂ OH C: NO ₂
A: CH ₂ OH B: Br	Br CH ₂ OH CH ₂ OH
A: CH_2OH B: Br	Br CH ₂ OH CH ₂ OH
A: CH_2OH B: Br	Br CH ₂ OH C: NO ₂

Question 5		
(a)(i)	Suggested solution:	



Hydrogen bond

- lone pair
- δ+ / δ-
- 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:

$$H_2N$$
—COO $^-$ Na $^+$ H_2N —

(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:

$$H_2N \longrightarrow COOH + H^+ \longrightarrow H_2N \longrightarrow COO^- + H_2O$$

OR

$$H_3^{\dagger N} \longrightarrow COO^- + H^+ \longrightarrow H_3^{\dagger N} \longrightarrow COO^- + H_2O$$

$$H_3^{\dagger N} \longrightarrow COO^- + OH^- \longrightarrow H_2^{\dagger N} \longrightarrow COO^- + H_2O$$

Suggested solution:	
Information / Type of reaction	Deductions
Compound G , C ₆ H ₉ O ₂ N, is a neutral compound with the ability to rotate plane polarised light.	As G contains N and is neutral, G is like the an amide.
	G contains <u>at least 1 chiral carbon.</u>
G reacts with aqueous sodium	Alkaline hydrolysis
hydroxide to form pungent gas H that turned moist red litmus blue.	Alkaline gas H : CH₃NH₂(g).
	(J has 1 less carbon than G)
Upon acidification with aqueous	
hydrochloric acid, J C ₅ H ₈ O _{4.}	J has 2 <u>carboxylic acid</u> groups.
	G is cyclic <u>amide</u> .
J reacts with LiA/H ₄ to form \mathbf{K} , $C_5H_{12}O_2$.	K has 2 is primary <u>alcohol</u> groups.
On heating with excess concentrated H_2SO_4 , K forms L , C_5H_8 . L does not exhibit cis-trans isomerism.	K undergoes <u>elimination</u> of H ₂ O to form with 2 alkene groups. Most likely terminal alkenes as no isomerism.
When L is heated with acidified KMnO ₄ solution, M , $C_3H_4O_3$ is formed.	L undergoes <u>oxidative cleavage</u> to f C ₃ H ₄ O ₃
M reacts with aqueous Na₂CO₃ to	acid-base reaction
produce effervescence that forms a white precipitate in limewater.	M contains a <u>carboxylic acid</u> .
M also forms a yellow precipitate when warmed with alkaline aqueous I ₂ .	M contains <u>CH₃CO- group.</u> (must be ketone as it is a product of cleavage of a C=C)
G CH ₃	Ј СООН Н
$0 \sim C$	$CH_3NH_2^{CH_3NH_2}$ H_3C C

K	L	М
CH ₂ OH H H ₃ C——C———C——CH ₂ OH H H	$CH_2 \\ H_3C - C - C = CH_2 \\ H$	O H ₃ C-C-COOH

	NATIONAL JUNIOR COLLEGE SH2 Year-End Practical Examination Higher 2	
CANDIDATE NAME		
SUBJECT CLASS	REGISTRATION NUMBER	
CHEMISTRY		9729/04
Paper 4 Practical		14 August 2018
Candidates answ	Candidates answer on the Question paper 2 hours 30 minute	

READ THESE INSTRUCTIONS FIRST

Write your identification number and name.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

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

Additional Materials: As listed in the Confidential Instructions

The use of an approved scientific calculator is expected, where appropriate. You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 18 and 19.

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	/ 14	
2	/ 6	
3	/ 13	
4	/ 9	
5	/10	

/3

/ 55

Presentation

Total

Shift

Laboratory

This document consists of **19** printed pages including this cover page.

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

1 Determination of the average relative formula mass of a mixture of two copper salts

In this experiment, you will determine the average relative formula mass of a mixture of two copper salts by titration.

A solution of the copper salts mixture reacts with excess acidified potassium iodide, producing iodine.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_2(aq)$$

This iodine is then titrated with aqueous sodium thiosulfate, using starch indicator.

FA 1 is an aqueous solution of the copper salt prepared by dissolving 26.0 g of the salt mixture to make 1.00 dm³ of solution.

FA 2 is dilute sulfuric acid, H₂SO₄.

FA 3 is aqueous potassium iodide, KI.

FA 4 is 1.50 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$. starch indicator

(a) Preparation of diluted FA 4

- 1. Pipette 25.0 cm³ of **FA 4** into the 250 cm³ graduated flask.
- 2. Make up the contents of the flask to the 250 cm³ mark with deionised water.
- 3. Stopper the flask and mix the contents thoroughly to ensure a homogeneous solution.

This prepared solution is diluted FA 4.

Titration

- 1. Fill the burette with **diluted FA 4**.
- 2. Pipette 25.0 cm³ of **FA 1** into a conical flask.
- 3. Use the measuring cylinder to add approximately 10.0 cm³ of **FA 2** to the same conical flask.
- 4. Use the measuring cylinder to add approximately 20.0 cm³ of **FA 3** to the mixture in the conical flask. The mixture will appear brown, due to iodine produced in the reaction.
- 5. Begin your rough titration by adding **diluted FA 4** from the burette until the intensity of the brown colour decreases.
- 6. Add 10 drops of starch indicator. The mixture will become darker.
- 7. Continue titrating until the dark colour is discharged. The mixture should appear off-white. This is the end-point.
- 8. Add **one** drop of starch indicator to check that no traces of dark colour are produced.
- 9. If the mixture stays off-white, the titration is completed. If some dark colour is produced, because iodine is still present, continue the titration until mixture appears off-white.
- 10. Record your burette readings and the rough titre in the space below.
- 11. Carry out as many accurate titrations as you think necessary to obtain consistent results.

- 12. Make sure any recorded results show the precision of your practical work.
- 13. Record in a suitable form below all of your burette readings and the volume of **diluted FA 4** added in each accurate titration.

71	1	
[7]	II	
	Ш	
	IV	
	٧	
	VI	
	VII	

From your accurate titration results, obtain a suitable value for the volume of **diluted FA 4** to be used in your calculations.

Show clearly how you obtained this value.

The iodine produced required cm³ of **diluted FA 4**. [1]

(b) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of sodium thiosulfate, Na₂S₂O₃, in the volume of **diluted FA 4** obtained in **(a)**.

moles of $Na_2S_2O_3$ = mol [1]

(ii)	Balance the ionic equation for the reaction of iodine with sodium thiosulfate. State symbols are not required.
	$ \; I_2 \;\; + \; \;\; S_2 O_3^{2-} \;\; \to \;\; \;\; S_4 O_6^{2-} \;\; + \; \;\; I^-$
	Hence calculate the number of moles of iodine that reacted with the number of moles of $Na_2S_2O_3$ calculated in (i).
	moles of I_2 = mol [1]
(iii)	Using your answer to (ii), calculate the number of moles of copper(II) ions in 25.0 cm 3 of FA 1 .
	moles of Cu ²⁺ ions = mol [1]
(iv)	Using your answer to (iii) and the information on page 2, calculate the average relative formula mass of the copper salts in FA 1.
	Average Mr of copper salts =[1]
(v)	Write the full electronic configuration of 29Cu in CuI.

[1]
Hence, explain why solid CuI appears white in colour.
[1]
[Total: 14]

2 Qualitative analysis

In this question, you will deduce the two anions present in **FA 1.** Perform the tests described in **Table 2** and record your observations in the table. Test and identify any gases evolved.

If any solution is warmed, a boiling tube MUST be used.

Table 2

	Test	Observations
(a)	To a 1 cm depth of FA 1 in a test- tube, add aqueous silver nitrate.	
(b)	To a 0.5 cm depth of FA 1 in a boiling tube, add aqueous sodium hydroxide and add one piece of aluminium foil and warm.	
(0)	To a 1 cm depth of FA 1 in a test- tube, add aqueous barium chloride followed by nitric acid.	
(d)	To a 1 cm depth of FA 1 in a test-tube, add an equal volume of sulfuric acid followed by KMnO ₄ .	
		[3]
(e)	From your observations, state the a	nions present in FA 1 . Explain your answers.
	First anion:	Second anion:

[3]

[Total: 6]

3 Investigation of thermal decomposition of sodium hydrogencarbonate

Sodium hydrogencarbonate, NaHCO₃, is used as baking soda in cooking. Baking soda may also contain small amounts of other chemicals.

When baking soda is heated, carbon dioxide is produced. In this experiment, you will investigate the reaction taking place when the sodium hydrogencarbonate in baking soda is thermally decomposed.

FA 5 is baking soda (impure NaHCO₃).

(a) Method

Record all your readings in the space below.

- 1. Weigh the crucible with its lid.
- 2. Transfer all the **FA 5** from the container into the crucible.
- 3. Weigh the crucible, lid and **FA 5**.
- 4. Calculate and record the mass of FA 5 used.
- 5. Place the crucible and contents on a pipe-clay triangle.
- 6. Heat gently, with the lid off, for approximately one minute.
- 7. Heat strongly, with the lid off, for a further three minutes.
- 8. Replace the lid and leave the crucible to cool for about ten minutes.

While the crucible is cooling, you should work on other questions.

- 9. When it has cooled down, weigh the crucible with its lid and contents.
- 10. Heat strongly, with the lid off, for a further two minutes.
- 11. Replace the lid and leave the crucible to cool for ten minutes.
- 12. When it has cooled down, weigh the crucible with its lid and contents.
- 13. Calculate and record the mass of residue obtained.
- 14. This residue is FA 6. Keep this for use in 3(d).

Results

IIIIIIV

(b)	Calculations													
	(i)	Given that the percentage purity by mass of FA 5 is 95.8%, calculate the mass of sodium hydrogencarbonate in the sample of FA 5 that you weighed out.												
		mass of NaHCO ₃ in FA 5 weighed out = g												
	(ii)	Calculate the mass of impurity present in your sample of FA 5 .												
		mass of impurity =g												
	(iii)	The impurity in FA 5 does not decompose when it is heated.												
		This means that the residue, FA 6 , contains the mass of impurity calculated in (ii) together with the solid decomposition product of sodium hydrogencarbonate.												
		Calculate the mass of the solid decomposition product.												
		mass of solid decomposition product = g												
(c)	Why	was the lid put on while the crucible and its contents were cooled?												
		[1]												
		ניו												

(d)	(i)	Ah Beng carried out the experiment by heating 84.0 g of pure NaHCO ₃ to constant mass, he obtained 53.0 g of the solid decomposition product.
		Ah Hock then suggested the following equation for the thermal
		decomposition of sodium hydrogencarbonate.

$$NaHCO_3(s) \rightarrow NaOH(s) + CO_2(g)$$

Explain why Ah Hock's suggestion is **incorrect**. Show working in order to explain your answer.

[A_r: C; 12.0; Na; 23.0; H, 1.0; O: 16.0]

[1]

(ii)	Add 1 cm depth of sulfuric acid into a test-tube. Add some FA 6 from the crucible to the acid in the test-tube. Record all your observations. Use your observations to identify the anion present in FA 6 .	
(iii)	State the assumption you have made in (ii).	[2]

[1]

(iv)	Steam is one of three products obtained when sodium hydrogencarbonate is thermally decomposed.
	Use your answer in (ii) to complete and balance the equation for the thermal decomposition of sodium hydrogencarbonate. Include state symbols.
	NaHCO ₃ () \rightarrow H ₂ O() +CO ₂ () +
(v)	State whether the balanced equation in (iv) agrees with Ah Beng's results.
	Show working in order to explain your answer.
	[1]
	[Total: 13]

4 Determination of the enthalpy change of a reaction, ΔH_r

FA 7 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃

FA 8 is 2.00 mol dm⁻³ sodium hydroxide, NaOH

FA 9 is 2.00 mol dm⁻³ sulfuric acid, H₂SO₄

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in Tables 4.1 and 4.2.

Experiment A

Reaction between FA 7, NaHCO₃, and FA 8, NaOH.

Reaction 1 NaHCO₃(aq) + NaOH(aq)
$$\rightarrow$$
 Na₂CO₃(aq) + H₂O(l) $\triangle H_{\text{reaction 1}}$

The molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with NaOH.

- 1 Using a measuring cylinder, transfer 30.0 cm³ of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 7**, T_{FA7} .
- 3 Using another measuring cylinder, measure 20.0 cm³ of **FA 8.**
- 4 Stir and measure the temperature of this **FA 8**, T_{FA8} .
- Add **FA 8** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.
- Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 7** and **FA 8** using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA8} \times T_{FA8})}{(V_{FA7} + V_{FA8})}$$

	Experiment A
T _{FA7} /°C	
T _{FA8} /°C	
Taverage /°C	
T _{max} /°C	
ΔT _{max} /°C	

Table 4.1

Experiment B

Reaction between FA 7, NaHCO₃, and FA 9, H₂SO₄.

The molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with H₂SO₄.

- Using a measuring cylinder, transfer 30.0 cm³ of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 7**, T_{FA7} .
- 3 Using another measuring cylinder, measure 20.0 cm³ of **FA 9.**
- 4 Stir and measure the temperature of this **FA 9**, T_{FA9} .
- Add **slowly**, the **FA 9** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.
- **6** Using the thermometer, stir the mixture continuously until a maximum/minimum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 7** and **FA 9** using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA9} \times T_{FA9})}{(V_{FA7} + V_{FA9})}$$

	Experiment B
T _{FA7} /°C	
T _{FA9} /°C	
Taverage /°C	
T _{max} /°C	
ΔT _{max} /°C	

Table 4.2

(a)		e purpose of calculations, you should assume that the mixture has a density 0 g cm $^{-3}$ and specific heat capacity, c, of 4.18 J g $^{-1}$ K $^{-1}$.
	(i)	Use your results from Table 4.1 to calculate a value for the molar enthalpy change for reaction 1 , $\Delta H_{\text{reaction1}}$.

$\Delta H_{\text{reaction 1}}$	=			 									 					
															[2	2]	

(ii)	Use your results from Table 4.2 to calculate a value for the molar enthalpy
	change for reaction 2 , $\Delta H_{\text{reaction2}}$.

 $\Delta H_{\text{reaction2}} = \dots$

[2]

(b) Ionic equations for neutralisation, reaction 1, and reaction 2 are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	$\Delta H_{\text{neu}} = -57.1 \text{ kJ mol}^{-1}$
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{ m reaction 1}$
$HCO_3^-(aq) + H^+(aq) \to H_2O(l) + CO_2(g)$	$\Delta H_{ m reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3
$$CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2HCO_3^{-}(aq) \quad \Delta H_{reaction3}$$

Using your calculated answers in (a), together with the given value of enthalpy change of neutralisation, ΔH_{neu} , construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{\text{reaction}3}$.

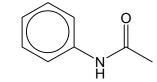
 $\Delta H_{\text{reaction3}} = \dots$

[3]

[Total: 9]

5 Planning

The structure of *N*-phenylethanamide is shown below:



N-phenylethanamide, C₆H₅NHCOCH₃

The preparation of N-phenylethanamide from phenylamine is termed acylation. Ethanoic anhydride, $(CH_3CO)_2O$ is commonly used as an acylating agent as its low reactivity relative to ethanoyl chloride allows the reaction rate to be more easily controlled.

Phenylamine is most conveniently used in the form of the salt phenylammonium chloride, C₆H₅NH₃C*l*.

The reaction is performed in **two** stages:

Stage 1:

Phenylamine can be prepared from phenylammonium chloride and sodium ethanoate in an aqueous medium under room temperature.

The reaction is as shown below:

phenylammonium chloride

phenylamine

[1]

The reaction mixture needs to be continuously stirred for 3 minutes.

Stage 2:

Phenylamine then reacts with ethanoic anhydride to form solid *N*-phenylethanamide together with ethanoic acid. The addition of ethanoic anhydride to the reaction mixture may be violent.

This mixture is heated under reflux for about 15 minutes, before the crude solid product is removed by filtration and purified by recrystallisation from hot water. The melting point of N-phenylethanamide is 114 $^{\circ}$ C.

(-)	State the type of reaction taking place in stage 1.
	[1
(ii)	Write an equation for the reaction of phenylamine with ethanoic anhydride i stage 2 .
	(ii)

(b) The above reaction between phenylamine and ethanoic anhydride in stage **2** gives an 80% yield.

Assuming phenylammonium chloride is completely converted to phenylamine in stage **1**, determine the mass of phenylammonium chloride required to prepare 2 g of *N*-phenylethanamide.

(A_r: C: 12.0, H: 1.0, N: 14.0, O: 16.0, C*l*: 35.5)

[2]

(c) Write a full description of the procedure to carry out stages 1 and 2. You do not need to describe the recrystallization process to obtain a pure sample of N-phenylethanamide in stage 2.

You may assume that you are provided with:

- 30 cm³ of water for use as solvent
- 6.0 g of hydrated sodium ethanoate
- 2.0 cm³ of ethanoic anhydride
- Apparatus normally found in a school or college laboratory

Your plan should include details of:

- (i) appropriate quantities of reactants
- (ii) appropriate choice of apparatus
- (iii) drawing of reflux set-up

[5]
Suggest a method to check the purity of <i>N</i> -phenylethanamide obtained.
[1]
ניו

[Total: 10]

(d)

Qualitative Analysis Notes

[ppt. = precipitate]

(a) Reactions of aqueous cations

action	reaction with		
cation	NaOH(aq)	NH₃(aq)	
aluminium, A <i>β</i> +(aq)	white ppt. soluble in excess	white ppt. insoluble in excess	
ammonium, NH₄⁺(aq)	ammonia produced on heating	-	
barium, Ba ²⁺ (aq)	no ppt. (if reagents are pure)	no ppt.	
calcium, Ca ²⁺ (aq)	white ppt. with high [Ca ²⁺ (aq)]	no ppt.	
chromium(III), Cr ³⁺ (aq)	grey-green ppt. soluble in excess giving dark green solution	grey-green ppt. insoluble in excess	
copper(II), Cu ²⁺ (aq)	pale blue ppt. insoluble in excess	blue ppt. soluble in excess giving dark blue solution	
iron(II), Fe ²⁺ (aq)	green ppt., turning brown on contact with air insoluble in excess	green ppt., turning brown on contact with air insoluble in excess	
iron(III), Fe ³⁺ (aq)	red-brown ppt. insoluble in excess	red-brown ppt. insoluble in excess	
magnesium, Mg ²⁺ (aq)	white ppt. insoluble in excess	white ppt. insoluble in excess	
manganese(II), Mn ²⁺ (aq)	off-white ppt., rapidly turning brown on contact with air insoluble in excess	off-white ppt., rapidly turning brown on contact with air insoluble in excess	
zinc, Zn²+(aq)	white ppt. soluble in excess	white ppt. soluble in excess	

(b) Reactions of anions

anions	reaction
carbonate, CO ₃ ²⁻	CO ₂ liberated by dilute acids
chloride, CF(aq)	gives white ppt. with Ag ⁺ (aq) (soluble in NH ₃ (aq))
bromide, Br (aq)	gives pale cream ppt. with Ag ⁺ (aq) (partially soluble in NH ₃ (aq))
iodide, I ⁻ (aq)	gives yellow ppt. with Ag ⁺ (aq) (insoluble in NH ₃ (aq))
nitrate, NO ₃ -(aq)	NH₃ liberated on heating with OH⁻(aq) and A/ foil
nitrite, NO ₂ ⁻ (aq)	NH₃ liberated on heating with OH⁻(aq) and A/ foil; NO liberated by dilute acids (colourless NO → (pale) brown NO₂ in air)
sulfate, SO ₄ ²⁻ (aq)	gives white ppt. with Ba ²⁺ (aq) (insoluble in excess dilute strong acids)
sulfite, SO ₃ ²⁻ (aq)	SO ₂ liberated by dilute acids; gives white ppt. with Ba ²⁺ (aq) (soluble in dilute strong acids)

(c) Tests for gases

gas	test and test result
ammonia, NH ₃	turns damp red litmus paper blue
carbon dioxide, CO ₂	gives white ppt. with limewater (ppt. dissolves with excess CO ₂)
chlorine, CI ₂	bleaches damp litmus paper
hydrogen, H ₂	"pops" with a lighted splint
oxygen, O ₂	relights a glowing splint
sulfur dioxide, SO ₂	turns aqueous potassium manganite(VII) from purple to colourless

(d) Colour of halogens

halogen	colour of element	colour in aqueous solution	colour in hexane
chlorine, CI ₂	greenish yellow gas	pale yellow	pale yellow
bromine, Br ₂	reddish brown gas / liquid	orange	orange-red
iodine, I ₂	black solid / purple gas	brown	purple

2018 SH2 H2 Chemistry P4 Solutions

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

1 Determination of the average relative formula mass of a mixture of two copper salts

In this experiment, you will determine the average relative formula mass of a mixture of two copper salts by titration.

A solution of the copper salts mixture reacts with excess acidified potassium iodide, producing iodine.

$$2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow 2CuI(s) + I_{2}(aq)$$

This iodine is then titrated with aqueous sodium thiosulfate, using starch indicator.

FA 1 is an aqueous solution of the copper salt prepared by dissolving 26.0 g of the salt mixture to make 1.00 dm³ of solution.

FA 2 is dilute sulfuric acid, H₂SO₄.

FA 3 is aqueous potassium iodide, KI.

FA 4 is 1.50 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$. starch indicator

(a) Preparation of diluted FA 4

- 1. Pipette 25.0 cm³ of **FA 4** into the 250 cm³ graduated flask.
- 2. Make up the contents of the flask to the 250 cm³ mark with deionised water.
- 3. Stopper the flask and mix the contents thoroughly to ensure a homogeneous solution.

This prepared solution is diluted FA 4.

Titration

- 1. Fill the burette with diluted FA 4.
- 2. Pipette 25.0 cm³ of **FA 1** into a conical flask.
- 3. Use the measuring cylinder to add approximately 10.0 cm³ of **FA 2** to the same conical flask.
- 4. Use the measuring cylinder to add approximately 20.0 cm³ of **FA 3** to the mixture in the conical flask. The mixture will appear brown, due to iodine produced in the reaction.
- 5. Begin your rough titration by adding **diluted FA 4** from the burette until the intensity of the brown colour decreases.
- 6. Add 10 drops of starch indicator. The mixture will become darker.
- 7. Continue titrating until the dark colour is discharged. The mixture should appear off-white. This is the end-point.
- 8. Add **one** drop of starch indicator to check that no traces of dark colour are produced.
- 9. If the mixture stays off-white, the titration is completed. If some dark colour is produced, because iodine is still present, continue the titration until mixture appears off-white.
- 10. Record your burette readings and the rough titre in the space below.

- 11. Carry out as many accurate titrations as you think necessary to obtain consistent results.
- 12. Make sure any recorded results show the precision of your pract
- 13. Record in a suitable form below all of your burette readings and of **diluted FA 4** added in each accurate titration.

I All the following data is recorded initial and final burette readings for **two** (or more) titrations

Il Titre values recorded for accurate titrations, and Appropriate headings and units

- initial / start (burette) reading
- final / end (burette) reading
- titre or volume used / added (not "difference")

unit: / cm³ (for each heading) or cm³ unit given for each volume recorded.

III: All burette readings are recorded to the nearest 0.05 cm³. (2 d.p) (Rough reading do not need 2 d.p)

including 0.00 cm³ (if this was the initial reading).

Do **not** award if: (reverse burette readings)

- 50(.00) is used as an initial burette reading
- more than one final burette reading is 50.(00)

any burette reading is greater than 50.(00)

IV: at least two titres within 0.10 cm³

[7]

Ш

IV

VΙ

VII

From your accurate titration results, obtain a suitable value for the volume of **diluted FA 4** to be used in your calculations.

Show clearly how you obtained this value.

Candidate calculates the mean correctly.

- Candidate must take the average of two (or more) titres within 0.10 cm³.
- Working / explanation **or** ticks must be shown
- The mean should be quoted to **2 d.p**, and be rounded to nearest 0.01 cm³.

(e.g. 26.667 cm³ must be rounded to 26.67 cm³)

The iodine produced required cm³ of **diluted FA 4**.

[1]

(b) Calculations

Show your working and appropriate significant figures in the final answer to **each** step of your calculations.

(i) Calculate the number of moles of sodium thiosulfate, Na₂S₂O₃, in the volume of **diluted FA 4** obtained in (a).

No of moles of thiosulfate used = $1.50 \times \frac{25.0}{250} \times \text{mean titre} / 1000$

Or No of moles of thiosulfate used = 0. 150 × mean titre / 1000 (expressed to 3 or 4 sig fig)

moles of
$$Na_2S_2O_3$$
 = mol [1]

(ii) Balance the ionic equation for the reaction of iodine with sodium thiosulfate. State symbols are not required.

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

Hence calculate the number of moles of iodine that reacted with the number of moles of $Na_2S_2O_3$ calculated in (i).

Equation balanced I_2 + **2** $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$ + **2** I^- no of moles of I_2 = 0.5 × ans. in (i)

moles of
$$I_2$$
 = mol

(iii) Using your answer to (ii), calculate the number of moles of copper(II) ions in 25.0 cm³ of **FA 1**.

No of moles of copper(II) ions = 2 × answer (ii) (expressed to 3 or 4 sig fig)

moles of
$$Cu^{2+}$$
 ions = mol [1]

(iv) Using your answer to (iii) and the information on page 2, calculate the average relative formula mass of the copper salts in **FA 1**.

Average Mr = [26.0 / ans (iii)] × 25 / 1000

Average Mr of copper salts =[1]

(v) Write the full electronic configuration of 29Cu in CuI.

 $1s^22s^22p^63s^23p^63d^{10}$

- (vi) Hence, explain why solid CuI appears white in colour.
 - d subshell is fully filled, no vacant / half-filled d orbitals
 - electrons cannot be promoted from lower energy d orbitals to higher energy d orbitals / d-d transition not possible
 - No wavelength of visible spectrum is absorbed, hence solid appears white

[1]

[Total: 14]

2 Qualitative analysis

In this question, you will deduce the two anions present in **FA 1.** Perform the tests described in **Table 2** and record your observations in the table. Test and identify any gases evolved.

If any solution is warmed, a boiling tube MUST be used.

Table 2

	Test	Observations
(a)	To a 1 cm depth of FA 1 in a test-tube, add aqueous silver nitrate.	Solution remained blue / no ppt
(b)	To a 0.5 cm depth of FA 1 in a boiling tube, add aqueous sodium hydroxide and add one piece of aluminium foil and warm.	Blue ppt formed, insoluble in excess sodium hydroxide Black ppt formed upon heating Colourless, pungent gas / gas evolved turns (damp red) litmus blue
(c)	To a 1 cm depth of FA 1 in a test-tube, add aqueous barium chloride followed by nitric acid.	White ppt formed and insoluble in excess nitric acid
(d)	To a 1 cm depth of FA 1 in a test-tube, add an equal volume of sulfuric acid followed by KMnO ₄ .	FA 1 remained blue. Purple KMnO₄ remained/ not decolourised

[3]

(e) From your observations, state the anions present in ${\bf FA}$ 1. Explain your answers.

Nitrate NO₃⁻ + Sulfate SO₄²⁻ <u>Explanation for NO₃</u>⁻

Both Nitrate or Nitrite is reduced by Al foil in NaOH(aq) to give NH₃ gas + Since KMnO₄ remained purple, **FA 1** does not contain reducing agent NO₂⁻.

Or

Since no brown NO₂ gas is evolved with nitric acid, **FA 1** contains Nitrate NO₃⁻

Explanation for SO₄²=

Since a white ppt is formed with BaCl₂, **and** remained in nitric acid, anion in FA1 cannot be SO₃²⁻.

Since Since KMnO₄ remained purple, **FA 1** does not contain reducing agent SO₃²⁻.

[3]

[Total: 6]

3 Investigation of thermal decomposition of sodium hydrogencarbonate

Sodium hydrogencarbonate, NaHCO₃, is used as baking soda in cooking. Baking soda may also contain small amounts of other chemicals.

When baking soda is heated, carbon dioxide is produced. In this experiment, you will investigate the reaction taking place when the sodium hydrogencarbonate in baking soda is thermally decomposed.

FA 5 is baking soda (impure NaHCO₃).

(a) Method

Record all your readings in the space below.

- 1. Weigh the crucible with its lid.
- 2. Transfer all the **FA 5** from the container into the crucible.
- 3. Weigh the crucible, lid and **FA 5**.
- 4. Calculate and record the mass of **FA 5** used.
- 5. Place the crucible and contents on a pipe-clay triangle.
- 6. Heat gently, with the lid off, for approximately one minute.
- 7. Heat strongly, with the lid off, for a further three minutes.
- 8. Replace the lid and leave the crucible to cool for about ten minutes.

While the crucible is cooling, you should work on other questions.

- 9. When it has cooled down, weigh the crucible with its lid and contents.
- 10. Heat strongly, with the lid off, for a further two minutes.
- 11. Replace the lid and leave the crucible to cool for ten minutes.
- 12. When it has cooled down, weigh the crucible with its lid and contents.
- 13. Calculate and record the mass of residue obtained.
- 14. This residue is FA 6. Keep this for use in 3(d).

Results

Four weighings recorded and correct headings given and mass of FA 5 used and mass of residue recorded

Mass	/g
Crucible + lid	a
Crucible + lid + FA 5 before heating	р
Crucible + lid + content after 1st heating	С
Crucible + lid + content after 2nd heating	d
FA 5 used	b-a = e
Residue OR FA 6	d-a = f



If 'mass' not written then 'g' must be with each entry.

Use of lid must be consistent

П

- All weighings recorded to 3 decimal places
- Mass of FA 5 and FA 6 / residue must be correctly subtracted

[4]

(b) Calculations

(i) Given that the percentage purity by mass of **FA 5** is 95.8%, calculate the mass of sodium hydrogencarbonate in the sample of **FA 5** that you weighed out.

Mass NaHCO₃ = $(95.8 / 100) \times \text{mass of } \mathbf{FA 5} \text{ used}$

mass of NaHCO₃ in **FA 5** weighed out = g

(ii) Calculate the mass of impurity present in your sample of **FA 5**.

Mass impurity = mass of FA 5 – answer (i) or mass impurity = $4.2/100 \times \text{mass FA 5}$

mass of impurity = g

(iii) The impurity in **FA 5** does not decompose when it is heated.

This means that the residue, **FA 6**, contains the mass of impurity calculated in **(ii)** together with the solid decomposition product of sodium hydrogencarbonate.

Calculate the mass of the solid decomposition product.

Mass of decomposition solid = mass of residue (**FA 6**) from table – mass of impurity (ii) and expressed to 3 d.p / 3 s.f

or mass of decomposition solid = mass of NaHCO₃ – mass **lost** on heating **[(i)** – (mass **FA 5** – mass **FA 6**)]

mass of solid decomposition product = g

(c) Why was the lid put on while the crucible and its contents were cooled?

Lid reduces / stops absorption of water (vapour) by solid / residue / **FA 5** while cooling/ prevents reaction with carbon dioxide.

Do not accept: falling impurities/ loss of solid due to wind/oxidation in the air. [1]

(d) (i) Ah Beng carried out the experiment by heating 84.0 g of pure NaHCO₃ to constant mass, he obtained 53.0 g of the solid decomposition product.

Ah Hock then suggested the following equation for the thermal decomposition of sodium hydrogencarbonate.

$$NaHCO_3(s) \rightarrow NaOH(s) + CO_2(g)$$

Explain why Ah Hock's suggestion is **incorrect**. Show working in order to explain your answer.

[A_r: C; 12.0; Na; 23.0; H, 1.0; O: 16.0]

If Ah Hock is **correct**., (84 g) NaHCO₃ would give **40** g residue / NaOH

mole ratio of NaHCO₃: NaOH is 1:1.3 (so not 1:1)

10

Answers could refer to mass lost / moles of CO₂

(ii) Add 1 cm depth of sulfuric acid into a test-tube.

Add some **FA 6** from the crucible to the acid in the test-tube.

Record all your observations.

Use your observations to identify the anion present in **FA 6**.

Any observation below + gas forms white ppt in limewater

Do NOT accept milky / chalky / cloudy

- fizzing / effervescence / bubbling
- · solid dissolves / colourless solution formed

FA 6 contains carbonate ion / CO₃²⁻

[2]

(iii) State the assumption you have made in (ii).

Complete decomposition of NaHCO₃.

OR

There is no leftover NaHCO₃.

[1]

(iv) Steam is one of **three** products obtained when sodium hydrogencarbonate is thermally decomposed.

Use your answer in (ii) to complete and balance the equation for the thermal decomposition of sodium hydrogencarbonate. Include state symbols.

$$\mathbf{2}\mathsf{NaHCO}_3(\mathsf{s}) \to \mathsf{H}_2\mathsf{O}(\mathsf{g}) + \mathsf{CO}_2(\mathsf{g}) + \mathsf{Na}_2\mathsf{CO}_3(\mathsf{s})$$
 [1]

(v) State whether the balanced equation in (iv) agrees with Ah Beng's results.

Show working in order to explain your answer.

(From equation) 84.0 g NaHCO₃ should give 0.5×106 g residue (= 53.0 g) And this agrees with Ah Beng's 53.0 g [1]

[Total: 13]

4 Determination of the enthalpy change of a reaction, ΔH_r

FA 7 is 1.00 mol dm⁻³ sodium hydrogen carbonate, NaHCO₃

FA 8 is 2.00 mol dm⁻³ sodium hydroxide, NaOH

FA 9 is 2.00 mol dm⁻³ sulfuric acid, H₂SO₄

An acid-base neutralisation reaction involves reacting the two solutions, to produce water molecules. The equation for this neutralisation reaction is given below.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

You will follow the instructions to perform two experiments, **Experiment A** and **Experiment B**. Record your results in Tables 4.1 and 4.2.

Experiment A

Reaction between FA 7, NaHCO₃, and FA 8, NaOH.

Reaction 1 NaHCO₃(aq) + NaOH(aq)
$$\rightarrow$$
 Na₂CO₃(aq) + H₂O(l) $\triangle H_{\text{reaction 1}}$

The molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with NaOH.

- 1 Using a measuring cylinder, transfer 30.0 cm³ of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 7**, T_{FA7} .
- 3 Using another measuring cylinder, measure 20.0 cm³ of **FA 8**.
- 4 Stir and measure the temperature of this **FA 8**, T_{FA8} .
- Add **FA 8** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.
- Using the thermometer, stir the mixture continuously until a maximum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 7** and **FA 8** using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA8} \times T_{FA8})}{(V_{FA7} + V_{FA8})}$$

	Experiment A
T _{FA7} /°C	
T _{FA8} /°C	
T _{average} /°C	
T _{max} /°C	
ΔT _{max} /°C	

Table 4.1

Experiment B

Reaction between **FA 7**, NaHCO₃, and **FA 9**, H₂SO₄.

Reaction 2 NaHCO₃(aq) +
$$\frac{1}{2}$$
H₂SO₄(aq) \rightarrow $\frac{1}{2}$ Na₂SO₄(aq) + H₂O(l) + CO₂ (g) $\Delta H_{reaction2}$

The molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction 2}}$, is the enthalpy change when 1.00 mol of NaHCO₃ reacts completely with H₂SO₄.

- Using a measuring cylinder, transfer 30.0 cm³ of **FA 7** into a Styrofoam cup. Place this cup inside a second Styrofoam cup, which is placed in a 250 cm³ glass beaker. Place the lid on the cup.
- 2 Stir and measure the temperature of this **FA 7**, T_{FA7} .
- 3 Using another measuring cylinder, measure 20.0 cm³ of **FA 9.**
- 4 Stir and measure the temperature of this **FA 9**, T_{FA9} .
- Add **slowly**, the **FA 9** from the measuring cylinder to the **FA 7** in the Styrofoam cup. Immediately replace the lid.
- **6** Using the thermometer, stir the mixture continuously until a maximum/minimum temperature is reached. Read and record this temperature T_{max} .
- 7 Calculate the weighted average initial temperature, *T*_{average}, of **FA 7** and **FA 9** using the formula given below:

$$T_{\text{average}} = \frac{(V_{FA7} \times T_{FA7}) + (V_{FA9} \times T_{FA9})}{(V_{FA7} + V_{FA9})}$$

	Experiment B
T _{FA7} /°C	
T _{FA9} /°C	
T _{average} /°C	
T _{max} /°C	
ΔT _{max} /°C	

Table 4.2

[2]

All temperature readings are recorded to the nearest 0.1 $^{\circ}$ C. (for both Tables 4.1 & 4.2)

 $\Delta T_{\text{max/min}}$ must be correctly calculated i.e. T_{max} – average initial temperature. (for both Tables 4.1 & 4.2)

- (a) For the purpose of calculations, you should assume that the mixture has a density of 1.00 g cm⁻³ and specific heat capacity, c, of 4.18 J g⁻¹ K⁻¹.
 - (i) Use your results from **Table 4.1** to calculate a value for the molar enthalpy change for **reaction 1**, $\Delta H_{\text{reaction1}}$.

$$q = (20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{max}$$
 $n(NaHCO_3) = 1.00 \times 30.0/1000 = 0.03 \text{ mol}$

$$\Delta H_{reaction1} = - q / n(NaHCO_3) \quad \text{(this reaction is exothermic)}$$

$$\Delta H_{\text{reaction1}} = \dots$$
 [2]

(ii) Use your results from **Table 4.2** to calculate a value for the molar enthalpy change for **reaction 2**, $\Delta H_{\text{reaction2}}$.

$$q = (20.0 + 30.0)(1.00) \times 4.18 \times \Delta T_{min}$$
 $n(NaHCO_3) = 1.00 \times 30.0/1000 = 0.03 \text{ mol}$
 $\Delta H_{reaction1} = + q / n(NaHCO_3)$ (this reaction is endothermic)

$$\Delta H_{\text{reaction2}} = \dots$$

[2]

(b) Ionic equations for neutralisation, **reaction 1**, and **reaction 2** are shown below.

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	$\Delta H_{\text{neu}} = -57.1 \text{ kJ mol}^{-1}$
$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$	$\Delta H_{ m reaction1}$
$HCO_3^-(aq) + H^+(aq) \to H_2O(l) + CO_2(g)$	$\Delta H_{ m reaction2}$

Carbon dioxide reacts with solutions of carbonate ions according to the following equation.

reaction 3
$$CO_2(g) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2HCO_3^{-}(aq) \quad \Delta H_{reaction3}$$

Using your calculated answers in (a), together with the given value of enthalpy change of neutralisation, ΔH_{neu} , construct an energy cycle to determine a value for the enthalpy change for this reaction, $\Delta H_{\text{reaction}3}$.

$$CO_{2} + 2H_{2}O + CO_{3}^{2} \rightarrow 2HCO_{5} + H_{2}O$$

$$AH_{1}2 \uparrow \qquad \qquad \uparrow AH_{1}$$

$$HCO_{3}^{-} + H^{+} + CO_{3}^{2} + H_{2}O \leftarrow 2HCO_{5}^{-} + H^{+} + OH^{-}$$

$$AH_{1}I$$

$$\Delta H_{\text{reaction3}} = (-(a)(ii)) + (-(a)(i)) + (-57.1)$$

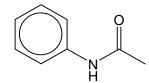
 $\Delta H_{\text{reaction3}}$ =

[3]

[Total: 9]

5 Planning

The structure of *N*-phenylethanamide is shown below:



N-phenylethanamide, C₆H₅NHCOCH₃

The preparation of N-phenylethanamide from phenylamine is termed acylation. Ethanoic anhydride, $(CH_3CO)_2O$ is commonly used as an acylating agent as its low reactivity relative to ethanoyl chloride allows the reaction rate to be more easily controlled.

Phenylamine is most conveniently used in the form of the salt phenylammonium chloride, $C_6H_5NH_3Cl$.

The reaction is performed in two stages:

Stage 1:

Phenylamine can be prepared from phenylammonium chloride and sodium ethanoate in an aqueous medium under room temperature.

The reaction is as shown below:

phenylammonium chloride

phenylamine

The reaction mixture needs to be continuously stirred for 3 minutes.

Stage 2:

Phenylamine then reacts with ethanoic anhydride to form solid N-phenylethanamide together with ethanoic acid. The addition of ethanoic anhydride to the reaction mixture may be violent.

This mixture is heated under reflux for about 15 minutes, before the crude solid product is removed by filtration and purified by recrystallisation from hot water. The melting point of N-phenylethanamide is 114 $^{\circ}$ C.

(a) (i) State the type of reaction taking place in stage 1.

Acid base reaction/ neutralisation

[1]

(ii) Write an equation for the reaction of phenylamine with ethanoic anhydride in stage 2.

 $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3 + CH_3CO_2H.$

[1]

(b) The above reaction between phenylamine and ethanoic anhydride in stage **2** gives an 80% yield.

Assuming phenylammonium chloride is completely converted to phenylamine in stage **1**, determine the mass of phenylammonium chloride required to prepare 2 g of *N*-phenylethanamide.

(A_r: C: 12.0, H: 1.0, N: 14.0, O: 16.0, C*l*: 35.5)

Amount of N-phenylethanamide = 2/ 135= 0.01481 mol

Amount of phenylamine = 0.01481 mol

Mass of phenylammonium chloride = 0.01481 x (72 + 8 + 14 + 35.5) x 100/80 = 2.398 g

[2]

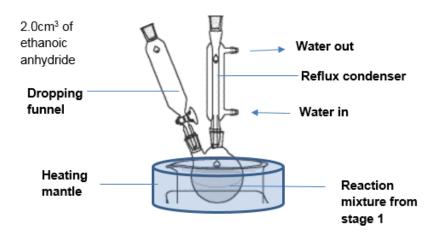
(c) Write a full description of the procedure to carry out stages 1 and 2. You do not need to describe the recrystallization process to obtain a pure sample of *N*-phenylethanamide *in stage* 2.

You may assume that you are provided with:

- 30 cm³ of water for use as solvent
- 6.0 g of hydrated sodium ethanoate
- 2.0 cm³ of ethanoic anhydride
- Apparatus normally found in a school or college laboratory

Your plan should include details of:

- (i) appropriate quantities of reactants
- (ii) appropriate choice of apparatus
- (iii) drawing of reflux set-up



- 1. **Weight out** accurately about **2.40 g** of phenylammonium chloride in a clean and dry weighing bottle.
- 2. Measure 30 cm³ of water using a 100 cm³ measuring cylinder.
- 3. **Dissolve/Add** this completely in 30 cm³ of water in a clean and dry 250 cm³ round bottom flask.
- 4. Weigh out 6.0 g of hydrated sodium ethanoate in a weighing bottle.
- 5. Add sodium ethanoate to the solution in (3) and **stir the mixture for three minutes** using a magnetic stirrer.
- 6. Measure 2.0 cm³ of ethanoic anhydride using a 10 cm³ measuring cylinder.
- 7. Introduce 2.0 cm³ of ethanoic anhydride slowly using a dropping funnel/dropwise using dropper /(using ice bath for the reaction) and connect the reaction mixture to the reflux condenser as shown in the set up below inside a fumehood.
- 8. Carry out the reflux for 15minutes.
- 9. Filter off the crude product and wash it with a little cold water
- (d) Suggest a method to check the purity of *N*-phenylethanamide obtained.

Determine the melting point and verify it against literature data/ value of 114 $^{\circ}$ C. If the melting point is within \pm 2 $^{\circ}$ C of literature data/ 114 $^{\circ}$ C, it is pure

[Total: 10]